**Lightweight, strong, and super-thermal insulating polyimide composite aerogels under high temperature**

Wei Fan, Xiang Zhang, Yi Zhang, Youfang Zhang, Tianxi Liu*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Innovation Center for Textile Science and Technology, Donghua University, 2999 North Renmin Road, Shanghai 201620, PR China

**ABSTRACT**

High-performance thermally insulating materials is highly desirable for many applications in which heat transfer should be strictly restricted. Traditional organic or inorganic insulation materials are limited by either poor thermal stability or mechanical brittleness. Here, SiO₂ nanoparticles crosslinked polyimide aerogels synthesized by one-pot freeze-drying are presented, which show excellent mechanical properties and super-insulating behavior in a wide temperature range. The highly porous structure of the aerogel and nanosized components benefit the significant reduction of thermal conductivity through inhibiting gas conduction and imparting interfacial thermal resistance, respectively. The PI/SiO₂ composite aerogel with a density of 0.07 mg cm⁻³ can achieve a low thermal conductivity of 21.8 mW m⁻¹ K⁻¹, which is lower than the most common super-insulating criterion (25 mW m⁻¹ K⁻¹). More importantly, the PI/SiO₂ aerogel exhibits good thermal insulation performance at elevated temperatures, with a thermal conductivity still lower than 35 mW m⁻¹ K⁻¹ even at 300 °C. Therefore, the mechanically strong and super-insulating PI/SiO₂ composite aerogels are promising candidates for practical thermal insulation applications.

**Keywords:**

A: Polymer-matrix composites (PMCs)
B: Mechanical properties
A: Nano composites
B: Thermal properties
A: Aerogels

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**1. Introduction**

Decreasing heat transfer via advanced thermal insulators is one efficient approach to improve the energy efficiency and reduce the world's total energy consumption, which contributes to a lower carbon footprint [1–3]. Advanced thermal insulators are also urgently needed for many optical, electrical and space applications in which heat transfer should be strictly restricted [4–8]. Therefore, developing materials with a superior insulation performance is highly desirable, which possess thermal conductivity (λ) values below those of commercially available insulation materials, such as polyurethane (PU) foam, expanded polystyrene, mineral wool and fiberglass (λ = 30–50 mW m⁻¹ K⁻¹).

Aerogels are believed to be ideal candidates for thermal insulation due to their high porosity (80.0–99.9%) and low apparent density (0.003–0.15 g cm⁻³) [9–11]. Currently, typical silica aerogels are widely studied and exhibit good thermal insulation properties with a low λ of 17–21 mW m⁻¹ K⁻¹ under ambient conditions, but their potential applications are severely restricted by the poor mechanical properties [12–17]. The emerging organic aerogels show better mechanical properties, but have a slightly higher thermal conductivity of 20–40 mW m⁻¹ K⁻¹ as compared to silica aerogels [18]. Moreover, typical organic aerogels, such as PU aerogels [19,20], cellulose aerogels [21–23], poly(vinyl alcohol) aerogels [24,25], exhibit poor thermal insulation performance under elevated temperatures, which tend to collapse at temperature above 200 °C. Although the thermal stability of organic aerogels can be improved by incorporating inorganic fillers, such as silicate and clays, current organic aerogels cannot be stable over 300 °C [26–30]. More recently, some works have presented super-insulating materials (λ, as low as ~21 mW m⁻¹ K⁻¹) such as bioinspired polymeric woods [31] and anisotropic nanowood [1], but their insulation behavior at elevated temperature has not been studied. Therefore, aerogel materials with both excellent thermal insulation behavior under a wide temperature range and good mechanical properties are urgently required, which is highly desirable in many applications where much higher using temperatures are needed.

Polyimide (PI) aerogels exhibiting excellent mechanical properties (Young's modulus over 100 MPa), low thermal conductivity (30–60 mW m⁻¹ K⁻¹) and high-temperature stability (up to 600 °C) have drawn much attention recently [32–37]. These properties make robust PI aerogels promising candidate for thermal insulation applications, especially under high-temperature circumstance. However, further decreasing the thermal conductivity of PI aerogels has reached a plateau since it would lead to compromises in mechanical properties...
and fabricating complexity. Typically, PI aerogels have been synthesized from dianhydrides and diamines, followed by chemical imidization and supercritical drying [38]. Normally polyimide aerogels prepared from supercritical carbon dioxide drying exhibit a nanofibrous structure while their porous structure cannot be well controlled. Different from supercritical drying, freeze-drying method is a promising alternative since it is cost effective and environmentally friendly [39,40]. However, the formation of PI aerogels usually suffers from large shrinkage, which contributes to the loss of porosity and strength. Since the thermal insulation performance of aerogels is highly related to their porous structure, alternative approaches to fabricate PI aerogels with less shrinkage and well-organized porous structure via freeze-drying is still a challenge.

Previous work has shown that inorganic nanoparticles, such as clay nanoplatelets and graphene sheets, can perform as crosslinking agents for polymer gels, which helps to improve structural stability and mechanical properties of the gel [41,42]. The inorganic nanoparticles behaving like crosslinkers could inhibit shrinkage and maintain the high porosity of aerogels, which favors the improvement of thermal insulation. More importantly, it has been reported that the use of nanosized components can effectively reduce heat conduction of pore walls through imparting interfacial thermal resistance [2]. More recently, hollow mesoporous silica nanoparticles crosslinked PI aerogels have been reported with improved mechanical properties and low thermal conductivity via supercritical carbon dioxide drying [43]. Therefore, incorporating inorganic nanoparticles into PI aerogels could further reduce their thermal conductivity, without sacrificing the mechanical properties and thermal stability. However, the effect of crosslinkers on the porous structure as well as corresponding thermal properties have not been studied yet.

Herein, inorganic SiO2 nanoparticles crosslinked polyimide aerogels have been synthesized by one-pot freeze-drying followed by thermal imidization. SiO2 nanoparticles as crosslinkers could effectively control the porous structure and subsequently optimize thermal properties of aerogels. The crosslinking points formed from interactions between amino functionalized SiO2 nanoparticles and PI chains favor the formability of PI/SiO2 composite aerogels, which exhibit a little shrinkage (<20%) and a well-organized honeycomb-like porous structure. The thermal conductivity of PI/SiO2 composite aerogel can be optimized by tuning the porous structure via crosslinking points, achieving a low thermal conductivity of 21.8 mW m−1 K−1. More importantly, the thermal conductivity of PI/SiO2 aerogel only shows a slight increase as the temperature goes up, with a thermal conductivity still lower than 35 mW m−1 K−1 at 300 °C. The super-insulation properties of PI/SiO2 composite aerogel at room and high temperatures make them promising candidates for thermal insulation applications.

2. Experimental section

2.1. Fabrication of PI/SiO2 composite aerogels

Silica nanoparticles were first functionalized by 3-aminopropyltriethoxysilane (3-APTS) to obtain amino functionalized silica nanoparticles (NH2-SiO2) (see details in supporting information). PI/SiO2 composite aerogels were prepared according to our previous work [39,40]. Briefly, water-soluble poly(amic acid) (PAA) oligomer (synthesis procedure illustrated Fig. S1), was mixed with functionalized silica nanoparticles to obtain a homogenous PAA/SiO2 sol. PI/SiO2 composite aerogels was obtained by subsequent freeze-drying and thermal imidization process. PI composite aerogels with 0, 10, 20, and 30 wt% loading amount of NH2-SiO2 nanoparticles were fabricated, and denoted as PI, PI/SiO2-1, PI/SiO2-2, and PI/SiO2-3, respectively.

3. Results and discussions

Different from the usually used supercritical drying method, a green freeze-drying method is employed to prepare PI aerogels in this work. Water-soluble poly(amic acid) oligomer is dissolved in deionized water and kept for gelation at room temperature. The PAA hydrogel is subsequently freeze-dried and thermally imidized to obtain PI aerogel. The influence of the concentration of PAA in the hydrogel on the morphology of as-obtained PI aerogel is first investigated. SEM images of PI aerogels prepared from PAA concentration of 10, 7, 5, 4 wt% are shown in Fig. S2 and the corresponding pore size distribution are shown in Fig. S3. It can be observed that honeycomb-like porous structures are formed for all the aerogels. However, PAA with high concentrations exhibits high viscosity, which lead to non-uniform ice growth rate in the freeze-drying process, resulting in the inhomogeneous porous structure and thick pore walls of corresponding PI aerogel (Figs. S2a and 2b).

PI aerogels prepared from PAA hydrogel with 5 wt% concentration show a much more uniform porous structure (Fig. S2c) with smaller pore size mainly centered in 15 μm (Fig. S3c) and less shrinkage (Fig. S4). Further decreasing the concentration of PAA results in the increase of pore size (30 μm) of PI aerogel since diluted solution favors formation of larger ice crystals (Figs. S2d and 3d). Therefore, unless specifically stated, PI aerogels prepared from PAA hydrogel with 5 wt% concentration, exhibiting uniform porous structure and less shrinkage, are used in the following text.

Before fabricating PI/SiO2 composite aerogels, SiO2 nanoparticles were first functionalized by 3-APTS to enhance the interaction between SiO2 nanoparticles and polymer chains. SEM image shows SiO2 nanoparticles are 10–20 nm in size (Fig. S5a) and FTIR spectra prove successful functionalization of SiO2 nanoparticles (Fig. S5b). Compared with pure SiO2, additional peaks located at 2980-2850 cm−1 and 1190 cm−1 of functionalized SiO2 are associated to C-H and C-N stretching modes, indicating that amino groups (−NH2) are grafted onto SiO2 nanoparticles. The NH2-SiO2 nanoparticles were subsequently mixed with PAA precursor to fabricate PI/SiO2 composite aerogels as illustrated in Fig. 1.

The morphology of PI/SiO2 composite aerogels with different loading of SiO2 is shown in Fig. 2a–d. All the aerogels exhibit honeycomb-like porous structures with the pore size varied by adding different amount of SiO2. Neat PI aerogel shows a large pore size in the range of 10–20 μm with a broad distribution (Fig. 2a). With SiO2 nanoparticles, the composite aerogels exhibit smaller pore sizes and more uniform distributions, with PI/SiO2-2 composite aerogel exhibiting the smallest pore size of ~9 μm among those samples (Fig. 2b and c). TEM images of PI/SiO2-2 aerogels (inset in Fig. 2c and Fig. S6) verify SiO2 loaded in PI and indicate the uniform dispersion of SiO2 nanoparticles in PI matrix. However, further increasing the amount of SiO2 nanoparticles leads to the slight increase of pore size (~13 μm) as for PI/SiO2-3, which is probably due to the aggregation of SiO2 nanoparticles in PI matrix as indicated by the inset in Fig. 2d. The smaller pore size of PI/SiO2-2 composite aerogel is attributed to the strong interaction between polymer chains and functional groups on SiO2 nanoparticles as well as steric effect of inorganic SiO2 as schematically illustrated in Fig. 2e. Theoretically speaking, the porous structure of aerogels is highly dependent on structural planarity and intermolecular interaction formed during the gelation process [44]. In the PAA/SiO2 hydrogel, physical or chemical interactions between PAA and NH2-SiO2 nanoparticles through hydrogen bond and amide bond can form crosslinking points, which could maintain the 3D interconnected structure during the freeze-drying process, thus forming a porous structure. More functional groups on SiO2 nanoparticles lead to increased crosslinking points formed in the hydrogel, thus forming a smaller pore size in the final aerogel. The chemical interaction between PAA chain and NH2-SiO2 nanoparticles can be inferred from the XPS characterization (Fig. S7).

As compared with PAA, the intensity of C-N bond increased while the intensity of O-C==O bond decreased for PAA/SiO2 composite, indicating more amide bond formed between PAA chains and NH2-SiO2 nanoparticles.

The structural formability and mechanical properties of PI/SiO2...
Composite aerogels are investigated in Fig. 3 and Table S1. The aerogels show very low density of ∼0.07 g cm$^{-3}$ and good structural formability, which can be shaped into letters of DHU (Fig. 3a). The lightweight aerogel can withstand 7000 times of its own weight, indicating excellent anti-compressibility (Fig. 3b). As shown in Fig. 3c, the shrinkage of PI/SiO$_2$ composite aerogels is less than 20%, much smaller than that (32%) of neat PI aerogel. Silica nanoparticles in polyimide matrix are treated as the crosslinker, which play dual roles for reducing the shrinkage of the polyimide gels. First, crosslinking points formed between PAA and functionalized SiO$_2$ would maintain the 3D interconnected structure during drying. Second, SiO$_2$ nanoparticles help to inhibit the stacking between polymer chains (steric effect), which inhibits the shrinkage and maintain a uniform porous structure. Consequently, PI/SiO$_2$-2 aerogels exhibit a high porosity up to 96%. The strain-stress curves shown in Fig. 3d indicate that the PI/SiO$_2$ aerogels can be compressed by 80% or more without catastrophic collapse. The compression modulus calculated from the linear part of strain-stress curve of PI/SiO$_2$-2 composite aerogel is about 30.4 ± 2.9 MPa, which is much higher than that (0.7–12 MPa) of previously reported polyimide-silica hybrid aerogels with similar density [45,46]. The specific compression modulus represents the ratio of compression modulus to apparent density, which can better indicate the mechanical properties for ultralight materials. The specific modulus of PI/SiO$_2$-2 aerogel is 384 kN m kg$^{-1}$, which is substantially higher than most aerogel materials as listed in Fig. 3e, normally exhibiting specific modulus less than 100 kN m kg$^{-1}$.

Aerogels are one of the most excellent thermal insulation materials, with significantly low thermal conductivity due to their high porosity. As shown in Fig. 4a, pure PI aerogel with a density of ∼0.1 g cm$^{-3}$ shows a thermal conductivity (λ) of 52.8 mW m$^{-1}$ K$^{-1}$, which is comparable to the commercial insulation materials like expanded poly(styrene) (35–55 mW m$^{-1}$ K$^{-1}$) and glass wool (38–50 mW m$^{-1}$ K$^{-1}$).
Adding SiO₂ nanoparticles into PI aerogels can further decrease the thermal conductivity. The PI/SiO₂-2 composite aerogel with a density of 0.07 mg cm⁻³ can achieve a lower thermal conductivity of 21.8 mW m⁻¹ K⁻¹, in contrast to 26.0 mW m⁻¹ K⁻¹ for air, 30.8 mW m⁻¹ K⁻¹ for aromatic polyimide aerogels [34], 26 mW m⁻¹ K⁻¹ for polyimide fiber sponges [5], 31.8 mW m⁻¹ K⁻¹ for polyimide aerogels [47] under ambient conditions. This super-insulation property of PI/SiO₂-2 composite aerogel can be explained by the following factors. The thermal conductivity can be divided into several contributions related to conduction (λ-cond), convection (λ-conv), and radiation (λ-rad). Due to the low application temperature, radiative heat transfer is neglected in the following analysis. A simple theoretical model can be used to estimate the effective thermal conductivity of the PI-based aerogels:

\[ \lambda = \frac{\lambda_\text{g} \lambda_\text{s}}{(1 - \phi)\lambda_\text{g} + \phi \lambda_\text{s}} \]  

(1)

where \( \phi \) is the porosity of aerogel, \( \lambda_\text{g} \) is the thermal conductivity of gas, and \( \lambda_\text{s} \) is the solid thermal conductivity, respectively.

The thermal conductivity of gas is strongly dependent on the pore size and can be estimated according to the following equation:

\[ \lambda_\text{g} = \frac{\lambda_{\text{g,0}}}{1 + 2\alpha l/D} \]  

(2)

where \( \lambda_{\text{g,0}} = 26.0 \text{ mW m}^{-1} \text{ K}^{-1} \) is the thermal conductivity of gas in the free space, \( \alpha = 2 \) for air, \( l \) is the mean free path of gas (~70 nm at ambient condition) and \( D \) is the mean pore size.

PI/SiO₂-2 composite aerogel exhibits a high porosity up to 96%, which contributes to low thermal conductivity according to Eq. (1). Furthermore, PI/SiO₂-2 composite aerogel has a smaller pore size as compared with the other samples (Fig. 2), which favors the reduction of gas conduction (\( \lambda_\text{g} \)) according to Eq. (2). Furthermore, smaller pore size contributes to numerous solid-air interfaces, which leads to tortuous photon conduction and multiple scattering at interfaces, resulting in enhanced thermal insulation behavior. In addition, the incorporation of nanosized components (SiO₂) leads to interfacial thermal resistance, the so-called Kapitza resistance, resulting reduction of the solid conduction of the walls [2]. Therefore, benefiting from its high porosity and tortuous porous channels, reduced pore size as well as nanostructure, the PI/SiO₂ composite aerogel exhibits excellent thermal insulation behavior at ambient temperature, much better than that (25 mW m⁻¹ K⁻¹) of the most common super-insulating criterion.

Owing to the excellent thermal stability of PI/SiO₂ composite aerogel, which exhibits a high decomposition temperature up to 560 °C (Fig. S8), it shows good thermal insulation performance even at high temperatures. The thermal conductivity of PI/SiO₂-2 composite aerogel only shows a slight increase as the temperature goes up, with a low thermal conductivity of 33.2 mW m⁻¹ K⁻¹ at 300 °C (Fig. 4b). In contrast, pure PI aerogel shows a much faster increase of thermal conductivity, with a thermal conductivity more than 100 mW m⁻¹ K⁻¹ at 300 °C. This high-temperature insulation performance of PI/SiO₂ composite aerogel offers great superiority over current insulating materials. Fig. 4c compares PI/SiO₂-2 composite aerogel with many frequently used organic aerogel materials in thermal conductivity versus maximum working temperature. As shown in Fig. 4c, most polymeric insulation materials such as PU, cellulose or resorcinol-formaldehyde (RF) aerogels are easily collapsed at temperatures above 400 °C, which limit their further application under high temperatures. In contrast, our
PI/SiO₂ composite aerogel can be stable up to 480 °C while still remaining a low thermal conductivity. It is worth to mention that although the maximum working temperature of this organic PI based aerogel is lower than traditional ceramic aerogels, such as SiO₂, Al₂O₃, and ZrO₂, which exhibit excellent heat resistance up to 1200 °C, our PI/SiO₂ composite aerogel shows much better mechanical properties (Fig. 3e) that is very important for practical applications. As a proof of concept for thermal insulation applications, the PI/SiO₂ composite aerogel is placed on a hot stage comparing to commercial PI foam. After stabilization for 10 min, the temperature distribution of the PI/SiO₂ composite aerogel upon heating is monitored by infrared camera. As indicated in Fig. 4d, the top of PI/SiO₂ composite aerogel (20 mm thick) maintains a relatively low temperature of about 55 °C after being placed on a 300 °C heating stage, much lower than that (78 °C) of PI foam. Moreover, with the height increase, the PI/SiO₂ aerogel exhibits a much quicker temperature decrease inside as compared to PI foam (Fig. 4e), indicating its excellent thermal insulation ability even at a small thickness. Therefore, their outstanding thermal insulation in a wide temperature range and the excellent mechanical performance place PI/SiO₂ composite aerogels among the state-of-the-art thermal insulators.

4. Conclusions

In summary, thermal insulating PI/SiO₂ composite aerogels have been synthesized by freeze-drying method followed by thermal imidization. The amino functionalized SiO₂ nanoparticles behaving like crosslinkers could inhibit shrinkage (< 20%) and maintain high porosity (> 95%) of aerogels, resulting in PI/SiO₂ composite aerogels with good structure stability and a uniform porous structure. The highly porous structure and nanosized components (SiO₂ nanoparticles) benefit the reduction of thermal conductivity through inhibiting gas conduction and imparting interfacial thermal resistance, respectively. Consequently, the PI/SiO₂ aerogel with a low density exhibits good mechanical properties with specific compression modulus as high as 334 kN m kg⁻¹, which is among the highest level in aerogel materials. More importantly, the PI/SiO₂ composite aerogels show super-insulation properties in a wide temperature range with a low thermal conductivity of 21.8 and 33.2 mW m⁻¹ K⁻¹ at room temperature and 300 °C, respectively. The PI/SiO₂ composite aerogel with excellent mechanical and super-insulation properties may find broad applications in many civil and military fields.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compscitech.2019.01.025.

References


