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An overview of aerogels as advanced thermal insulation materials

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I. Introduction

Thermal insulation is a key factor in the design of buildings, and it is also important in appliances and pipelines; conductivity is directly related to the energy efficiency of the construction. Insufficient thermal insulation in the residential sector leads to the emission of around thirty percent of the total greenhouse gases worldwide and it is linked to the performance of the insulating materials used; their thermal conductivity and thickness.^{1,2} The most common insulating materials for buildings are mineral wool, synthetic polymer foams, and natural fibres with the best (i.e. lowest) thermal conductivity in the range of 0.030 - 0.035 W m⁻¹ K^{-1,3} Vacuum insulation panels possess thermal conductivity below that of air at room temperature (<0.025 W m⁻¹ K⁻¹),⁴ and apart from that, only aerogels are known to be intrinsically thermal superinsulating materials in ambient conditions, due to the high porosity and fine pore structure.⁵⁻⁷ Silica aerogels were the first aerogels studied for their very low thermal conductivity (around 0.015 W m⁻¹ K⁻¹). Improvement of the synthesis strategies over the years has resulted to subcritically dried materials with "aerogels like" morphology.⁸ The high cost of fabrication and the poor mechanical properties of silica aerogels are the main barriers for their extensive application in the building market. Superinsulating aerogel blankets are produced in industrial scale, but the release of dust is still a drawback. Other aerogel materials that possess low thermal conductivity can be found in the literature, but they are linked to high toxicity.⁹⁻¹¹ Thus, there is a need for the development of new materials to overcome the disadvantages mentioned above.

Sustainability and environmental friendliness along with cost efficiency, which will allow easy and massive adoption by the industry, are important factors to consider in parallel with high performance. Academic and industrial research aims to develop greener procedures to replace materials made from non-renewable fossil resources and materials with high carbon footprint. As alternatives for materials fabrication, natural resources can be used, such as polysaccharides (e.g., cellulose, starch, alginate, pectin), proteins (e.g., egg white protein, collagen, silk fibroin, milk proteins), etc. The potential of bio-based aerogels as insulation materials was revealed in the last decade and several polysaccharide aerogels were shown to have thermal conductivity below that of the air in ambient conditions.⁶ Among them, pectin aerogels are very promising new materials for thermal insulation applications since they exhibit extremely low thermal conductivity (0.015 - 0.020 W m⁻¹ K⁻¹), the optimal value attained for polysaccharide aerogels.^{12,13} WORKING PAPER

II. Aerogels

1. Definition and historical notes

The exact definition of the term *aerogels* is not yet given in a way to satisfactory describe aerogel materials. According to IUPAC, aerogel is a "gel comprised of a microporous solid in which the dispersed phase is a gas".¹⁴ This means that aerogels can only be microporous, excluding "typical" mesoporous silica aerogels, which points out the necessity for a new definition. Debate on this topic is currently in progress, and several research groups are working to come up with a more precise definition.¹⁵ A better description of aerogels can rather be the following: a solid open pores network expanded throughout its entire volume by a gas and possessing high porosity, high specific surface area (at least 100 m² g⁻¹), and very low bulk density.

S.S. Kistler was the first to introduce the term aerogels in 1932 to describe wet gels, where the solvent inside the pores was exchanged with gas without the collapse of the porous network.¹⁶ While until then wet gels were dried mainly with solvent evaporation, Kistler applied a new technique using supercritical fluid. The procedure of supercritical drying included putting the sample in the conditions in which the liquid in the pores exceeds the critical point (critical temperature, T_c and critical pressure, P_c), followed by a slow evacuation of the supercritical fluid as a gas. This procedure prevented the formation of liquid-vapor menisci during solvent evaporation. These menisci are responsible for the pressure on the pore walls and resulted in pore collapse and gel shrinkage. Their absence made it possible to obtain the dried solid network with morphology being a replica of the initial wet material. In his founding work, Kistler studied aerogels of various chemical compositions.¹⁷ Silica aerogels were first synthesized, followed by other inorganic and organic aerogels. The liquid that was used for supercritical drying was varied, too. Ethanol was the first fluid used, other organic and liquid CO₂ followed. After this work, the chemical compositions of aerogel materials were progressively diversified. A wide family of silica and silica composites was synthesized¹⁸ and a variety of oxides, new organic and carbon aerogels were investigated.¹⁹⁻²¹ The evolution of the sol-gel chemistry led to a more diversified nature of aerogels. Nowadays, there is extensive work on aerogel materials, their properties, and applications, including organic aerogels based on biopolymers. More precisely, natural polymers have gained much attention due to their sustainability, biodegradability, often biocompatibility, and low cost and opening the

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possibility to replace existing materials that come from synthetic polymers. The general synthetic procedures of inorganic and organic aerogels are presented in Figure 1.



Figure 1. The main synthetic procedure for (a) inorganic and synthetic polymer aerogels, (b) aerogels synthesized by bio-polymer solution, and (c) aerogels synthesized by bio-based nanoparticles.22

2. Drying processes

Drying is a critical step which consists in removing the liquid phase contained inside the porous network of the gel to obtain, ideally, a self-standing aerogel. Every time liquid-gas menisci appear inside the pores, capillary stresses (P₂) are developed during the evaporation of the liquid. Because of the low fraction of solid matter (thus the weak mechanical properties) and the very small size of the large majority of the pores of the wet gels, it is important to avoid capillary stresses for the preservation of the open pore structure of the final dry material. Capillary pressure increases with smaller pore size and greater liquid-gas surface tension, and they can reach very high values (e.g., for the extreme case where θ = 0 (maximum tension that can be applied) and for pore diameter 5 nm, P_c = 960 bar for water, P_c = 280 bar for isopropanol, and P_c = 240 bar for hexane).²³ In a simplified model, the pores are considered cylindrical and the pressure P_c applied during liquid evaporation on the pore walls with pores of radius R is given by the Young-Laplace equation (1): WORKING PAPER

$$P_c = rac{2\sigma_{
m lg}\cos heta}{R}$$

where σ_{lg} is the liquid-gas surface tension and θ is the angle between the pore wall and the surface of the liquid.

The three most common methods used for drying are evaporation in so-to-say ambient conditions (Figure 2, (2)), freeze-drying (Figure 2, (1)), and supercritical drying (Figure 2, (3)).^{23,24} During evaporative drying (crossing the liquid–gas equilibrium curve), and as the gel dries, the porous network usually collapses, resulting in a remarkable increase in the density of the material. The most important factors affecting the network collapse are the nature of the solid, the nature of the solvent, and the rate of evaporation. There are several cases where dried samples maintain high porosity and Brunauer–Emmett–Teller (BET) surface area,^{25,26} but in most of the cases these values are much lower than the analogous supercritically dried aerogels. The gels dried with evaporative drying will be named *xerogels*.





Freeze-drying is one way to prevent the formation of liquid-vapor interfaces. During freeze-drying the liquid in the pores bypasses the triple point in the phase diagram as sublimation of the solvent prevents the creation of liquid-gas menisci. In the first step, it consists of freezing the liquid in the pores of the network which is removed by sublimation under low pressure. The resulting materials will be named *cryogels*. Freezing of the solvent, in particular, of water, creates several problems in the nanostructure of the gels, as ice crystals' growth and stress development in the liquid phase can cause damage to the solid network. This phenomenon is very characteristic when water is used as a solvent and with the decrease in temperature water crystals are created expanding the size of the pores and leading to dried materials with a high portion of very large macropores.

(pore diameter >> 50 nm).²⁷ Other solvent systems, including organic solvents such as tert-butanol, have been proposed over the years to avoid these changes in the porous network.^{28,29} Freeze-drying is a time-consuming process, as vapor diffusion occurs in low temperatures and vapor pressures are so small that the pressure gradient cannot yield high mass flow rates.

The most efficient drying technique to preserve the porosity of the solid network is supercritical drying. During this procedure, it is possible to obtain monolithic, dry *aeroge/s* with high porosity, close to that of the wet gels; there is no formation of liquidgas menisci, and the capillary stresses are eliminated so-that the mechanical stress. Drying with supercritical fluid can follow a hot process in different organic solvents, i.e., ethanol or acetone (critical temperature > 240°C),¹⁶ or a cold process using supercritical CO_2 (critical temperature \approx 31°C) close to ambient temperature conditions.³⁰ The latest is the method widely used for the drying of wet gels to obtain aerogels.

The process of "low-temperature" supercritical drying includes the exchange of the solvent in the pores of the gel with CO_2 in liquid state in a closed pressure chamber and heating above the critical conditions. The solvent exchange to CO_2 can be performed also in the supercritical state. After equilibrium of the supercritical state is achieved, slow isothermal release of the fluid, first in its supercritical state and then in its gaseous phase, is performed. Bypassing the critical point in the phase diagram there are no more capillary tensions, and at the end, the solvent is completely removed, leaving an open porous fine structure of the resulting material. However, this process is time and money consuming and so it is not yet widespread in the industry. An example of cellulose aerogels and the effect of the drying process on the pore structure is presented in Figure 3.



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Figure 3. SEM images of alginate bead aerogels (a, b, c), and cryogels (d, e, f).³¹

3. Properties and applications

Aerogels are by definition porous solid nanostructured networks. They can be microporous (pore diameter < 2 nm), mesoporous (pore diameter between 2 to 50 nm), or macroporous (pore diameter > 50 nm). They have typically very high porosities, as high as 99% v/v in some particular cases and as a result, they are lightweight materials.³² One of the main properties of aerogels is their high specific surface area which distinguishes them from foams. Therefore, the term aerogels does not refer to a particular substance, but to its properties.³³ Aerogels can be derived from a wide variety of substances, such as silica,³⁴ main group metal oxides (e.g., tin oxide³⁵), transition metal oxides (e.g., iron oxide³⁶), lanthanide and actinide oxides,³⁷ synthetic organic polymers (e.g., polyureas,³⁸ polyacrylates,³⁹ polystyrenes,⁴⁰ polyurethanes,⁴¹ polyamides,⁴² polyimides⁴³), biopolymers (e.g., pectin,⁴⁴ cellulose,⁴⁵ alginate,⁴⁶ chitosan⁴⁷), carbon (e.g., carbonized organic aerogels,⁴⁸ graphene,⁴⁹ nanotubes⁵⁰), or metals.⁵¹ They can be single component or composite or even hybrid materials.^{52,53} Aerogels densities are typically in the range of 0.01 to 0.2 g cm⁻³ and specific surface areas range from around 100 to greater than 1000 m² g⁻¹. Properties such as transparency, color, mechanical strength, etc. are primarily dependent on the chemical composition and synthesis parameters (e.g. concentration of solid matter in solution). Finally, they can have various shapes like monoliths, beads, powders, and films.

Due to their high porosity and the structural nature of microscopic and macroscopic features, aerogels can possess unique properties, such as ultralow thermal conductivity, specific acoustic properties, ultralow refractive index, ultralow dielectric constant, high specific surface area and wide adjustable ranges of the density and the refractive index. Aerogels can possess thermal conductivity below that of air and so, they are considered excellent thermal insulators.⁶ It should be noted that changes in the synthesis procedure result in very different final structures and properties of the material. Consequently, thermal conductivity, as all properties mentioned above, can be adjusted by varying the preparation conditions.¹³

Aerogels are very attractive candidates for a very wide variety of applications in the industry, due to their spectacular properties. These include thermal insulators,⁸ acoustic insulators,²² batteries electrodes,⁵⁴ (super)capacitors electrodes,⁵⁵ piezoelectric transducers,⁵⁶ hydrogen storage,⁵⁷ absorbents,⁵⁸ drug carriers,⁵⁹ space applications,^{60,61} catalysts,⁶² and catalyst supports.⁶³ However, few applications have been industrialized, concerning mostly silica aerogels, due to the high cost of the material fabrication. The most "widespread" industrialized application of aerogels is for thermal insulation. Aerogel

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blankets are aerogels reinforced with very long and interconnected fibers (so-called "mat") that provide flexibility to the material and make installation easier while degrading slightly the thermal performances when compared to their "pure" counterpart. Blanket route can also permit to maintain macroscopic cohesion when a subcritical evaporative processing route is applied. Other aerogel materials available for thermal insulation are provided as boards, renders, or granulates and they can have various compositions such as silica, polyurea, polyimide, or polyurethane. For building constructions, aerogels are usually valuable in space-challenging environments like historical buildings or dynamic buildings. Aerogels are preferred for thermal insulation in some sectors like space or airline, due to their lightweight nature and thermal stability in harsh environments.^{60,61,64-67}



III. Aerogels for thermal insulation applications

Thermal insulating material is a material that can "stop" or remarkably reduce heat flow, while a thermal conducting material is able to transfer easily heat flow between "hot" and "cold" surfaces. The ability to transfer heat is expressed through thermal conductivity (λ), which is an intrinsic property of the material. Thermal conductivity is defined by the heat flow through a piece of the material of area A and thickness d with an effective temperature difference ΔT acting on the two surfaces. The units of λ are [W m⁻¹ K⁻¹]. Examples of good thermal conductors are metals, with λ values in the range of tens to hundreds W m⁻¹ K⁻¹; polymers and organic materials are poor thermal conductors, with λ values in the range of tens W m⁻¹ K⁻¹. The thermal conductivity values of insulating materials are typically below 0.07 W m⁻¹ K⁻¹. The materials available for building insulation exhibit λ values mostly in the range of 0.030 – 0.035 W m⁻¹ K⁻¹ (Table 1).^{3,68,69} During the material selection the factors to be considered along with thermal insulation efficiency are numerous for instance cost, durability, climate factor, availability, and the ease level of installation.

Material	Thermal conductivity (W m ⁻¹ K ⁻¹)
Mineral wool	0.033-0.045
Fiberglass	0.033-0.04
Extruded polystyrene	0.034-0.038
Expanded polystyrene	0.033-0.040
Polyurethane foam	0.024-0.035
Aerogels*	0.013-0.015
Vacuum insulation panels*	0.002-0.008

Table 1. Materials available for building insulation and their thermal conductivity.^{3,68}

^{*}Superinsulating materials with thermal conductivity below that of air in ambient conditions (< 0.025 W m⁻¹ K⁻¹). WORKING PAPER

1. Thermal conductivity of porous materials

The thermal conductivity (λ) of an isotropic porous material is described, in the first approximation (i.e. in moderate temperature conditions where conduction and radiative transports are not coupled), by the sum of tree components: the conduction via the solid backbone (λ_{solid}), the heat transfer in the gas phase present in the open-pores aerogel structure (λ_{gas}) and the radiative heat transfer (λ_{rad}) (equation 2).^{6,70-74} A schematic representation of the mechanisms involved in heat transfer is presented in Figure 4. The heat transfer by convection is not considered because when the size of the pores is below 1 mm the phenomenon is negligible.



$$\lambda = \lambda_{solid} + \lambda_{oas} + \lambda_{rad}$$
(2)

Figure 4. Schematic representation of the heat transfer mechanisms of a porous material. Heat is transferred via the solid backbone (indicated by the red chain), by thermal radiation (red arrows), and by gas molecules present in the porous structure (blue dots).⁷⁵

The solid conduction (λ_{solid}) is describing the heat transfer through the solid backbone of the porous material and it is dependent on the structure, connectivity, and chemical composition of the skeleton and is strongly affected by the density of the porous material. The lower the density the lower the thermal conductivity via solid conduction. Heat transfer in the gaseous phase is influenced by the porosity (φ) and the pore size (D), at a given temperature and pressure (equation 3):

$$\lambda_{gas} = \frac{\varphi \,\lambda_{g_0}}{1 + 2\,\beta \,l_m/D}$$

(3)

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where $\lambda_{_{g_0}}$ is the conduction of the free gas, eta is a constant related to the interactions between the pore walls and the gas molecules, it depends on the chemical nature of the solid skeleton, and it is usually around 1.5, and l_{m} is the mean free path of an air molecule, around 70 nm for free air in ambient conditions (equation 4).

$$l_m = \frac{k T}{\sqrt{2} \pi d_g^2 P_g} \tag{4}$$

where k is Bottzman's constant, T is temperature, d_{g} is the diameter of the gas molecule, and P_{g} is the pressure.

Since the pore size of aerogels is much below the micron scale, the heat transfer through the aerogel network is already reduced compared to the heat transfer of the free gas. Therefore, aerogels have the potential to realize thermal conductivity values far below the thermal conductivity of free air at ambient temperature (0.025 W m⁻¹ K⁻¹) with pore size below 70 nm. This phenomenon is described as the Knudsen effect and characterized by the Knudsen number, K_{n} .⁷³

Knudsen number, $K_n = l_m/D$

 $K_n >> 1 \rightarrow$ Molecular heat transfer: The average pore size is remarkably lower than the mean free path of gas molecules. The gas molecules collide predominantly with the solid network and the thermal conductivity in the gaseous phase is proportional to the number of gas molecules, i.e., the gas pressure.

 $K_{n} \ll 1 \rightarrow$ Diffusive heat transfer: The average pore size is way higher than the mean free path of gas molecules. The gas molecules collide predominantly with each other; this is the typical case of diffusive heat transfer. The thermal conductivity of the gaseous phase is equivalent to the thermal conductivity of the free gas, which is independent of the gas pressure for ambient and moderate pressures.

 $K_n \approx 1 \rightarrow$ Transition regime: The gas molecules collide with both the walls and each other and both effects are considered.

At a given temperature and pressure and for low-density materials, the lower the pore size, the lower the thermal conductivity.

Radiative heat transfer depends on the optical thickness of the material. For optically thick aerogels, as most bio-aerogels, this term is not significant, it is linked to the emittance of infrared radiation, and refers to the heat transfer due to the diffusion of phonons (equation 5). λ_{rad} increases significantly with temperature and decreases for higher values of density. WORKINGPARE

$$\lambda_{rad} = \frac{16 \sigma n^2 T^3}{\rho e} \tag{5}$$

where *n* is the effective refractive index of the porous material, σ is Stefan-Boltzmann constant, *T* is the temperature, and *e* is the specific extinction coefficient which depends on the chemical composition and structure of the material and is inversely proportional to the phonon mean free path. Substances that reduce the radiative heat transfer can be added in small quantities to the material. These substances are called opacifiers and they can make the material opaque, as they absorb or scatter the radiation. Commonly used opacifiers are TiO₂ and Carbon. As mentioned above, in bio-aerogels radiative thermal conductivity is very low in comparison with the solid and gas components, since the phonon mean free path is much lower than the material thickness. This mode of transfer can thus be neglected in first approximation.

For porous materials, a decrease in density will result in lower λ_{solid} , and a decrease in pore size will result in lower λ_{gas} . However, for aerogels, a decrease in density, usually by decreasing the concentration of the matter, leads to bigger pores, and smaller pores for the same volume means a higher density of the material. Thus, to achieve the best thermal properties, a compromise between these two factors is needed (Figure 5). The total thermal conductivity of aerogels as a function of density forms a U-shape curve. The minimum value of this curve is the key point to achieve superinsulating properties.





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2. Examples of thermal superinsulating aerogels

<u>Silica aerogels.</u> Silica aerogels among all aerogels were the first to be studied for their superinsulating properties. In recent years, silica aerogels are commercially available with thermal conductivity in the range of 0.013 - 0.020 W m⁻¹ K⁻¹. Hence, silica aerogels are found to possess the lowest thermal conductivity value of any insulator so far reported at atmospheric pressure. The steps for their synthesis include sol preparation, gelation, aging/solvent exchange, and drying. Silylation is applied before the drying step to make the surface hydrophobic and make possible the ambient drying, resulting in materials with similar thermal conductivity to the ones dried with supercritical fluid. The disadvantage in this process is that silulated silica gels are breaking during ambient pressure drying (so-called "spring-back" effect).8,76-80

However, silica aerogels are not easy to handle due to their mechanical properties and extensive work exists in the literature for silica composites and their thermal conductivity. The most common approach is the reinforcement of silica with fibres. As a general trend, an increase in the bulk density due to the fibre addition is observed, along with a significant improvement of the composites' mechanical properties compared to the native silica aerogels. On the other hand, the insulation properties tend to become slightly damaged. However, this is not always the case, and it is possible to receive composite silica aerogels with superinsulating properties. The fibres used can be of very different nature. Inorganic fibres are required for thermal barrier systems due to their stability in high temperatures. In this case, ceramic fibres are the most suitable.⁸¹⁻⁸³ Other examples of inorganic fibres include glass fibres,⁸⁴ and others based on metal oxides.⁸⁵ Organic fibres are used to donate higher flexibility to the silica aerogel for thermal insulation at ambient temperatures. Natural fibres are preferred due to the low environmental impact and low cost. Cellulose is very commonly used together with cotton, flax, and kenaf.^{86,87} An example of superinsulating silica aerogels reinforced with cellulose fibres is presented in Figure 6.

Bio-aerogels. The growth in bio-based aerogels field was followed by research to replace inorganic and synthetic polymer aerogels concerning all existing applications. As a result, several biopolymer aerogels have been studied for thermal insulation as a green alternative for silica aerogels. Nanocellulose, starch and pectin aerogels showed that superinsulating properties are possible using polysaccharides to synthesize aerogels.

Nanocellulose (cellulose I) aerogels with thermal conductivity below that of the air were first reported in 2014.⁸⁹ An interesting technique applied on cellulose aerogels to reach superinsulating properties was pore size harmonization by uniaxial densification.⁹⁰ WORKING PAPER A number of freeze-dried nanocellulose materials exhibited very low thermal conductivity, below 0.016 W m⁻¹ K^{-1.91} Neat cellulose II and chitin aerogels with thermal superinsulating properties are not reported in the literature. On the other hand, flexible chitosan aerogels have shown to exhibit thermal conductivity below that of air.⁹²



Figure 6. SEM images of silica-cellulose composite aerogels. From image (a) to image (f) there is an increase in the concentration of silica precursor (TEOS), as indicated.⁸

Pectin aerogels have a high performance as thermal insulating material reaching thermal conductivity values down to 0.015 W m⁻¹ K⁻¹. Complete study on the correlation of thermal conductivity of pectin aerogels with the structure was performed by tuning the conditions of the aerogel's synthesis. A U-shaped curve was revealed, similar to this of silica aerogels, with all the values being in the superinsulating area. Few works exist for thermal conductivity of starch aerogels. Pea starch aerogels possess the lowest thermal conductivity (0.021–0.023 W m⁻¹ K⁻¹) compared to waxy potato starch, regular potato starch and high amylose corn starch due to the lowest density and finest morphology.⁹³ Finally, some alginate aerogels have been reported as thermal superinsulating materials with conductivity around 0.018–0.022 W m⁻¹ K⁻¹.⁹⁴

Similar to silica aerogels, bio-aerogel composites have been studied for thermal insulation applications. The thermal conductivity of the composites is often lower than the neat material since silica is typically used as the second component.⁹⁵ When another component is used, the thermal conductivity moves to higher values.⁹⁶

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IV. Conclusions

Thermal insulation is a very important factor in the construction sector, and it is a very big contributor in the energy consumption. The most efficient common insulating materials for buildings have thermal conductivity in the range of 0.030 – 0.035 W m⁻¹ K⁻¹. Among insulations materials only aerogels, apart from vacuum insulation panels, posses thermal conductivity below that of air at room temperature (<0.025 W m⁻¹ K⁻¹) due to the high porosity and fine pore structure. Work on aerogels for thermal insulation applications has been done for years. The first family of aerogels that was studied on regard to this application was silica aerogels and their composites. Very low values of thermal conductivity were obtained (down to 0.013 W m⁻¹ K⁻¹) and effort has been made since then to improve their mechanical properties, typically by reinforcement of the network with fibres of different nature. In the last decades, as sustainability raises concern, biopolymer aerogels have been studied as thermal insulations and very interesting finding have come to light. Biopolymer aerogels can be superinsulating materials, with thermal conductivity close to the one of silica aerogels. Along biopolymer aerogels, pectin aerogels were obtained with the lowest thermal conductivity (down to 0.015 W m⁻¹ K⁻¹).



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