Recent advances in novel aerogels through the hybrid aggregation of inorganic nanomaterials and polymeric fibers for thermal insulation

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Abstract
Aerogel is a nanoporous solid material with ultrahigh porosity, ultralow density, and thermal conductivity, which is considered to be one of the most promising high-performance insulation materials today. However, traditional pure inorganic aerogels (i.e., silica aerogel) exhibit inherent structural brittleness, making their processing and handling difficult, and their manufacturing costs are relatively high, which limits their large-scale practical use. The recently developed aerogel based on polymer nanofibers has ultralow thermal conductivity and density, excellent elasticity, and designable multifunction. More importantly, one-dimensional polymer nanofibers are directly used as building blocks to construct the network of aerogels via a gelation-free process. This greatly simplifies the aerogel preparation process, thereby bringing opportunities for large-scale aerogel applications. The aggregation of inorganic nanomaterials and polymer nanofibers is considered to be a very attractive strategy for obtaining highly flexible, easily available, and multifunctional composite aerogels. Therefore, this review summarizes the recent advances in novel aerogels through the hybrid aggregation of inorganic nanomaterials and polymeric fibers for thermal insulation. The main processing routes, porous microstructure, mechanical properties, and thermal properties and applications of these aerogels are highlighted. In addition, various future challenges faced by these aerogels in thermal insulation applications are discussed in this review.

KEYWORDS
aerogels, aggregate, inorganic nanoparticles, polymeric nanofibers, thermal insulation

INTRODUCTION
High-porosity materials are very common in nature (from plants to animals) and have been used by humans for thousands of years. Aerogel, an artificial solid material with surprisingly high porosity (>95%), was created by Kistler in the 1930s. Typically, aerogel is derived from a gel in which the liquid components in the gel are ultimately replaced by a gas. The result is a solid with super-light density, ultrahigh porosity, ultralow thermal conductivity, and highly three-dimensional (3D) nanoporous network. Nowadays, a variety of aerogels with adjustable chemical composition, tailororable properties, and various complex shapes have been manufactured. Moreover, these new aerogels show strong application prospects in the fields of thermal insulation, sound absorption, purification and separation, energy conversion, and biomedicine.

Aerogels are nanostructured, open porous solids formed by slow replacement of liquid phase in a gel with gas through CO2 supercritical drying, freeze-drying, or ambient
Typically, most of the aerogels are prepared based on sol–gel process, including dissolution of precursors, sol–gel formation, and the subsequent gel drying as schemed in Figure 1. In the sol–gel process, nanosized sol particles (colloidal particles) are formed spontaneously in the precursor solution or through hydrolysis and polycondensation reactions initiated by a certain catalyst. The sol particles gradually gather and grow into small particle clusters, and the small particle clusters collide with each other to form a larger particle cluster, and finally form a continuous network. However, it exhibits inherent structural brittleness, making their processing and handling difficult, and their manufacturing costs are relatively high, which limits their large-scale practical use.

As we all know, silica aerogel is a highly porous and open-pored material made of amorphous silica nanoparticles by the sol–gel method, which are connected to each other in a 3D random network. However, it exhibits inherent structural brittleness, making their processing and handling difficult, and their manufacturing costs are relatively high, which limits their large-scale practical use. So far, Samiots et al.[8] reported a phase separation method. Most inorganic aerogels are obtained by the sol–gel method. As we all know, silica aerogel is a highly porous and open-pored material made of amorphous silica nanoparticles by the sol–gel method, which are connected to each other in a 3D random network. However, it exhibits inherent structural brittleness, making their processing and handling difficult, and their manufacturing costs are relatively high, which limits their large-scale practical use. Recent studies have shown that adding flexible organic polymers to a silica gel solution will be an effective mechanical reinforcement method for silica aerogels.

Polymer aerogel is a new type of aerogel material developed in recent years, which has ultralow thermal conductivity and density, excellent elasticity, and designable multifunction. As far as we know, most synthetic (Polyurethane (PU), polyurethane-acrylate (PUA), and polyimide (PI)) and natural polymer (cellulose, starch, and alginate) aerogels are manufactured through sol–gel technology. For polymer aerogels, another important preparation technology is the phase separation method.[7] Recently, Samiots et al.[8] reported a phase separation method for fabrication of polymeric aerogels. Polymer aerogels, such as Polystyrene (PS), PC (Polycarbonate), and polyacrylonitrile (PAN), can be successfully prepared by solvent replacement and subsequent drying after the polymer solution is transformed from a frozen state to a cold crystallization. However, complex chemical reactions and parameter control have brought huge challenges to the large-scale manufacturing of aerogels. In recent years, polymer nanofibers have provided a facile way for the production of aerogels. That is, there is no need for the gelation of the sol to form a network, but the polymer nanofibers themselves are used as building blocks for the 3D network of the aerogel through entanglement and crosslinking. This is the so-called gelation-free strategy for preparing polymeric aerogels. This method greatly simplifies the aerogel preparation process, thereby bringing opportunities for large-scale aerogel applications.

The unique pore structure, extremely low thermal conductivity, and ultralow density of aerogels determine their most important application as super-insulation materials. Aerogels have been widely used in tents, outdoor clothing, military uniforms, spacecraft, space suits, automobiles, buildings and constructions, pipelines, insulations, packaging, and so forth.[9, 10] Polymeric aerogels generally have excellent mechanical properties and elasticity but are not resistant to high temperatures. Inorganic oxide aerogels have the characteristics of transparency and high temperature resistance, but the mechanical properties are fragile. For example, native silica aerogels obtained via a sol–gel method often possess a typically unique microstructure, that is, a pearl necklace or beads-on-a-string aggregate of spherical silica nanoparticles while the neck regions composing of only a few Si–O–Si bonds. The weak bonding of the necks renders the silica aerogels’ fragile nature especially undergoing overloading or tensile strain. However, the above shortcomings limit the wide application of these aerogels in the ever-increasing thermal insulation market, especially those fields that require sufficient mechanical strength, flexibility, and high thermal stability. Therefore, the aggregation of inorganic nanomaterials and polymeric fibers is considered to be a very attractive strategy for obtaining highly flexible, easily available, and multifunctional composite aerogels.

In this review, we summarized the three aggregation strategies of inorganic nanomaterials/polymeric fibers for the production of composite aerogels for thermal insulation applications, as illustrated in Figure 2. The first strategy is to introduce organic polymer nanofibers into the inorganic aerogel skeleton to strengthen its network structure. The second strategy is to introduce inorganic nanoparticles/fibers into the main network of aerogels composed of polymeric nanofibers in a gelation-free manner to provide enhanced structure and thermal stability. The third strategy is to combine inorganic aerogel granules with nonwoven fabrics to form a series of aerogel blankets, which have extremely high flexibility and industrial application value. This review aims to describe and discuss the main processing routes, porous microstructure, and mechanical properties of the aerogels prepared via the hybrid aggregation of inorganic nanomaterials and polymeric fibers. It also highlights the challenges that need to overcome to enable the mass production of aerogels with tailored microstructure and properties for thermal insulation.
addition, the preparation methods of inorganic nanosized sol particles and polymeric nanofibers, the two basic units constituting the composite aerogel network, are also reviewed.

**PROCESSING STRATEGIES**

**Preparation methods of inorganic nanoparticles and nanofibers for aerogels**

**Preparation of inorganic nanoparticles**

SiO$_2$, Al$_2$O$_3$, TiO$_2$, and boron nitride (BN) aerogels are the most widely investigated and utilized inorganic aerogel materials.$^{[11]}$ It is well known that the SiO$_2$ aerogel was the first aerogel material created by Kistler in 1931.$^{[12]}$ Almost all inorganic aerogels are obtained using the same preparation method, the sol–gel process, which involves some key steps: the formation of colloidal solution (sol) from the hydrolysis of precursor molecules, the formation of a wet network (gel) by sol polycondensation, the aging of the wet gel, and the drying of the gel.$^{[13]}$ Figure 3 shows the general preparation process of silica sol nanoparticles.

Generally, there are three main sources of silicon used to prepare silica aerogels: water glass (i.e., sodium silicate solution), ion-exchange water glass (i.e., silicic acid solution), and silicon alkoxide (TEOS)$^{[14]}$. In the case of water glass as silicon source, the SiO$_2$ gel can be obtained according to the following reaction:

$$\text{Na}_2\text{SiO}_3 + 2\text{HCl} \rightarrow [\text{SiO}_2 \cdot x\text{H}_2\text{O}] + 2\text{NaCl}. \quad (1)$$
In this process, sodium chloride needs to be removed frequently, and the water solvent needs to be replaced. Thus, this time-consuming and expensive method of producing aerogels cannot attract enough attention. Soon later, Teichner et al. used the tetramethoxysilane (TMOS) as the silicon source and alcohol as the precursor fluid to avoid complicated solvent exchange, and successfully prepared SiO\textsubscript{2} aerogels by supercritical drying. The main reaction is as follows:

\[
\text{Si(OCH}_3\text{)}_4 + \text{H}_2\text{O} \rightarrow [\text{SiO}_2 \cdot \text{H}_2\text{O/CH}_3\text{OH}].\ (2)
\]

In this process, TMOS is dissolved into methanol, and water is added into the solution to initiate reaction. Due to this relatively facile process, the preparation technology of SiO\textsubscript{2} aerogel has been developed rapidly since then. In addition, TEOS (tetraethoxysilane) is a nontoxic silicon source and is generally regarded as the best alternative to TMOS. For sol–gel process with TEOS as silicon source, small oligomers are initially formed by the condensation reactions, and aggregating to form larger secondary particles, and then the particles eventually form the oxidic gel network. In this process, the alkoxy group (OR) is first hydrolyzed, but due to incomplete hydrolysis, the hydrolysis and condensation reactions can proceed simultaneously in the solution. Therefore, the resulting SiO\textsubscript{2} gel often possesses both alkox (OR) groups and hydroxyl (OH) groups.

For sol–gel process, precursors and pH value have a decisive effect on the wet gel and the resulting aerogel particles. For instance, Wagh et al.\cite{16-18} investigated the effects of three different precursors (TMOS, TEO, and PDS) on the properties of colloidal silica spheres. It is found that the unit size of silica spheres is closely related to the catalyst used for each precursor. Monodisperse silica spheres with uniform size can be prepared under the action of acid catalysts when TEO and PDS are used as precursors. Similarly, monodisperse silica spheres can be obtained by using TMOS as precursor under basic catalysts. The pore distribution of silica spheres made by TMOS and PDS is limited and uniform, and the colloidal particles are ball-shaped and smaller than TEOS-based silica spheres.

During aging stage of the sol–gel process, the wet gel will undergoes dehydration and aging. The dehydration is caused by further condensation reaction of the wet gel, resulting in further shrinkage of the gel network. The polycondensation will last for a long time due to the high concentration of active hydroxyl groups in the gel. If the two adjacent hydroxyl groups polymerize on the surface of the network and generate M–O–M groups, which will occupy a smaller space and cause the liquid to drain from the pores. The last step is drying, which is a vital process for successful achieving aerogel structure.\cite{21, 22} CO\textsubscript{2} supercritical drying, freeze-drying, and ambient drying are the common drying methods for production of inorganic aerogels.

Al\textsubscript{2}O\textsubscript{3} aerogel is a kind of promising inorganic aerogel due to its outstanding thermal stability and high dielectric insulation. The preparation process is similar to SiO\textsubscript{2}. Some organic aluminum salts are usually used as the aluminum resources, such as isopropanol aluminum, sec-butyl alcohol aluminum, and inorganocatalminol salts (i.e., AlCl\textsubscript{3}.6H\textsubscript{2}O, Al(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O). Table 1 lists in detail the preparation conditions of some inorganic nanoparticles for aerogels.

### Preparation of inorganic nanofibers

The structural fragility of traditional inorganic aerogels is mainly due to the weak interaction between the network nodes formed by the sol–gel process. As we known, when the diameter is reduced to nanometer level, the flexibility and specific surface area of the fiber will be significantly improved.\cite{34} Nanofibers have the characteristics of high aspect ratio and high surface activity, and can help in the nucleation of sol particles and participate in the construction of the gel network. Moreover, inorganic nanofibers also have the advantages of high melting point and high modulus, which can greatly improve the thermal stability and mechanical properties of aerogels. Therefore, inorganic nanofibers are expected to provide strong mechanical properties and high thermal stability for hybrid aerogel networks.

So far, the main preparation methods of inorganic nanofibers reported include 3D printing, self-assembly method, template method, chemical vapor deposition method, hydrothermal synthesis method, and electrospinning method.\cite{35-39} Meza et al.\cite{40} fabricated a 3D micron lattice framework with a thickness of 5–6 nm, wherein the framework is composed of numerous alumina ceramic hollow nanofibers. However, at present, the cost of this method is too high to expand production. Lin et al.\cite{41} successfully obtained BN-based aerogels through ultrasound-assisted self-assembly using melamine triborate as the precursor, followed by freeze-drying and subsequent pyrolysis. However, due to the large fiber diameter, poor diameter uniformity, and irregular disordered pore structure, the self-assembly method still has defects. As mentioned above, inorganic nanofibers can be manufactured through the 3D printing and self-assembly, but the shortcomings of the high cost and the complex processes limit the application. Direct spinning is a technique of directly depositing fibers through electrospinning or other spinning methods, and many inorganic nanofibers can be prepared by this method. According to Mi et al.,\cite{42} SiO\textsubscript{2} nanofibers were prepared by electrospinning, and then calcined at high temperature, piled up, and self-assembled to form a three-dimensional organic–inorganic hybrid aerogel. However, it is difficult to manufacture such inorganic nanofiber materials on a large scale by electrospinning.

### Preparation methods of polymeric nanofibers for aerogels

#### Preparation of biomass nanofibers

Biopolymers are of natural origins such as from plants, microorganisms, and animals and mainly include carbohydrates and proteins to provide structural support framework. In recent decades, most efforts have been devoted into biomass nanofiber due to their excellent biocompatibility, wide sources, inherent nontoxicity, and biodegradability performance, demonstrating great advantages in the applications ranging from microelectronic-sensing system to biomedical engineering fields.\cite{43, 44} However, with the emergence of
### Table 1: The synthesis conditions of some inorganic nanoparticles for aerogels

| Ref. | Chemical system | Synthesis procedures |
|------|-----------------|----------------------|
| SiNC\(^{24}\) | Silica precursor: tetramethoxysilane (TMOS) | Silica sol (containing TMOS, methanol, DI water, and ammonium hydroxide) added into a functionalized silsesquioxane (SiO\(_2\)-based) solution (5 mg/ml). |
| SiO\(_2\)\(^{25}\) | Silica precursor: TMOS | TMOS hydrolyzed in water (H\(_2\)O:TMOS, 4:1); mineral powders added after 3 h. Gelation: 3–5 h; aging: 24 h (in MeOH at RT); drying: MeOH-SCD |
| SiO\(_2\)\(^{26}\) | Silica precursor: fly ash, trimethylchlorosilane (TMCS) | Fly ash and trona, mixed and calcined, then washed in H\(_2\)SO\(_4\) obtained SiO\(_2\) gel. Put the gel into TMCS/MeOH/Hexane solution for 24 h and drying under ambient pressure. |
| SiO\(_2\)–Al\(_2\)O\(_3\)\(^{23}\) | Silica precursor: TEOS alumina precursor: aluminum isopropoxide (AIP) | Mixing alumina sol (in IPA and acetylacetone) and silica sol (in IPA and H\(_2\)O); gelation: 4 min to 4 h; Aging: 5 days at 40\(^\circ\)C; drying: isopropanol supercritical drying (IPA-SCD) |
| SiO\(_2\)–Al\(_2\)O\(_3\)\(^{27}\) | Silica precursors: TEOS, VTES aluminum source: Boehmite | TMOS hydrolyzed in 2-butanol with HCl (TMOS:H\(_2\)O [1:1]); addition of VTES (TMOS/Al\(_2\)O\(_3\):H\(_2\)O in NH\(_3\) solution:2-butanol [1:8:6]); aging: MeOH-SCD |
| SiO\(_2\)–Al\(_2\)O\(_3\)\(^{28}\) | Precursor: TEOS and AlCl\(_3\) \(\cdot\) 6H\(_2\)O | Preparation of alumina and silica sols; addition of PCM powders (0.18–0.45 g) and PO; aging: 1 day at RT; solvent exchange: EtOH–3 days. Drying: EtOH-SCD |
| GO\(^{31}\) | Graphene oxide (GO) source: GO, ethylenediamine (EDA) | Mixing aqueous graphene oxide (GO) suspension with ethylenediamine (EDA) as a reducing agent and sodium borate solution (SBS) as an enhancer. |

**Figure 4** Natural nanofibers extracted from bioresources: (left) plants (reprinted with permission\(^{48}\)) and (right) crabs (reprinted with permission\(^{49}\)).

Nanosized building blocks (e.g., nanofibers or nanowhiskers) based on renewable polymeric resources, there are now possibilities for the nanoscale engineering of renewable materials to generate low-density biobased foams and aerogels that have the potential for efficient thermal insulation.\(^{45}\) Some of the commonly used biomass nanofiber materials including cellulose, chitin, and their composites are discussed as follows.

Cellulose, as one of the most abundant bioresources (more than 100 billion tons annual production), is the main reinforcement material, along with protein, providing load-bearing function and dynamic nature to the cell wall (e.g., wood, agricultural residues, waste cotton linters). Cellulose is a homopolysaccharide comprising straight chains of connected anhydroglucose units. Some of the hemicelluloses and lignins in wood are formed from cellulose.

Cellulose is a homopolysaccharide comprising straight chains of connected anhydroglucose units. The cellulose chains are in extended chain conformation and organized in microfibrils of high molecular order and have a plant source-dependent diameter that ranges from 3 nm (e.g., native wood) to 20 nm (e.g., Valonia alga). As shown in Figure 4, the inter- and/or intramolecular hydrogen bonding between cellulose chains
Table 2: Extraction details of nanofiber materials from bioresources

| Natural polymers | Types of nanocomponents | Synonyms | Typical sources | Extraction method | Conditions | Average size | Ref. |
|------------------|--------------------------|----------|----------------|------------------|------------|--------------|------|
| Cellulose        | Nano- or microfibrillated cellulose | Microfibrillated cellulose, nanofibrils and microfibrils, nanofibrillated cellulose | Banana rachis, Sisal, Kapok, Pineapple leaf | Alkaline and bleaching treatments/acid hydrolysis | H₂SO₄/HCl | >1000 | 9–25 | [53, 54] |
|                  |                          |          | Spruce, Wood pulp | Mechanical homogenization, Grinding | HCl | >1000 | 1–100 | [55] |
|                  |                          |          | Palm leaf, Poplar, Spruce | Chemical pretreatment and mechanical microfluidization/ high-intensity ultrasonication | HCl/NaHCO₃ | ~0.5 × 10⁶ | 5–1000 | [56] |
| Nanocrystalline cellulose | | Cellulose nanocrystals, crystallites, whiskers, rod like cellulose, microcrystals | Tunicate, Rice straw, Pineapple leaf, Bacteria, Softwood pulp, Sugarcane, bagasse, Tunicate | Acid hydrolysis | H₂SO₄/HCl | 121–2300 | 3.5–60 | [57, 58] |
|                  |                          |          | Cotton linter pulp, Bamboo pulp, Softwood pulp, Cotton linter pulp, Tunicate | Mediated oxidation with ultrasonic treatment, enzymatic hydrolysis | 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) | 100–800 | 5–25 | [59] |
| Bacterial nanocellulose | | Bacterial cellulose, microbial cellulose, bio-cellulose | A. xylinum, G. medellensis, G. xylinus | Bacterial synthesis | Carbon source: glucose, mannitol, fructose | 0–1000 | 2–83 | [60, 61] |
| Chitin            | Chitin nanowhisker or chitin nanofiber | Animal sources | Crab, Shrimp, Squid, Prawn | Acid hydrolysis (HCl), electrospinning, mechanical treatment, ultrasonication, self-assembly, ultrasonication | 80–120°C, pH 3–4, 30–40 min | 150–800 | 2–670 | [62, 63] |
|                  |                          |          | Tube worm | Irradiation, electrospinning, gelation, regeneration, deacetylation/cationization, mediated oxidation, mechanical treatment | 0–100°C 120–240 min | 10–390 | 5–222 | [64] |
|                  |                          |          | Mushroom lobster | Acid hydrolysis (HCl), mechanical treatment, high pressure homogenizer | 100°C, 90 min, pH 7/1000 bar | 300–1000 | 10–100 | [65, 66] |

Induces further aggregations of microfibrils, leading to bigger units such as macrofibrils (15–60 nm) and cellulose fiber (20–50 μm) and giving strength and stiffness to the plant framework. [46–48] Nanocellulose can be disintegrated from wood pulp through three distinct methods including acid hydrolysis, enzymatic hydrolysis, and chemical treatment processes. Among these, the chemical isolation method for cellulose nanofiber (CNF) has been extensively investigated and the resulting nanofibers are typically aggregates of the 4–5 nm wood microfibrils. Additionally, as shown in Table 2, the source of cellulose and isolation process strongly influence the morphologies and properties of CNFs. Compared to traditional synthetic nanofiber materials, the natural derived nanocellulose can be functionalized in their natural state without altering their original molecular structure, resulting in great dispersibility in polymeric composites. [47] Chitin, as the second abundant bioresource (after cellulose), is made of β-(1,4)-2-acetamido-2-deoxy-D-glucose and mainly obtained from the exoskeletons of numerous organisms including marine shrimp and crabs, insects, crabs, fungi, and yeasts. As shown in Figure 4, chitin is a nanocomponent embedded in the shells of crustaceans in the form of mechanically functional chitin microfibrils (nanofibers) with the diameter ranging from 3 to 40 nm and length longer than 5 μm. [49, 50] Chitin nanofiber can be directly produced from chitin compounds through top-down approaches including chemical, mechanical, or chemical–mechanical routes, which not only give all the aforementioned beneficial properties
of chitin but also bring optical transparency and high reinforcing capability.\(^{51}\) Furthermore, because of fascinating features including high aspect ratio, strong hydrogen bonding, extended crystalline structures, and other remarkably unique characteristics of nanomaterials along with the aforementioned properties of chitin, chitin nanofibers offer great opportunity for building aerogels with tailored pore structure and multifunctionality.\(^{52}\)

Preparation of synthetic polymeric nanofibers

Nanotechnology is a leading and rapidly growing technology among all other technologies in the today’s world. In general, a variety of fabrication technique has been used to prepare polymeric nanofibers, including electrospinning, centrifugal spinning, sea-island bicomponent spinning, and phase separation. The principles, preparation process parameters, advantages, and disadvantages of various preparation methods are briefly introduced in this section. The schematic diagrams of these nanofibers fabrication techniques are shown in Figure 5. Moreover, Table 3 compares the characteristics of the three main nanofiber preparation technologies so far, including the types of nanofibers that can be produced, the common solvents used to prepare nanofibers, and the efficiency of nanofiber production.

So far, electrospinning is one of the most commonly used methods to produce nanofibers. This technique uses
The sea–island melt-spinning also provides a method to produce polymer nanofibers. The principle is to select two partially miscible or immiscible thermoplastic polymers, mix them, and melt-spin them through traditional spinning machines. By adjusting the viscosity ratio of the mixture, composition, and spinning conditions, a mixture fiber with a sea–island structure is produced. Nanofibers can be obtained by dissolving and removing the sea phase of the mixed fiber. However, the traditional sea–island spinning method to prepare thermoplastic nanofibers has many limitations, such as requiring expensive conjugate spinning machines, complicated spinneret designs, and two polymers that can form sea–island structures. In addition, there are environmental and economic problems in the process of dissolution and separation of island components. So far, the traditional sea–island bicomponent spinning can only prepare PET and PA66 fibers with diameters above 700 nanometers. The melt extrusion phase separation method is a special example of sea-island melt spinning, which has been developed by Dong Wang and Gang Sun et al. Based on the phase separation of immiscible cellulose ester with thermoplastic polymer blends, this is a novel, high-production, environment-friendly, thermoplastic nanofiber manufacturing process. In this process, the two thermodynamically incompatible polymers are stretched and deformed under the action of the combined force field of shear and stretching in the twin-screw melt extruder, and finally form nanofiber bundles. The matrix polymer in the nanofiber bundle is then removed with a solvent to obtain the desired thermoplastic nanofibers. The method can be used to produce nanofibers such as polyester, polyolefin, polyamide, polyelectrolyte copolymer, and thermoplastic polyurethane with a fiber diameter ranging from 80 to 500 nm. This technique successfully breaks the bottleneck of polymer nanofiber preparation.

| Techniques                          | Producing nanofibers | Solvents                                      | Diameters (nm) | Productivity | Ref.       |
|------------------------------------|----------------------|-----------------------------------------------|----------------|--------------|------------|
| Electrospinning                    | Poly(vinyl alcohol) (PVA), PI, PC, Poly(acrylic acid) (PAA), PU, Polybenzimidazole (PBI), Polyvinyl chloride (PVC), Poly(methyl methacrylate) (PMMA), polyamide 6 (PAA) | Dimethylformamide (DMF), Tetrahydrofuran (THF), Formic acid (FA), Acetic acid (AC) | 50–1000         | Low          | [68, 77]   |
| Centrifugal spinning               | Chitosan, Silk, Chitin, Collagen | Hexafluoropropylene (HFP), Hexafluorosopropyl (HFIP), FA, AC |                |              |            |
| Melt extrusion phase separation    | Polyolefins (Polyethylene (PE), Polypropylene (PP), Ethylene-propylene (EP) copolymer), Polyesters (poly(ethylene terephthalate (PET)), Polytrimethylene terephthalate (PTT), Polybutylene terephthalate (PBT), Ecolflex), Polyamide, Copolymers (poly(vinyl alcohol-co-ethylene ((PVA-co-PE), Poly(ethylene-co-glycidyl methacrylate) (PE-co-GMA)) | Acetone, isopropanol, and water | 50–500         | Very high    | [73–76]   |
Preparation methods of nonwoven textile with polymeric fibers

Nonwoven textile is a fabric with a web structure formed without spinning or weaving, which is made up of randomly entangled short fibers or filaments, and then reinforced by physical or chemical methods. Nonwoven textile is widely used in the fields of medical protective clothing, blankets, garments, air filters, packaging, automobiles, geotextiles, drapes, wound dressing, crop covers, masks, and wet tissues as a result of the advantages of light weight, high output, moderate strength and stability, good stability, and low cost. Nonwoven textile can be divided into melt-blown, needle-punched, spun-bonded, spun-laced, and thermal-bonded nonwoven textile according to the difference in the fabrication method and process. There are a variety of polymers that can be used to manufacture nonwoven textile, such as polypropylene (PP), polyester (PET), polylactic acid (PLA), polyamide (PA), and so on. Currently, polypropylene (PP) and polyester (PET) are widely used in the fabrication of nonwoven textile.

Compared with melt-blown nonwoven textile, spun-bonded nonwoven textile composes of continuous filaments with the diameter range of medium to coarse, and have more uniform quality. The polymer melt is first extruded from a spinneret and stretched to form continuous filaments. The filaments are then laid into a web structure, and reinforced by self-bonding or mechanical or thermal bonding to form spun-bonded nonwoven textile. Spin-bonded PET nonwoven textile has various excellent properties, such as dimensional stability, high strength, high elasticity, and UV resistance. In addition, the needle-punched nonwoven textile has become popular due to the diverse mechanical and physical properties that can provide different thickness and densities to meet various requirements. The short fibers are opened, carded, and laid into a web structure, and then reinforced by using needle with barbs repeatedly punching to form needle-punched nonwoven textile. The needle-punched PET nonwoven textile has the advantages of excellent abrasion resistance, UV resistance, and thermal stability. In some cases, needle-punched PET nonwoven textile could be used in place of wool. The bonding process of spun-bonded and needle-punched nonwoven textile is shown in Figure 6.

Preparation strategy of forming aerogel through the aggregation of inorganic nanomaterials and polymer fibers

In this section, we mainly introduce the preparation strategy of aerogel materials formed by organic–inorganic composite: inorganic nanoparticles as the aerogel network structure, organic polymeric nanofibers as the aerogel network, and nonwoven fabric as the base material.

Introducing nanofibers into inorganic aerogels

The inorganic aerogel fabricated by the sol–gel method has a pearl necklace–like skeletal network. Therefore, the mechanical properties of inorganic aerogels exhibit stiff and brittle nature due to the weak interactions between the inorganic particles. The intrinsic fragility greatly limits its practical applications. To solve this problem, researchers employed flexible fibers to construct aerogels to enhance the mechanical properties.

Inorganic nanofibers can be added to the network of the inorganic aerogels to strengthen the structure. Generally, inorganic fibers and particles can be introduced into the aerogel network via a gradual assembling. Figure 7A shows a core–shell structure of SiC/SiO2 nanowire aerogel constructed by SiC nanowire and SiO2 mold. After annealing under ambient conditions, the adjacent nanowires are fused together through the oxide layer. This fusion and anisotropic microstructure of nanowires lead to high compression resilience. Furthermore, the inorganic sol nanoparticles can also act as crosslinkers, forming a stable crosslinking structure between the nanofibers and nanoparticles. Dou et al. fabricated a hierarchical cellular-structured ceramic nanofibrous aerogels with SiO2 nanoparticles and nanofibers as shown in Figure 7B. The flexible Si–O–Si bonds generated between the SiO2 nanoparticles and nanofibers endow the aerogels rapid recovery from 80% strain and zero Poisson’s ratio.

In addition, the directional freeze-drying technique provides an oriented structure for aerogels during the growth of ice crystals. The aerogels fabricated by directional freeze-drying technique obtain a neat microstructure and impressive mechanical properties. The core–shell structure of SiC/SiO2 nanowire aerogels adopts directional freeze casting and subsequent heating. Compared with inorganic nanofibers, the polymeric nanofibers have excellent flexibility, high aspect ratio, and abundant active groups, so they can provide inorganic aerogels with high flexibility and versatility. For example, Si et al. utilized PAN nanofiber to reinforce SiO2 aerogel, as shown in Figure 7C. The crosslinked composite aerogel represented excellent flexibility that can be compressed 1000 cycles at a large ε of 60%. Liu et al. reported a graphene-based aerogel that uses PVA-co-PE nanofiber and PVA to enhance 3D network structure by hydrogen bonding. The composite aerogel overcomes the poor mechanical properties and high compressibility of pure graphene. Mi et al. fabricated a fluorinated hybrid aerogel consisting of graphene oxide, cellulose nanofibrils, and silica nanoparticles by a one-pot hydrothermal synthesis method. The
FIGURE 7 Introducing fiber into inorganic aerogels: (A) inorganic nanofiber reinforce inorganic aerogel (reprinted with permission[96]); (B) directional freeze drying method provide oriented structure (reprinted with permission[93]); (C) organic nanofiber reinforce inorganic aerogel (reprinted with permission[94])

flexible cellulose nanofibrils in the composite aerogel can prevent volume shrinkage and offer a very large specific surface area, whereas the GO sheets provide mechanical strength for the aerogel. The silica particles and cellulose nanofibrils form hierarchical structures on pore walls, and the grafted fluoro chains greatly reduce the surface energy.

Introducing inorganic nanomaterials into polymeric nanofibers-based aerogels

Introducing inorganic fillers, such as graphene oxide (GO) and carbon nanotube (CNT), aluminum oxide (Al₂O₃), silicon carbide (SiC), aluminum nitride (AlN), BN, metal–organic framework (MOF), and so forth into polymeric nanofibrous aerogels has often been considered as an effective strategy to improve their mechanical properties and functions. Among them, the widely investigated graphene and carbon nanotubes processing superb thermal conductivity are the two promising candidates for highly efficient thermal management of high-power devices. For example, Wang et al.[98] have first incorporated the fluorinated CNT into nanofibrillated celluloses as the thermally conductive fillers via a facile vacuum-assisted filtration method. The film shows a well-organized multilayer structure with strong interfacial interactions, leading to simultaneous accessibility of high in-plane thermal conductivity of 14.1 W/m·K.

Cao et al.[99] designed a nanocomposite aerogel that comprises 3D interconnected hierarchical microstructure with the surface-functionalized PAN nanofiber as the support framework throughout the graphene networks, which shows a highly porosity and excellent compressive stress of 43.5 kPa (Figure 8A). Particularly, due to the high porosity and thermal stability of the MOFs, Zhou et al.[100] reported a novel type of CNF@MOF aerogels constructed via an interfacial synthesis and stepwise assembly approach (Figure 8B). The unique core–shell architecture comprising the continuous MOFs shell layers and nanocellulose core substrate endows the aerogel with high specific compression modulus of ~200 MPa·cm³/g and specific stress of ~100 MPa·cm³/g, whereas the cellular network structure and hierarchical porosity render the aerogels with relatively low thermal conductivity of ~40 mW/m·K.

Many approaches have been established to enhance the polymer nanofiber matrix via using low dimensional inorganic nanofillers. However, random distribution of the inorganic nanocomponents (e.g., metallic, carbon-based materials and/or other constructing thermal transport networks yielded materials) often leads to a lower thermal conductivity than theoretically predicted.[101] Alternatively, by fabricating the organic/inorganic nanocomposites with novel alignment or specified core–shell architecture using mechanical stretching, electrospinning, nanoscale templating, and externally applied electrical/magnetic-field induced self-assembly technologies, the thermal conductivities were observed to be further improved as compared to the traditional one.[102, 103] To combine the features of polymers nanofibers and inorganic materials, a bilayer aerogel structure has been designed by employing naturally abundant cellulose nanofibrils as basic building blocks to achieve sustainability and biodegradability as well as employing a CNT cover layer for efficient solar utilization (Figure 8C). The aerogel possesses an ultralow density of 9.6 mg/cm³ and a high porosity of 99.4%, resulting in a high solar-energy conversion
efficiency of 76.3\% and 1.11 kg/m²/h at 1 kW/m² (one sun) solar irradiation performance, which can be comparable to most of the reported thermal management devices (e.g., solar steam generation).\[104\]

Integration of inorganic aerogels on textiles (aerogel blankets)

Nowadays, some newly engineered blankets have combined the innovative thermal properties of aerogels and the extremely high flexibility of textiles, providing versatile products with lowest thermal conductivity. Currently, there are some large manufacturers in the production of commercial aerogel blankets, including but not limited to Aspen Aerogel, Inc., Cabot Corporation, Svenska Aerogel AB, Acoustiblok UK Ltd., Active Space Technologies, and Airglass AB.\[105\] For example, Thermal-Wrap™ is a product made by Cabot Corporation with available thicknesses of 5–8 mm and a thermal conductivity of 0.023 W/m·K.\[105\] These aerogel blankets are nonwoven fabrics composed of fibers and inorganic aerogel granules. The fibers used to construct the nonwoven scaffold include polymer fibers, glass fibers, carbon fibers, and their composite fibers. The most commonly used aerogel granules are SiO₂. Obviously, different applicable temperatures and application scenarios have specific requirements for the types of fibers that make up the aerogel blanket. Nonwoven fabrics made of polymer fibers are lighter, more flexible, and easier to manufacture on a large scale. In this section, we will focus on the aggregation technology of polymeric fibers and SiO₂ aerogel granules to form aerogel blankets. Figure 9 shows the schematics of three typical routes for developing aerogel blankets based on nonwoven. The first route is the lamination method as shown in Figure 9A. Specifically, the aerogel particles are sprayed on the surface of the nonwoven fabric, and then a layer of nonwoven fabric or nanofiber mesh is hot pressed on the surface of the nonwoven. For example, Xiong et al.\[106\] prepared an aerogel blanket with a layered structure by spraying a layer of SiO₂ aerogel granules uniformly on a needle-punched PET nonwoven, and then hot pressing a layer of PAN nanofiber wet gel to cover the surface of the granules. The aerogel blanket shows excellent thermal insulation properties. Bhuiya et al.\[107\] reported silica aerogel-integrated nonwoven protective fabrics for chemical and thermal protection and thermophysiological wear comfort. The silica aerogel (IC3120) that was used was purchased from Cabot Corporation. These aerogel powders have a hydrophobic surface with a size of 100–1200 μm, a particle density of 120–150 kg/m³, and a pore size of about 20 nm. They first used a carding machine to form a dry-laid web with a fiber mixture of viscose fiber and polyester staple fiber. After that, the web was heat-set at 140°C/6.0 kPa to form a nonwoven fabric. Then, aerogel particles were spread on the nonwoven fabric through a perforated roller, and a fusible lining was used to firmly fix the particles and the edges of the fabric. The other side of the nonwoven fabric was also covered with aerogel particles and a lining in the same way, so as to finally form an aerogel-integrated sandwich structure.

The second route is to mix aerogel granules and polymer masterbatches in a solution or molten state through an electrospinning process or a nonwoven web consolidation process to form an aerogel mat. Newly, Bhuiyân et al.\[108\] reported an electrospun polyacrylonitrile-silica aerogel coating on viscose nonwoven fabric for versatile protection and thermal comfort as shown in Figure 9B. As reported, commercial silica aerogel particles were first mechanically milled to reduce particle size to 35–340 microns. Then, the refined silica aerogel particles were added to a PAN polymer spinning solution, and the PAN–aerogel hybrid nanofiber membrane is obtained by electrostatic spinning. That is, the silica particles were consolidated in the PAN nanofibers. Subsequently, the PAN–aerogel hybrid nanofiber membrane was sandwiched between two layers of nonwoven fabrics, and then a fusible
interlining was used to heat-set the fabrics at 40°C/6.0 kPa for 3 min to form the aerogel textile.

As shown in Figure 9C, the third route is to mix the nonwoven fabric with pre-gel mixture or gel precursor to form an impregnated fiber network, and then obtain the aerogel mat through a drying process. In a typical preparation process, a commercial polymer nonwoven fabric is first immersed in a silica sol with TEOS as the precursor. The composite system then undergoes hydrolysis, gelation, aging, solvent exchange, surface modification, washing, and drying and finally forms a soft aerogel/nonwoven composite blanket. For an instance, Talebi et al. prepared silica aerogel blankets by in situ synthesis of silica aerogel on PET nonwoven fabrics via a two-step sol–gel process of TEOS, which was followed by drying at ambient pressure. It is worth noting that most commercial aerogel blankets require surface modification to obtain a hydrophobic surface, such as the use of tetramethylchlorosilane (TMCS) modification.

In general, the vast majority of commercial aerogel blankets are based on the assembly of silica aerogel particles and nonwoven fabrics (with glass or polyester fibers). Strictly speaking, aerogel blankets are not real aerogel materials. However, there is some exciting news about the progress of aerogel nonwovens. Recently, the F-Textiltechnik Institute (ITA) of RWTH Aachen University has developed a continuous aerogel filament nonwoven fabric manufacturing process to develop high-porosity aerogel nonwoven fabric, as shown in Figure 10. The project was funded by the German Research Foundation (DFG). At present, the main components of the aerogel nonwoven fabric are cellulose and polyacrylate (PAN). This technology is based on the expansion of wet spinning technology, that is, the spinning solution is directly coagulated into a gel form through the wet spinning process, and then dried by supercritical drying. Researchers believe that there is still space to improve the PAN aerogel filaments by optimizing the spinning bath conditions, the spinning nozzle, and the technical machine concept.
POROUS STRUCTURE AND MECHANICAL PROPERTIES

Pore size and porosity

The pore size and distribution and porosity are extremely important physical parameters to characterize the pore structure of aerogels, which have a strong influence on their density, mechanical properties, and thermal conductivity. The terms “Aerogel” and “foam” are often used interchangeably to refer to solid materials with porous structures. However, according to Kirk-Othmer encyclopedia of Chemical Technology, the definition of aerogel seems to be stricter. That is, the aerogel should have an open-pore structure with a nanoscale pore size. However, the foam can have a closed cell structure with a pore size of micrometers, such as polystyrene foam. In view of the open pore structure of aerogel, the pore size of aerogel does not have a definite geometric size but is more similar to a statistical size in a physical sense. According to the definition of UPAC, a microporous material is a material with pores less than 2 nm in diameter, a macroporous material is a material with pores greater than 50 nm in diameter, and a mesoporous material is a material with pores with a diameter between 2 and 50 nm. Macropores can generally be measured by mercury intrusion method, whereas mesopores and micropores can be measured by gas adsorption method. As mentioned, the pore size of an aerogel is in the nanoscale. Therefore, the pore size and size distribution in an aerogel can be estimated by the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the nitrogen adsorption and desorption curve. The gas adsorption method uses the principle of capillary condensation and volume equivalent substitution, that is, the amount of liquid nitrogen filled in the measured pores is equivalent to the volume of the pores. Assuming that the apparent volume of the aerogel is \( V_a \) and the skeleton volume (real volume) is \( V_s \), then the pore volume of the aerogel is \( V_a - V_s \), and the porosity can be defined as

\[
\text{Porosity} = \frac{V_a - V_s}{V_a} \times 100\%.
\]  

(3)

wherein \( V_a \) can be directly calculated from the geometric dimensions of the sample, and \( V_s \) needs to be measured. If the skeleton material of the aerogel is a pure solid component with a weight mass of \( m_o \) and a definite theoretical density of \( \rho_s \), the porosity \( (P) \) can be estimated by the following equation:

\[
P = \left(1 - \frac{m_o}{\rho_s V_a}\right) \times 100\%.
\]  

(4)

Table 4 Mechanical properties of some inorganic nanoparticles-based aerogels

| Aerogel                        | Density (g/cm³) | Porosity (%) | Compressive modulus (MPa) | Elasticity modulus (MPa) | Elastic recovery performance |
|-------------------------------|----------------|--------------|---------------------------|-------------------------|-----------------------------|
| TiO₂                          | 0.3–1          | 78–90        | –                         | –                       | –                           |
| ZrO₂                          | 0.2–0.3        | 84–96        | –                         | –                       | –                           |
| ZrO₂–SiO₂                     | 0.52           | –            | 1.36                      | –                       | –                           |
| ZrO₂–SiO₂                    | 1.25–1.3       | 62.6         | 53.86                     | –                       | –                           |
| SiC–SiO₂ fiber (61)          | 6.5            | 98           | 0.03                      | 0.016                   | √                           |
| SiO₂ fiber (122)             | 200            | 99.9         | 0.01                      | 0.007                   | √                           |
| SiO₂ fiber (93)              | 250            | 98.989       | 0.004                     | 0.006                   | √                           |
| Ceramic fiber (123)          | 150            | 99.993       | 0.01                      | 0.02                    | √                           |
| SiO₂–PAN (60)                | 0.086          | 95           | 0.025                     | –                       | √                           |

If we define the apparent density \( \rho^s = m_o/V_0 \), then Equation (2) can be written as Equation (5):

\[
P = \left( 1 - \frac{\rho^s}{\rho_s} \right) \times 100%,
\]

where the \( \rho^s/\rho_s \) is reviewed as the relative density of an aerogel. Obviously, the porosity is inversely proportional to relative density. That is, the lower the relative density, the greater the porosity. However, if the skeleton material is a multiphase or multicomponent material, and its theoretical density cannot be obtained directly, the porosity can be calculated by Equation (3), wherein the pore volume can be measured by the equivalent substitution of helium using a true densitometer.

**Mechanical properties**

Assuming that structure collapse was due to densification of the porous structure, Gibson and Ashby [113] had developed a scaling law to evaluate the mechanical properties of the aerogels or foams with cellular porous structure. The compressive strength of aerogels with open cells can be described by following equations [114]:

\[
E^s/E_s \propto (\rho^s/\rho_s)^n, \quad (6)
\]

\[
\sigma^s/\sigma_s \propto (\rho^s/\rho_s)^m, \quad (7)
\]

where \( E^s \) and \( \sigma^s \) are the are Young’s modulus and yield stress of the aerogels, respectively; \( n \) and \( m \) are the scaling exponents; and \( E_s \) and \( \sigma_s \) represent Young’s modulus and the yield stress of the solid skeleton materials, respectively. Typically, \( n = 2 \) and \( m = 2/3 \) are demonstrated for open cell aerogels.

**Porous structure and mechanical properties of inorganic nanoparticles-based aerogels**

As mentioned above, the poor mechanical property of inorganic aerogel limited the application. Using flexible fiber materials to build aerogel structure can strengthen the mechanical property but still have lots of limitation. Thus, a combination of some reinforcements and aerogels will effectively improve the mechanical properties of aerogels and avoid its disadvantages. Aerogel composites generally refer to aerogels as substrates, and some materials such as fibers, wafers, carbon nanotubes, whiskers, or particles are added as reinforcement in the preparation process [115, 116]. Otherwise, the structure elasticity-back property of inorganic aerogel has been significantly improved by the directional freeze-drying method, which can orient the growth of ice crystals and result in the entanglement fiber. The basic performance of composite inorganic aerogel has been shown in Table 4.

The inorganic aerogels that were enhanced by organic materials can effectively improve the mechanical property of inorganic aerogel. Organic materials that are present in abundance have been considered as promising materials to enhance the bonding structure of aerogels [117, 118]. The organic nanofibers act as structural reinforcement or surface functionalizing agents in inorganic-based scaffolds through physical or chemical cross-linking. As reported, Si et al. [119] utilized the polyacrylonitrile fibers to strengthen the network assembled by silica particles and successfully overcome the brittleness of the original structure.

**Porous structure and mechanical properties of nanofiber-based aerogels**

Nanofiber-based aerogels constructed from polymeric nanofibers and low-dimensional inorganic materials have been demonstrated to have huge potential applications in many fields, due to their integrated advantages of excellent and ultralight porosity, extreme flexibility, enhanced mechanical strength, and structural tenability. However, the widespread uses of nanofibrous aerogels for practical thermal management applications are often restricted mainly due to their poor mechanical properties and regulated thermal conductivities. Actually, the morphologies of nanofiber-based aerogels are the main influential factors to the mechanical properties, and which are in agreement with the larger pore size of 3D network and the lower resulting mechanical strength.

For instance, silica-based aerogel is a highly thermal insulating material with a thermal conductivity as low as 0.013 W/m-K; however, its poor mechanical stability limits its use in versatile applications. The high porosity of nanofibrous mesh enables it to trap air, which potentially gives it a good thermal insulation property. These behaviors are confirmed by the thermal conductivity tests that decreasing fiber diameter leads to an increase in the thermal resistance of
aerogels. However, at high compression level, the amount of air trapped within the interfiber pockets is reduced, resulting in a decrease in its insulating performance. Microstructural characteristics of the inorganic/organic hybrid aerogels collected from recent literatures are displayed in Table 5. In general, pore sizes of the aerogels are closely dependent on the precursor concentrations and construct approaches. In some cases, the aerogel morphology is also affected by the synthesizing conditions including the types of precursors, additive materials, drying method, cooling speed, and other physical conditions. Typically, by using a supercritical CO$_2$ drying method and applying with a rapid cooling rate, the CNF-based aerogels have been successfully fabricated, while showing extremely small pores ($\sim$3 nm), ultrahigh porosities (97.3%–99.7%), and more homogeneity.[124–126] As reported by Liu et al.,[5] a PVA-co-PE nanofiber-based aerogel (NFA) has been fabricated with a mean pore size of about 15 nm and pore diameter ranging from 5 to 100 nm. Moreover, by increasing the concentrations of precursor materials, the higher density of aerogels would be obtained, and which can be mainly explained by the regular structure origins from their smaller pore sizes. Svagan et al.[127] reported that the addition of starch to the CNF-based aerogel can alter their porous architecture, resulting in a 65% reduction of their average pore size.

Actually, the aerogels sometimes are sensitive to the moisture environmental conditions (e.g., handling and storage), and likely to become more brittle with ageing and exhibit stress relaxation behaviors. To avoid the collapse of aerogels during cyclic compression, the semi-interpenetrating frameworks have been developed to improve their elasticity by forming bonding points between each nanofiber (seen in Figure 11A).[135] Compared to traditional aerogels, nanocelulose with low shrinkage and higher crystallinity often been used as the supporting material and integrated with the other components, resulting in a diverse novel material inherent mechanical property.[126] The nanomaterials (e.g., nanofibers) can be further functionalized to increase their interfacial interactions with the matrix, resulting a three-dimensional interconnected hierarchical microstructure and enhanced mechanical strength of the aerogels. (seen in Figure 11B).[99]

**TABLE 5** Microstructure information of the inorganic/organic hybrid aerogels collected from recent literatures

| Hybrid aerogels                | Density (mg/cm$^3$) | Porosity (%) | Pore size (nm) | Specific surface area (m$^2$/g) | Ref.   |
|-------------------------------|----------------------|--------------|----------------|---------------------------------|-------|
| Zinc oxide–cellulose          | 20                   | 98.7         | 10             | 92                              | [128] |
| Silica nanoparticle–cellulose | 10                   | 98           | –              | –                               | [129] |
| Polypyrrole/silver nanoparticles–cellulose | 6.32         | 99.5         | –              | 263.2                           | [130] |
| Graphene oxide–cellulose      | 5.9                  | –            | 652            | 47.3                            | [131] |
| Ag$_2$O–chitin                | 2.19                 | 99.85        | 15             | 179.71                          | [132] |
| Graphene oxide–chitin         | –                    | –            | 17             | 146.2                           | [133] |
| Carbon nanotubes–aramid nanofiber | 43                 | –            | 30             | 232.8                           | [134] |

**THERMAL PROPERTIES AND APPLICATIONS**

**Characterizations of thermal conduction**

Thermal conductivity in aerogels

Aerogels with ultralow thermal conductivities (<0.1 W/m-K) are regarded as promising thermal insulators. Thermal conductivity is a physical material property that describes the ability to conduct heat. According to Fourier’s law, the total heat transfer of porous materials (foams or aerogels) can be described as a summation of contributions from the solid

**Porous structure and mechanical properties of aerogel blankets**

Generally, aerogel blankets have a high-porosity structure and are soft and bendable, which enables them to meet the requirements of folding or wrapping insulation components, such as pipe insulations.
FIGURE 11  Reinforcing elasticity of the aerogels with: (A) semi-interpenetrated networks (reprinted with permission\cite{135}) and (B) inorganic fillers (reprinted with permission\cite{99}).

FIGURE 12  (A) The typical appearance of a commercial aerogel blankets product (Aspen Aerogel, Inc.) (reprinted with permission\cite{137}). (B) The microstructure of a commercial aerogel blanket (TW800, Cabot, Germany) (reprinted with permission\cite{137}; copyright © 2018, ASM International). (C) Contact angle image showing hydrophobic surface of a silica aerogel/polyester aerogel blanket (reprinted with permission\cite{110}; copyright © 2019 Elsevier Ltd.) and the typical FESEM images of fracture surface of a commercial aerogel blanket (TW800, Cabot, Germany) after (D) tensile and (E) tear tests (reprinted with permission\cite{137}; copyright © 2018, ASM International).
conduction ($\lambda_{sc}$), gas conduction ($\lambda_{gc}$), heat radiation ($\lambda_{r}$), and thermal convection ($\lambda_{c}$) by gas flow.[45] The schematic diagram of the thermal conduction mechanism of an aerogel has been shown in Figure 13. Regarding solid conduction ($\lambda_{sc}$), the heat transfer in solids is mainly carried by electrons and phonons. For polymer fibers or inorganic nanomaterials, $\lambda_{sc}$ mainly comes from the scattering of phonons. Phonons are energy quantum related to the acoustic vibration modes of the crystal structure, which can be created and destroyed through random energy fluctuations. Point defects, dislocations, stacking faults, and grain boundaries are the most common crystal defects in condensed materials. It is generally believed that the phonons–defect interaction plays a decisive role in thermal conductivity, especially when the material’s dimension is reduced to the nanoscale.[138] Aerogels are solid materials with 3D nanoporous structure. Therefore, the scattering of phonons by the solid–solid or solid–gas interfaces in an aerogel structure will reduce the contribution of $\lambda_{sc}$ to thermal conductivity. Due to the large number of multilevel solid–solid interfaces (skeleton composed of nanoscale units) and solid–gas (pores) interfaces, aerogels always show strong phonon scattering characteristics, thereby resulting in a low solid conductivity. As for thermal convection ($\lambda_{c}$), its contribution to the thermal conductivity of an aerogel is almost negligible. This is because the pore size in aerogels is usually at the nanometer scale, so the heat transfer area of the surface is very small. The contribution of radiation ($\lambda_{r}$) to thermal conductivity for an aerogel under ambient temperature and pressure can almost be ignored. But under vacuum conditions, the contribution of radiation needs to be taken seriously.[136] Under most atmospheric conditions, gas conduction ($\lambda_{gc}$) has a dominant contribution to the thermal conductivity of aerogel materials. The gas conduction is governed by the average pore size in aerogels and the mean free path of air molecules.[45] For aerogels, the mesoporous (2–50 nm) pore favors the Knudsen effect, which means the circulation of air molecules is confined inside pores (i.e., pore size smaller than the mean free path of air molecules), thus resulting in a very low gas conduction. Taken silica aerogel as example, the low thermal conductivity and high insulative capability can be attributed to the presence of nanosized pores full of air, as well as the small, scattered clusters of silica solid.

**Thermal conductivity measurement for aerogels**

Generally, there are two methods that are most commonly used for thermal conductivity testing of aerogels, namely, the heat flux method (HFM) and the transient planar source (TPS) method. HFM method is a steady-state method used to determine the heat transfer characteristics of the material through the heat flow meter device.[139] This method can be applicable to other flat slab insulating materials, such as solids, foams, and textiles with thermal conductivities from 0.005 to 0.5 W/m·K over a temperature range of –20 to 70°C. The heat flow method is considered an accurate thermal characterization technique. However, the disadvantage is that they take a long time to perform and require larger samples, which are not suitable for testing small-sized materials.[12]

Transient Planar Source (TPS) methods can evaluate thermal performance at a faster rate, and they can be used for samples of even a few millimeters. This method is also often referred to as the hot-disk method.[12] But for high-thermal-insulation materials, it is worth noting that this method may affect the TPS results, sometimes leading to overestimation of thermal conductivity.
Applications

Applications of inorganic nanoparticles-based aerogels

The pore size of most inorganic aerogels is in the range of 2–100 nm, same as mesoporous materials. These tiny holes contribute to the Knudsen effect and allow its thermal conductivity as low as 0.014 W/m⋅K and the sintering temperature as high as 1600 °C under environmental conditions. Table 6 summarizes the thermal insulation performance of some SiO2-based aerogels. Due to their unique advantages, the inorganic aerogels can be utilized in various applications ranging from aerospace to solar thermal receivers (or translucent windows). The most well-known examples of the application of silica-based aerogels in the aerospace field are the collection of ultrahigh-speed particles in the “Stardust Project” of the National Aeronautics and Space Administration (NASA) and the thermal insulation of the electronic box in the Mars Rovers.[140]

The aerospace-related thermal applications include cryogenic fluid containers, rocket, space craft, rovers, space habitats, Cherenkov radiators, skylights and windows, extravehicular activity suits, and so forth.[141, 142] Regarding aerospace applications, the conditions of use of materials are very harsh. Because the ambient temperature of aerospace varies from −250 to 2000 °C, there are few materials that can meet the conditions of use.[11, 143] The silica aerogels had been proven to withstand large temperature fluctuations and harsh environments. Among all inorganic aerogels, alumina–silica-based aerogels with excellent insulating properties are considered to be suitable substitutes for aerospace applications. Ji et al.[130] prepared a Al2O3–SiO2-based aerogel by using Al(H2O)3(NO3)3 and TEOS as precursors. The densification of the constituent particles leading to viscous sintering and pore collapse is prevented by the introduction of Al2O3. The surface area and total pore volume still remain after heating at 1100 °C for 2 h. In addition, different kinds of low thermal conductivity inorganic aerogels have been fabricated. For example, Xu et al.[123] fabricated a ceramic aerogel that exhibited an ultralow thermal conductivity (~20 mW/m⋅K) and excellent mechanical properties (95% compressibility and complete resilience) by hexagonal BN. Remarkably, the usage temperature can reach as high as 1400°C, which was much higher than the verified on-space operations.

Although pure silica inorganic aerogels seem to be particularly suitable for space applications due to their high temperature resistance, the brittleness of their structure makes their survival in the planetary environment a greater challenge.[144] Sufficient mechanical strength and flexibility of the aerogels are necessary. The durable aerogels with higher strength and stiffness can be obtained by proper selection of silane precursors and by reinforcement with polymers.[142] Sabri et al.[144] reported polyurea crosslinked (covalently bonded) aerogels as a substitute for room temperature vulcanizing–based chromatic calibration targets for spacecraft. The strength of the resulting aerogel is 300 times stronger than the silica skeleton. Recently, Kim et al.[145] achieved a silica aerogel strengthened with polyvinylidene fluoride nanofibers showing high flexibility, low thermal conductivity (0.028 W/m⋅K), and fire retardancy. Due to the light weight, high flexibility, and outstanding elasticity, nanofiber-reinforced inorganic aerogels are considered to be excellent candidates for aerospace-related applications under extreme conditions. As shown in Figure 14, newly reported novel silica aerogels can withstand the test of fire (high temperature) or liquid nitrogen (severe cold atmosphere) and shows excellent elastic recovery.[93,122,140] Moreover, high-performance lightweight insulation materials are required. The bulk density of the aerogel also influences the thermal conductivity. The increase of the fiber content in the aerogel will lead to an increase in its density, which in turn leads to high insulation performance. Therefore, the density and thermal insulation properties of inorganic-based aerogels can be customized by changing the synthesis conditions (such as low pH, longer aging time, or surface modification).

Silica-based inorganic aerogels are usually transparent across the solar spectrum and have an ultralow solid thermal conductivity, making them suitable for use in solar windows, such as solar thermal receivers.[146, 147] By optimizing nanostructure of the silica aerogel, Zhao et al. successfully achieved nonevacuated transparent aerogels with excellent optical transparency while maintaining ultralow thermal conductivity as a solar thermal receiver. The receiver can achieve over 50% efficiency at 200°C, showing promising application prospects in industrial process heat, solar fuel production, desalination, and solar cooling.

Applications of nanofiber-based aerogels

The nanofiber-based aerogel has commonly been regarded as one of the most promising higher performance thermal insulation materials for building applications in recent decades.
Comparing to the traditional and commercially dominating materials including the expanded polystyrene, polyurethane foams, and glass wool, the nanofiber-based aerogels and foams show the super-insulating performance and significantly better heat transport properties, which has raised a rapidly increasing research activity. Specifically, polymeric nanofiber-based aerogels always exhibit extremely low thermal conductivity (∼13 mW/m·K), and show the extraordinary advantages of combining high porosity, ultra-high specific surface area, and excellent flexibility, thus achieving a great prospect in on-demand fire retardant and heat insulation of vehicles/buildings, thermal management of devices, and thermal regulation apparels.

One of the thermal management applications of aerogels is the thermal insulation and fire protection of vehicles. For vehicles, all parts of the vehicle must be protected from high temperatures. Aerogel materials can be used for fire protection and heat insulation while occupying minimal space and weight in the vehicle. Both silica-based and fiber-based aerogels can be used for vehicle insulation. Silica-based aerogels can withstand higher temperatures, whereas fiber-based aerogels are lighter, more flexible, and can withstand severe deformation.

Novel polymeric aerogels with high transmittance to visible light can be applied to smart windows and skylights in energy-saving building systems as shown in Figure 15A. Additionally, Zhou et al. reported an elastic hybrid CNF@MOF aerogels fabricated by a stepwise assembly approach involving the coating and crosslinking of CNFs with continuous nanolayers of MOFs (Figure 15B). Interestingly, the unique crosslinked structure can give the aerogel excellent mechanical properties (80% maximum recoverable strain, high specific compression modulus of ∼200 MPa cm³/g, and specific stress of ∼100 MPa cm³/g) and relatively low thermal conductivity ∼40 mW/m·K, demonstrating its great potential as an efficient heat insulation and flame-retardant material. According to Liu et al., the NFA exhibits a thermal conductivity ranging from 0.033 to 0.044 W/m·K as density increases from 6.56 to 24.08 mg/cm³. The optimized NFA aerogel has a conductivity of 0.036 W/m·K, which is comparable to those of polymeric aerogels for thermal insulation made by conventional freeze-drying (0.03–0.05 W/m·K), and even better than those of commercially available insulators, such as polystyrene foam (PS) (0.04–0.06 W/m·K). They also put one hand directly on the aerogel to intuitively evaluate the thermal insulation capability. It is amazing that the temperature difference between the lower and upper surface of the aerogel remains about 100°C (Figure 15C). The thermal conductivity of the boron nitride nanosheets (BNNS)/CNFs hybrid.
aerogel (referred to as CNF/BNNS) is about 0.50 W/m·K, which is much greater than 0.105 W/m·K of the pure CNF aerogel.[151] Polymeric-based aerogels can also be used for cryogenic systems; a multifunctional Janus Cu/MnO$_2$/cellulose @layered double hydroxide fiber membrane with symmetrical characteristics of infrared radiation for on-demand personal thermal management has been developed.[152] Specifically, the low-emissivity Cu nanowires (inside layer, 0.476) could be used to reduce the human thermoradiation, whereas the high-emissivity cellulose@layered double hydroxide (outward layer) is served to enhance the human thermoradiation. Moreover, the Cu nanowires layer processes great electrical conductivity and endows the superior Joule heating for extra warmth of 19°C using a low supply voltage around 8.4 V to enhance the thermal comfort in the cold environment.

Fiber-based aerogels also have great potential in thermal management textiles and clothing due to its ultralight weight, high flexibility air permeability, and high capacity of holding air.[153] Arat et al. reported that silica–aerogel-integrated polyacrylonitrile (PAN) nanofibers show high excellent thermal insulation and hydrophobicity, which can be suitable for use in thermal insulation protective clothing. Zhu et al.[154] developed ultralight, flexible, and multifunctional PVA nanofiber-based aerogels, providing ideal material for ultralight thermal clothing. It is worth noting that there are some international manufacturers of aerogel clothing, such as Oros, Supild, and so on, which mainly provide gloves, jackets, coats, jackets, and snow pants for outdoor adventures. They can also be used in winter lightweight cold-proof military uniforms.

**Applications of aerogel blankets**

In order to have an intuitive understanding of the thermal insulation performance of aerogel blankets, Table 7 lists the specific insulative thermal properties of some commercial aerogel blankets.[124, 136] Currently, the main application area of aerogel blankets is pipeline insulation in the oil and gas industry, one example[163] as shown in Figure 16A. High-temperature steam, gas, oil, and fluid medium pipelines are important equipment in the fields of chemical industry, oil refining, and thermal power. Using aerogels as pipe insulation materials can protect pipes from the huge heat loss when exposed to high temperature or cold environment and ensure the quality of the conveyed products. Up to now, some large global petrochemical companies such as ExxonMobil, Shell, PetroChina, and other companies have adopted aerogel blankets as pipe insulation materials. However, in the future, the market for aerogel blankets in the building and construction industry is expected to grow significantly. Besides, the aerogel blankets also have important applications in areas such as vehicle fire and heat insulation, ski resorts, fire-resistant clothing, outdoor clothing, and military applications. Some application cases of the aerogel blankets have been shown in Figure 16 B-C.

**Insulation for buildings and constructions**

A significant amount of energy consumption and CO$_2$ emissions in Middle and Northern European countries in high latitude are mainly due to heating of buildings, of which more than one third of household energy is used for indoor heating.[156, 157] In particular, older buildings generally have poor thermal insulation, resulting in high energy
TABLE 7 The main thermal insulative properties of some commercial aerogel blankets available on the market

| Type                          | Manufacture   | Fiber composition | Thickness (mm) | Density (g/cm³) | Thermal conductivity (mW/m·K) | Maximum temperature (°C) | Ref |
|-------------------------------|---------------|-------------------|----------------|----------------|------------------------------|--------------------------|-----|
| Cryogel (x201, Z, space loft) | Aspen Aerogels| Polyester/Glass fiber | 5 or 10        | 0.13–0.2       | 14–17                        | 200                      | [105, 136] |
| Thermal Wrap                  | Cabot         | Polyester and PET  | NA             | 0.07           | 23                           | NA                       | [24] |
| Key-on Aerogel Felt           | Key-on-Nano-Anhui |              | 3, 6, or 10    | <0.22          | <20                          | <800                     | [155] |
| Silica aerogel                | Joda          | Ceramic fiber     | NA             | 0.3            | 16                           | NA                       |     |

(A) Aerogel blanket (Aspen Aerogels, Inc.) as an example of industrial insulation materials[163] (i.e., regasification pipes and equipment). (B) (Top) Aerogel insulation for retrofitting of an old brick dwelling and a thermographic image of a timber wall where the studs of the top floor are insulated with a thin layer of aerogel insulation (reprinted with permission[156]; copyright © 2010 Elsevier B.V. All rights reserved.); (down) the proposed aerogel-based composite system applied to retrofit the concrete wall at the exterior side and at the interior side (reprinted with permission[164]; copyright © 2019 Elsevier Ltd.). (C) (Top) The burning frequencies (shown in numbers) of different positions of the firefighter’s protective clothing (FPC) and the various fabric layers in FPC (reprinted with permission[36]; copyright © 2018, Springer Science Business Media, LLC, part of Springer Nature); (down) configuration of firefighter clothing assemblies, images of aerogel-treated firefighter clothing before and after instrumented manikin testing (reprinted with permission[159]).

consumption and poor thermal comfort in the building. Therefore, heat insulation inside and outside buildings is very important for these countries. As far as we know, Spaceloft® aerogel blanket is a commercial product produced by Aspen aerogels company designed for insulating buildings and apparel. It has a very low density of 0.15 g/cm³ and a low thermal conductivity of 14 mW/m·K. The maximum temperature for this blanket is 200°C. As they claim, the blanket is flexible, hydrophobic, and breathable, which can be used in a wide range of applications including walls (internal and external), floors, ceilings, dormers and pitched roofs, terrace and balcony, gutter and soffit, window, door and
fenestration inserts, point, repeating and linear thermal bridging treatment, and services such as ducts and hot water pipework. Figure 16B shows aerogel insulation for retrofitting of an old brick dwelling and a thermographic image of a timber wall where the studs of the top floor are insulated with a thin layer of aerogel insulation. One proposed aerogel-based composite system applied to retrofit the concrete wall at the exterior side and at the interior side is illustrated in Figure 16B. So far, many European universities and institutions have been engaged in the research of aerogels in building renovation.

Michal Ganobjak et al. reviewed the technical properties of commercially available aerogel materials—such as blankets, boards, and renders—and their use scenarios in heritage buildings. They illuminated that low thermal conductivity, vapor diffusion openness, hydrophobicity, and good fire ratings make aerogels appropriate materials for application in historical buildings. In particular, the open porous structure of aerogel is beneficial to heritage buildings due to the diffusion of vapors, so as to avoid indoor humidity and possible bacterial growth.

### High temperature–protective clothing

So far, aerogel-based nonwoven clothing used in cold climates has been successfully commercialized. The potential application of aerogel in high-temperature protective clothing (such as firefighter’s protective clothing [FPC]) has also received extensive attention. As we know, normal human body temperature is around 37°C. Human skin starts to feel pain at 44°C, suffers first-degree burns when it reaches 48°C, and suffers irreversible second-degree burns when the temperature reaches 55°C, and is immediately destroyed when the epidermal temperature reaches 72°C. The time interval between feeling pain (44°C) and receiving irreversible burns (55°C) is the escape time for the firefighter to withdraw from a dangerous situation. As shown in Figure 16c, Jin et al. evaluated the effect of aerogel on thermal protective performance (TPP) of fire fighter clothing, showing that aerogel-treated fire fighter clothing exhibited higher TPP than the existing firefighter clothing. Recently, Shaid et al. investigated protective performance of aerogel nonwoven as reinforcement and batting material for FPC. The SiO2 aerogel nonwoven was purchased online from Buyaerogel.com with a fabric weight of 285 g/m and a thermal conductivity of ∼23 mW/m·K. They found that aerogel nonwoven for FPC will provide a firefighter with more than 1 min of escape time to withdraw from a danger situation, while it can only provide 5 s for commercial FPC with existing thermal lining and reinforcement materials. Therefore, it has been strongly proved that the use of aerogel can significantly improve the protective performance of FPC.

Except for thermal liner for fire protective garments, the aerogel blankets also gained attention for apparel application, such as spacesuit insulation, cold weather clothing, clothing with versatile protection and thermal comfort, and military applications (gloves, insoles, jacket, trousers, etc.).

### Insulation for ski resorts

Aerogels are also used to keep cold in public sports facilities, such as ski resorts. Apart from low thermal conductivity, aerogels should involve hermeticity, lightness, easy mounting and maintenance, durability, bacterial and fungal resistance, and temperature differential resistance. Karapet Ter-Zakaryan et al. reported the use of aerogel blankets to protect and conserve snow on the mountainsides and plateaus of ski resorts in Russia. For example, polyethylene foam rollers are used for butt connection and mechanically fixed to form a seamless thermal insulation coating covering the entire mountainside. The insulation system can be maintained during the positive temperature period during the off-season from March to September.

### CONCLUSIONS AND PERSPECTIVES

Here, we reviewed the recent advances in novel aerogels through the hybrid aggregation of inorganic nanomaterials and polymeric fibers for thermal insulation. For a better understanding, Figure 17 highlights the three aggregation strategies and summarizes the most promising thermal insulation application scenarios for different aerogels. As shown, the first strategy involves embedding polymeric nanofibers in a wet gel network composed of inorganic sol nanoparticles during the sol–gel process. The most typical inorganic sol nanoparticle is SiO2. The second strategy is to incorporate or bond inorganic nanofibers into the network structure formed by polymer nanofibers. The third strategy is to combine inorganic aerogel particles with nonwoven fabrics to obtain aerogel blankets, so as to realize the industrial-scale production and application of aerogel products. Of course, these three strategies all require subsequent drying processes to obtain the final aerogel material, such as vacuum drying, carbon dioxide supercritical drying, or ambient pressure drying. The work done so far shows that the hybrid aggregation of polymer fibers and inorganic nanomaterials provides a multifunctional platform with a controllable microstructure, sufficient mechanical strength and flexibility, and customized functions for versatile thermal insulation application scenarios. But we have also noticed that a variety of aerogel materials used in the field of thermal insulations are far beyond what we have summarized. Therefore, we will discuss the advantages and disadvantages of aerogel materials obtained by these three strategies and some new surprising trends outside of the strategies.

As for the composite silica aerogels obtained via the first strategy, the introduction of nanofibers provides the resulting aerogels with higher strength and toughness. In this case, polymeric nanofibers participate in the construction of the colloidal network during the gelation process, and the fibers often act as nucleating agents, reducing the time of gelation and aging, and can also reduce gel shrinkage and cracking during drying. Therefore, the composite aerogel may reduce the manufacturing cost of the aerogel. However, the influence of polymeric nanofibers on the gel process and the final nanopore structure is still worthy of further study and evaluation. In addition, the interaction between polymer nanofibers and adjacent silica networks is also worthy of discussion. Most of the current composite aerogel networks are mainly based on the electrostatic force, Van der Waals force, and hydrogen bonds between the two to crosslink each other. However, it is foreseeable that if the polymer
nanofibers and silica are covalently bonded, the composite aerogel can provide higher mechanical strength. The aerogel obtained by this method is translucent, usually with high flexibility and ultralow thermal conductivity, which makes it very suitable for translucent windows with light transmission and flame retardancy, or for aerospace insulation in harsh environments. However, the actual cost is too high when applied to heat-insulating translucent windows. This is mainly due to the high production cost of silica aerogels.\textsuperscript{[167]} In addition, the cost of preparing polymer nanofibers is also very high. If micron polymer fibers are used, the transparency and pore structure of the aerogel may be lost. It can be expected that if the polymer nanofibers prepared by the melt phase separation method are used to replace the commonly used cellulose nanofibers, the cost may be greatly reduced. This work is under consideration in our research. Commercially, translucent heat-insulating windows based on aerogel particles are mainly developed by ZAE Bayern (Germany).\textsuperscript{[156]} The supplier of translucent windows based on monolithic aerogel is mainly Okalux.\textsuperscript{[156]} The visible light transmission can reach 0.40 and the sound reduction of this window is 52 dB.\textsuperscript{[168]}

The aerogel material obtained by the second aggregation strategy is soft, light, easy to form, and multifunctional. This kind of aerogel has application prospects in thermal comfort clothing, flame-retardant insulation fabrics, and fire warning. For example, Chen et al.\textsuperscript{[114]} newly developed an ultrasensitive fire-warning and high fire-resistance chitosan/montmorillonite/carbon nanotube composite aerogel (CCA) via freeze-drying. The CCA achieved a hitherto shortest fire-warning response time (\(\sim 0.25\) s) and
exhibited excellent flame retardancy and self-extinguished in the vertical burning test. However, most of the reported aerogel materials are still laboratory products, and it is difficult to reach industrial production scale. As mentioned above, the F-Textiletechnik Institute (ITa) of RWTH Aachen University has developed a continuous aerogel filament nonwoven fabric manufacturing process to develop high-porosity aerogel nonwoven fabric in a pilot scale.[111] This may pave the way for the commercialization of polymer fiber-based aerogels.

The aerogel product obtained by the third aggregation strategy, commonly known as aerogel blanket or aerogel nonwoven fabric, is currently the most commercialized aerogel product. This type of product has been successfully used in pipeline insulation, building insulation walls, high-temperature protective clothing, and other fields. It perfectly integrates the advantages of simple manufacturing process and low cost of traditional nonwoven fabrics and the characteristics of low thermal conductivity of silica aerogel granules, enabling the large-scale production of aerogel products. But at present, the world’s commercial companies that can produce excellent performance aerogel blankets are limited to a few well-known companies, such as Aspen Aerogel, Inc. and Cabot Corporation. However, for the vast number of developing countries, the current cost is still high. Therefore, reducing the manufacturing cost of silica aerogel granules and accurately regulating the porous structure of the aerogel blankets on demand is the key to the successful development of such products.

Although up to now, cheap aerogel materials that can be obtained on a large scale still have a long way to go. But there is no doubt that with the advancement of technology and the enhancement of global energy conservation awareness, the demand for environmentally friendly and degradable new thermal insulation materials with ultralow thermal conductivity will continue to grow. It can be foreseeable that this demand growth will focus on energy saving of industrial pipelines, safety protection of new energy vehicles, fire and heat insulation of rail transit trains and ship hulls, heat flow management in the semiconductor industry, special coldproof clothing, high-temperature protective clothing, space shuttle insulation materials, and various building insulation materials.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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REFERENCES

1. S.S. Kistler, Nature (1931), 127(3211), 741.
2. J. Stergar, U. Mavor, J. Sol-Gel Sci. Technol. (2016), 77(3), 738.
3. M.A. Hasan, R. Sangasheethy, A.C.M. Esther, S.B. Patil, B.N. Sherikar, A. Dey, J. Inst. Eng. India Ser. D (2017), 98(2), 297.
4. T. Linhares, M.T.P. de Amorim, L. Durares, J. Mater. Chem. A (2019), 7(40), 22768.
5. Q. Liu, J. Chen, T. Mei, X. He, W. Zhong, K. Liu, W. Wang, Y. Wang, M. Li, D. Wang, J. Mater. Chem. A (2018), 6(8), 3692.
6. H. Maleki, L. Durares, A. Portugal, J. Non Cryst. Solids (2014), 385, 55.
7. B. Babiarczuk, D. Lewandowski, A.Szczurek, K. Kierzek, M. Mefert, D. Gerthsen, J. Kaleta, J. Krzak, J. Supercrit. Fluids (2020), 166, 104997.
8. S. Samitsu, R. Zhang, X. Peng, M.R. Krishnan, Y. Fujiy, I. Ichinose, Nat. Commun. (2013), 4(1), 1.
9. I. Fracke, T. Tillotson, Thin Solid Films (1997), 297(1-2), 212.
10. S.M. Jones, J. Sol-Gel Sci. Technol. (2006), 40(2-3), 351.
11. C. Ziegler, A. Wolf, W. Liu, A.K. Hermann, N. Gaponik, A. Eychmuller, Angew. Chem. Int. Ed. Engl. (2017), 56(43), 13200.
12. A.A. Trofimov, J. Aitchley, S.S. Shrestha, A.O. Desjarlais, H. Wang, J. Porous Mater. (2020), 27(6), 1791.
13. M. Ganobjak, S. Brunner, J. Wernery, J. Cult. Herit. (2020), 42, 81.
14. A. Stojanovic, S. Zhao, E. Angelica, W.J. Malfait, M.M. Koebel, J. Sol-Gel Sci. Technol. (2019), 9(1), 57.
15. G. Nicolaon, S. Teichner, Bulletin de la Société Chimique de France (1968), 5, 1900.
16. A.V.B.G. Vrij, J. Colloid Interface Sci. (1992).
17. S. Kim, C.F. Zukoski, J. Colloid Interface Sci. (1990), 139(1), 198.
18. G.H. Bogush, C.F.Z. Iv, J. Colloid Interface Sci. (1991), 142(1), 1.
19. Q. Tang, T. Wang, J. Supercrit. Fluids (2005), 3(5), 91.
20. W.J. Malfait, S. Zhao, R. Verel, S. Iswar, D. Rentsch, R. Fener, Y. Zhang, B. Milow, M.M. Koebel, Chem. Mater. (2015), 27(19), 6737645.
21. N. Hüsing, U. Schubert, Angew. Chem. Int. Ed. (2010), 57(1-2), 22.
22. W. Cao, A.J. Hunt, Appl. Phys. Lett. (1994), 64(18), 2376.
23. H. Tamon, T. Sone, M. Mikami, M. Okazaki, J. Colloid Interface Sci. (1997), 188(2), 493.
24. M. Aghajamali, M. Iqbal, T.K. Purkait, L. Hadidi, R. Sinelnikov, Mater. Lett. (2017), 212, 1.
25. C. Rütiser, S. Komarneni, R. Roy, Mater. Lett. (1994), 19(5-6), 221.
26. G.S. Kim, S.H. Hyun, J. Mater. Sci. (2003), 38(9), 1961.
27. A.S. Shalygin, I.V. Kozechevnik, E.Y. Gerasimov, A.S. Andreev, O.B. Lapina, O.N. Martyanov, Micro porous Mesoporous Mater. (2017), 251, 105.
28. J. Ma, F. Ye, C. Yang, J. Ding, S. Lin, B. Zhang, Q. Liu, Mater. Des. (2017), 131, 226.
29. T.M. Fears, C. Sotiriou-Leventis, J.G. Winiarz, Leventis, J. Sol-Gel Sci. Technol. (2015), 77(1), 244.
30. X. Ji, Q. Zhou, G. Qiu, C. Yue, M. Guo, F. Chen, M. Zhang, Ceram. Int. (2018), 44(11), 11923.
31. X. Xu, Q. Zhang, Y. Yu, W. Chen, H. Hu, H. Li, Adv. Mater. (2016), 28(41), 9223.
32. D.B. Mahdaki, K.Y. Lee, R.V. Ghorpade, H.H. Park, Sci. Rep. (2018), 8(1), 1.
33. P.B. Wagh, R. Begag, G.M. Pajonk, A.V. Rao, D. Hanarath, Mater. Chem. Phys. (1999), 57(3), 214.
34. S. Wen, H. Ren, J. Zhu, Y. Bi, L. Zhang, J. Porous Mater. (2018), 26(4), 1027.
35. R. Liu, X. Dong, S. Xie, T. Jia, Y. Xue, J. Liu, W. Jing, A. Guo, Chem. Eng. J. (2019), 360, 464.
36. A. Shaid, L. Wang, P. Padhaye, M.R. Bhuyian, J. Sol-Gel Sci. Technol. (2018), 87(1), 95.
37. X. Tang, A. Sun, C. Chu, M. Yu, S. Ma, Y. Cheng, J. Guo, G. Xu, Mater. Des. (2017), 115, 415.
38. R. Zhang, C. Ye, B. Wang, J. Porous Mater. (2017), 25(1), 171.
39. X. Hou, R. Zhang, D. Fang, Ceram. Int. (2017), 43(12), 9547.
40. L.R. Meza, S. Das, J.R. Greer, Science (2014), 345(6202), 1322.
41. J. Lin, X. Yuan, G. Li, Y. Huang, W. Wang, X. He, C. Yu, Y. Fang, Z. Liu, C. Tang, ACS Appl. Mater. Interfaces (2017), 9, 44732.
42. H.Y. Mi, X. Jing, H.X. Huang, L.S. Turung, Mater. Lett. (2017), 204, 45.
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