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Aramid fibers reinforced silica aerogel composites with low thermal conductivity and improved mechanical performance

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Abstract

Aramid fibers reinforced silica aerogel composites (AF/aerogels) for thermal insulation were prepared successfully under ambient pressure drying. The microstructure showed that the aramid fibers were inlaid in the aerogel matrix, acting as the supporting skeletons, to strengthen the aerogel matrix. FTIR revealed AF/aerogels was physical combination between aramid fibers and aerogel matrix without chemical bonds. The as prepared AF/aerogels possessed extremely low thermal conductivity of 0.0227 ± 0.0007 W·m⁻¹·K⁻¹ with the fiber content ranging from 1.5% to 6.6%. Due to the softness, low density and remarkable mechanical strength of aramid fibers and the layered structure of the fiber distribution, the AF/aerogels presented nice elasticity and flexibility. TG-DSC indicated the thermal stability reaching approximately 290 °C, can meet the general usage conditions, which was mainly depended on the pure silica aerogels. From mentioned above, AF/aerogels present huge application prospects in heat preservation field, especially in piping insulation.

Keywords

A. Aramid fibers; A. Nanocomposites; B. Mechanical properties; B. Thermal properties

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1. Introduction

Aerogels are fascinating solid materials made up with over 95% air and less than 5% skeletons [1]. With the advantages of an extremely low density of 0.003-0.5 g·cm⁻³, a low thermal conductivity of 0.017-0.021 W·m⁻¹·K⁻¹ and a high specific surface area of 500-1200 m²·g⁻¹ [1-3], aerogels have enormous application potential in various fields, such as thermal insulators, energy conservation, catalyst supports, biomedical engineering and aerospace applications [3-9]. However, the actual aerogel applications have been hindered seriously due to the inherent low density and fragility which also complicate handling or processing aerogels without catastrophic fracture.

Therefore, improving mechanical properties of aerogels is the foundation for potential applications. For this purpose, extensive efforts have been made. In general, two primary strategies for mechanically reinforcing aerogels are: (i) strengthening skeletons of aerogels using nanoengineering and (ii) developing aerogel composites. For strengthening aerogel skeletons, organic polymers, usually as reinforcing agents, are applied to the “necks” between nano-particles in the aggregate structure of aerogels [10]. Leventis’s group [11-14], Randall et al. [3], Nguyen et al. [15], etc., made an excellent research on this aspect. Besides, using surface initiated atom transfer radical polymerizations to prepare mechanically robust aerogels was achieved [16]. For developing aerogel composites, growing interests concentrated on the multiphase composites in the form of X/aerogels (X represents the reinforcements in aerogel composites). In this respect, polyvinyl alcohol/silica aerogels (PVA/silica aerogels) [17], polyimide/silica aerogels [18], ZrO₂/silica aerogels [19], etc., for silica aerogel composites and epoxy/graphene aerogels [20], PVA/cellulose nanofibrils/graphene oxide nanosheets aerogels [21], carbon fibers/carbon aerogels [22], etc., for carbon
aerogel composites were investigated extensively. Furthermore, carbon nanotube sponges were synthesized, as a type of soft aerogel, achieving a high flexibility [23].

Actually, due to the inexpensive silicon source, silica aerogels have been studied and used at the earliest which is now expected to have a wide variety applications especially in super-thermal insulators. The same issue of the fragility and low strength is still confronted. According to a lot of research and the practice, using fibers as reinforcements to generate fibers/silica aerogel composites is one of the most frequent and effective way to solve the fragility nature of silica aerogels. For fibers/silica aerogels, most of the selected reinforcements concentrate on inorganic fibers, mainly including mineral fibers [24], ceramic fibers [25, 26] and glass fibers [27-29]. On this aspect, most researchers focus on the compressive strength of the aerogel composites with neglecting the requirement of flexibility. However, the specific flexibility requirement for some actual applications is pretty common, especially in piping insulation. The addition of inorganic fibers indeed improves the compressive strength, but does nothing to improve the flexibility owing to the brittleness of inorganic fibers themselves which are not suitable for bearing flexural stress. Simultaneously, due to a larger density of the inorganic fibers, the obtained composites usually sacrifice the advantages of low density and low thermal conductivity unexpectedly [24, 30].

To data, adopting flexile organic fibers as reinforcements is rarely reported. The most important parameter for choosing organic fibers is thermal stability which should be higher than that of pure silica aerogels, about 300 ~ 330 °C for tetraethoxysilane (TEOS) based aerogels [31-33]. As it is known, aramid fibers are an excellent organic fibers with a low density, a low thermal conductivity and a high mechanical strength which are usually used as reinforcements. Above all, the pyrolysis temperature in air of
aramid fibers reaches up to 430 ~ 480°C according to the technical manual of Kevlar, a type of aramid fiber produced by DuPont, which can easily satisfy the choice criterion. So aramid fibers were chose as reinforcements and TEOS were used as precursor in this research respectively at last.

In this paper, aramid fibers reinforced silica aerogel composites (AF/aerogels) were fabricated via ambient pressure drying (APD) which showed the integrated, crack-free appearance and the significant flexibility. Mechanically reinforced AF/aerogels improved both the compressive strength and flexural strength of silica aerogels and avoided impairing the inherent excellent properties of silica aerogels simultaneously. The aramid fiber distribution, pore structure, pore size distribution (PSD), chemical properties, dimensions, density, porosity, mechanical properties and thermal properties were discussed in detail.

2. Experimental section

2.1. Raw materials

Aramid fibers in excess of 10 cm were KEVLAR®-49, DuPont™, used as reinforcements. A fiber opening machine was used to make the aramid fibers fluffy which were subsequently pressed to form aramid fiber layers and then tailored the size to fit the mould. TEOS used in the experiments were chemical pure grade which were purchased from Sigma-Aldrich (USA). Other chemicals including ethanol (EtOH), n-hexane, hydrochloric acid (37%) and ammonia (27%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC, China). Deionized water was used to prepare 0.1 mol/L HCl (aq) and 0.5 mol/L NH₃·H₂O (aq) which were used as the acid and base catalysts, respectively.
2.2. Preparation of AF/aerogels

TEOS, EtOH, H₂O and 0.1 mol/L HCl (aq) were mixed together stirring for 10 min in a beaker. After sufficient hydrolysis in a 45 °C water bath for 12 h, 0.5 mol/L NH₃·H₂O (aq) was added into the precursor mixed solution and stirred for 10 min. The molar ratio of TEOS: EtOH: H₂O: HCl: NH₃·H₂O was fixed at 1:9.6:2.16:1.6×10⁻³:9.7×10⁻³. The obtained alcosol was poured into the rectangular mould with the size of 87 mm ×57 mm ×25 mm (Length × Width × Thickness) and aramid fiber layers were added into the alcosol with a layer by layer subsequently along the length of the mould. Then the mould was made air-tight to perform condensation and the gelation generally occurred in 30 min. The generated AF/alcolegs were aged with EtOH for 12 h, exchanged with n-hexane for 12 h and surface modification with TMCS/n-hexane solution for 12 h in turn, respectively. At last, the wet AF/alcolegs were dried under ambient pressure at 80 °C and 100 °C for 8 h, respectively, to get the AF/aerogels. The composites with various fiber content (denoted as FC) were prepared for performance characterization.

2.3. Methods of characterization

The microstructure of the composite was observed by field emission scanning electron microscope (SEM, SIRION200, FEI). Several surfaces derived from various directions of the composites were taken as specimens to survey the microstructure and fiber distribution. Furthermore, the nanoporous structure of the pure silica aerogels prepared with the same recipe were studied by nitrogen adsorption-desorption test, measured at 77 K using a Tristar II 3020M analyzer (Micromeritics, USA). Pore parameters of silica aerogels were calculated using the Brunauer–Emmitt–Teller (BET) analytical method. FTIR (Nicolet 8700, TFS) was employed to study the chemical
bonds of the samples. Electronic dynamic and static fatigue testing machine (E3000K8953, Intron) was used for mechanical property test at room temperature including uniaxial compression tests and three-point bending tests. Considering the possible mechanical damage when handling or processing the test specimens, the as-prepared rectangular AF/aerogels specimens with the size of 85 mm ×55 mm ×10 mm were used for three-point bending tests while the specially prepared cylindrical AF/aerogels specimens with the size of Φ48 mm ×12 mm were used for uniaxial compression tests. For each specific FC, more than three specimens were tested and the average values were regarded as the final test results. The thermal conductivity of the composites was measured with a thermal constants analyzer (Hot-Disk 2500, Sweden) at 25 °C. The thermal stability analysis was tested using TG-DSC (SDT Q600, TA) with a heating rate of 10 °C/min from room temperature to 800 °C in air.

3. Results and discussion

3.1. Structure analysis

Fig. 1a shows a single aramid fiber with the diameter of approximately 13 μm. It is known that the size of nanoparticles in silica aerogels ranges from 2 nm to 5 nm [1] which is much smaller than that of aramid fibers. So broad cylindrical side of aramid fibers provides beddings for nanoparticles to attach. Fig. 1b presents that the aramid fibers are inset in the aerogel matrix acting as reinforcements. Although the fibers distribute disorderly in the aerogel matrix, the fibers still present directionality to some extent. Namely, the fibers along the L axis are much more than the fibers along the W axis and the fibers along the T axis are the least. Meanwhile, the fiber distribution presents a layered structure as shown in Fig. 1c, marking with different color arrows. Though it is not uniform, fibers gather in various layers obviously. This is caused by the
preparation technology of AF/aerogels. Due to the pretreatment on the aramid fibers, most of the aramid fibers in an aramid fiber layer distributed in the layer plane, only with a few perpendicular to the layer plane. Furthermore, aramid fiber layers were paved into sols a layer by layer along the length. So most part of the fibers keep lying in a layer and it is hardly to see the fibers perpendicular to a layer.

Fig. 2a shows a single aramid fiber stretching out of the aerogel matrix with one end wrapped around a block of aerogels. Seen from the bonding interface between the aerogel matrix and fibers, the two phases combine tightly. The more microcosmic structure is showed in Fig. 2b that the aramid fiber is wrapped by an aerogel lamella which consists of the porous and continuous nanoparticles revealed in Fig. 2d. The formed aerogel lamella affords the foundation for the growth of aerogel network in aerogel matrix. The 3-D nanoporous network of the aerogel block is presented in Fig. 2c which represent the microstructure of the aerogel matrix. And it is simultaneously demonstrated that the introduction of fibers does not change the porous structure of the aerogel matrix.

In Fig. 3a, the adsorption-desorption isotherms of the aerogel matrix are of type IV, belonging to mesoporous materials and the hysteresis loops of type H3 indicating the probable presence of slit-like interparticle pores [34] which can be verified in Fig. 2a. Fig. 3b reveals the most probable pore diameter is approximately 9 nm demonstrating that the diameter of most pores ranges between 6~12 nm which belongs to the PSD region of mesoporous materials. Detailed pore parameters are given in Table 1.

3.2. Dimensions, density and porosity

Fig. 4 shows the variations of the length, width, thickness, volume and mass with the increasing fiber content. It is distinct that with the fiber content increasing, the
length and width obey exponential growth while the thickness complies with linear growth in Fig. 4a. The fitted equations for length, width, thickness are listed as follow.

\[ L = 85.87 - 15.43e^{-0.72FC} \quad (1) \]
\[ W = 55.86 - 5.59e^{-0.46FC} \quad (2) \]
\[ T = 9.73 + 0.22FC \quad (3) \]

In which, \( FC \) is the fiber content. \( L, W \) and \( T \) are the length, width, thickness, of the AF/aerogels, respectively. With the \( FC \) increasing, the length, width and thickness of the composites all increase while the increasing rates of the length and width slow down as it is seen in Fig. 4a. When \( FC \geq 6.0\% \), the length and width nearly do not increase any more while the thickness still keeps linear growth. Since the aramid fibers are added into the aerogel matrix, they not only resist the lateral compressive stresses during APD but also act as the supporting skeletons, both of which contribute to reducing the volume shrinkage. The increase in fiber content leads to the increasing volume and mass, as shown in Fig. 4b. However, the increase of mass can be neglected because of the low density of aramid fiber itself and a smaller content in the AF/aerogels. At last, the density of the AF/aerogels is mainly depended on the volume.

Fig. 5 shows, as \( FC \) increases, the density decreases to about 0.14 g·cm\(^{-3}\) in accordance with negative exponent, and it almost keeps invariant with further increasing. The porosity presents an opposite trend with increasing to the maximum of approximately 84\%. The fitted equations for porosity and density are listed as follow.

\[ P = 83.87 - 4.55e^{-0.48FC} \quad (4) \]
\[ \rho = 0.14 + 0.04e^{-0.48FC} \quad (5) \]

In which, \( P, \rho \) are the porosity and density of the AF/aerogels, respectively. In the preparation process, the added aramid fibers should be guaranteed of immersing in the sols. When \( FC \rightarrow 8\% \), fibers are already hard to immerge into the sols, namely, \( FC \)
reaches the maximum limit. At this moment, $L_{\text{max}} = 85.82\text{mm}$, $W_{\text{max}} = 55.72\text{mm}$, $T_{\text{max}} = 11.49\text{mm}$, $\rho_{\text{min}} = 0.14g\cdot\text{cm}^{-3}$ and $P_{\text{max}} = 83.77\%$.

In order to state the effects of incorporating aramid fibers concisely, a matrix unit is taken out from a lamina of AF/aerogels for force analysis, as presented in Fig. 6. It is all known that huge lateral compressive stress is the direct inducement of the collapse of the gel network during APD. In the shrinkage process, the matrix unit shrinks towards an assumed contraction center which is marked in the center of the lamina. As referred before, fibers and aerogel matrix have a well interfacial bonding, as shown in Fig. 2a. So the shrinkage towards the center has to conquer the adhesive forces between aramid fibers and aerogel matrix and resistance from the introducing aramid fibers. To be specific, as presented in Fig. 6 (a), the adhesive forces and resistance in the lamina plane can be divided into tensile stress, $\sigma_{11}$, and thrust, $\sigma_{12}$, produced by the fibers along the width and two shear stresses, $\tau_{1}$ and $\tau_{2}$, induced by the fibers along the length, respectively. Out of the lamina plane, the resistance along the thickness mainly derives from the adhesive force between aerogel matrix and fibers, as shown in Fig. 6 (b), corresponding to four shear stresses, i.e., $\tau_{13}$, $\tau_{12}$, $\tau_{33}$ and $\tau_{34}$. All of these resistance hinder the aerogel matrix’s shrinkage. As the fiber content increases, more fibers crowd into the aerogel matrix leading to an increasing resistance which contributes to resisting the volume shrinkage.

With the further increase of fiber content, the increasing rates of length and width inversely decrease, approaching to zero gradually, which indicates that the resistance reaches to the maximum and more fibers can not play an increasing effect on resisting the volume shrinkage any more. Due to this changing process, the length and width both present exponential growth at last. On account of the quantitative superiority on length,
the growth rate of the length is larger than that of the width at the same fiber content. The resistance in the thickness mostly depends on the quantity of aramid fibers. As the aramid fibers increase, the resistance in the thickness also increases, resulting in the thickness keeping a steady increasing rate with the fiber content, i.e., a linear growth.

3.3. Chemical properties

FTIR spectrums of the aramid fiber, silica aerogel and AF/aerogels are depicted in Fig. 7. In FTIR spectra of the silica aerogel, the absorption region from 1100 cm\(^{-1}\) to 1000 cm\(^{-1}\) is the prominent peak corresponding to the asymmetric and symmetric modes of silicon dioxide [35]. The faint peak around 1632 cm\(^{-1}\) and the broad absorption band around 3444 cm\(^{-1}\) are due to the Si-OH groups [33]. The observed peak around 2963 cm\(^{-1}\) is due to the stretching and bending of C-H bonds [36] while the Si-C peaks at 1258 cm\(^{-1}\), 847 cm\(^{-1}\) and 758 cm\(^{-1}\) are due to the Si-(CH\(_3\))\(_3\) groups modified by TMCS which contains three non-hydrolysable -CH\(_3\) groups [30, 36]. In FTIR spectra of the aramid fiber, the broad absorption peak at 3318 cm\(^{-1}\) is attributed to the N-H group [37] while the observed peaks at 1653 cm\(^{-1}\), 1539 cm\(^{-1}\) and 1307 cm\(^{-1}\) respectively correspond to the amide I band (stretching vibration of C=O bond), amide II band (coupling between stretching vibration of C-N bond and bending vibration of N-H bond) and amide III band (coupling among C-N bond, N-H bond and C-C bond vibrations) [38]. The inconspicuous peak around 2929 cm\(^{-1}\) and 2849 cm\(^{-1}\) are due to the stretching vibrations of methylene and methyl groups respectively [37].

The FTIR spectra of the aramid fiber pulled out from the composite reveals the chemical composition of the AF/aerogels. From FTIR spectra of the composite, the peaks at 3318 cm\(^{-1}\), 2929 cm\(^{-1}\), 2849 cm\(^{-1}\), 1653 cm\(^{-1}\), 1539 cm\(^{-1}\) and 1307 cm\(^{-1}\) are all observed on the FTIR spectra of pure aramid fibers and the two FTIR spectrograms are
almost the same. No significant new peak is appeared on FTIR spectra of the composite. The FTIR spectra analysis demonstrates that the composite is just a physical combination of aramid fibers and silica aerogels [39]. In spite of no chemical bonds existing, the favorable interfacial adhesion is still formed which is probably maintained by the Van der Waals' force between the two phases.

3.4. Mechanical properties

Fig. 8 describes a typical uniaxial compression stress-strain curve of AF/aerogels. The whole loading compression process can be divided into three parts: the contact stage, the linear stage and the elastic-plastic stage. The contact stage mainly concentrates on the strain below 20% which is caused by the unsmooth surface of the tested specimen. As it is, the compression bar could not press on the entire composite surface initially and the two surfaces contact closely with the increasing load during this stage. The linear stage distributes over the strain being 20% to 30%, with an almost fixed slope. The linear stage presents the elasticity of AF/aerogels which is derived from the aerogel matrix and fiber layers alternating in AF/aerogels caused by the layered structure. During the linear stage, the main load bearing part is ascribed to the open nanopores of silica aerogels [26] while the fibers act as supporting skeletons to maintain the integrity of AF/aerogels. The elastic-plastic stage mainly concentrates on the strain above 30% which is the mixture of the yield stage and the densification stage. At this stage, the stress rises rapidly with the increasing strain, during which the aerogel matrix and fibers resist the compressive stress together.

The uniaxial compression tests including loading and unloading of the AF/aerogels with various FC are shown in Fig. 9. All of the stress-strain curves can be divided into three parts. From the inset, the strain from 25% to 30% present preferable linearity
corresponding to the linear stage. Further analytical data including $\sigma_{25\%}$ and $\sigma_{30\%}$ corresponding to the compressive stress at 25\% and 30\% strain, and the elastic modulus calculated from $\varepsilon_{25\%}$ to $\varepsilon_{30\%}$ are presented in Table 2. As the FC increases, $\sigma_{25\%}$, $\sigma_{30\%}$ and elastic modulus decrease at first and then increase with the increasing FC, in which the composite shows the best elasticity at FC = 6.04\%. As the FC increases, more fibers are inlaid in the aerogel matrix and play the role of supporting skeletons which contribute to combining each part of the aerogel matrix together and sustaining the integrity of the AF/aerogels. Furthermore, the aramid fiber skeletons disperse and transfer the external force to the whole composite, avoiding stress concentration, which help to conquer the fragility of the aerogel matrix [25]. This effect is gradually enhanced with the FC increasing to 6.04\%. For further increasing FC, more fibers crowd into the aerogel matrix. Under this circumstance, aramid fibers hinder the aerogel matrix from playing the role of the main load bearing part. On the contrary, aramid fibers themselves bear the main external force while silica aerogels in composites only act as fillers. At last, the dense fibers lead the AF/aerogels an increasing rigidity and a decreasing elasticity gradually.

As most of the aramid fibers distributed in the fiber layer plane due to the layered structure, the mechanically reinforced effect on the aerogel matrix leads to an increasing flexural strength. Fig. 10a is the flexural stress-strain curves of the AF/aerogels with various FC. It is clear seen that flexural stress of each curve shows an initial increase until reaching the maximum and then followed by a rapid decline, indicating that the tested specimen has lost its strength, leading to the final material failure. The maximum flexural stress during a bending test is defined as flexural strength, $\sigma_{fM}$, corresponding to the highest point of the flexural stress-strain curve. It is found that the $\sigma_{fM}$
approximates linear growth with the increasing FC, as shown in Fig. 10b. Flexural strain at flexural strength indicates the maximum nominal fractional change in length of the tested specimen at midspan which is denoted as $\varepsilon_{\text{fm}}$. The $\varepsilon_{\text{fm}}$ increase gently and then faster as the FC increases in Fig. 10c, which accords with the dash line through the highest points in Fig. 10a. Flexural modulus expressed in $E_f$, is the ratio of the stress difference to the corresponding strain difference. Fig. 10d shows that $E_f$ approximates linear increase with the increasing FC. Seen from Fig. 10, the three parameters including $\sigma_{\text{fm}}$, $\varepsilon_{\text{fm}}$ and $E_f$, all increase with the increasing FC. As the FC increases, more fibers added into the aerogel matrix to strengthen the entire composite, and the existing layered structure of the fiber distribution, both contribute to improving the flexibility of the AF/aerogels. So during the flexural tests, the flexural strength increases nearly linearly as the FC increases. The flexural strain at flexural strength keeps the same tendency and so does the flexural modulus. Besides, the as-prepared samples even can exhibit an outstanding flexibility by a large deflection bending test. The nice flexural property is just the advantage for the piping insulation.

3.5. Thermal properties

Before the FC reaching 4.1% in Fig. 11, the thermal conductivity fluctuates around 0.0224 W·m$^{-1}$·K$^{-1}$ and then increases slightly with the FC rising up. As aramid fibers are added into the aerogel matrix, not only the network is reinforced but also more heat transfer passageways are provided by the increasing fibers. So more heat transfers through aramid fibers instead of the aerogel matrix which leads to an increasing thermal conductivity. In spite of this, the distribution of fibers lying in the layer plane greatly diminishes the heat transfer passageways compared to the fibers perpendicular to the layer plane when subjecting a heat flux commonly perpendicular to the layer plane in
AF/aerogels. As presented in Fig. 11, the thermal conductivity of AF/aerogels with the maximal FC being 6.6% is just 0.0026 W·m⁻¹·K⁻¹ larger than that of the compact pure silica aerogel powder. Actually, the thermal conductivity of AF/aerogels possess extremely low thermal conductivity of 0.0227 ± 0.0007 W·m⁻¹·K⁻¹ with FC ranging from 1.5% to 6.6% which even does not exceed the thermal conductivity of still air at 25 °C. The outstanding characteristic of low thermal conductivity of AF/aerogels present the huge application prospects in the field of heat insulation.

Fig. 12 shows the TG-DSC analysis of the typical AF/aerogels and pure silica aerogels. The whole processes of weight loss can be separated into two parts for pure silica aerogels and three parts for AF/aerogels respectively, which have been labeled in Fig. 12. For the pure silica aerogels in Fig. 12a, there is a negligible weight loss from 50 °C to 270 °C in Part I, declaring the evaporation of water and the remained organic solvent in the AF/aerogels. The main weight loss in Part II is considered to be the oxidation of ≡Si-CH₃ groups on the aerogel surface which results in the primary exothermic peak [40]. For the AF/aerogels in Fig. 12b, the Part I is almost the same as the pure silica aerogels. In Part II, the main weight loss between 288 °C and 418 °C is also ascribed to the oxidation of ≡Si-CH₃ groups on the silica aerogel which leads to the first exothermic peak. The primary weight loss from 418 °C to 635 °C in Part III is attributed to the thermolysis of aramid fibers and the remained oxidation of ≡Si-CH₃ groups, in which the former causes the second exothermic peak [41].

The beginning temperatures of the two exothermic reactions are denoted as $T_{\text{onset-1}}$ and $T_{\text{onset-2}}$, respectively. The $T_{\text{onset-1}}$ are about 270 °C for the pure silica aerogels and about 288 °C for the AF/aerogels, both of which indicate the beginning temperature of the oxidation of ≡Si-CH₃ groups on the silica aerogels. When exceeding the $T_{\text{onset-1}}$, the
hydrophobicity of the silica aerogels would translate to hydrophilia which results in absorbing the moisture in air and deteriorating with time going by. The $T_{\text{onset-2}}$ is approximately 463 °C which indicates the beginning temperature of the thermolysis of aramid fibers in AF/aerogels. Thus, it can be seen that the thermal stability of the aramid fibers is better than that of the pure silica aerogels. In this regard, the thermal stability of AF/aerogels is mainly depended on the pure silica aerogels. From the TG-DSC analysis, it is revealed that the highest usage temperature of the AF/aerogels is 288 °C which still can satisfy the general environmental conditions of the heat insulation.

3.6. Comparison of various fibers reinforced silica aerogel composites

Table 3 is the physical properties of various fibers reinforced silica aerogel composites. Compared to inorganic fibers reinforced silica aerogel composites, it is clear seen that the as prepared AF/aerogels possess the minimum density and thermal conductivity, approximating to that of pure silica aerogels which indicates the best thermal insulation property. This is because that the aramid fiber itself owns a low density, 1.44 g·cm$^{-3}$, and a low thermal conductivity, $\sim 0.04$ W·m$^{-1}$·K$^{-1}$, which are far lower than that of the inorganic fibers. So the density and thermal conductivity of the AF/aerogels will not increase too much due to the introduced aramid fibers. On the aspect of mechanical property, inorganic fibers reinforced silica aerogel composites can improve the compressive strength and flexural strength higher than AF/aerogels. However, the aramid fibers, as a representative of the organic fibers, are more beneficial to improve the elasticity and flexibility which is demonstrated by a smaller elastic modulus and flexural modulus. For some special use conditions with the requirement of flexibility, organic fibers used as the reinforcements is a better choice.
4. Conclusions

Using flexible organic fibers as reinforcements had been tried out and aramid fibers reinforced silica aerogel composites were prepared successfully via ambient pressure drying. Though AF/aerogels were physical combination between aramid fibers and aerogel matrix, microstructure analysis presented a favorable interfacial adhesion with aramid fibers inlaying in the aerogel matrix and porous nano-structure of aerogels covering on the surface of aramid fibers. On basic parameter aspects, dimensions, porosity and thermal conductivity increased with the fiber content increasing while the density presented an opposite trend. The extremely low thermal conductivity of 0.0227 ± 0.0007 W·m⁻¹·K⁻¹ was obtained and can be adjusted by the fiber content. The softness, low density and remarkable mechanical strength of the aramid fiber itself and the layered structure contributed to improving the elasticity as well as the flexibility, which conquered the bending problem in the thermal insulation application. TG-DSC analysis revealed the thermal stability of AF/aerogels was mainly depended on the pure silica aerogels, reaching up to approximately 288 °C, which can meet the general conditions of usage in heat preservation field.

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References


**Figure Captions**

Fig. 1. A single aramid fiber (a), overall view of the composite (b) and the layered structure of the fiber distribution (c).

Fig. 2. A single aramid fiber in AF/aerogels (a), fiber surface covered with aerogels (b), porous nanostructure of the matrix (c) and aerogel nanoparticles on the fiber surface (d).

Fig. 3 Nitrogen adsorption-desorption isotherms (a) and PSD of the aerogel matrix (b).

Fig. 4. Variation of the dimensions (a), v (b) with the fiber content.

Fig. 5. Variations of the density and porosity with the fiber content.

Fig. 6. An idealized model for AF/aerogels and force analysis of the matrix unit.

Fig. 7. FTIR spectrums of the aramid fiber, silica aerogel and AF/aerogel composite.

Fig. 8. A typical uniaxial compression curve of AF/aerogels.

Fig. 9. Uniaxial compressions of the composites with different FC.

Fig. 10. Flexural stress-strain curves (a), flexure strength (b), flexure strain at flexure
strength (c), and flexure modulus (d) of the composites with the various FC.

Fig. 11. Effect of fiber content on thermal conductivity of the AF/aerogels.

Fig. 12 TG-DSC analysis of the pure silica aerogels (a) and AF/aerogels (b).

Tables

Table 1. Pore parameters of the aerogel matrix.

Table 2. Analytical data of compressive stress-strain curves of the composites.

Table 3. Physical properties of various fibers reinforced silica aerogel composites.

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Fig. 10. Flexural stress-strain curves (a), flexure strength (b), flexure strain at flexure strength (c), and flexure modulus (d) of the composites with the various FC.
Fig. 11. Effect of fiber content on thermal conductivity of the AF/aerogels.

Fig. 12. TG-DSC analysis of the pure silica aerogels (a) and AF/aerogels (b).
Table 1. Pore parameters of the aerogel matrix.

<table>
<thead>
<tr>
<th>Component</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerogel matrix</td>
<td>973.34 ± 9.84</td>
<td>2.13 ± 0.14</td>
<td>8.86 ± 0.31</td>
</tr>
</tbody>
</table>

Table 2. Analytical data of compressive stress-strain curves of the composites.

<table>
<thead>
<tr>
<th>Fiber Content (%)</th>
<th>σ₂₅% (kPa)</th>
<th>σ₃₀% (kPa)</th>
<th>Elastic Modulus (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.58</td>
<td>43.67 ± 3.02</td>
<td>65.56 ± 2.30</td>
<td>437.69 ± 14.41</td>
</tr>
<tr>
<td>3.09</td>
<td>34.52 ± 1.86</td>
<td>55.68 ± 2.95</td>
<td>423.07 ± 21.82</td>
</tr>
<tr>
<td>6.04</td>
<td>19.07 ± 2.06</td>
<td>25.92 ± 1.52</td>
<td>137.06 ± 10.82</td>
</tr>
<tr>
<td>8.76</td>
<td>22.19 ± 1.74</td>
<td>34.58 ± 2.47</td>
<td>247.79 ± 14.63</td>
</tr>
<tr>
<td>11.40</td>
<td>26.19 ± 1.54</td>
<td>43.58 ± 2.44</td>
<td>347.62 ± 18.23</td>
</tr>
<tr>
<td>Reinforcements</td>
<td>Density (g/cm³)</td>
<td>Thermal Conductivity (W·m⁻¹·K⁻¹)</td>
<td>Elastic Modulus (MPa)</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------</td>
<td>-----------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>Pure aerogels [1]</td>
<td>0.10</td>
<td>0.017-0.021</td>
<td>1.00</td>
</tr>
<tr>
<td>Aramid fibers</td>
<td>0.14</td>
<td>0.022</td>
<td>0.14±0.01</td>
</tr>
<tr>
<td>Sepiolite fibers [24]</td>
<td>0.21</td>
<td>0.025</td>
<td>-</td>
</tr>
<tr>
<td>Ceramic fibers [25, 26]</td>
<td>-</td>
<td>-</td>
<td>106</td>
</tr>
<tr>
<td>Glass fibers [27, 28]</td>
<td>0.41</td>
<td>0.025</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.17</td>
<td>0.025</td>
<td>-</td>
</tr>
</tbody>
</table>