High-Performance Nano Insulation Materials for Energy-Efficient Buildings

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ABSTRACT

High-performance nano insulation materials (Hi-Per NIM) may be developed by exploiting the Knudsen effect for reduced thermal conductivity and thus making air-filled nanoporous thermal insulation materials with a nanoporous air-filled structure. NIMs with very low thermal conductivity values will enable the use of normal or thin wall thicknesses in energy-efficient buildings. Especially for energy renovation of existing buildings, the reduced insulation thickness is of high interest. This study will present an exploration of attempting to achieve NIMs through experimental laboratory development of hollow silica nanospheres (HSNS), hollow silica nanofibres (HSNF) and hollow silica integrated nanospheres and nanofibres, alongside theoretical modelling and sustainability investigations.

Keywords: nano insulation material, NIM, hollow silica nanosphere, hollow silica nanofibre, thermal conductivity.

1 INTRODUCTION

Two state-of-the-art thermal insulation solutions and materials are vacuum insulation panels (VIP) and aerogel-based materials [1-3]. Fresh VIPs can have a thermal conductivity as low as 4 mW/(mK), while various aerogel products typically have thermal conductivity values between 12 - 18 mW/(mK) at ambient pressure. Both can be used for insulating e.g. buildings, pipelines and storage tanks, but both also have serious drawbacks.

The efficiency of a VIP will be dramatically reduced if the enclosing foil is broken, resulting in loss of vacuum. Hence, VIPs cannot be cut and fitted on the building site, and perforation with e.g. a nail would be detrimental. In addition, diffusion of air and moisture through the VIP foil into the VIP core will with time increase the thermal conductivity due to loss of vacuum (up to 20 mW/(mK) when punctured and full loss of vacuum). This drawback is partly solved for aerogels. They are highly porous nanomaterials where the gas thermal conductivity is reduced due to the small size of the internal pores. Aerogels may be more user-friendly than VIPs, but they exhibit substantially higher thermal conductivities, and dust formation can be a problem. Their areas of use are limited by high manufacturing costs and poor mechanical strength.

A *key challenge* is therefore to develop environmentally friendly high-performance insulation materials with superior mechanical properties, lower thermal conductivity and lower cost than the currently available aerogel products, which is the overall aim of the *High-Performance Nano Insulation Materials (Hi-Per NIM)* project presented herein. The current status of our attempts to develop nano insulation materials (NIM) by the sacrificial template method producing hollow silica nanospheres (HSNS) will be given. Moreover, challenges and opportunities related to possible development of hollow silica nanofibres (HSNF) and combinations of HSNS and HSNF will also be treated. Finally, some aspects regarding theoretical modelling and environmental impact of NIM will be illuminated.

2 THE KNUDSEN EFFECT

The thermal transport through a porous material when exposed to a temperature gradient may be quantified by the material's total thermal conductivity λ_{tot} (W/(mK)), which may be represented as a sum of conductivities associated with the following different thermal transfer mechanisms:

$$\lambda_{tot} = \lambda_{sol} + \lambda_{gas} + \lambda_{rad} + \lambda_{conv} + \lambda_{coup} \quad (1)$$

where λ_{sol} is the solid state thermal conductivity, λ_{gas} is the gas thermal conductivity, λ_{rad} is the radiation thermal conductivity, λ_{conv} is the convection thermal conductivity, and λ_{coup} is the thermal conductivity coupling term accounting for second order effects. To minimize the thermal conductivity, the sum of the above contributions must be minimized. The coupling effect can be rather complex. Theoretical approaches to thermal performance of VIPs usually assume this coupling effect to be negligible, see e.g. the study by Heinemann [4]. Gas convection will be negligible for porous materials with very small pores.

For VIPs, the difference between 4 W/(mK) (non-aged, pristine condition) and 20 mW/(mK) (punctured) of 16 mW/(mK) is due entirely to gas thermal conductivity (omitting any changes to the solid core due to the 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 somewhat lower as there is still a very small concentration of air inside a VIP causing gas conduction. Hence, as it is possible to make materials with such a very low solid state and radiation conductivity, there are rather good opportunities to make a high-performance thermal insulation material functioning at atmospheric pressure by lowering the gas thermal conductivity.

Thus, the stage is set for the opportunities to exploit the Knudsen effect, where the gas thermal conductivity $\lambda_{gas+gas/solid}$, also including the gas and solid state pore wall interaction, may be written in a simplified way as [1,2,5]:

$$\lambda_{gas+gas/solid} = \frac{\lambda_{gas,0}}{1+2\beta Kn} = \frac{\lambda_{gas,0}}{1+\frac{\sqrt{2}\beta k_B T}{\pi d^2 p \delta}} \qquad (2)$$

where $\lambda_{gas,0}$ is the gas thermal conductivity in the pores at STP (standard temperature and pressure) (W/(mK)), β is a coefficient characterizing the molecule-wall collision energy transfer (in)efficiency (between 1.5 - 2.0), k_B is the Boltzmann's constant ($1.38 \cdot 10^{-23}$ J/K), T is the temperature (K), d is the gas molecule collision diameter (m), p is the gas pressure in pores (Pa), δ is the characteristic pore diameter (m), σ_{mean} is the mean free path of gas molecules (m), and $Kn = \sigma_{mean}/\delta$ is the Knudsen number.

Hence, by decreasing the pore size within a material below a certain level, i.e. a pore diameter of the order of 40 nm or below for air, $\lambda_{gas+gas/solid}$ may become very low even with air-filled pores, i.e. where the mean free path of the gas molecules is larger than the pore diameter. The solid state and gas interaction is taken care of by the β coefficient in Eq.2. Thus, the resulting $\lambda_{gas+gas/solid}$, also including the gas and pore wall interaction, versus pore diameter, may be calculated in this simplified model [1,2].

3 EXPERIMENTAL RESULTS AND POSSIBLE PATHWAYS

3.1 Spheres, Fibres and Combinations

A possible pathway is to make NIMs by assembling hollow nanostructures. These structures can be hollow nanospheres (HNS) (Fig.1) or hollow nanofibres (HNF) (Fig.1), where both material systems show great promise in lowering the bulk thermal conductivity. Further improvement is expected by combining the two systems to form a nanocomposite, as depicted in Fig.1.

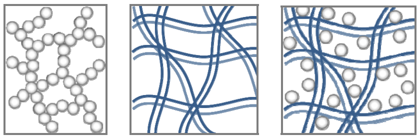

Figure 1. Schematic depiction of thermal insulation materials based on HNS (left), HNF (middle) and combined integrated HNS and HNF (right).

The material porosity must be optimized to reduce the solid contribution to thermal conductivity, i.e. shells must be thin, and still maintain strength to avoid sphere/fibre collapse. The distance between the hollow building blocks should be < 100 nm to minimize gas thermal conductivity.

Additional requirements for practical use include safe and easy handling and possibility for fitting on building site. Condensation of water within the pores must be avoided, thus the material should be hydrophobic.

3.2 Initial Experimental Pathways

Miscellaneous experimental pathways may be followed for manufacturing nanoporous thermal insulation materials by utilizing the Knudsen effect. Three of these are the membrane foaming, the internal gas release and the 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. However, our initial membrane foaming attempts were not successful as the reaction was too slow and no suitable surfactant systems were found to stabilize alcohol-based foams. 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. Due to very demanding experimental conditions, work along this path has so far been terminated. The processes would require simultaneous formation of gas bubbles with a narrow size distribution throughout the reaction system, very homogeneous system temperature, rapid shell formation (before Ostwald ripening process), and extremely reactive chemicals requiring strict humidity control. Although experimental investigations along both the template foaming and internal gas release pathways have been abandoned so far, it should be noted that future experiments may prove different, though.

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. In contrast to the two other methods, experimental work following the template method proved to be manageable and has provided interesting results.

3.3 Hollow Silica Nanospheres

The experimental work following the sacrificial template method has so far been concentrated on making hollow silica nanospheres (HSNS) by applying polyacrylic acid (PAA) and polystyrene (PS) as sacrificial templates, where the templates PAA and PS have been removed by a chemical washing and a heating process, respectively (the template materials diffusing and evaporating through the silica shell). Experimental procedures and details concerning various fabrications of HSNS are found in our earlier studies [6-8]. The principle behind the HSNS synthesis is illustrated in Fig.2 alongside scanning electron microscope (SEM) images of corresponding actual fabricated materials. Close resemblance between theoretical concepts and experimental practice is observed.

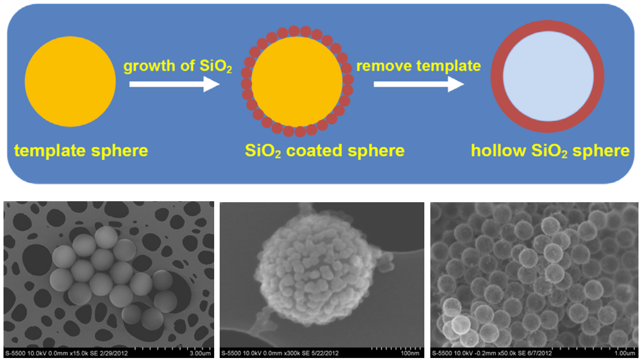

Figure 2. A principle drawing of the sacrificial template method for HSNS synthesis (top). SEM images (left to right) of PS templates, small silica particles coated around a spherical PS template, and HSNS after removal of PS.

The measured thermal conductivity for various powder samples of HSNS has typically been in the range 20 to 90 mW/(mK), though some uncertainties in the Hot Disk apparatus measurement method have to be clarified [9]. The specific powder packing of the HSNS in the bulk condition is also an issue to be addressed in this respect. Lowering the thermal conductivity is currently being attempted by a parameter variation and optimization of the hollow silica sphere inner diameter and wall (shell) thickness.

HNS materials must be hydrophobic in order to avoid water condensation, which is detrimental for thermal conductivity. Functionalization can be done during the production or structuring of HNS by adding hydrophobic silanes at appropriate steps in the reaction. It is also possible to apply a post-treatment, either by immersing the material in an impregnating bath or by gas phase transport of active components to external and internal surfaces.

3.4 Hollow Nanofibres

High-performance thermal insulation materials may also be achieved with hollow nanofibres (HNF). Structuring of HNF into a bulk material is expected to be less challenging than that for the HNS counterparts as long fibres tend to entangle together as depicted in Fig.1. This may also help to improve the corresponding mechanical strength compared to HNS based materials. Previous studies have revealed that the thermal conductivity of HNF is primarily dependent on their wall thickness [10], thus highlighting the importance of controlling the wall thickness of HNF through different experimental pathways. It is also reasonable that controlling other structural or compositional parameters, such as the wall materials and the packing manner/density of the HNF, would have an impact on the overall thermal conductivity of the resulting materials.

Several synthesis routes are available for HNF [11], such as self-assembly, electrospinning, and template-assisted approaches. Among these, the template-assisted method, which has also been used for the preparation of HNS, is considered to be specially promising, e.g. for control of the wall thickness. Various inorganic and organic nanofibres will be tested for use as template materials; in particular, the organic nanofibres may be produced via electrospinning, which is a continuous process well suited for up-scaling. It is important that for thermal insulation applications HNF materials must be hydrophobic to avoid water condensation. Surface functionalization methods similar to those used for HNS (in situ modification, liquid and gaseous post treatments) will be tested.

3.5 Sphere and Fibre Integration

Fibres are widely used to reinforce materials. Since the thermal conductivity of HNF is lower than that of their solid counterparts, HNF may be used as reinforcements for HNS-based NIMs as depicted in Fig.3, thus combining the advantages of HNS and HNF within one material.

Several methods are available for HNS-HNF composite synthesis. One possibility is to prepare dispersions of HNS and use them to impregnate HNF mats. Capillary forces during drying should be avoided by surface functionalization, proper solvent selection and well-controlled solvent removal to achieve evenly distribution of HNS throughout the HNF material.

Overall function and installation requirements will determine whether flexible foils are needed to support the HNS, HNF and/or composites (Fig.3). The foils could have several functions, e.g. provide mechanical support, prevent nanoparticulate dust during handling, control transport of water vapour and limit thermal radiation.

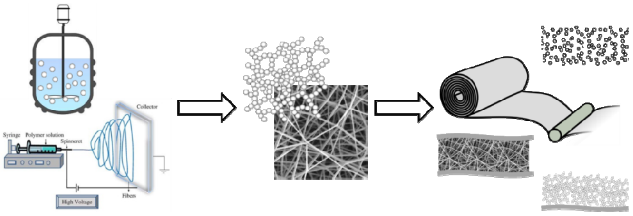

Figure 3. A possible schematic production route for low-density, hydrophobic, flexible NIM mats.

4 THEORETICAL MODELLING

Thermal properties of nanostructured materials are governed by processes at different scales. A decisive factor is the thermal conductivity of the solid phases, which is primarily limited by phonon scattering. Phonons are not only scattered by impurities and phonon-phonon interactions, but also when they reach the surfaces. Surface scattering may dominate at the nanometre scale. As a first estimate of these surface effects, we computed the thermal conductivity of a thin plate of α-quartz from first-principles quantum mechanics using the temperature dependent effective potential method [12-14]. The surface scattering was accounted for by using Minnich's approach [15]. A temperature range of 50 to 800 K was investigated. All underlying quantum mechanical computations were carried out using the PBE96 [16] density functional and the VASP program package [17]. The longer c-axis was assumed to lie in the plane, and thermal conductivity was studied along this axis. At 300 K the thermal conductivity is halved relative to bulk values when the film thickness is 4 nm. For more complex structures at more relevant size scales, Monte Carlo simulations may be used [18,19].

5 ENVIRONMENTAL IMPACT

Preliminary life cycle analysis (LCA) of NIM as HSNS has been carried out [6,7,20], and follow-up investigations are currently being conducted. Simplified health, safety and environmental (HSE) evaluations will be actively used to evaluate the sustainability and safety of possible production routes. Initial evaluations will be based on comparisons of chemical and environmental properties of alternative reactants, solvents, by-products and products associated with material production. Detailed HSE evaluation of the most promising materials and production routes will be carried out. The aim is to reduce risks associated with all stages of the materials' life cycle: Material production, use and end-of-life waste management and recycling, including safety measures for industrial production, which may differ from those for laboratory scale synthesis.

Full LCA will be performed as a part of selecting the most promising production routes. The assessment will include energy and material consumption, emissions of heat, emissions to air and water, and solid waste, in addition to the product. Then we will assess thermal conductivity and durability for the completion of the LCA, and compare the NIMs with conventional thermal insulation products.

6 CONCLUSIONS

In the on-going quest for high-performance nano insulation materials, hollow nano spheres and fibres and their possible integration represent promising stepping-stones towards developing new thermal insulation materials. Important issues being addressed are chemical synthesis and optimization, theoretical models for thermal transport, health, safety, environmental aspects and life cycle assessment.

ACKNOWLEDGEMENTS

This work has been supported by the Research Council of Norway within the Nano2021 program through the SINTEF and NTNU research project ”High-Performance Nano Insulation Materials” (Hi-Per NIM).

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