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Thermal Conductivity of Silica Aerogel Thermal Insulation Coatings

Fang He[1] · Zhentao Qi[1] · Wei Zhen[2] · Juying Wu[3] · Yuhong Huang[3] · Xianwen Xiong[2] · Ruizhu Zhang[2]

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Abstract
In this study, silica aerogel microspheres were prepared through sol–gel method with tetraethyl orthosilicate as the silicon source. Thermal insulation coatings were prepared by mixing silica aerogel and acrylic emulsion. The relationships between the thermal conductivity and volume fractions, densities, sizes, and interfaces of silica aerogel microspheres were investigated through scanning electron microscopy and thermal conductivity analysis. The thermal insulation mechanism of composite coating was discussed in detail. Results showed that the aggregations prevented the decrease of thermal conductivity in the coating when the volume fraction of silica aerogel microspheres was lower than 30 %. However, the pores in the coating reduced the thermal conductivity when the volume fraction was higher than 30 %. The porosity of silica aerogel increased with the declining density, which improved the thermal insulation performance of silica aerogel and reduced the thermal conductivity of the coating. The thermal conductivity of the coating with large microspheres was lower than that with small microspheres at low volume fractions. However, the thermal conductivity of the coating with small silica aerogel microspheres was low because of their large interfacial thermal resistance at high volume fractions. Wetting agents were beneficial in improving the compatibility of hydrophobic aerogel microspheres and polymer, improving the volume fractions of silica aerogel microspheres in the coating, and reducing the thermal conductivity of the coating.

Keywords Silica aerogel · Thermal conductivity · Volume fraction · Wetting agent

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✉ Fang He
hefang@haut.edu.cn

[1] College of Material Science and Engineering, Henan University of Technology, Zhengzhou 450001, Henan Province, China

[2] College of Mechanical Engineering, North China University of Water Conservancy and Electric Power, Zhengzhou 450011, Henan Province, China

[3] Institute of Systemic Engineering, China Academy of Engineering Physics, Mianyang 621900, Sichuan Province, China

1 Introduction

Silica aerogel, which is made of nanoporous matrices with interconnected amorphous silica nanoparticles, is a highly nanoporous and open cell structure material. Silica aerogel has been widely used as super thermal insulators [1] and super insulating material in industrial applications [2] because of its low thermal conductivity (less than 0.02 $W\cdot(m\cdot K)^{-1}$ at ambient conditions). However, silica aerogel is unsuitable as insulating materials because of its low strength. Therefore, a second phase, such as fibers [3–5], is usually added to improve the strength of silica aerogel, and a polymer could be used as a new carrier of silica aerogel. At the same time, the polymers is used to bind inorganic powders because of its high corrosion resistance, chemical stability, and electric insulation property. Thus, the strength of silica aerogel would be improved, and its application could be expanded when silica aerogel particles or powders are filled with the polymer.

The composite of polymer and silica aerogel particles as a type of newly developed energy-saving materials has excellent thermal insulation performance [6, 7]. However, its thermal conductivity is affected by many factors; for example, the thermal conductivity will change with the arrangement of particles, especially when a parallel or series structure of particles is generated in the composite [8, 9]. The thermal conductivity may be affected by interfacial thermal resistance, which changes with the sizes of particles. Many researchers have experimentally and analytically investigated the thermal performance of the composite of silica aerogel particles and polymer. Kim et al. [10] studied the thermal conductivity of aerogel–PVB composites and found that the thermal conductivity of composites increased because a heat channel with low thermal resistance was formed by the polymer coated on the surface of aerogel particles. Ge et al. [11] investigated the thermal insulation performance of silica aerogel/epoxy composite and found that the thermal conductivity of the composite increased because part of silica aerogel powders was immersed by epoxy as observed by transmission electron microscopy. In the above research, the factors about the thermal conductivity of silica aerogel composite were systematically investigated and extensively discussed. However, previous studies have not evaluated the thermal conductivity of the composite of silica aerogel particles and polymer and have not conducted a systematic discussion about silica aerogel particles.

In the present study, a thermal insulation composite coating was prepared using silica, aerogel microspheres, and polymer emulsion. The thermal conductivity of the composite was measured and analyzed. The relationships between the thermal conductivity and volume fractions, densities, sizes, and interfaces of silica aerogel microspheres were investigated through scanning electron microscopy (SEM) and thermal conductivity analysis. The thermal insulation mechanism of the composite coating was discussed.

2 Experimental Investigation

2.1 Preparation of Silica Aerogel Microspheres

In this experiment, 208.33 g tetraethyl orthosilicate (TEOS), 322 g anhydrous ethanol, and 72 g deionized water were mixed, and 1 ml nitric acid with 65 % mass fraction was added. The viscous fluid, namely, silica sol, was obtained by mixing well and holding it in a water bath at 60 °C for 2 h. Then, the silica sol was sprayed into the peanut oil using an atomizer, and the peanut oil was continuously stirred. The volume of silica sol injected each time was maintained below 20 % of peanut oil to ensure its dispersion. Then, small amount of ammonia water with 2 % mass fraction was added into the mixture of peanut oil and silica sol and held for 3 min to obtain its natural gel. The gel was allowed to stand at room temperature for 3 days to separate the pure gel from the mixture. At the same, the gel was soaked in an organic solvent for 2 days to remove the residual organic impurities on the gel surface and was cleaned with ethanol. The silica gel microspheres were soaked in a mixture of TEOS, anhydrous ethanol, and deionized water with a volume ratio of 10:39:1 and aged in an autoclave at 105 °C for 5 days. The sizes of microspheres were adjusted by changing the used atomizing nozzle model. The silica gel microspheres were modified by trimethylchlorosilane (TMCS) and cleared with deionized water to remove Cl^- produced in the reaction. The hydrophobic silica gel microspheres were dried under supercritical conditions with ethanol as the medium. Then, the silica aerogel microspheres were prepared.

2.2 Preparation of Silica Aerogel Thermal Insulation Coatings

As crosslinking agent, the acrylic emulsion was mixed with wetting agents, dispersing agents, antifoaming agents, and thickener at room temperature. The mass ratio of silica aerogel microspheres, acrylic emulsion, and auxiliaries (wetting, dispersing, antifoaming, and thickening agents) was 1:4:0.01. Silica aerogel microspheres were filled with acrylic emulsion, a curing agent was added into the mixture and stirred, and the mixture was filled into the mold and dried at room temperature for 2 days. Then, the sample of silica aerogel thermal insulation coatings was obtained. Commercially available acrylic emulsion and additives, such as wetting agents, dispersing agents, antifoaming agents, thickener, and curing agent, were used to prepare the coatings. The dosages of additives were less than 0.3 wt % of the total weight of the coating.

2.3 Characterization

The stacking density of silica aerogel microspheres was measured on the basis of weight and volume. The average sizes of aerogel microspheres were evaluated by using a laser particle detector (Micro S3000), and the particle size distribution was recorded. The microstructure of the coating and the distribution of the microspheres in the coating were investigated through SEM (JSM 7500F). The thermal conductivities of coatings were measured by a transient plane source method using the Hot Disk TPS 2500 s thermal conductivity measurement equipment. The size of the sample was

5 mm × 50 mm × 50 mm. The thermal conductivity was calculated by using built-in formulas, and the thermal environment temperature was defined at 21 °C.

3 Results and Discussions

3.1 SEM Photographs of the Coating

3.1.1 Microstructure of the Coating with Various Volume Fractions of Silica Aerogel Microspheres

The coatings with various volume fractions of silica aerogel microspheres were prepared by changing the content of silica aerogel microspheres, and the microstructures of the coatings were observed through SEM.

The microstructures of the coatings with various volume fractions of hydrophobic silica aerogel microspheres are shown in Fig. 1. Aggregations of aerogel microspheres appeared in the coating, especially when the volume fraction of silica aerogel microspheres was low. The significant aggregations were caused by the compatibility between silica aerogel microspheres and polymer in the acrylic emulsion. In this experiment, the microspheres treated by TMCS had excellent hydrophobic property [12], making them difficult to be coated by the hydrophilic polymer and resulting in the occurrence of aggregations. However, the initial aggregations were replaced by a complete accumulation of microspheres in the coating at high volume fractions because of the increase of silica aerogel microspheres, as shown in Fig. 1c, d, and e. In particular, dense accumulation of silica aerogel microspheres appeared when the volume fraction of the silica aerogel reached 70 %, as shown in Fig. 1f.

Figure 1 shows the occurrence of macropores in the coatings because of water evaporation and polymer shrinkage. The formation of pores is related to the increase of silica aerogel volume faction. At low volume fractions, the microspheres or aggregations could be wrapped by polymer. However, the polymer cannot fill the pores of silica aerogel microspheres at high volume fractions. After the curing of polymer, the water evaporated, and macropores remained in the coating.

3.1.2 Coatings with Different Sizes of Silica Aerogel Microspheres

In this research, silica aerogel microspheres of different sizes were prepared by changing the nozzles during atomization [13]. Two sizes of silica aerogel microspheres were filled with acrylic emulsion, and the dispersion of microspheres was investigated through SEM.

The distribution of silica aerogel microspheres in the coating is shown in Fig. 2. SEM photographs showed that significant aggregations appeared in the coating with 24 μm size microspheres, whereas no aggregations appeared in the coating with 49 μm microspheres. This condition implied that large microspheres had better dispersion in the coating. For hydrophobic silica aerogel microspheres, small particles had higher surface energy than large particles because of their larger special surface areas, making it easier for large silica aerogel microspheres to be covered with the polymer than small

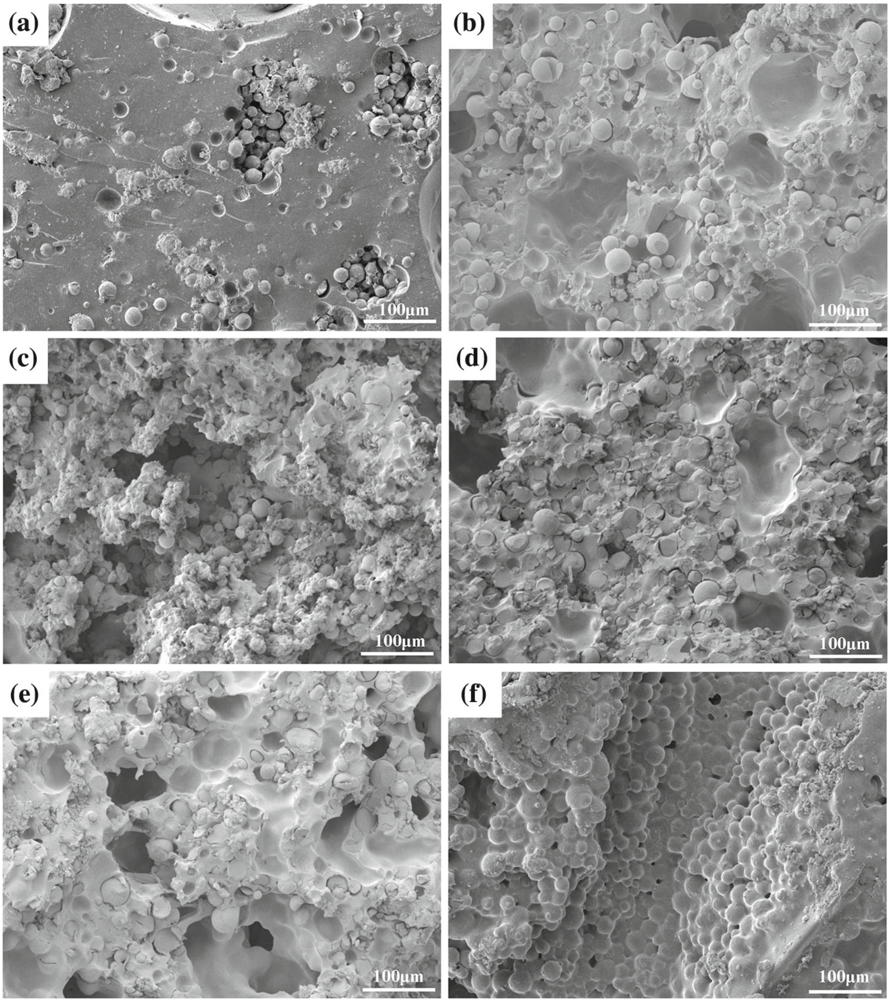

Fig. 1 SEM photographs of the coating (a, b, c, d, e, and f represent 20 %, 30 %, 40 %, 50 %, 60 %, and 70 % volume fractions of aerogel microspheres in the coating, respectively)

microspheres during the preparation of coatings. Then, after the curing of polymer, good dispersibility appeared in the coating with large silica aerogel microspheres, whereas agglomeration occurred in the coating with small microspheres.

3.1.3 Interface of Silica Aerogel Microspheres and Polymer in the Coating

In this research, silica aerogel microspheres were treated with TMCS. The original hydrophilic groups on the silica aerogel were substituted by the hydrophobic groups, such as $–CH_3$ and $–CH_2CH_3$. A wetting agent was added into the coating to investigate the effect of the interface on thermal conductivity. In addition, a coating without wetting agent was prepared for comparison in this experiment.

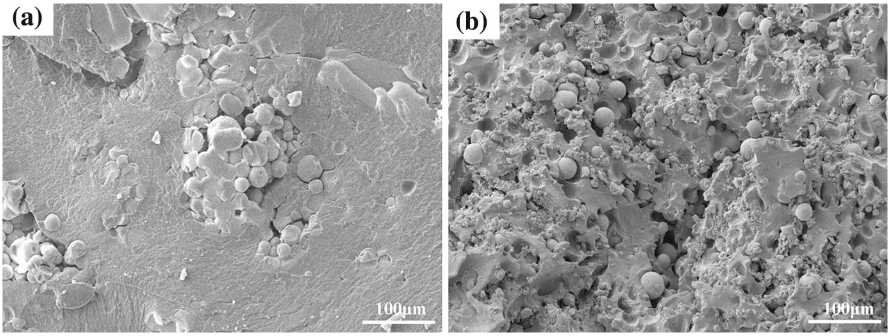

Fig. 2 Distributions of microspheres in the coatings (a and b represent the coatings with silica aerogel microspheres with average sizes of 24 and 49 μm, respectively)

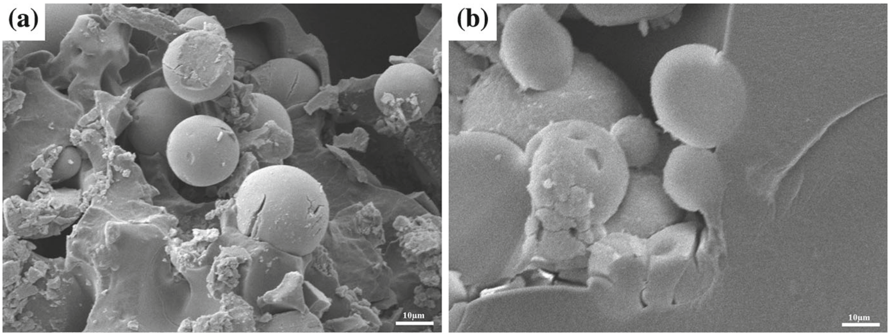

Fig. 3 Interfaces of the coatings (a and b represent the coating without and with wetting agent, respectively)

The interfaces of the coatings with and without wetting agent are shown in Fig. 3. A poor interfacial compatibility was observed in the coating without wetting agent, as shown in the SEM photograph. Obvious gaps existed at the interface between the silica aerogel microspheres and polymer. Some microspheres dropped off from the polymer. The perfect combination of silica aerogel microspheres and polymer was observed in the coating with wetting agent. This condition indicated that the wetting agent improved the compatibility of hydrophobic microspheres and polymer [14].

3.2 Thermal Conductivities of the Coatings

3.2.1 Thermal Conductivities of Coatings with Different Volume Fractions of Silica Aerogel Microspheres

Figure 4 shows the change of thermal conductivities of the coatings with the increasing volume fraction of silica aerogel microspheres. The thermal conductivity slowly decreased when the volume fraction was lower than 30 % because of the aggregations in the coating. The mechanism was that the heat cannot transfer through the silica aerogel because of the excellent thermal insulation property of silica aerogel

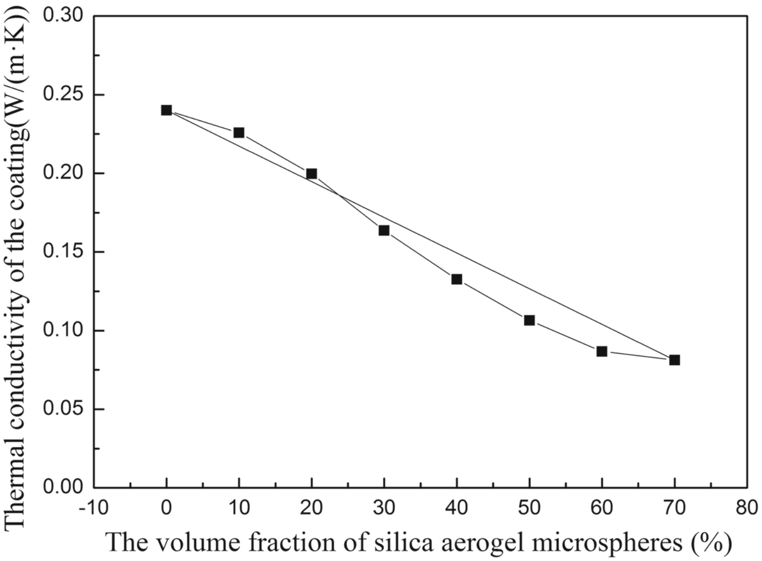

Fig. 4 Thermal conductivities of coatings with various volume fractions of silica aerogel microspheres

microspheres. Most of the heat went through the polymer, which possessed low thermal resistance. When the aggregations appeared in the coating, the length of the heat path was seriously shortened compared with that when the silica aerogel microspheres were uniformly dispersed in the coating. Correspondingly, the thermal resistance of the coating was reduced, and the thermal conductivity of the coating became high. Thus, the aggregations prevented the decline of the composite coating with the increasing volume fraction of silica aerogel. The thermal conductivity rapidly decreased when the volume fraction was higher than 30 %. The pores in the coating, which increased with the rise of the volume fractions of silica aerogel, reduced the thermal conductivity of the coating because the air in the pores had low thermal conductivity of approximately 0.023 W·(m·K)$^{-1}$.

3.2.2 Thermal Conductivities of the Coatings with Different Densities of Silica Aerogel Microspheres

Silica aerogel was prepared by sol–gel method with TEOS as the silicon source and ethanol as the solvent [15–17]. In the reaction, the ethanol increased the distance between the reactants and reduced the hydrolysis reaction rate of TEOS. The density of silica aerogel was adjusted by changing the proportion of ethanol in the raw materials. In this experiment, three silica aerogel microspheres with different densities were prepared with molar ratios of TEOS, water, and ethanol as 1:4:4, 1:4:7, and 1:4:10. The results are listed in Table 1.

Silica aerogel microspheres with three different densities were filled with the polymer to prepare the thermal insulation coating. The thermal conductivities of the coatings are shown in Fig. 5. As shown in Fig. 5, the thermal conductivity of the

Table 1 Density of silica aerogel microspheres

TEOS:water:ethanol (mol)	Density (g·cm^{-3})
1:4:4	0.23
1:4:7	0.18
1:4:10	0.15

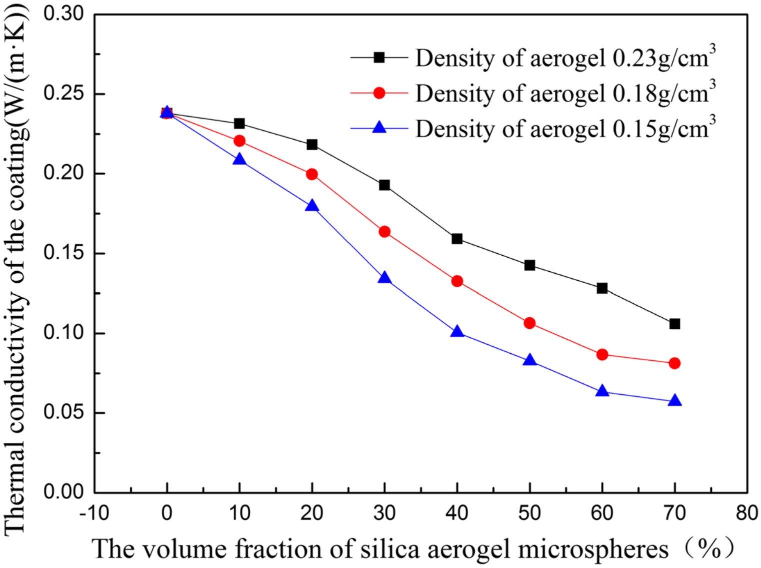

Fig. 5 Thermal conductivities of the coatings with different densities of silica aerogel microspheres

coating decreased with the declining density of silica aerogel microspheres. The coating with 0.15 g·cm^{-3} silica aerogel microspheres had the lowest thermal conductivity. The difference of thermal conductivity increased with the increasing volume fraction of silica aerogel microspheres. At 10 % volume fraction, the difference of thermal conductivities between the coatings with 0.23 and 0.18 g·cm^{-3} silica aerogel microspheres was approximately 0.01 W·(m·K)$^{-1}$, whereas at 60 % volume fraction, the difference was approximately 0.04 W·(m·K)$^{-1}$. Thus, the density of silica aerogel microspheres had an important influence on the thermal conductivity of the coating, especially at high volume fractions.

A reasonable explanation should be given to interpret the difference. The thermal insulation property of silica aerogel is attributed to its unique nanoporous structure. The gas molecules are fixed into the nanopores of silica aerogel, and the heat-transfer efficiency during the collision between gas molecules is reduced when the heat flux goes through the silica aerogel. The larger the number of nanopores per unit volume, the lower the thermal conductivity of silica aerogel. In other words, the increase of porosity improves the thermal insulation performance of silica aerogel.

On the basis of the structural characteristics of silica aerogel, a fixed relationship between the porosity and density is given as follows:

$$\phi = \left(1 - \frac{\rho}{\rho_s}\right) \times 100\% \tag{1}$$

where ϕ and ρ represent the porosity and density of silica aerogel, respectively, and ρ_s represents the density of the silica matrix. As shown in Formula 1, porosity increases with the declining density of silica aerogel microspheres. Ping et al. [18] discussed the relationship between the density and thermal conductivity of silica aerogel. An approximate formula for the thermal conductivity of silica aerogel was given as follows [19]:

$$\lambda = \frac{\lambda_1 \lambda_2 \rho_s}{\lambda_1 \rho_s - (\lambda_1 - \lambda_2)\rho} \tag{2}$$

where λ_1 and λ_2 represent the thermal conductivities of silica matrix and air, respectively, and are constant. As shown in Formula 2, the thermal insulation performance of silica aerogel improves with the declining density. Thus, the thermal conductivity of the coating decreases with the improvement of the thermal insulation performance of silica aerogel microspheres.

3.2.3 Thermal Conductivities of the Coatings with Different Sizes of Silica Aerogel Microspheres

Three curves represented the change of thermal conductivities with the size of silica aerogel microspheres, as shown in Fig. 6. The thermal conductivity of the coating with 49 μm microspheres was lower than that of the coating with 24 μm microspheres when the volume fraction of silica aerogel microspheres ranged from 0 % to 30 %. This is because there were more aggregations in the coating with 24 μm microspheres than those with 49 μm microspheres, as shown in Fig. 2. The aggregations reduced the thermal resistance, as analyzed in Sect. 2.2.1. The thermal conductivity of the coating with 24 μm microspheres was lower than that of the coating with 49 μm microspheres when the volume fraction ranged from 30 % to 70 %. This result was attributed to the change of the microstructure of the coating. At high volume fractions (60 % to 70 %), the thermal conductivity of the coating with 24 μm silica aerogel microspheres was lower that that of 49 μm microspheres, aggregations disappeared, and a complete accumulation of microspheres occurred in the coating, enabling silica aerogel microspheres to overcome the polymer and coating. The thermal resistance of the coatings was equal at the same time. However, the interfacial thermal resistance, which was considered an important factor in the study of the thermal conductivity of composites, especially at high volume fraction, was ignored. The interfacial thermal resistance was closely related to the sizes of silica aerogel microspheres [20–22]. The interfacial thermal resistance of small particles was larger than that of large particles because of their higher special surface areas. Thus, the thermal conductivity of the coating with 24 μm silica aerogel microspheres was lower than that with 49 μm microspheres when the volume fraction ranged from 60 % to 70 %.

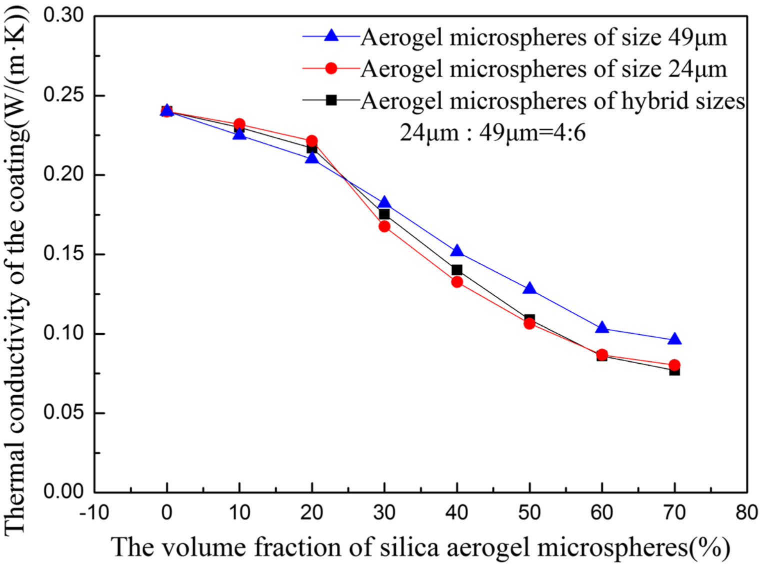

Fig. 6 Thermal conductivities of the coatings with different sizes of silica aerogel microspheres

In this experiment, hybrid silica aerogel microspheres were prepared by mixing 24 and 49 μm microspheres at the volume ratio of 4:6. They were filled with acrylic emulsion to prepare the thermal insulation coating. The thermal conductivities of the coatings are shown in Fig. 6. As shown in Fig. 6, the thermal conductivity of the coating with hybrid microspheres was lower than that with 49 μm microspheres and higher than that with 24 μm microspheres when the volume fraction ranged from 0 % to 30 %. By contrast, the condition was opposite when the volume fraction ranged from 30 % to 50 %. The aggregations had important influence when the volume fraction ranged from 0 % to 30 %, and the interfacial thermal resistance became the key factor when the volume fraction ranged from 30 % to 50 %. However, the difference of thermal conductivities between the coatings with 24 μm microspheres and those with hybrid microspheres rapidly decreased when the volume fraction ranged from 50 % to 70 %. At 70 % volume fraction, the thermal conductivity of the coating with hybrid microspheres was lower than that with 24 μm microspheres. This unexpected phenomenon was because of the mixture of different sizes of microspheres, which increased the stacking density of silica aerogel microspheres in the coatings at high volume fractions.

3.2.4 Thermal Conductivities of the Coatings with Different Interfaces

The thermal conductivities of the coatings with and without wetting agents are shown in Fig. 7. The volume fraction of silica aerogel microspheres in the coating without wetting agent did not exceed 40 %. This condition was because of the hydrophobic property of silica aerogel microspheres, which prevented them to be wetted. By contrast, the volume fraction of silica aerogel microspheres in the coating with wetting

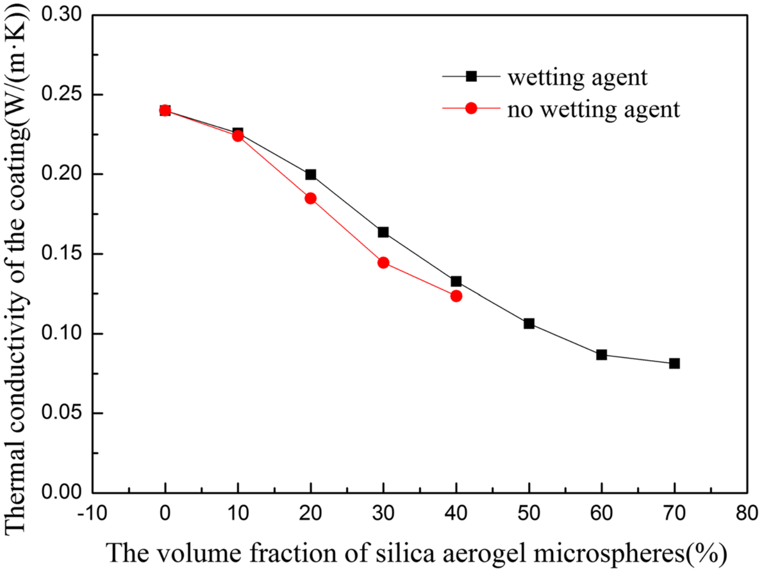

Fig. 7 Thermal conductivities of the coatings with and without wetting agent

agent reached 70 %. Obviously, the surface tension of silica aerogel microspheres was reduced by the wetting agent. The difference of thermal conductivities was caused by the pores when the volume fraction ranged from 0 % to 40 %, which reduced the thermal conductivities of the coatings because of the air they contained.

4 Conclusions

In this study, the thermal insulation coatings were prepared using hydrophobic silica aerogel microspheres, and the factors of the thermal conductivity of the coatings, including the volume fractions, densities, sizes, interfaces of silica aerogel microspheres, and the interface of the composite, were discussed.

1. The thermal conductivity slowly decreased when the volume fraction was lower than 30 % because of the aggregations in the coating. This condition was because the aggregations in the coatings increased the thermal conductivity by extending the length of the heat-transfer path compared with the uniformly dispersed silica aerogel microspheres. However, the thermal conductivity rapidly decreased when the volume fraction was higher than 30 %. This condition was because the pores in the coating increased with the increasing volume fraction of the microspheres, which reduced the thermal conductivity of the coating.
2. The thermal conductivity of the coating decreased with the declining density of silica aerogel microspheres because the porosity of silica aerogel increased with the decline of the density, which improved the thermal insulation performance of silica aerogel.

3. At low volume fractions, the thermal conductivity of the coating with small silica aerogel microspheres was higher than that with large microspheres because the aggregations easily formed with small particles. At high volume fractions, the thermal conductivity of the coating with small microspheres was lower than that with large microspheres because of the larger interfacial thermal resistance of the former. The thermal conductivity of the coating with hybrid silica aerogel microspheres decreased with the increasing stacking density of the microspheres and the porosity of the coating.
4. Wetting agents improved the interfacial compatibility of hydrophobic silica aerogel microspheres and the polymer, which improved the volume fraction of silica aerogel microspheres and reduced the thermal conductivity of the coating.

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