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Air-Filled Nanopore Based High-Performance Thermal Insulation Materials

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Abstract

State-of-the-art thermal insulation solutions like vacuum insulation panels (VIP) and aerogels have low thermal conductivity, but their drawbacks may make them unable to be the thermal insulation solutions that will revolutionize the building industry regarding energy-efficient building envelopes. Nevertheless, learning from these materials may be crucial to make new and novel high-performance thermal insulation products. This study presents a review on the state-of-the-art air-filled thermal insulation materials for building purposes, with respect to both commercial and novel laboratory developments. VIP, even if today's solutions require a core with vacuum in the pores, are also treated briefly, as they bear the promise of developing high-performance thermal insulation materials without the need of vacuum. In addition, possible pathways for taking the step from today´s solutions to new ones for the future using existing knowledge and research are discussed. A special focus is made on the possible utilization of the Knudsen effect in air-filled nanopore thermal insulation materials.

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Keywords: High-performance thermal insulation; Nano insulation material; NIM; Aerogel; Vacuum insulation panel; VIP.

1. Introduction

Immediate priorities and future goals will need to reflect the enhanced energy efficiency options combined with a decarbonized power sector that may reduce the CO_2 emission in the building sector. However, given constraints on

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resources there is a call to focus more on efficient building envelopes to keep energy use down. The building envelope determines the amount of energy needed to heat and cool a building, and hence needs to be optimized to keep heating and cooling loads to a minimum. The importance of heating and cooling in total building energy use is very diverse with this share varying between 20% and 80%. Thus, thermal insulation with significantly lower thermal conductivity may contribute largely to an increased thermal resistance and hence an overall reduced energy consumption in buildings.

This study starts with giving an overview of the theoretical background of the process of heat conduction in thermal insulation materials applied in building envelopes, which helps developing an understanding of how such materials behave when used to achieve improved insulation properties. Furthermore, the study demonstrates the theoretical principle by utilizing the Knudsen effect for reduced thermal gas conductance in nanopores that has considerable impact on the overall thermal conductivity.

Secondly, this study presents the state-of-the-art solutions for building purposes, e.g. aerogels and vacuum insulation panels, discussing both benefits and drawbacks. The solutions are investigated with respect to both commercially available products and the global research front, and all property values are retrieved from sources late 2016. The final part will offer some recommendations and ideas on the direction in which the development could proceed, providing a pathway to further advance towards the goal of achieving the improved thermal insulation materials of tomorrow with a substantially lowered thermal conductivity value utilizing the Knudsen effect.

2. Heat transfer in materials

All materials have specific properties when it comes to conduction of heat, and this is irrespective to whether one are looking at solids, liquids or gases. Heat flows spontaneously from a higher temperature body to a lower temperature body, and this will happen as a result of solid state and gas conduction, radiation and convection [1]. The relation between the different contributions are often described as in the following [2]:

$$\lambda_{total} = \lambda_{solid} + \lambda_{gas} + \lambda_{rad} + \lambda_{conv} + \lambda_{coup} + \lambda_{leak} \tag{1}$$

where λ_{solid} is solid state conductivity, λ_{gas} is gas conductivity, λ_{rad} is radiation conductivity, λ_{conv} is convection conductivity, λ_{coup} is conductivity due to coupling effects between the other terms in Eq.1, and λ_{leak} is (air) leakage thermal conductivity.

In addition, it is important to identify which of the terms contribute most to the thermal transport. As we will see later for vacuum insulation panels (VIP), the gas conduction part is very large and the most dominant when the VIP is punctured.

3. The Knudsen effect

Conventional thermal insulation materials are produced so the effects of conduction, radiation and convection are minimized. Using low-radiative surfaces and porous structures reduces radiation, convection and solid conduction, but due to the size of the pores and the open-porous material, the gaseous thermal conduction is limited to the conductivity of air [3]. A solution to this is to utilize the Knudsen effect. This effect is explained by the equations in the following, and implies that a reduction of the pore size in the material to the nano range will effectively reduce the thermal conductivity [4]:

$$\lambda_{gas} = \frac{\lambda_{gas,0}}{1+2\beta Kn} \tag{2}$$

where

$$Kn = \frac{\sigma_{mean}}{\delta} = \frac{k_B T}{\sqrt{2}\pi d^2 p \delta} \tag{3}$$

where λ_{gas} is a combination of thermal conductivity of the gas inside the pores on nanoscale and the energy transfer when molecules collide with pore walls (the latter from the β factor), $\lambda_{gas,0}$ is the thermal conductivity for air at standard temperature and pressure (STP), β is a unitless number between 1.5 and 2.0 which describes the (in)efficiency of energy transfer between molecules and pore walls when colliding [5], Kn is the Knudsen number, σ_{mean} is the mean free path of gas molecules, δ is the pore size of the material, d is the collision diameter of the gas molecules, p is the gas pressure inside the pores, k_B is the Boltzmann's constant, and T is the temperature [6]. It is clear from Eq.2 and 3 that for pores only a few nanometres in diameter the Knudsen number becomes large. This results in a low λ_{gas}. For example, a material with pore size of about 100 nm would achieve a λ_{gas} of somewhat below 8 mW/(mK). Note that the value for stagnant air at STP is 26 mW/(mK) [6].

The Knudsen effect is achieved when the pores have a dimension comparable or smaller than the mean free path of the gas molecules inside the pores. Knowing how to utilize and exploit the Knudsen effect will be very important in the development of high-performance thermal insulation materials based on air-filled pores for building applications.

4. Thermal insulation materials

Materials used as thermal insulation in buildings try to benefit from solutions that create products with low thermal conductivity. This can be achieved by reducing one or several of the contributions shown in Eq.1. In mineral wool, i.e. glass and rock wool products, such a reduction is achieved by bounding fibres together with the use of suitable resins, hence creating complex pore structures with limited/obstructed ways for heat transfer through the material [7]. Manufacturers have come a long way in creating porous materials with low thermal conductivities, e.g. mineral wool products with thermal conductivity values down to 32 mW/(mK).

The drawback with these materials appear together with the higher requirements to thermal insulation in buildings. For example, to achieve a U-value of e.g. 0.22 W/(m^2K) (minimum requirement for wall insulation in Norway per 26th of November 2016 [8]) with a standard mineral wool material, a thickness of approximately 150 mm is needed. For low-energy or zero emission buildings the requirements are even lower U-values. This may result in an insulation layer of more than 250 mm in thickness, which hence takes up valuable space and introduces challenges with convection between the wind and vapour barrier enclosing the insulation layer.

An increased research in the field of thermal building insulation materials have resulted in new materials with better performance in some areas. Aerogels and VIP are examples of materials that have noticeably lower thermal conductivity values [7].

4.1 Aerogels

Aerogels were discovered in 1931 by Samuel S. Kistler and are a silica gel where all the liquid components are replaced by air through a complex drying process. The remaining material creates a nanoporous structure with low thermal conductivity [9]. The solid thermal conductivity of silica is relatively high, but the silica aerogel has only a small fraction of solid silica. With a good purity and production method pore sizes of 5 to 70 nm are possible, where the air-filled pores will take up between 85 to 99.8% of the volume [4]. Pure aerogels have a low thermal conductivity typically between 12-20 mW/(mK).

Aerogels are constantly being developed, both regarding the production process and the final material product itself. Challenges with the material for building purposes have been inherent low density and thus high fragility, which complicates the handling process without fracturing the aerogel products. Therefore numerous different composites have been made in order to create a more robust material [10]. Mineral wool and aerogel have been mixed, with a resultant thermal conductivity of 19 mW/(mK) [7]. Hayase et al. report a development of another composite aerogel with a density of 20 kg/m^3 and a thermal conductivity of 15 mW/(mK) [11]. Also note that as aerogels may be produced as either opaque, translucent or transparent materials, these products may be used for several different building applications, e.g. in opaque walls, translucent solar walls or glazing systems and transparent windows or glazing systems. Table 1 gives an overview of the findings of several different variants of aerogels and their characteristics.

Table 1. Examples of aerogels, listed with important characteristics.

Aerogel	Density (kg/m^3)	Thermal conductivity (mW/(mK))

Stone wool and aerogel [7]	-	19
Polymethylsilsesquioxane-cellulose nanofibre bicomposite aerogels [11]	20	15
Aramid fibre reinforced silica aerogel [10]	150	22.7
Monolithic silica aerogels [12]	-	≈ 13

4.2 Vacuum insulation panels

Vacuum insulation panels (VIP) consist of a multilayer envelope that encloses an open-porous material, also known as the VIP core. To increase the thermal resistance of the panel, vacuum is formed inside the core [7]. The core material could consist of glass fibre, open-cell polyurethane foam, open-cell polystyrene foam, precipitated silica or aerogel. For achieving the lowest thermal conductivity, precipitated silica, fumed silica or aerogel should be used [13]. Numerous VIP are produced, and many of them can be purchased on the market from various suppliers [14].

VIP have several challenges that may make it difficult for them to become the thermal insulation material of the future. One of the main disadvantages is to keep the vacuum intact. This makes it hard to adapt panels at the building site, and the risk of punctures is always present. Thus, the VIP must be handled carefully [15]. Furthermore, the VIP envelope creates a thermal bridging effect [16]. A solution to reduce this problem is to put double, overlapping layers of panels, but this creates more work and higher material usage. Another problem with the envelope is that it is not absolutely air and vapour tight, thus air and water vapour will diffuse into the core as time passes, hence reducing the insulation performance substantially over time. Research is being carried out on how to create better envelopes with respect to the tightness. However, for most of these there will still be a diffusion process of air and water vapour through the VIP envelope and into the VIP core, which may be decreased but not fully stopped.

If the panel is perforated, the core material will still have a rather low thermal conductivity, i.e. VIP with an air-filled fumed silica core will have a thermal conductivity of around 20 mW/(mK). Note then that the difference between 4 mW/(mK) (pristine condition) and 20 mW/(mK) (punctured) of 16 mW/(mK) is due entirely to gas thermal conductivity (not considering any changes to the solid due to loss of vacuum). That is, the combined solid state and radiation thermal conductivity of fumed silica is as low as 4 mW/(mK) or in principle lower (as there is still a very small concentration of air inside a VIP, a small part of the 4 mW/(mK) value is due to gas conduction). Hence, as it is possible to make materials with such a very low solid state and radiation conductivity, lowering the gas thermal conductivity should be a good opportunity to make an air-filled nanopore based high-performance thermal insulation material at atmospheric pressure.

5. Thermal insulation materials of the future

Aerogel and VIP have very good characteristics as insulating materials for buildings. Low thermal conductivity results in both space and energy saving solutions. Much research has been carried out in recent years to improve structural properties of both materials, e.g. making aerogel more robust with the use of different fibres and try different core solutions for VIP. Both materials are commercially available for purchase from several suppliers, and represent some of the best alternatives for building insulators on the market today. However, as mentioned earlier, there remains several stumbling-blocks to a future widespread use of such materials as main insulators in buildings.

As seen in VIP and aerogels, low thermal conductivity values are possible to achieve with the materials already available when using lowered (near-vacuum) pressures. Once the low thermal conductivity values have been achieved, the most important issue in choosing insulators remains to be the long-term thermal performance. The concept of nano insulation materials (NIM) seem to represent a leap forward for the next generation of thermal insulation materials. One such example is found through the studies conducted by Gao et al. [12,17], Jelle et al. [5] and Sandberg et al. [6] where hollow silica nanospheres (HSNS) may be a possible foundation or stepping-stone for the development of the NIM of tomorrow. One distinctive advantage of HSNS NIM over conventional thermal insulators is the controllability of thermal properties by modifying their structural parameters like e.g. particle size, porosity, inner diameter and shell thickness. HSNS utilize physical principles such as the Knudsen effect to reduce the thermal conductivity of the material to a minimum. Nevertheless, it must be noted that turning the laboratory-made HSNS NIM into practical thermal insulation materials for building applications may require substantial research efforts dedicated to this field.

One may also imagine to apply hollow silica nanofibres (HSNF) in such NIMs, e.g. for increased mechanical strength purposes.

A thermal insulation material should be light-weight, and have a certain strength for transport and handling on the building site. Fibre reinforcing of aerogel is one principle that is well documented [10,11], and the right combination of fibre material and aerogel could result in a stronger and, at the same time, a material with a reduced thermal conductivity. Reinforcement often leads to a higher thermal conductivity, as seen from Table 1. Hence, a new material should consist of a homogenous, porous substance. To implement pores in already uniform materials would be an interesting research topic. Possible ways to perform this could be to implement closed pores individually using small valves or by implementing a membrane with holes of the desired size (which is removed at a later stage). Another solution may be to create a material that becomes open-porous when inflated. An inflation process, e.g. by chemical means, from within a bulk material creating a closed nanopore structure could also be imagined and feasible in the future.

In summary, one may categorize some of the promising experimental methods into membrane foaming, internal gas release and sacrificial template methods. The membrane foaming method is using a membrane to prepare a foam with nanoscale bubbles, followed by hydrolysis and condensation of a precursor within bubble walls to make a solid structure. The internal gas release method uses a controlled decomposition or evaporation of a component to form nanobubbles in a liquid system, followed by formation of a solid shell along the bubble perimeter. The sacrificial template method is based on the formation of a nanoscale liquid or solid structure, followed by reactions to form a solid shell along the template perimeter. The sacrificial template core is then chemically or thermally removed, thus resulting in a hollow sphere. Scanning electron microscope (SEM) images of the different steps in the template method when synthesizing HSNS are depicted in Fig.1, where polystyrene (PS) is used as the sacrificial template material.

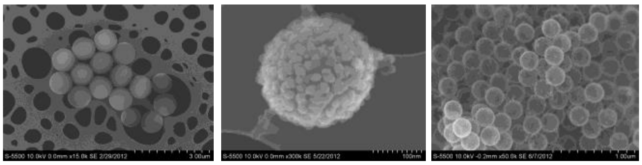

Figure 1. The different steps in the template method with SEM images (left to right) of PS templates, small silica particles coated around a spherical PS template, and HSNS after removal of PS.

6. Conclusions

There are many thermal insulation materials and solutions, both on the market and still at a research level. This study is briefly summarizing the information on today's high-performance thermal insulation for building applications. Aerogel and vacuum insulation panels (VIP) have several satisfying characteristics, such as low weight and low thermal conductivity. On the other hand, the challenges with brittle structures (aerogels) and loss of vacuum (VIP) will always be present with these solutions. Thus, risk of failures which then subsequently will lead to increased thermal conductivities and thus a higher heat transfer through the building envelope. The next generation of thermal insulation materials should be evolved so the various disadvantages are removed. A solution may be to manufacture a material with nanopores implemented by a controlled process.

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