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Synthesis of Hollow Silica Nanospheres

Nano Insulation Material for Energy-Efficient
Buildings

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Abstract

Increased attention is given to the global energy use and emissions of greenhouse gases (GHG) since research has shown that this is highly related to the increasing global temperature. A temperature rise of only 2 °C compared to pre-industrial level may have serious consequences for the global climate. The building sector accounts for up to 40% of the global energy use and GHG emissions, and has therefore experienced more investigations for energy saving measures in the last decades. Here, high-performance thermal insulation materials, with low thermal conductivity, in the building envelope may be a promising improvement for both new and existing (as retrofit) buildings.

This study first gives an introduction to thermal insulation materials and the state-of-the-art high-performance solutions such as aerogels and vacuum insulation panels. Since these materials have their disadvantages has the knowledge obtained from this research later been used in the experimental work of producing a nano insulation material (NIM). NIM is regarded as a promising path for development of new materials. In this work has sacrificial polystyrene templates been used for synthesis of hollow silica nanospheres (HSNS), which is a silica-based NIM. The procedure is a multistep process where adjustments can be made to reduce inner diameter or shell thickness of the spheres. Some of these modifications have been investigated and the thermal conductivity of the product has been measured with the use of a Hot Disk apparatus. These HSNS may be a possible stepping-stone in the work towards high-performance NIM, and with a measured thermal conductivity of 20 mW/(mK) for spheres with an inner diameter of 46.3 nm is there a reason for expectations. Suggestions for further research have also been included.

Keywords

Thermal insulation
Nano insulation material
NIM
Knudsen effect
Hollow silica nanospheres
HSNS


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Norwegian abstract

Den globale energibruken og utslippet av drivhusgasser har fått økt oppmerksomhet etter at det ble kjent at dette er sterkt knyttet til den globale oppvarmingen. En temperaturøkning på bare 2 °C sammenlignet med førindustrielle verdier, kan ha alvorlige konsekvenser for det globale klimaet. Byggesektoren er ansvarlig for opptil 40 % av den globale energibruken og utslippene av drivhusgasser. De siste tiårene har derfor denne sektoren opplevd en økning i forskning som leter etter energisparende tiltak. Isolasjonsmaterialer med svært lav termisk ledningsevne for bruk i bygningsskallet blir sett på som en mulig forbedring for både nye og eksisterende bygninger.

Dette studiet gir først en introduksjon til isolasjonsmaterialer og deres virkemåte, deretter blir dagens produkter med lavest termisk konduktivitet, som aerogel og vakuumsisolasjonspaneler, presentert. Siden disse løsningene har sine svakheter benyttes kunnskapen om dem i et eksperimentelt arbeid for å utvikle nanoisolasjonsmaterialer (NIM). NIM er sett på som en lovende teknologisk utvikling. I dette arbeidet har polystyrenekuler blitt brukt som offermal for å lage hule silikananosfærer (HSNS), som er et silikabasert NIM. Prosedyren er en prosess med flere steg hvor forskjellige justeringer er mulig for å endre faktorer som innvendig diameter eller skalltykkelse på sfærene. Noen av disse justeringene har blitt undersøkt og termisk ledningsevne er målt ved bruk av et Hot Disk-apparat. Disse HSNS kan være et steg i retningen av NIM med meget gode isolerende egenskaper for bruk i bygninger. Målinger gjort viser en ledningsevne på 20 mW/(mK) for HSNS med en innvendig diameter på 46.3 nm, noe som gir grunn til forhåpninger. Underveis er det også gitt forslag til videre forskning.

"We shape our buildings, and afterwards, our buildings shape us."

- Winston Churchill (1943)

"Nanotechnology is an idea that most people simply didn't believe."

- Ralph Merkle (2000)

Preface

This master thesis concludes my five years of studies at the Norwegian University of Science and Technology (NTNU). The work is done as the final requirement in the five-year Master of Science program of Civil and Environmental Engineering (Bygg- og miljøteknikk) during the spring of 2017.

The work in this thesis is done as a part of the NANO2021 program by the Research Council of Norway through SINTEF and NTNU. More specifically the research project "High-Performance Nano Insulation Materials" (Hi-Per NIM). The work has been to synthesize hollow silica nanospheres (HSNS) with the use of sacrificial polystyrene templates, characterize the HSNS and measure the thermal conductivity in order to see if this is a possible stepping-stone for the next generation Hi-Per NIM.

The results are presented in the form of scientific articles, two already are approved for publication in Energy Procedia through 11th Northern Symposium on Building Physics 2017 in Trondheim, Norway and CISBAT 2017 in Lausanne, Switzerland. The final text is written in the style of a scientific article, and was submitted in June 2017 for potential publication in *Construction and Building Materials*. Since this is not meant for a very restricted conference paper, it can be longer and explain things more thoroughly.

I would like to thank my supervisor Bjørn Petter Jelle for introducing me to the topic of nano insulation materials and contributing with good advice and feedback. He also gave me the challenge of writing scientific articles, a new and interesting test for me. I am very happy for the opportunity and the belief he had in me. I would also like to thank my co-supervisor PhD candidate Sohrab Alex Mofid for training me in laboratory work and contributing with his results to the project. The work presented in this thesis would not be possible to do without his knowledge. He has also been an important contact person, and has come with great input to the articles. Finally, I have to thank my girlfriend, family and friends for their continuous support during this semester. They have kept my motivation up throughout these months.



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Process report

Master thesis, Haakon Fossen Gangåssæter

Introduction

This process report covers the work on the articles "Air-Filled Nanopore Based High-Performance Thermal Insulation Materials", "Synthesis of Silica-Based Nano Insulation Materials for Potential Application in Low-Energy or Zero Emission Buildings" and "Synthesis and Characterization of Hollow Silica Nanospheres for Thermal Insulation in Buildings", written during winter 2016/2017 and spring 2017.

Expectations

Since the work with the article "Air-Filled Nanopore Based High-Performance Thermal Insulation Materials" was mostly done during the late 2016/early 2017 I knew the physics of heat transport and the functioning of thermal insulation materials. This was a scientific review article on the state-of-the-art of thermal insulation materials for application in building envelopes for the 11th Northern Symposium on Building Physics 2017 (NSB2017). Hence, my knowledge on article structuring, citations, references and literature studies was good. This basis was crucial to have before I started on the work synthesis and characterization of hollow silica nanospheres (HSNS).

The difference is that the master thesis consists of experimental work which involves a lot of physics and chemistry. The plan was to be with PhD candidate Sohrab Alex Mofid in the laboratory to learn the procedures and the basic chemistry for the first period, then work more independent afterwards. Together we should produce HSNS, characterize them in microscopes and nano particle analysers and measure thermal conductivity. The results should be presented in different scientific articles were we should alternate on being author and co-author.

Work progress

The first phase of the work with this master thesis consisted of finishing the article for NSB2017 since the deadline was set to the beginning of February 2017. The work with the article was started during the authors project thesis in the autumn, but the article went through major changes in review period. When this was done, the training started in the laboratory and the author began with chemistry studies. Even though this is not directly used in this thesis it is important to know the background of the

work to be able to identify what different adjustments make to the final product.

The synthesis of HSNS is a multistep process with three main steps. These are production of polystyrene (PS) spheres, silica coating and drying of PS and measuring of thermal conductivity. February/Mars was mostly used for production of PS spheres in the chemistry lab at SINTEF, which proved to be give both positive and negative answers to some important questions. For the coating process we found out that NTNU NanoLab had instruments that could help us. This is a restricted certified cleanroom area after ISO 5-7 cleanroom standards. These standards guarantees certain maximum level of contaminants in the room, which is very important for work on nanoscale. We were first granted access after sufficient equipment traning, theory course and guided tour. The work in the NanoLab was time consuming since every synthesis only gives a fraction of what is needed for thermal conductivity mearsurements. This means that there was needed a lot of repetitive work. When the sufficient amount of HSNS was produced we measured thermal conductivity using a Hot Disk TPS 2500S apparatus at SINTEF in April/May. This was the final part of scientific work for me, but the research continues of Sohrab and his PhD project.

When we had the first laboratory results, the article "Synthesis of Silica-Based Nano Insulation Materials for Potential Application in Low-Energy or Zero-Emission Buildings" was written to the CISBAT conference in Lausanne, Switzerland. An abstract submitted in February was already approved and the article explaining the synthesis and obtained results was submitted 30th April 2017 and approved for publishing and presentation at CISBAT early June 2017. Since this was a short conference paper with a six page restriction, a more comprehensive article was made to go more thoroughly through the synthesis and results. More background theory and figures were also included. This article, "Synthesis and Characterization of Hollow Silica Nanospheres for Thermal Insulation in Buildings", was written in May and submitted to the journal Construction and Building Materials in June.

Summary

The work with this master thesis has learnt me that experimental work is very time consuming and might sometimes be frustrating. Especially when the work is not going according to plan or you have unexpected results. On the contrary, there are few things better than having promosing results after hard work. The last few months have been very different from what I have done earlier in my studies, but at the same time has this semester been very interesting and educational. Working in the frontiers of research and publish articles under my name is a very giving process.

Introduction

Today our buildings have become more complex than ever. What was earlier just a barrier against the outdoor climate is now a high-performance structure that should provide humans with everything from shelter and comfort to esthetics. The increased demands we have to our buildings have made every step from material manufacturing to construction and use requiring high amounts of energy. Hence, have energy saving measures in the building sector had an increased attention, and therefore also the research on high-performance insulation materials. Better insulation in buildings has been shown to be both an effective energy and a money saving measure [1–3].

To understand the development of the next generation thermal insulation materials, a basic knowlegde of thermal conductivity and todays materials is crucial. A short introduction will be given here. A more comprehensive explanation can be read in the articles presented from page 7 in this thesis.

Thermal conductivity

It is important to understand the physics behind heat transport in order to know what to look for in an insulation material. The total thermal conductivity, λ_{total} , in porous materials consists of different contributions and is often easiest described by use of the following:

$$\lambda_{total} = \lambda_{gas} + \lambda_{solid} + \lambda_{conv} + \lambda_{rad} + \lambda_{leak} + \lambda_{coup} \quad (1)$$

where λ_{gas} is the gaseous thermal conductivity, λ_{solid} is the solid solid state conductivity, λ_{conv} is convection conductivity, λ_{rad} is radiation conductivity, λ_{leak} is leakage thermal conductivity and λ_{coup} is thermal conductivity due to coupling effects [4, 5]. The different contributions are described more to detail in article number 1 and 3. Here, the important thing to notice is that every part of Equation 1 is rather well limited in most existing thermal insulation materials, except from λ_{gas} . Due to the pore sizes is this limited to the value of air (26 mW/(mK) at standard temperature and pressure, STP) [6, 7]. This makes it difficult to create air-filled insulation materials with low thermal conductivity, but there might be a solution to decrease the gaseous thermal conductivity substantially. This possible, and promosing, solution is based on the Knudsen effect.

The Knudsen effect

The Dane Martin Knudsen (1871-1949) discovered this effect in 1910 [8], and it is a consequence of small, gas-filled pores. An important factor is the mean free path of the gas, which is the average distance a gas molecule travels before it collides with another molecule [9]. If the pores are smaller than the mean free path of the gas inside will the gas molecules hit the pore walls more often than the other gas molecules. The gaseous thermal conductivity, λ_{gas} will be significantly lowered due to the ineffective energy transfer from molecule to pore wall [6, 10]. The Knudsen effect states that the thermal conductivity of gas is given by the following:

$$\lambda_{gas} = \frac{\lambda_{gas,0}}{1 + 2\beta Kn} \quad (2)$$

where,

$$Kn = \frac{l_{mean}}{\delta} \quad \text{and} \quad l_{mean} = \frac{k_B T}{\sqrt{2}\pi d_{gas}^2 P_{gas}} \quad (3)$$

where $\lambda_{gas,0}$ is the thermal conductivity of stagnant air at STP and β is a constant expressing the (in-)efficiency of energy transfer between molecules and pore walls. β has a value between 1.5 and 2.0. Kn is the Knudsen number, l_{mean} is the mean free path of the gas inside the pore, δ is the pore diameter, T is the temperature, d_{gas} is the collision diameter of the gas molecules and k_B is the Boltzmann's constant¹ [10, 11]. It can easily be seen that a decrease in pore diameter increases the Knudsen number. Hence, a smaller pore diameter will reduce the gaseous thermal conductivity.

Thermal insulation materials

There are many different insulation materials on the market today. The most commonly used materials are different sorts of mineral wool (i.e. glass or rock wool), but also cellulose fibers, polyurethane, cork and extruded and expanded polystyrene is used [4, 9]. These materials have good strength properties and adaptability on the building site, but they have a relatively high thermal conductivity (30–40 mW/(mK)) [12].

The increased focus on energy and space saving has pushed the building sector in to more use of materials with lower thermal conductivity, such as aerogels, vacuum

¹The value of Boltzmann gas constant is approximately $1.381 \times 10^{-23} \text{ JK}^{-1}$

insulation panels (VIP) or gas-filled panels (GFP) [5,13,14]. The problem is that most of these materials all have disadvantages. Mineral wool has a rather high thermal conductivity, aerogels are brittle and expensive, while VIP/GFP loose performance over time due to the inevitable loss of vacuum/gas because of air and moisture diffusion into the core over the lifetime.

Next generation high-performance thermal insulation materials

In this thesis has the state-of-the-art in thermal insulation materials been investigated, both commercially and on research level. Based on previous research and on the knowledge behind heat transfer in porous materials has there been worked on developing the next generation thermal insulation material based on nano technology and utilization of the Knudsen effect. More specifically has the work been to look at hollow silica nanospheres as a possible solution or stepping-stone on the way to nano insulation materials. Results from the work will be presented in this thesis as scientific articles.

Articles

Introduction to articles

For this master thesis has three articles been produced where the author of the thesis is the responsible author of the article. This page will give a short introduction to all the articles.

1. Air-Filled Nanopore Based High-Performance Thermal Insulation Materials

This article was submitted to the 11th Northern Symposium on Building Physics 2017 (NSB2017) after review and finalizing in January 2017. The work originally started during the autumn 2016 when the author was working on his project thesis which was a study of the high-performance thermal insulation materials available for building envelopes, but due to extensive work and major changes in the review period was it natural to include it in this thesis.

The article was approved for publishing in March 2017 and will be a part of a separate issue of Elsevier's Energy Procedia after the conference medio June 2017.

2. Synthesis of Silica-Based Nano Insulation Materials for Potential Application in Low-Energy or Zero Emission Buildings

This article was submitted to CISBAT 2017, a conference in Lausanne on energy efficient buildings and implementation of nanoscale materials in the building sector. It explains the synthesis of hollow silica nanospheres (HSNS) and presents some of the findings from the research done this spring. The article was limited to a six page restriction, and the information presented had to be carefully chosen.

The article was approved for publishing in May 2017 and will be a part of a separate issue of Elsevier's Energy Procedia after the conference in September 2017.

3. Synthesis and Characterization of Hollow Silica Nanospheres for Thermal Insulation in Buildings

This article can be seen as an extension of article 2, including also the important background theory. Some of the basics of heat transport from the first article was included to give a better understanding for the reader. This article presents the same results as in article 2, but with even more, and promising, findings and discussions.

Article 3 was submitted in June to the international scientific journal Construction and Building Materials for potential publication.

**Article 1: Air-Filled Nanopore Based High-Performance Thermal
Insulation Materials**

Accepted for publication in Energy Procedia and to be presented at the
Northern Symposium of Building physics 2017 in Trondheim.

11th Nordic Symposium on Building Physics, NSB2017, 11-14 June 2017, Trondheim, Norway

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 CO₂ 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]:

$$\lambda_{total} = \lambda_{solid} + \lambda_{gas} + \lambda_{rad} + \lambda_{conv} + \lambda_{coup} + \lambda_{leak} \quad (1)$$

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]:

$$\lambda_{gas} = \frac{\lambda_{gas,0}}{1+2\beta Kn} \quad (2)$$

where

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

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), $\lambda_{\text{gas},0}$ 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/(m²K) (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/m³ 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.

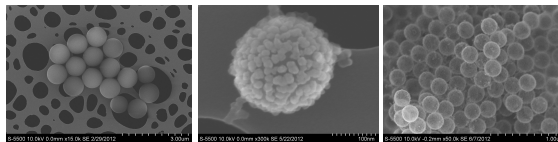


Figure 1. The different steps in the template method with SEM images (left to right) of PS templates, small silica particles coated around a spherical PS template, and HSNS after removal of PS.

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.

Acknowledgements

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Article 2: Synthesis of Silica-Based Nano Insulation Materials for Potential Application in Low-Energy or Zero Emission Buildings

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Synthesis of Silica-Based Nano Insulation Materials for Potential Application in Low-Energy or Zero Emission Buildings

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Abstract

Sacrificial polystyrene (PS) templates have been used for synthesis of silica-based nano insulation materials (NIM). The PS was synthesized by a simple procedure where parameters as polyvinylpyrrolidone/styrene ratio and potassium persulfate amount were adjusted. Thereafter the PS templates were coated with silica by using tetraethyl orthosilicate (TEOS). The time used for adding TEOS was varied to investigate the effect on how the silica particles attached to the PS surface and the resulting silica spheres. By modifying the process, different PS templates were obtained. The thermal conductivity was measured for hollow silica spheres originating from the coating process of 198 nm PS templates, and the results showed thermal conductivities around 38 mW/(mK) for long-time measurements (160–640 s). Controlled synthesis of this silica-based NIM might be a stepping-stone on the path to a new generation of high-performance thermal insulation materials with low thermal conductivity, which can be used in the building envelope of low-energy or zero emission buildings in the future.

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Peer-review under responsibility of the scientific committee of the scientific committee of the CISBAT 2017 International Conference – Future Buildings & Districts – Energy Efficiency from Nano to Urban Scale.

Keywords: Nano insulation material; NIM; Knudsen effect; Zero emission building; ZEB

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Peer-review under responsibility of the scientific committee of the CISBAT 2017 International Conference – Future Buildings & Districts – Energy Efficiency from Nano to Urban Scale.

1. Introduction

Increased global attention is given to environment in general, and especially sustainable development and energy use in buildings. This is regarded, in order to reach the goal set by the Intergovernmental Panel on Climate Change of limiting the global warming to 2 °C compared to pre-industrial level [1], as an important focus.

The building sector is often called the 40 % sector since it uses approximately 40 % of the materials and energy world-wide, and in addition accounts for 40 % of the annual global emissions of greenhouse gases (GHG) [2]. An important factor of the total energy use in a building is determined by the needs for heating and cooling, that has a varying share between 20 % and 80 %. This energy use is dependent on the building envelope. Thus, thermal insulation with significantly lower thermal conductivity than what is commonly used today may contribute to an overall reduced energy consumption in the building sector.

Today's commonly used solutions such as mineral wool and high-performance products as aerogel and vacuum insulation panels (VIP) all have their drawbacks. Mineral wool has a relatively high thermal conductivity, while aerogels are brittle and expensive and a VIP has the risk of puncture and in any case the inevitable vacuum loss over time due to diffusion of air and moisture into the VIP core, which can increase the thermal conductivity up to ten times the initial value. These disadvantages make it interesting to work with developing a new generation of thermal insulation materials.

A promising path to follow is to create nano insulation materials (NIM), where the goal is to utilize the Knudsen effect to reduce the thermal conductivity substantially [3]. NIM is proposed to be a homogenous structure with an overall conductivity of less than 4 mW/(mK). The structure can be both open or closed nanoporous [4]. For a VIP, the difference in thermal conductivity from pristine condition (4 mW/(mK)) to punctured (20 mW/(mK)) is entirely due to loss of vacuum, and therefore related to gaseous thermal conductivity. The heat transport within an insulation material is complex, but as VIPs illustrate may the gaseous thermal conductivity be of considerable importance. Reducing the pore diameter to nanoscale in a material may significantly reduce the thermal conductivity. An insulation material with considerable lower thermal conductivity than most commonly used materials today may not only save energy, but also money and space in every step from production and transport to installation, due to less material used.

The objective of this work is to attempt to have a controlled production of silica-based nanospheres using sacrificial polystyrene templates. Silica is used for many applications such as in medicine, electronics and water treatment on nano scale, and is shown to be a controllable and robust material [5–8]. Investigations for use in building envelopes, especially as core materials in VIPs, have also been conducted [9,10]. During the synthesis, several parameters are investigated in order to state their importance for the final product. Both the inner diameter of the spheres and the shell thickness may affect the thermal conductivity, and these are dependent on the size of the polystyrene spheres and the coating procedure, respectively. For the coating process may the time used for adding tetraethyl orthosilicate (TEOS) be important for the shell thickness.

2. Synthesis of silica-based nano insulation materials

The synthesis is carried out principally as described by Sandberg et al. [11], but with some modifications. The experimental work is explained in the following. The results from the different steps in the synthesis is showed in Figure 1.

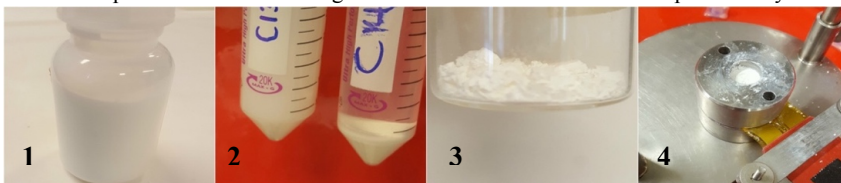


Figure 1: Results of the steps in the synthesis. The first and left photo shows the polystyrene templates produced (1), in the second photo the polystyrene spheres coated with silica particles are showed both before (left) and after (right) centrifuging (2), the third photo shows the dried silica spheres (3), and the fourth photo depicts the powder in the Hot Disk for measurement of thermal conductivity (4).

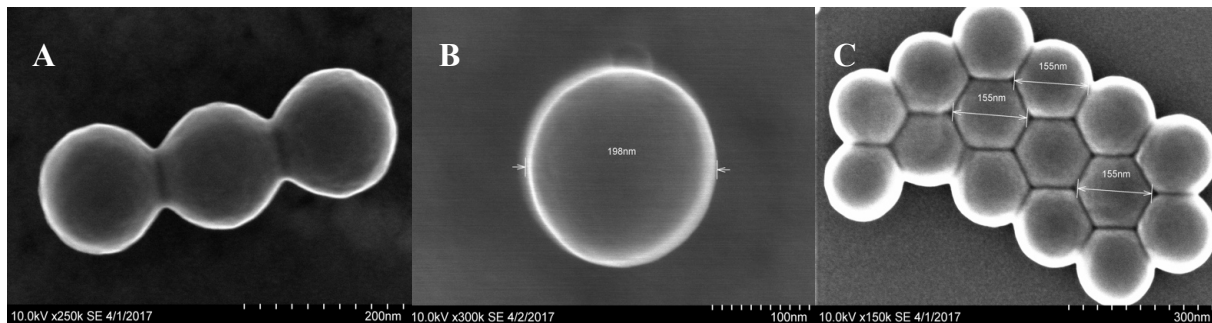


Figure 2: Scanning electron microscope (SEM) images of polystyrene templates A (160 nm), B (198 nm) and C (155 nm), dimensions referring to sphere diameter.

2.1. Materials

Polyvinylpyrrolidone (PVP), reagent grade styrene, potassium persulfate (KPS), tetraethyl orthosilicate (TEOS) as source for silica, ammonium hydroxide solution (NH_4OH , 28-30 wt%) and 96 % ethanol. Throughout the synthesis of the PS templates was distilled water used as a reaction medium.

2.2. Preparation of polystyrene templates

For the preparation of polystyrene (PS) templates, 10 g of styrene, 90 g of distilled water and a given amount of polyvinylpyrrolidone (PVP), were added in a single-neck round-bottom flask. The flask was immersed in an oil bath at 70 °C and magnetically stirred for 15 minutes before a KPS-water mixture (given amount of KPS in 10 g of distilled water) was added dropwise using a plastic pipette. The mixture was kept in the oil bath for approximately 24 hours, while magnetically stirred and heated at 70 °C. After this were the PS templates cooled down and stored at room temperature.

By varying the amount of KPS added, and the PVP/styrene-ratio, were different PS diameters achieved, see Table 1 and the scanning electron microscope (SEM) images in Figure 2.

Table 1: Average diameter of the polystyrene (PS) templates by varying the PVP/styrene-ratio and the amount of KPS.

Polystyrene sample	PVP/styrene-ratio	Amount of KPS (g)	Measured diameter (nm)
A	0.18	0.15	160
B	0.20	0.20	198
C	0.20	0.15	155

2.3. Coating of polystyrene templates

For coating of the PS spheres, 6 g of PS were added to 115 g of 96 % ethanol in a 500 ml round-bottom flask with extra horizontal opening for a syringe. The mixture was magnetically stirred at 500 rpm before 5 ml of NH_4OH was added. The flask was then closed with a ground glass stopper and vacuum grease to prevent evaporation. Then a 10 ml TEOS solution (5 ml TEOS and 5 ml 96 % ethanol) was added dropwise with the use of a syringe pump. The time used was adjusted to investigate possible changes. See Figure 3 for a photo of the setup. After the TEOS solution was added, the mixture was left over night while stirred. The solution was then centrifuged at 4500 rpm for 20 minutes to extract the silica coated PS templates. To remove the PS, was the sample dried at 475 °C for 12 hours.

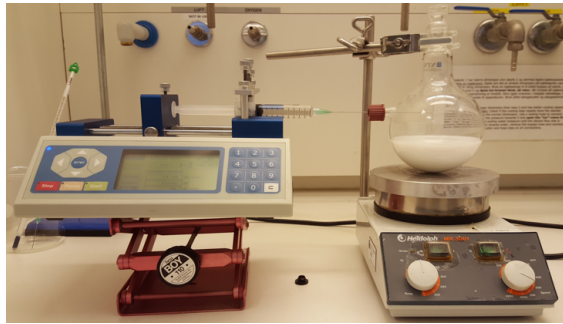


Figure 3: TEOS solution added dropwise to the round bottom flask with the use of a syringe pump, a 10 ml syringe and a horizontal opening in the flask.

2.4. Characterization

Size and morphology were characterized using a Hitachi S-5500 scanning electron microscope (SEM), which also has a transmission electron microscope (TEM) mode. A small sample of the synthesized material was solved in ethanol and dripped onto a TEM grid. The ethanol was evaporated in air before the grid was inserted in the SEM.

Thermal conductivity of the NIM was measured by the use of Hot Disk TPS 2500 S Thermal Constant Analyser. The sensor used had a diameter of 6.403 mm.

3. Results and discussion

3.1. Polystyrene templates

The importance of the PVP/styrene ratio has been reported in several earlier publications [11,12]. Both size and monodispersity of the PS are dependent on this relation, but the effect is higher for smaller ratios [11]. This is shown by comparing sample A and C from this work, where the ratio was increased from 0.18 to 0.20 ($\approx 11.1\%$) and the diameter was reduced from 160 nm to 155 nm ($\approx 3.2\%$). For higher PVP/styrene ratios were there no monodispersity in the PS sample, which is important for creating a homogenous insulation material.

In this work, the effect of KPS was also investigated. It was found that for a PVP/styrene ratio of 0.20 and an increase in KPS, had a negative effect on the result. When increasing the amount of KPS from 0.15 to 0.20 ($\approx 33.3\%$), the diameter of the PS increased from 155 nm to 198 nm ($\approx 27.7\%$).

3.2. Coating of polystyrene templates

The time used for applying the TEOS solution for coating of the PS samples was adjusted in the range of 1–5 hours to investigate if the time had any effect, and the results showed that the time was not of significant importance.

More important is the surface characteristics of the PS sample. Since silica particles have a tendency of being in the negatively charged range will they not attach to the PS surface unless the PS surface is positively charged [13].

In Figure 4 one can see an SEM image of silica spheres produced by coating of PS sample B, which under investigation with SEM proved to be the most monodisperse material and was therefore used for measurement of thermal conductivity. For this image, the sacrificial polystyrene templates have been removed by drying the sample in the oven for 12 hours.

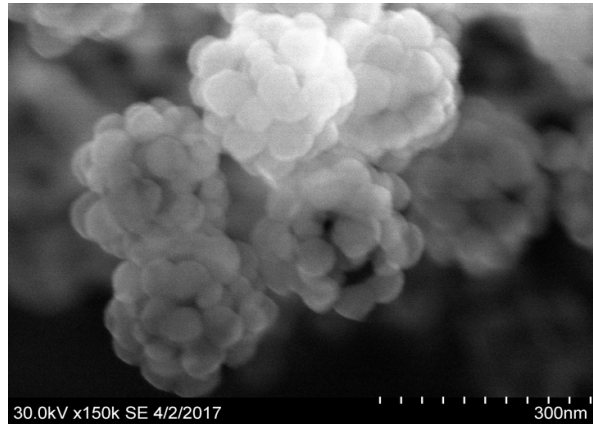


Figure 4: Scanning electron microscope (SEM) image of silica spheres produced by coating and drying of PS sample B.

3.3. Thermal conductivity measurements

The thermal conductivity measurements were carried out on silica spheres produced using the PS sample B as a sacrificial template. A SEM image can be seen in Figure 4. Four measurements were performed on the same sample where only the measurement time was varied. As seen in Table 2 the thermal conductivity was measured lower for longer measurement time. Since the start temperature (23 °C) and output power (50 mW) were the same for all the measurements it is assumed that the initial heating phase of the material has a minor role for longer measurements, hence the thermal conductivity measurement stabilizes in the range of 38 mW/(mK) over time. Naturally, for applications in building envelopes will these long-time measurement values represent the relevant performance. The value of 38 mW/(mK) is approximately 10 % higher than the lowest values for mineral wool in dry conditions (32–34 mW/(mK)) [14]. It is assumed that with smaller silica spheres, the exploitation of the Knudsen effect may be improved, thus lower thermal conductivity values may be obtained.

Table 2: Thermal conductivity measurements of insulation materials produced by coating of 198 nm PS spheres. The measurements were carried out by using a Hot Disk TPS 2500 S apparatus.

Measurement time (s)	Start temperature (K)	Output power (mW)	Thermal conductivity (mW/(mK))
80	296	50	42.1
160	296	50	38.9
320	296	50	38.0
640	296	50	37.9

An important notice for these measurements is that they are performed on the same sample, with the same packing density. The latter may affect the performance of the Hot Disk apparatus and alter the thermal conductivity measurements, and therefore also the obtained results. The influence of the packing density on the Hot Disk apparatus should be investigated in further studies.

4. Conclusions

The diameter of the polystyrene (PS) templates was adjusted by changes in the polyvinylpyrrolidone (PVP)/styrene ratio and potassium persulfate (KPS) amount used in the synthesis. A higher PVP/styrene ratio gave a smaller PS diameter, while an increase of KPS used gave an increase in the size of the PS templates.

For the coating process, it was discovered that the time used for adding the solution of tetraethyl orthosilicate (TEOS) and 96 % ethanol was not of significant importance and that the surface characteristics of the PS samples had a greater impact on the final results.

The thermal conductivity was measured to be in the range of 38 mW/(mK) when PS samples with sphere diameters of 198 nm were used. The thermal conductivity measurements were carried out over different time intervals, but on the same test sample with the same start temperature and the same output power for the Hot Disk TPS 2500 S apparatus. It is likely that the packing density of the silica powder can alter the thermal conductivity measurements in the Hot Disk apparatus. Hence, further studies should investigate the importance of this aspect.

Acknowledgements

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**Article 3: Synthesis and Characterization of Hollow Silica
Nanospheres for Thermal Insulation in Buildings**

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Synthesis and Characterization of Hollow Silica Nanospheres for Thermal Insulation in Buildings

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Abstract

Hollow silica nanospheres (HSNS) have been synthesized using sacrificial polystyrene (PS) templates to investigate this solution as a possible stepping-stone towards high-performance nano insulation materials (Hi-Per NIM). The synthesis is a multi-step process where PS first was produced by a straight forward procedure. Parameters as polyvinylpyrrolidone/styrene ratio and potassium persulfate amount have been adjusted to see the effect on the PS diameter, which is determining the inner diameter of the HSNS. Different PS spheres were obtained and used for coating. When coating the PS the time used for adding the tetraethyl orthosilicate solutions was varied to see if there was any difference in shell characteristics such as e.g. thickness. The produced HSNS were measured for their thermal conductivity using a Hot Disk TPS 2500S apparatus. The results were approximately 20, 31 and 38 mW/(mK) for HSNS with inner diameters of about 46, 151 and 209 nm, respectively. A controlled production of HSNS with small inner diameters might be a promising path towards Hi-Per NIM based on air-filled pores. This can potentially be used in building envelopes after further research, for both new low-energy and zero emission buildings or as a retrofit energy saving measure in existing buildings.

Keywords

Nano insulation material, NIM, Hollow silica nanosphere, HSNS, Thermal insulation, Knudsen effect

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1. Introduction

The energy consumption and carbon emissions of the building sector have become crucial issues with respect to the global climate, and the construction sector is responsible for more than 40 % of the global energy-use and 33 % of the global greenhouse gas (GHG) emissions [1,2]. In order to reach the goal of The Intergovernmental Panel on Climate Changes (IPCC) on reducing the global warming to a 2°C increase compared to pre-industrial levels, the global emissions of GHG must be reduced [3]. Studies have shown that investments in implementation of energy efficiency and renewable energy measures like improved heating systems and new or retrofit insulation can reduce the energy-use substantially [4,5]. The later shows that the total energy use in a building is dependent on the insulating effect of the building envelope.

The commonly used insulation materials today, such as mineral wool, vacuum insulation panels (VIP) and aerogels, all have their inconveniences or shortcomings. Mineral wool has a relatively high thermal conductivity between 30 and 40 mW/(mK) [6]. VIPs and aerogels have a lower thermal conductivity, but they must be handled with care. While aerogels are expensive and brittle, will a VIP has the constant risk of puncture under transport and installation, and will anyway loose performance due to the inevitable vacuum loss over time because of air and moisture diffusion into the core. This can increase the thermal conductivity up to ten times the initial value. The challenge of making a material with the same insulating effect as a VIP in pristine condition, while keeping the material robust and possible to adapt on building site is very interesting. This is where a new generation of thermal insulation materials comes in.

Nano insulation materials (NIM) is a promising path to follow. A NIM is proposed to be a homogenous, open or closed porous structure with an overall thermal conductivity of less than 4 mW/(mK) [7]. The goal with NIM is to utilize the Knudsen effect where gaseous thermal conductivity is reduced, and therefore also the overall thermal conductivity, substantially [8]. The potential can be shown by using VIP as an example. In pristine condition is the thermal conductivity only 4 mW/(mK), but when punctured it is increased to 20 mW/(mK) [6]. This is entirely due to loss of vacuum.

Heat transport within an insulation material is a complex matter, but the example with the VIP shows that the gaseous part may be of considerable effect. Hence, utilization of the Knudsen effect might be significant in the development of new materials. A development where the work presented in this article might be a stepping-stone.

The objective of this study is to attempt to have controlled production of hollow silica nanospheres (HSNS) with an in-situ procedure. Which means that particles are growing in a solution [9]. Here, sacrificial polystyrene (PS) templates are produced and coated with silica, then dried to remove the PS template, and HSNS are obtained. Silica is showed to be rather controllable on nano scale, and has been used for many applications from drug carrier in medicine to water treatment and electronics [10–13]. For building envelopes has especially the use of silica as core material in VIP be investigated [14–16]. During the synthesis' have several parameters been varied to study the effect on the final thermal conductivity. Factors that may affect this can be the inner diameter of the spheres and the shell thickness. The thought is that this can be adjusted with different PS templates and coating techniques, respectively.

2. Thermal conductivity

Heat flows through a materials as a result of solid state and gas conduction, radiation and convection, and the direction of flow is from a higher temperature body to a lower temperature body [17]. The different contributions to a material's thermal conductivity, and their relations, are described in and the following text and equation [6]:

$$\lambda_{total} = \lambda_{solid} + \lambda_{gas} + \lambda_{rad} + \lambda_{conv} + \lambda_{coup} + \lambda_{leak} \quad (1)$$

where λ_{solid} and λ_{gas} are solid state and gas conductivity, λ_{rad} is radiative conductivity, λ_{conv} is convection conductivity, λ_{coup} is conductivity due to coupling effects and λ_{leak} is leakage thermal conductivity.

2.1. Solid state conduction

Solid state conduction is when heat is transferred as kinetic energy through the structure of an atomic solid-state lattice. The temperature will spread through the media since atoms with high kinetic energy will transfer some of the energy to neighbouring atoms with less energy. Such transfer of energy in the solid part may be viewed upon as flow of free electrons (as in metals) and/or as vibration of the solid-state lattices made up of atoms held together by electron bounds [18].

2.2. Gas conduction

In gaseous conduction heat is transferred from molecule to molecule when two molecules with different energy level collide. Energy is transferred from a high-energy molecule to a molecule with a lower energy level [6].

2.3. Radiation

Thermal radiation may occur to gases, liquids and solids, and all body surfaces are influencing the transfer of energy by either absorbing, transmitting, emitting or reflecting electromagnetic radiation [19,20]. The electromagnetic radiation takes place due to molecular and atomic agitation, and the radiation has wavelengths in the range of 2 to 80 μm when looking at temperatures up to 100 $^{\circ}\text{C}$ [21]. This range covers what buildings are exposed to.

2.4. Convection

For buildings convection will be air flowing along the building envelope, but as a more general definition convection is when heat is transferred between a surface and a moving fluid with different temperatures [6]. The flowing substance can be both liquid and air, where the latter is of course most relevant for buildings. The movement of the liquid is due to different temperatures in the media and the heat transfer is characterized by the movement inside the media of particles and molecules with different energy levels [22].

2.5. Coupling

The coupling effect can be quite complex and is often neglected, but it can be included to take account for second order effects related to the different contributions to the total thermal conductivity as given in Equation 1 [6].

2.6. Knudsen effect

The aim of producing NIM is to utilize the Knudsen effect, which may lower the total thermal conductivity substantially. For conventional thermal insulation materials are the effects of solid conduction, radiation and convection reduced using low-radiative surfaces and porous structures. But the effects of gaseous conduction is limited to 26 mW/(mK), which is the conductivity of stagnant air at standard temperature and pressure (STP), because of the pore size and the open material structure [8,23]. The Knudsen effect is achieved when the pores of the material has a diameter smaller than, or comparable to, the mean free path of the gas molecules inside. Knowing how to utilize and exploit the Knudsen effect may be an important stepping-stone when developing the next generation high-performance thermal insulation materials.

The Knudsen effect is explained by Equation 2 and 3, and shows how a smaller pore diameter will decrease the gaseous conduction, λ_{gas} , which is a combination of thermal conductivity of the gas inside the pores and the transfer of energy when molecules collide with pore walls, where the latter is given from the factor β :

$$\lambda_{gas} = \frac{\lambda_{gas,0}}{1+2\beta Kn} \quad (2)$$

where

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

where $\lambda_{gas,0}$ is the thermal conductivity of stagnant air at STP and β gives the inefficiency of energy transfer between molecules and pore walls when colliding. The β is a unit less number between 1.5 and 2.0. Kn is the Knudsen number, σ_{mean} is the mean free path of the gas molecules, δ is the pore diameter, T is the temperature, d is the collision diameter of the gas molecules and k_B is the Boltzmann's constant [23,24]

As seen from Equation 2 and 3 will the Knudsen number become large for small pore diameters, and this results in a lower λ_{gas} . If the pores can be reduced to have a smaller diameter than the mean free path of air (≈ 70 nm at STP) the thermal conductivity may be substantially decreased without applied vacuum or low-conductive gases [15]. This possibility is what is being investigated with the production of HSNS in different sizes.

3. Synthesis of hollow silica nanospheres

The synthesis principally follows the procedure as described by Sandberg et al. [23], but with some modifications. Figure 1 shows a schematic drawing of the synthesis principles, while Figure 2 shows pictures of the results from each step.

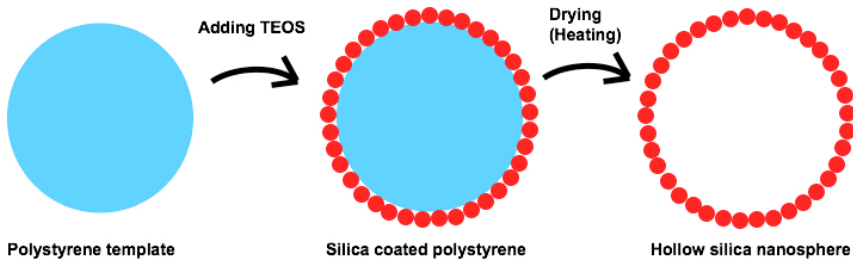


Figure 2: Schematic illustration of the synthesis from polystyrene template to hollow silica nanosphere using an in-situ coating technique and heated drying.

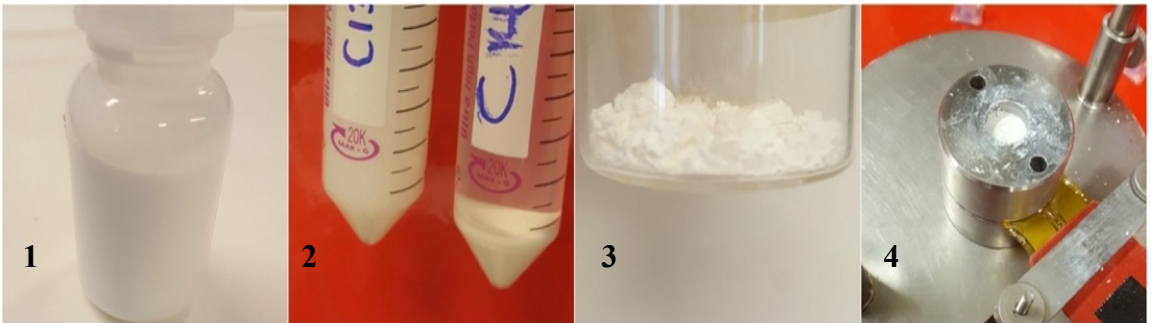


Figure 1: Results of the steps in the synthesis. The first and left photo shows the polystyrene templates produced (1), in the second photo the polystyrene spheres coated with silica particles are showed both before (left) and after (right) centrifuging (2), the third photo shows the dried silica spheres (3), and the fourth photo depicts the powder in the Hot Disk for measurement of thermal conductivity (4).

3.1. Materials

Polyvinylpyrrolidone (PVP), reagent grade styrene, potassium persulfate (KPS), tetraethyl orthosilicate (TEOS) as source for silica, ammonium hydroxide solution (NH_4OH , 28-30 wt%) and 96 % ethanol were the chemical substances. Throughout the synthesis of the PS templates distilled water was used as a reaction medium.

3.2. Preparation of polystyrene templates

Polystyrene (PS) templates were prepared by mixing 10 g of styrene and 90 g of distilled water together with a given amount of polyvinylpyrrolidone (PVP) in a single-neck round-bottom flask. The flask was immersed in an oil bath keeping 70°C and magnetically stirred at 500 rpm for 15 minutes before a KPS-distilled water mixture was added dropwise using a plastic pipette. The KPS amount was varied, but the distilled water was kept at 10 g. After this the mixture was kept in the 70°C oil bath and stirred for approximately 24 hours. Then the obtained PS was bottled and kept at room temperature for further use. Figure 2 shows the PS nanosphere suspension in picture 1 (leftmost picture) and Figure 3 shows a scanning electron microscope (SEM) picture of PS spheres.

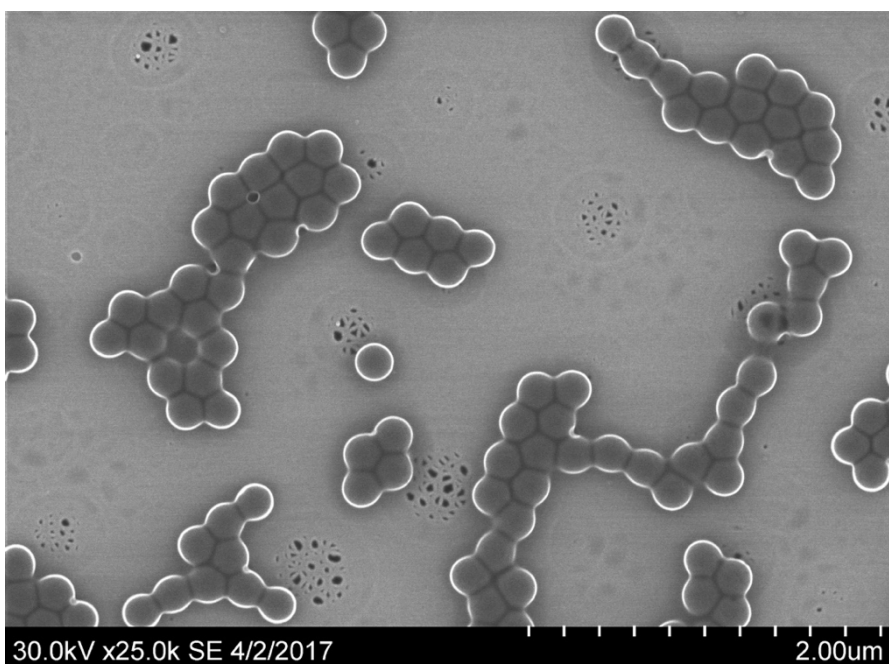


Figure 3: Scanning electron microscope (SEM) picture of PS spheres with a sphere diameter in the range of 209 nm.

3.3. Coating of polystyrene templates

The silica coating of the PS templates is done by using TEOS as the silica source. For the process is 6 g of PS added to 115 g of 96% ethanol in a 500 ml round-bottom flask with an extra horizontal, silicone-covered opening for syringes. The mixture was magnetically stirred at 500 rpm for 5 minutes before 5 ml of NH_4OH was added. Then, the flask was sealed with a ground glass stopper with vacuum grease to prevent evaporation of the ethanol. The 10 ml TEOS solution (5 ml of TEOS and 5 ml of 96 % ethanol) was added dropwise through the horizontal opening. A syringe pump was used to adjust the time between each drop for the different synthesis to investigate possible changes. Figure 4 shows a photo of the setup.



Figure 4: TEOS solution added dropwise to the round bottom flask with the use of a syringe pump, a 10 ml syringe and a horizontal opening in the flask.

With the TEOS solution added the mixture left was over night while it was kept stirred at 500 rpm. The mixture was then centrifuged at 4500 rpm for 20 minutes to extract the silica coated PS templates. The sacrificial PS was removed by drying the sample at 475 °C for 12 hours.

3.4. Characterization

For characterization of size and morphology for both the PS templates and the HSNS a Hitachi S-5500 scanning electron microscope (SEM) was mainly used. The SEM also has a transmission electron microscope (TEM) mode that was used to investigate shell thickness for the HSNS. For both SEM and TEM a small sample of the material was dissolved in ethanol and dripped onto a TEM grid. The grid was kept still until the ethanol had evaporated in air. A NanoSight Nanoparticle Analysis system with LM10 unit and blue laser was used to investigate the size and monodispersity of the PS templates.

For measuring the thermal conductivity of the synthesized HSNS a Hot Disk TPS 2500 S Thermal Constant Analyser with a sensor with a radius of 6.403 mm was used.

4. Results and discussions

As seen is the synthesis of HSNS a multistep process with a lot of room for research on different techniques that may influence the final product. For this work, the importance of the PVP/styrene ratio and the amount of KPS used for the PS templates, was investigated. For the coating process the time for adding the TEOS solution was studied, and how the PS size and surface affect the coating. Finally, the thermal conductivity of different HSNS was measured and compared. All results are presented in the same order as the synthesis process in the following.

4.1. Preparation of sacrificial polystyrene templates

The PS templates are very important for the final HSNS. They decide the inner diameters of the spheres, and their surface characteristics are very important for the coating process. First in this work, the PVP/styrene ratio was investigated. The importance of this has been reported in several publications earlier, and both the average size of the PS and the monodispersity are dependent on this ratio [23,25]. In Table 1 the PS samples produced in this work are listed together with their PVP/styrene ratios, KPS amount and obtained sphere diameters. SEM was used for analysing and investigation of the surfaces of the PS spheres. The pictures of the samples can be seen in Figures 5-7.

Table 1: Average diameter of the polystyrene (PS) templates by varying the PVP/styrene-ratio and the amount of KPS. Commercially purchased PS samples from Corpuscular Inc., New York, used for the coating process, are also listed as sample D.

Polystyrene sample	PVP/styrene-ratio	Amount of KPS (g)	Average diameter (nm)
A	0.18	0.15	$\approx 160^*$
B	0.20	0.15	$150.6 \pm 3.7^{**}$
C	0.20	0.20	$209.1 \pm 1.2^{**}$
D (Corpuscular Inc. (commercially product))	-	-	46.3^{***}

*Only measured using Hitachi S-5500 SEM due to a scarce amount of sample.

** Average diameter given with the standard error of mean.

*** Size given by manufacturer Corpuscular Inc., New York, USA, and controlled by us in SEM.

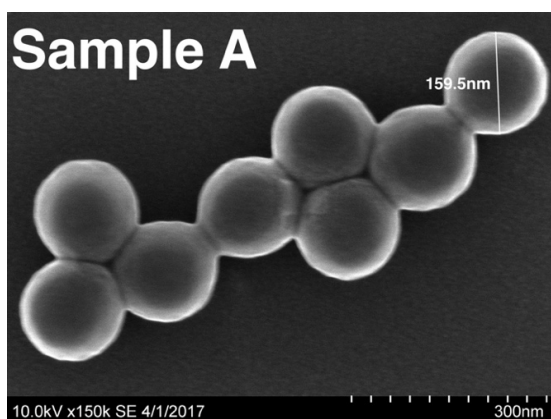


Figure 5: SEM picture of PS sample A. Obtained with the use of the Hitachi S-5500 with a TEM-grid.

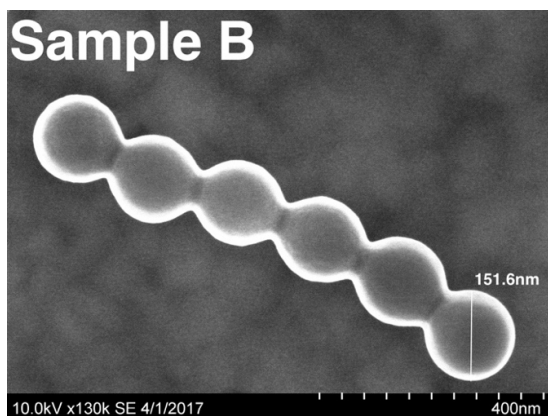


Figure 6: SEM picture of PS sample B. Obtained with the use of the Hitachi S-5500 with a TEM-grid.

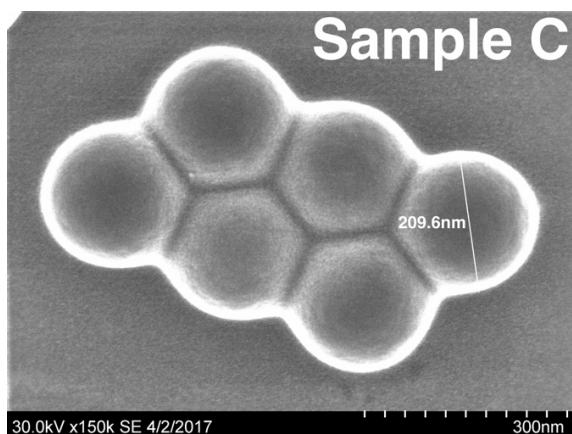


Figure 7: SEM picture of PS sample C. Obtained with the use of the Hitachi S-5500 with a TEM-grid.

By comparing sample A with B, that has the same amount of KPS, it is possible to see that the increased PVP/styrene ratio gave a smaller diameter of the PS. The ratio was increased from 0.18 to 0.20 ($\approx 11.1\%$) and this gave a reduction of about 10 nm ($\approx 6.3\%$). The role of the PVP in the synthesis is to be a stabilizer absorbed on the particle surface of the polystyrene particles [25]. Hence, the increasing amount of PVP to styrene (which is the monomer) results in a decrease in particle size. In this work, a limit on the PVP/styrene ratio of 0.20 was found, since a higher ratio gave no polymerization or samples with high polydispersity.

The monodispersity obtained from the particle size analyser of sample B and C can be seen in Figure 8 and 9. By comparing the two graphs can it be seen that both samples have a rather high degree of monodispersity, but sample B is slightly more polydisperse. The NanoSight particle analyser showed a small concentration of particles around 90 nm for sample B. The same tendency can be seen in Figure 9 for sample C as well, but not as clear as for sample B. This might be a result of the high PVP/styrene ratio or the higher amount of KPS (will be commented later). As explained will a higher ratio of PVP to

styrene in principle give smaller particles, which also was shown by comparing sample A to B. If the PVP is absorbed on some particle surfaces before the particles has grown to desired size, a result as shown in Figure 8 may be obtained.

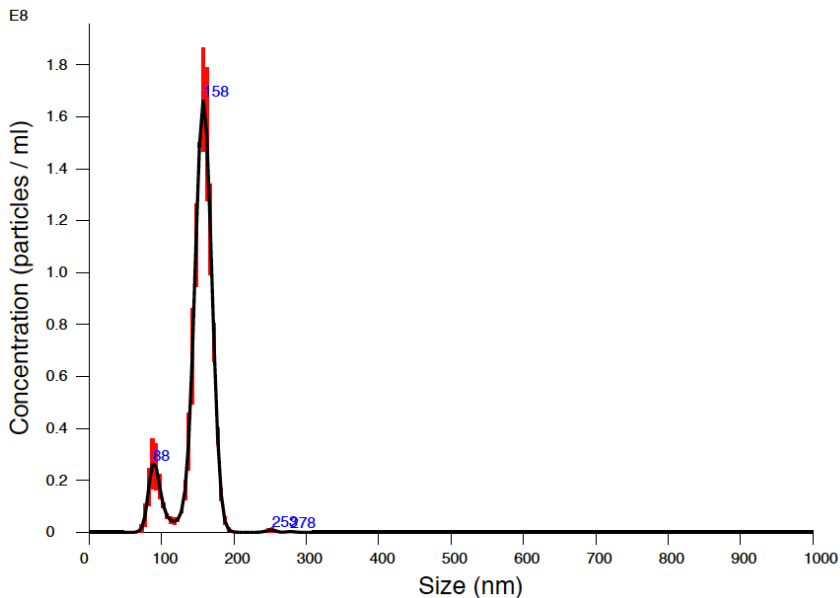


Figure 8: Particle size distribution of PS sample B. The red lines indicate ± 1 standard error of the mean.

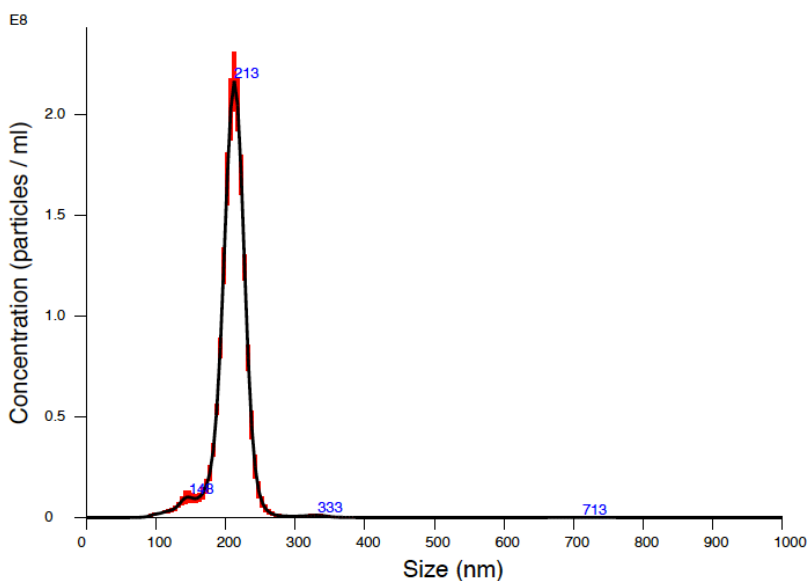


Figure 9: Particle size distribution of PS sample B. The red lines indicate ± 1 standard error of the mean.

The effect of the KPS amount was also investigated. KPS works as an initiator in the synthesis and, as seen from Table 1, an increased amount of KPS increased the size of the PS samples. The increase from 0.15 g to 0.20 g ($\approx 33.3\%$) resulted in an equally high increase in sphere diameter (150.6-209.1 nm, $\approx 38.8\%$). The higher amount of KPS makes the production of ionic groups produced from the decomposition of the initiator higher, and this changes the stabilization of the monomer (unstable monomer is produced) [26]. These unstable components give longer oligomeric chains and larger nuclei and particles [26]. Therefore, larger PS spheres were obtained when the KPS amount was increased. It should be noted that too low amounts of KPS would result in less production of initiator radicals, which further leads to less conversion of styrene [27].

For further research only PS sample B and C was used for coating and measurement of thermal conductivity. This is due to the time-consuming process of coating where small amounts of material are produced in each process. Since sample A and B were rather similar in size it was decided to work further with the smaller of the two. Sample C was used to investigate possible differences in inner diameter of the spheres and corresponding thermal conductivity. The same goes for a commercial sample from Corpuscular Inc. presented in Table 1 (sample D), which PS templates are considerably smaller in diameter than the ones produced by us, so coating and measurement of these are very interesting for comparison reasons.

4.2. Coating of sacrificial polystyrene templates

In this work, the coating process was investigated with focus on the time for adding the TEOS solution. The time was adjusted by using a syringe pump and a round-bottom flask with a horizontal opening as shown in Figure 4. The thought of changing the time was to investigate if a longer adding time would result in a different coating, and in the next step try to investigate if there was any difference in thermal conductivity.

The results from this work showed that longer time for adding the source of silica (in this case TEOS) did not necessarily result in a better or more even coating. In Figure 10, SEM images of a successful coating of PS sample B are given. This result was obtained by adding the 10 ml TEOS solution at a rate of $35\ \mu\text{l}/\text{min}$ (give a total adding time of 286 min). For higher rates similar results were achieved. Problems of successful coating occurred when the TEOS solution was added slower than $35\ \mu\text{l}/\text{min}$.

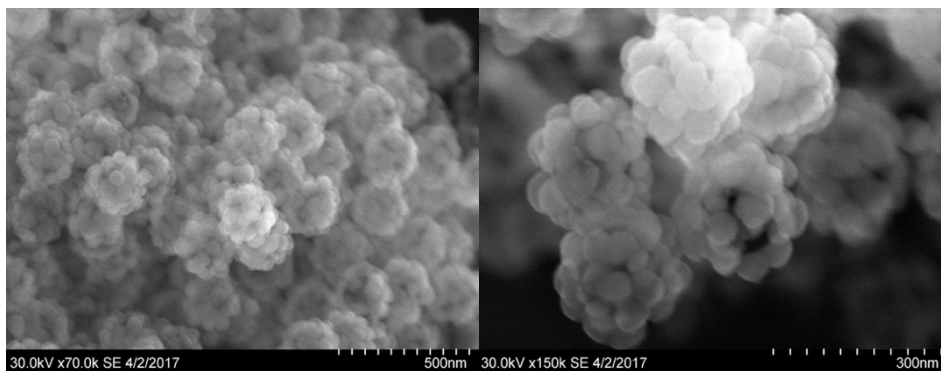


Figure 10: SEM images of hollow silica nanospheres obtained from a successful coating (adding 10 ml TEOS solution at a rate of $35\ \mu\text{l}/\text{min}$) and drying of sample B.

Figure 11 presents a TEM picture of an unsuccessful coating and Figure 12 gives a comparison between a successful and unsuccessful coating. It can clearly be seen that the silica has not formed a uniform shell around the PS in Figure 11, but has been deposited more randomly on the PS or on other silica particles. For thermal insulation materials, this is not preferred since there are no pores to utilize the Knudsen effect. Also, the solid/pore ratio will be too high and therefore the solid-state conductivity will also be high. The result will be an increased total thermal conductivity.

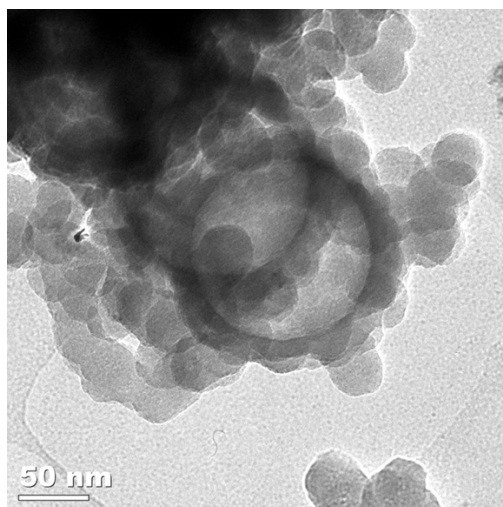


Figure 11: TEM image of an unsuccessful coating of PS sample B. It can clearly be seen that the silica has not created an even sphere shell, but has been deposited randomly on and between the PS spheres.

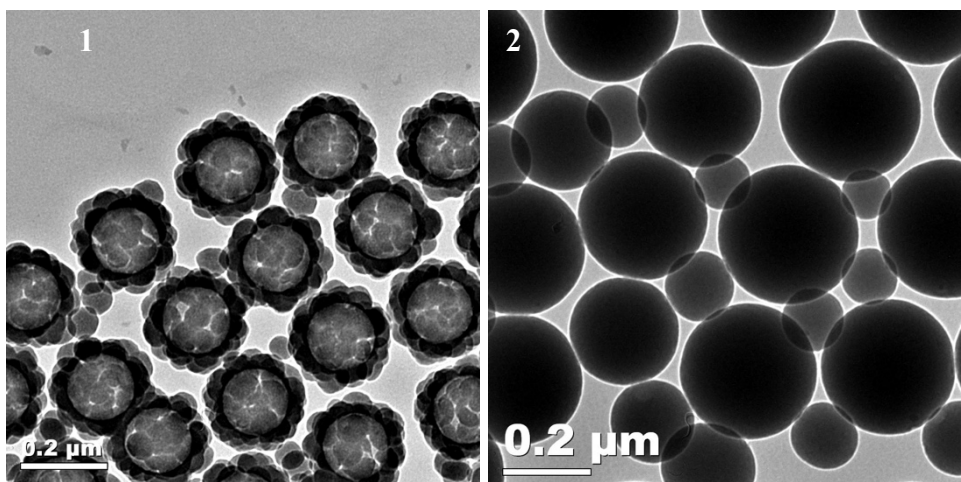


Figure 12: TEM pictures of successful, (1, left) and unsuccessful, (2, right) attempts to coat polystyrene spheres with silica. A uniform shell of silica has been obtained around the PS spheres (1), whereas the silica (smallest spheres) are randomly deposited between the PS spheres (2).

There might be several reasons for the uneven coating for longer adding time of the silica source. It is known that the characteristics of the PS sample is important, especially the charging of the surface. Silica particles has a tendency of being in the negatively charged range. Thus, a positively charged PS surface is necessary for the silica particles to attach themselves to the PS [28]. Similar coatings as in Figure 11 and 12 (right picture) has been the result when the charging of the surface has not been right. Then the silica particles are not connected in spheres around the PS templates and after the drying are no HSNS made. A possibility for this result for long-time adding of TEOS is that the first silica particles added somehow neutralize the PS spheres charging, and therefore the silica added later will not be attracted to a positively charged surface.

The final drying process for removing the PS templates has not been investigated in this work. First the samples were centrifuged to separate the solid particles from the ethanol that the coating process was taking place in. Then the samples have been left over night (12 hours) at 475 °C in an oven. The most important aspect here is that the polystyrene is completely dried out. Silica has a much higher melting point than the polystyrene, and the HSNS will be the only remaining. Ethanol and ammonia hydroxide will also evaporate in the oven.

4.3. Thermal conductivity of hollow silica nanospheres

The Hot Disk TPS 2500 S apparatus and belonging computer software have the option of adjusting several parameters for measuring thermal conductivity. For these measurements, the output power from the sensor were set to 50 mW for every measurement for consistency reasons. It was chosen to measure every sample with four different durations. This was conducted because the observed thermal conductivity measured was reduced with increasing time.

The reason for changing the time of measurement is to see the effect of the initial heating of the sample, and remove it from the results. Every test started with the same temperature and the sample was exposed to the same output power. The fact that the thermal conductivity measured for longer exposing periods approaches a constant value illustrates that the thermal conductivity stabilizes together with the operating temperature. The initial heating phase of the material plays a minor role in the longer measurements. For building applications, these long-time thermal conductivities are the most relevant, since buildings are exposed to gradually temperatures changes over long-time periods.

The results from the measurements of the three samples are given in Table 2 to 4, and Figure 13 gives a graphical illustration for easier comparison of the results.

Table 2: Thermal conductivity of HSNS produced by coating of 209.1 nm PS spheres (sample C). The measurements were carried out by using a Hot Disk TPS 2500 S apparatus with a sensor with a radius of 6.403 mm.

Measurement time (s)	Start temperature (K)	Output power (mW)	Thermal conductivity (mW/(mK))
80	296	50	42.1
160	296	50	38.9
320	296	50	38.0
640	296	50	37.9

From Table 2 can it be seen that the thermal conductivity of the HSNS obtained from sample C approaches ≈ 38 mW/(mK), which is approximately 10 % higher than for the lowest values of commercially available mineral wools in dry conditions (32-34 mW/(mK)) [29].

Table 3: Thermal conductivity of HSNS produced by coating of 150.6 nm PS spheres (sample B). The measurements were carried out by using a Hot Disk TPS 2500 S apparatus with a sensor with a radius of 6.403 mm.

Measurement time (s)	Start temperature (K)	Output power (mW)	Thermal conductivity (mW/(mK))
80	296	50	39.6
160	296	50	32.9
320	296	50	30.9
640	296	50	30.6

Thermal conductivity of the HSNS from coating of sample B (150.6 nm) approached ≈ 30 mW/(mK). This is a value below what is to be expected from mineral wools, extruded polystyrene, expanded polystyrene and other conventional insulation materials [6]. This thermal conductivity is also lower than for the larger HSNS from sample C, which is according to the theory that smaller pores lowers the thermal conductivity [7].

Table 4: Thermal conductivity of HSNS produced by coating of 46.3 nm PS spheres (sample D, commercially purchased sample from Corpuscular Inc.). The measurements were carried out by using a Hot Disk TPS 2500 S apparatus with a sensor with a radius of 6.403 mm.

Measurement time (s)	Start temperature (K)	Output power (mW)	Thermal conductivity (mW/(mK))
80	296	50	22.3
160	296	50	21.7
320	296	50	21
640	296	50	19.9

The HSNS produced with the commercially PS templates gave the lowest thermal conductivity measurements. For the long-time measurements, it was found that the thermal conductivity approached approximately 20 mW/(mK). This shows that the theory behind the Knudsen effect is actually in work for these hollow spheres, even though the thermal conductivity values are a bit higher than expected for HSNS with an inner diameter of less than 50 nm. In general the thermal conductivity measured for these HSNS is somewhat higher than the aerogel values [30,31]. There might be several reasons for the obtained thermal conductivity, and these will be discussed after the graphical presentation of the results.

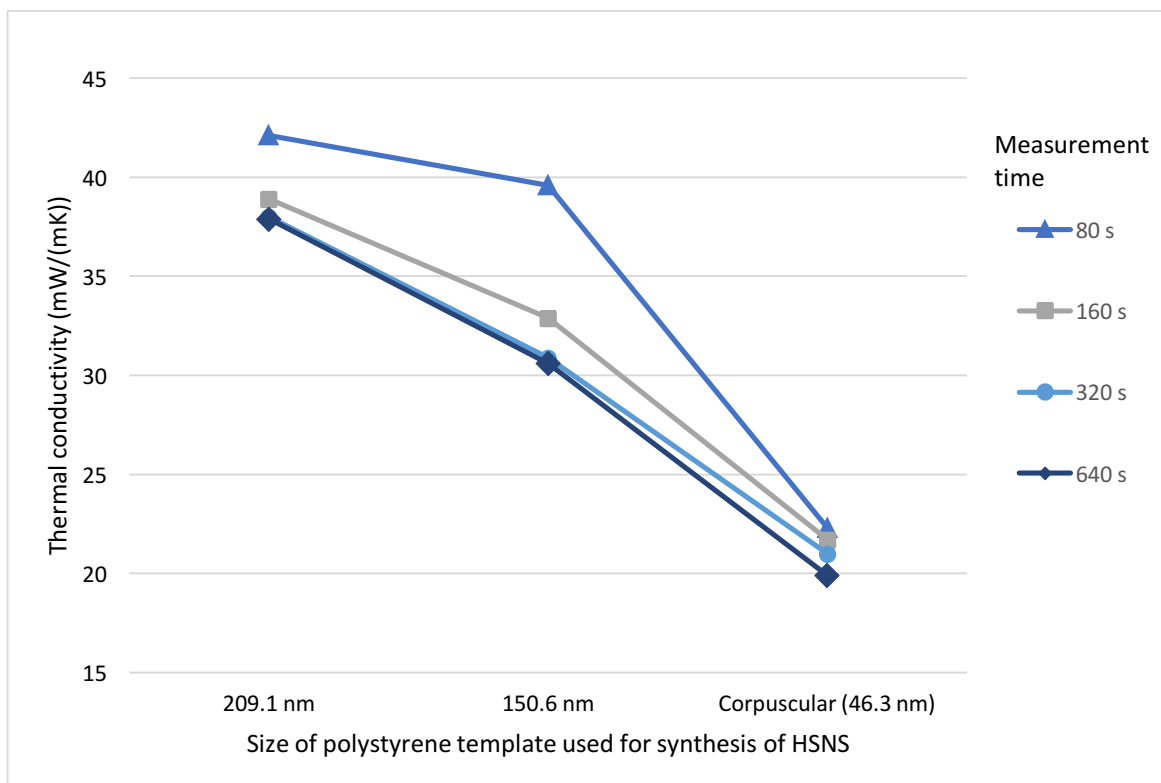


Figure 13: Graphical presentation of the thermal conductivity of the HSNS measured in the Hot Disk apparatus.

From the Knudsen equation given in Equation 2 and 3 a smaller pore diameter should decrease the gaseous thermal conduction, and therefore also the total thermal conductivity. This is illustrated in this work by comparison of HSNS obtained from PS sample B (template diameter 150.6 nm), C (template diameter 209.1 nm) and the PS templates from Corpuscular Inc. (diameter 46.3 nm). For the three samples a decrease in pore diameter of $\approx 28\%$ (209.1 nm to 150.6 nm) gave a decrease in thermal conductivity of $\approx 19\%$. For the reduction from 150.6 nm to 46.3 nm ($\approx 69\%$ reduction in inner sphere diameter) the thermal conductivity was reduced approximately 33%. These changes correspond rather well to the Knudsen equation when assuming all other variables than pore size to be constant.

For the measurements of HSNS a decrease in thermal conductivity was found with reduced inner diameter. This is according to the theory that smallest spheres should have the lowest thermal conductivity of the three samples tested due to better utilization of the Knudsen effect. This is also illustrated in Table 4 and Figure 13. However, the thermal conductivity was not as low as expected, and an even more significantly reduction in thermal conductivity could perhaps be obtained from HSNS with this size. Using the same numbers as Jelle et al. [31] in Eq. 2 and 3, calculations illustrated that for hollow spheres with inner diameters of 209, 151 and 46 nm the gaseous thermal conductivities and energy transfer from molecule to pore walls theoretically are as low as 12.1, 10.0 and 4.2 mW/(mK), respectively. For these calculations, air-filled pores at STP are also assumed. Shown by VIP, the gaseous thermal conductivity is dominant on these levels and lower

total thermal conductivities could therefore be expected.

A reason for these higher measured thermal conductivities might be that the HSNS do not have the shell characteristics as desired. Solid silica itself has a rather high thermal conductivity of 1500 mW/(mK) [29]. This means that thick shells of the HSNS, which gives a high solid/pore ratio, may contribute to an increased solid-state conductivity.

Another aspect to consider is the packing density of the powder when placed in the Hot Disk apparatus. The HSNS from the Corpuscular PS templates had a completely different texture than the two others. Where the HSNS from sample B and C was easy to pack in the cylindrical chamber, packing as seen in Figure 2, picture 4, the fine-grained texture of the smaller HSNS made it hard to obtain a perfect surface and density. The effect on thermal conductivity from particle packing is shown by several studies [33–35], and the contact area and contact resistance have been proven to have a significantly effect on the thermal conductivity. Therefore, it is likely that the packing density of the silica powder may alter the thermal conductivity measurements in the Hot Disk apparatus. That is, larger air pores between particles may affect the result. Hence, further studies should investigate the importance of this aspect and investigate other possibilities for measuring thermal conductivity.

4.4. Further research opportunities

Further work should focus on decreasing the size of the particles to try to utilize the Knudsen effect better. As shown in this work, smaller PS spheres for coating will give smaller inner diameters of the HSNS and therefore also lower the thermal conductivity, but the shell thickness must probably also be reduced for optimal effect. Optimizing the coating process is important to reduce the solid state thermal conductivity. For small HSNS the solid shell will contribute to a higher degree if its thickness is not reduced. An interesting possibility could also be to investigate the voids between the spheres to see if the Knudsen effect could also be utilized here for an even better insulation effect.

For this work HSNS have been obtained in a dry powder form. Since this is an impracticable substance to use as thermal insulation in building envelopes, a possible future research path is to study the possibility of gluing these particles together, or in any other way make a non-powder porous bulk material. A recommendation is to not use an envelope as for vacuum insulation panels since these are known to create thermal bridges and have the risk of punctures [24, 32,36–38]. Hence, a better solution could be to have a material with the texture characteristics as mineral wool, extruded polystyrene or expanded polystyrene. This would make the material better to handle at the building site.

Finally, the materials used and processed in the synthesis of HSNS should be explored to look for less energy consuming alternatives. Life cycle assessments (LCA) [37] of the processes related to the high embodied energy should therefore be investigated in further work. Either by changing the materials used, i.e. using waterglass (sodium silicate) as a silica source instead of TEOS, or changing the process, i.e. try to synthesis PS spheres in room temperature to save energy used for heating.

The authors also encourage research work looking for other solutions for developing NIM and other high-performance thermal insulation materials for implementation in building envelopes. Here, membrane foaming, internal gas release and other sacrificial template methods might be interesting aspects to investigate for creating open or closed nanoporous materials with as low thermal conductivity as possible.

5. Conclusions

All the synthesis steps of hollow silica nanospheres (HSNS) have been explained and modified to search for potential improvements. HSNS are made in a straight forward process with the use of sacrificial polystyrene (PS) templates that are coated with silica. The PS is then removed by drying in oven. The obtained HSNS were measured for their thermal conductivity in a Hot Disk apparatus.

For the PS templates, it was found that the diameter was decreased with increasing polyvinylpyrrolidone/styrene ratio up to 0.20, then spheres with diameters of ≈ 150 nm were obtained. For higher ratios, there were no successful synthesis. The amount of initiator used (in this work potassium persulfate (KPS)) also affects the size of the PS spheres. It was found that for higher amounts than 0.15 grams of KPS (to 10 grams of styrene) the sphere diameter was increased.

Tetraethyl orthosilicate (TEOS) was used as a silica source for the coating process, and it was investigated if the time used for adding the TEOS influenced the shell of the HSNS. A syringe pump was used for fully control over amount and time for TEOS added. For adding times over 5 hours no successful coatings were produced. There were not observed any substantial differences in the coating when adjusting the time in the lower time range (<4 hours), even though some coatings were unsuccessful for these as well. This indicates that the surface characteristics of the PS may have an impact due to the needed difference in charging between the positive PS surface and the negatively charged silica particles.

HSNS with inner diameters of about 209, 151 and 46 nm were successfully synthesized and the measurements in the Hot Disk TPS 2500S apparatus showed approximately 38, 30 and 20 mW/(mK) in thermal conductivity, respectively. These results illustrate that the final thermal conductivity is size-dependent as according to the theory of the Knudsen effect. However, the smallest HSNS have a higher thermal conductivity than what could be expected from spheres of that size. This could be a result of a higher solid-to-pore ratio than what is optimal, and the high solid state conduction of silica may negatively affect the results. Hence, further studies should investigate the coating process of PS spheres with diameters less than 50 nm to obtain smaller HSNS.

6. Acknowledgements

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Further work

The development of the next generation high-performance thermal insulation materials is in process with several possible solutions, where nano insulation material (NIM) is regarded as a promising one. In this work the synthesis of hollow silica nanospheres (HSNS) has been investigated for possible improvements, but there is a lot of work left.

For further research of HSNS should the coating of PS spheres with a diameter less than 50 nm be an important focus, because this is where the Knudsen effect is fully utilized as shown in this study. The shell thickness of HSNS with this size has to be adjusted so the ratio between solid silica and pore size is not too high. A lower shell thickness would also help reducing the solid-state thermal conductivity. Both the surface characteristics and the coating procedure might be very important for the obtained HSNS.

Shown by Gao et al. in [15] is this process of HSNS production relatively high in energy use. This can, to some extent, be reduced through an up-scale in production and recycling of materials, but the whole process should be investigated for possible energy-saving measures. An interesting proposal is to use waterglass, $(Na_2SiO_2)_nO$, as a silica source because of its lower energy-use during production.

Since the powder form of HSNS is not suitable for direct use in building envelopes should a process where the materials are glued together be developed. This way, the thermal conductivity could be measured for a solid material and not as a powder. A solution where an envelope is used, as for vacuum insulation panels, should be avoided because of the thermal bridging effect and the risk of rupture.

HSNS is only one possible way to develop NIM, where the basis is a sacrificial template method. Other ways may be internal gas release or membrane foaming methods. Here the latter is a process where a membrane is used to prepare a foam with nanoscale bubbles inside. Then a solid structure is obtained by hydrolysis and condensation of a precursor within the bubble walls. For production of NIM with the internal gas release method is the theory that 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, will create a nanoporous structure.

Conclusions

The state-of-the-art for thermal insulation materials for use in building envelopes have been investigated and it was found that despite some materials had very low thermal conductivities will all solutions available today have their drawbacks. The most commonly used mineral wool is very versatile, but has a high thermal conductivity. Aerogels and vacuum insulation panels (VIP) demonstrate that high-performance insulation materials with low thermal conductivity exists, but today's materials are brittle and loose performance over time. Hence, there are room for new solutions.

A promising path for high-performance thermal insulation is nano insulation materials (NIM), where the Knudsen effect is utilized to reduce the gaseous thermal conductivity. Hollow silica nanospheres (HSNS) were produced through a sacrificial template method, and investigated as a possible stepping-stone for developing high-performance NIM. All the steps of synthesis process of HSNS are described to detail and it was found that it is possible to adjust the size of the sacrificial polystyrene (PS) templates by varying the amount of potassium persulfate used and the polyvinylpyrrolidone (PVP)/styrene ratio. Up to a PVP/styrene ratio of 0.2 was PS templates successfully produced with the smallest diameter at 150 nm. For the amount of KPS was the higher limit found to be 0.15 g for the synthesis.

When the PS templates were coated, using tetraethyl orthosilicate (TEOS) as silica source, was the time used for adding the TEOS changed for different synthesis to investigate if this had any effect. The findings were that longer adding time for the TEOS did not give any different coatings. On the contrary, longer coating time gave non or uneven coating and for very long coating times (>6 hours) were no successful coating obtained. The optimal time was found to be less than 5 hours for these samples or, more general, adding the silica at a rate of > 35 μl .

Finally, and most important, was the thermal conductivity measured for the HSNS samples produced. The measurements done in the Hot Disk TPS 2500S apparatus showed approximately 38 mW/(mK), 31 mW/(mK) and 20 mW/(mK) for HSNS with inner diameter of 209.1 nm, 150.6 nm and 46.3 nm (commercially bought product from Corpuscular Inc., New York) respectively. The latter is a bit higher than what could be expected for this size, where factors can be that the shell is too thick and the solid-state thermal conductivity of the silica affects the result, or uncertainty in the thermal conductivity measurements, such as packing density in the Hot Disk apparatus. Anyway, the obtained results illustrate that smaller pores decreases the thermal conductivity, and show that NIM might be a promising path towards high-performance air-filled insulation materials for application in building envelopes.

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