EUDP 15-I, Thin vacuum insulation for post-insulation of buildings

Final report

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Acknowledgement

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Process

This project was structured into two phases:

1. Analysis
2. Experiments

The insulation analysis is structured into:

- Core insulation material
- Impermeable coating
- Business plan

During the analytic phase we have searched, found and studied more than a hundred scientific reports. Some are these reports are listed in the literature list at the end of this report

The experiments are focused around a particular process termed Thermally Induced Phase Separation (TIPS). During the experimental phase we have conducted more than 40 experiments (and experimental series) yielding in excess of hundred samples. Four of the most promising results have been tested for mechanical strength and thermal conductivity at ambient conditions and in vacuum.

The research within TIPS processes continues at DTI in collaboration with a master thesis project at KU by Martin Werge Willumsen, supervised by associate professor Kell Mortensen KU and PhD Kristian Sylvester Hvid DTI.

These extended experiments utilise experimental facilities established during the project, namely

- A newly designed autoclave setup employing transparent chambers allowing monitoring of the TIPS evolution visually in real-time.
- A 46 cm diameter autoclave chamber allowing the making of large amount of TIPS material

Additionally, a commercial track has been pursued with particular focus on

- Developing a business plan
- Mapping the freedom to operate in terms of existing patents within the area.

We have negotiated with X10 A/S and Syddansk Innovation A/S about venture capital. This process in pending until more knowledge on the TIPS material made is documented in order to substantiate a potential investment in the technology.

Executive summary

Figur 1: Model of the invented insulation cubes

The initial objectives of this research project is development of insulation with the following performance:

- 5-10 times better lambda value (3-6 mW/mK) than traditional materials.
- A material, which readily is shaped into 1cm thick panels that can be cut into shape at the construction site using ordinary construction tools.
- A material which does not deteriorate in terms of lambda over time as e.g. vacuum insulation panels.
- Price below 480 DDK/m2 excl. VAT (64 €/m2)

The initial invention

The project rests on an invention PCT/DK 2015/050307 describing 1 cm^3 cubes consisting of a core of super insulating material, subsequently covered with an impermeable coating allowing a permanent vacuum to be confined inside the cube.

The benefit of using evacuated cubes compared to Vacuum Insulation Panels (VIP) is that nail puncture due to mounting will only destroy the vacuum insulation performance in few cm^2 of in the entire panel. We knew from the beginning that we had to overcome two challenges in order to take advantage of the cube concept:

- While the VIP essentially is bagged powder, the cubes rely on a mechanically rigid super insulation material supporting the vacuum barrier on each face of the cube.

- The thermal bridge effect from the impermeable barrier is increased a hundred fold compared to VIPs due to the many cube surfaces. We had to identify a vacuum barrier with a hundred times smaller thermal conductivity.

The first year of the project proceeded according to the initial plan to produce the patented solution. The second year focussed on the core insulation material and particularly on how a polymer based core material could be made using the Thermally Induced Phase Separation (TIPS) process.

Core insulation material

The core material needed to be strong to support the pressure from the vacuum, and to be load bearing to be attractive as a building material. There is normally a conflict between strength and insulation performance. Stronger materials have a higher density and higher density materials have a poorer insulation performance.

We found however, two porous materials where the internal structure of the material is mechanically strong even at lower densities:

1. PMMA expanded with CO_2 into a foam
2. Thermally Induced Phase Separation (TIPS) processed PMMA

PMMA expanded with CO_2 into foam is well described in the research literature and has lately been developed by Dow chemicals. While it is fast to load CO_2 into water (sparkling water), it is very time consuming to load a large percentage CO_2 into PMMA in order to expanded it into a foam and thus not very practical for an industrial process.

We worked for a year in the laboratory on the development of a core insulation material made by an alternative process called Thermally Induced Phase Separation (TIPS) process. We succeeded in reducing the pore size from 150 micrometer to 200 nm using this process. That is an amazing almost thousand times reduction, bringing the pore size into a Knudsen regime. In this Knudsen regime, the gas trapped in the pores of the material ceases to conduct heat conducting heat as if was evacuated.

We have produced large samples of the TIPS insulation material with pores sizes in the range from 20-30 micrometer and porosity around 80%. The project funding was reduced compared to the applied budget and we ran out of money before we were able to produce large samples of TIPS with 200 nm pore size, so we could not test this super insulating material but expect it has a thermal insulation in the range of 17 mW/mK at ambient conditions.

Impermeable coating

Available scientific research, analyses, test and calculations documented that the thickness and thus the heat flow through the vacuum barrier of the surface of the cubes is roughly proportional to the largest pores in the surface.

Our research narrowed down the options available to cover the cubes with an impermeable coating to 1 micrometer graphene covered by a 10 micrometer waterproof polymer pain

The thermal bridge effect of introducing this vacuum coating, would at least add 0,007 W/mK to the heat flow of the material. Unfortunately, this almost balance the 0,009 W/mK gained by introducing vacuum into the cubes.

We found a (theoretical) solution, but it was not worthwhile going through several coatings to achieve a benefit of 0,002 W/mK. Even with pore size around 200 nm, the heat loss in the containment is about the same as the benefit from vacuum. It does not justify an expensive evacuation and coating process. It is furthermore very difficult to stay below a 200 nm maximum pore size, as there are always some much larger pores in surfaces among the otherwise small pores. Please note that there are 100 billion pores on one cm^2 surface.

The initial patented solution was consequently abandoned half way through the project. The patents granted protected the cube containment technology and it was consequently also abandoned.

Business plan

The commercial objectives were

1. Insulation 1 cm thin so your don't need to modify existing window frames, floor panels, electrical and heating installations
2. Do It Yourself mounting
3. Price below 480 DDK/m2 excl. VAT (64 €/m2)

We succeeded meeting all these goals.

We have named the TIPS insulation material Thinsu = Thin insulation

The unique selling point for Thinsu is a unique combination of:

- Good insulation like mineral wool and foam Reduce conductivity 72% from 0,14 W/mK in wood to 0,04 W/mK in the TIPS material
- Mechanical properties like wood
- Can be cast in any shape and profile
- Hydrophobic
- Completely inorganic, corrosion free and naturally white without painting
- Finished smooth durable surface.

Thinsu is not filled into a cavity in the construction, it is the construction

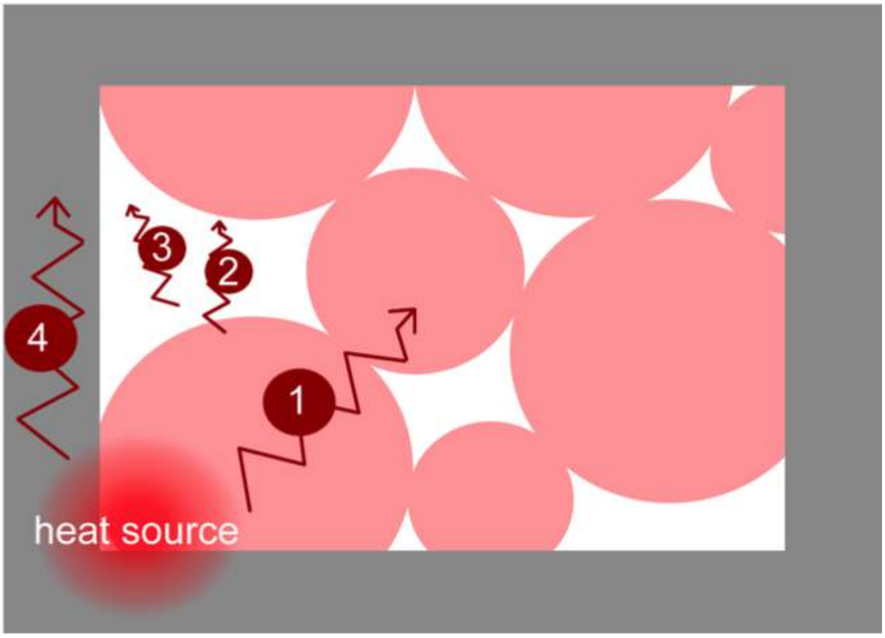
We don't know if the same mechanical performance is available when pore size is reduced from 20-30 micrometer to 200 nanometer as the 200 nm samples we have made are too small to be tested. If the mechanical properties prevail at small pore sizes we achieve a 90% reduction in conductivity compared to wood.

Our analysis point to the following core markets:

- A super insulating board you can cut, drill, and build with just like wood and wood board.
- Hard boards coloured straight through
- Supplied in floor to ceiling height as plasterboard and in smaller formats customers can pick up at an outlet and take home in the trunk
- Thinsu can be cast as click flooring with its own coloured durable and smooth surface and sold through building markets and on the Web in competition with laminate flooring
- Thinsu brings this product to the market through the wood floor manufacturers
- Thinsu can be glued to the back side of tiles made from thin gorilla glass, which can then be bonded with mortar. Thinsu can bring this product to the market through tile manufacturers.
- Window frames, window sills and linings can be made directly from Thinsu eliminating the thermal bridge in window constructions and thus ensure their isolation and their energy approval. This product Thinsu bring to the market through window manufacturers
- Refrigerators can be produced directly from Thinsu, cold storage modules, including refrigerated container and refrigerated trucks. This product Thinsu bring to market through manufacturers
- Thinsu can be cast in molds used for internal lining of ceilings, dashboard, doors, etc. in cars. This product Thinsu bring to the market through automakers. Good insulation properties will be particularly interesting in electric cars where no surplus energy is available for heating.
- Thinsu can be cast in profiles for glass roofs
- Thinsu can be cast as insulated pipes for HVAC, both for water and for air

Heat flows in insulation materials

We have used heat flow analysis to structure our systematic work with this new insulation material.



Figur 2: Parallel heat flows

Thermal insulation materials are porous and complex. The total conductivity is approximated by adding parallel heat flows (numbers relate to the figure)

1. Conductivity in the material, κM
2. Radiation trough the material, κR I
3. Conductivity in the gas, κG
4. Conductivity through thermal bridges, κB

I cavities larger than 5 mm there is furthermore gas convection but that is not relevant in this study of insulation materials

Some of these heat flows are related to porosity of the material.

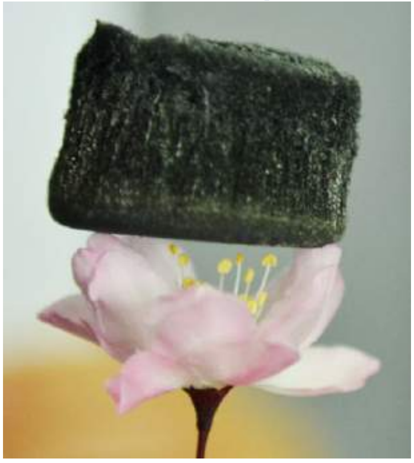
- Structures with high porosity contains more gas (low thermal conductivity) and less solid material (100-1000 times higher thermal conductivity)
- Vacuum insulation has an extra advantage from porosity because the gas conductivity converge to zero
- In materials with pore diameter below 100 nm the gas conductivity converge to zero
- Conductivity in the material pass through a cross section area. If the structure is thin and lattice shaped or fibres or powder only touch in point contact, this conductivity is reduced compared to bubbles or honeycomb structures

The radiation contribution in opaque materials is proportional to number of pore density. In opaque nano porous material radiation converge to zero. That is not the case in translucent and transparent materials like PMMA. Radiation can be reduced by adding black carbon powder material

The aim of this project was to

- **Eliminate the radiation, gas and convection contribution to the thermal conductivity**
- **Reduce the conductivity of the core material**
- **Minimise thermal bridges in the impermeable membrane**

6 different super insulation concepts



Figur 3: Carbon aerogel is so light that it doesn't even compress the flower

In order to find the right core material we investigated 4 physically distinct approaches to super insulation

1. Aerogels
2. Fag blown foams
3. Fibrous insulation
4. Powder insulation

Please notice the different structures possible within these categories

- Aerogels are like a nano scale hairball
- Fibres are like nano scale hay or "Mikado"
- Powder filler in VIP is like nano scale gravel
- Nanofoams are like ordinary insulation foam just with pores a thousand time smaller

Performance criteria for the core of the cubes were:

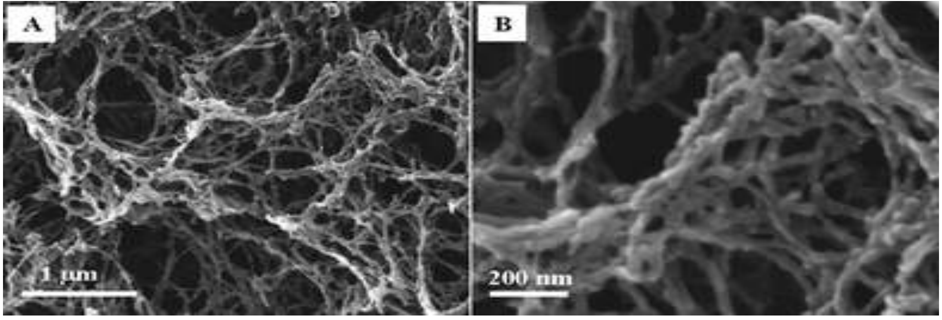
- Rigid (to support impermeable vacuum barrier coating)
- Permeable (to allow evacuation)
- Small pores in the surface to make thin coating possible
- Nano-scale pores for the Knudsen effect
- High porosity
- Low thermal conductivity of bases material
- No outgassing

These criteria tend to excluded each another.

- The rigid materials have a higher thermal conductivity due to higher density
- The rigid materials with reasonable conductivity like expanded Perlite has large pores in the surface which could not be coated with thin coating

When we zoom into the nano-scale world with a Scanning Electron Microscope (SEM) the smooth surfaces look like a mountain range. We assume that we can cover a cavity of 200 nm with a 5 times thicker layer of 1000 nm. The dilemma is however, that any kind of aerogel, powder composite or foam has a distribution of pore sizes. So, even if the average pore size is 40 nm there might 200 nm pores somewhere on the surface. One cubic cm of nanoporous material contains up to 10^{16} pores and the surface contains around 100 billion pores. It is highly unlikely that a vacuum barrier can be established over such a surface without any voids.

Aerogel



Figur 4: SEM image of silica aerogel

Aerogel is made from a gel, a kind of “pudding”, a solution of particles and chemicals in a fluid, where the particles and structures is growing into an ideal super thin nano-porous structure in a “zero gravity” environment because they a weightless in a fluid with the same density. This process takes days. The fluid is removed with super critically drying, a process where the fluid is transformed into a gas without boiling. Ethanol or fluid CO_2 is often used in this process. The entire process is rather complicated, time consuming and expensive. But the result is amazing. Carbon aerogel is lighter than air and when heated the air density decrease like in a hot air balloon and it can actually fly. Carbon aerogel is however not the best insulation material as carbon is electrically conductive and thus also thermally conductive.There is a fast and less expensive industrial process for production of aerogel powder. Drying powder is much easier than drying a thick material.

Aerogels can be made from many different materials:

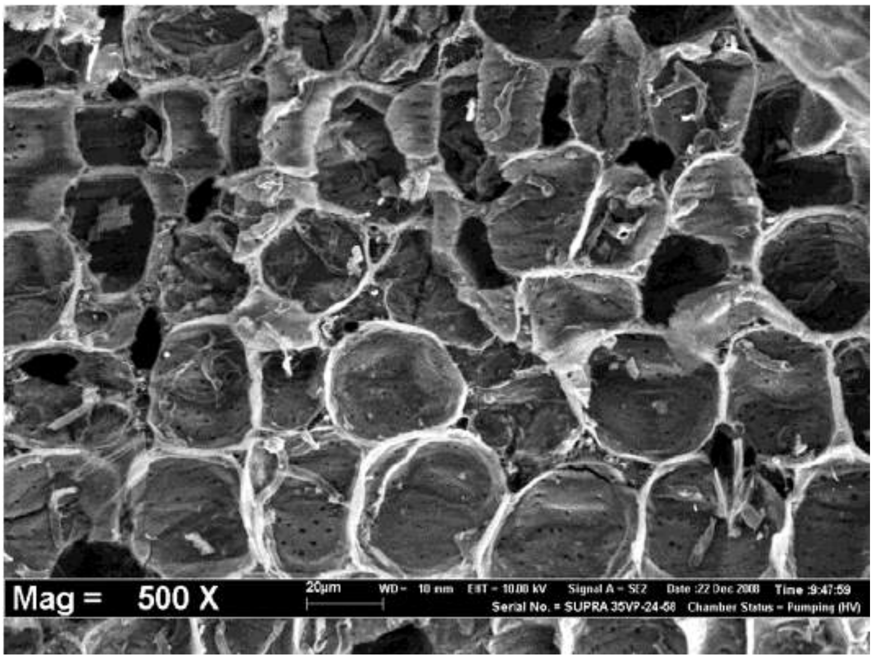
- Organic aerogel are made from pectin, gelatine, water melons and other similar “pudding” materials some of which have larger pores and are very soft. Others have pores down to 100 nm. They have excellent thermal conductivity down to 0,013 W/mK, but their soft and brittle nature render them of no practical use for the coated cubes.
- Carbon aerogel have nano-size pores and extremely low density of 0,00015 g/cm3 or 160 g for one m3. Air has 8 times higher density. It is one of the most porous materials known with a porosity of 99,9%, and hence very fragile. The conductivity is disappointing at 0,038 W/mK caused by the good electrical conductivity of carbon.
- Silica aerogel is fragile and brittle. The conductivity is excellent at 0,017 W/mK and it is used in VIP with conductivity down to 0,008 W/mK in high vacuum
- Polymer aerogel and cross-linked aerogel can be made quite strong, yet too flexible to be employed as core material for the cubes. Polymer aerogel with a conductivity of 0,014 W/mK are soft like a mattress. At 0,018 W/mK it is more like insulation foam. Slentite is made from cross-linked polymer aerogel and has a conductivity of 0,018 W/mK. The cross-linking increase mechanical strength but reduce insulation performance
- 3 phase silan aerogel can reach conductivity of 0,009 W/mK at ambient pressure. The aerogel has both small mesoporous pores (down to 10 nm) in the particles and larger pores, but still very small macroporous pores (around 100-200 nm) in the void between the particle structures

The size of pores in aerogel depends of:

- The chemistry of the molecules
- Acid (closed structures = smaller pores) or Basic (open structures = larger pores) growth condisions.

Aerogel is the best insulation material from a heat conductivity point of view, but it is fragile, soft and expensive. Aerogel is thus not a good candidate for the core of the cubes or for a material with a surface to be exposed in a building

Foams



Figur 5: SEM image of insulation foam

Foams are made from bubbles in a fluid. The bubbles are made from a gas, often CO_2 and this gas is either added to the fluid, produced by a chemical reaction or it can be absorbed in the fluid under pressure like CO_2 is absorbed in a soda, and released when the pressure drops. The fluid can be a material like acrylic in a glass phase, a two-component resin material like PUR, or a thermoplastic polymer. Either way, the material is temporarily a fluid or in glass phase when expanded and settles later and cures as a solid material.

Foam materials have a distribution of bubble size in the macroporous range (from a very seldom bubble size around 50 nm and upwards) Foams are usually inexpensive. The nano foams are however more difficult to produce because the blowing agent needs to be very perfectly distributed and the pressure relieve very well-defined. It takes long time to absorb the CO_2 into the acrylic.

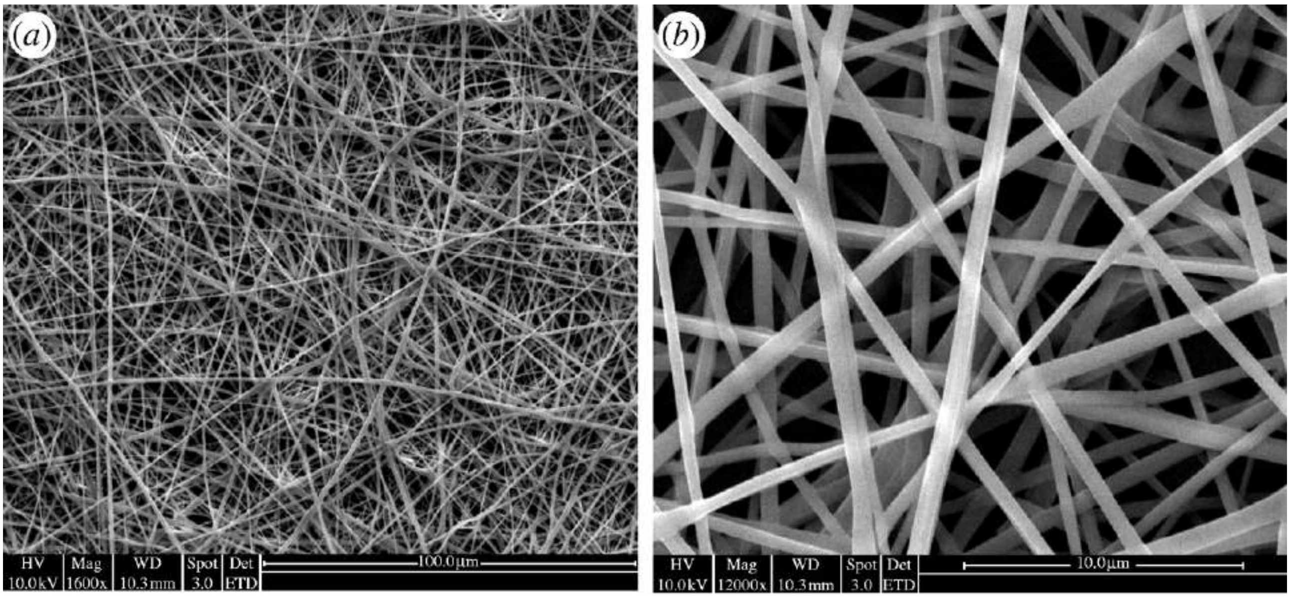
Using CO_2 or water for foaming will have a fire retarding effect compared to foams expanded with hydro carbons that will add a combustible component.

The best CO_2 blown PMMA (acrylic) has a thermal conductivity around 0,014 W/mK at ambient pressure. This material is almost as strong and rigid as solid PMMA although is has 90% porosity.

In foamed materials, the pore size is usually far from uniform and it can be difficult to assess. The maximum size of interconnected pores can be quite large. The maximum pores size in the surface of the same material depends of if the surface is cast or cut. Cutting the surfaces expose interconnected pores which in unfortunate cases will run parallel to the cut. With 100 billion pores in the surface of one cm^3 cube the risk is large that at least some pores are being interconnected in the cut surface.

Foam materials are second best from an insulation point of view, they are stronger than aerogels, keep their shape better, are often flexible rather than fragile and usually less expensive. The PMMA foam is not a good material for the core of the cubes because it is very difficult to evacuate. It could however be a good material for the construction sector. PUR foam is already a very common material in the construction sector

Fibre insulation



Figur 6: SEM image of mineral wool insulation

Composites like fiberglass and mineral wool are composed from fibres glued together. Their properties can be inferred from

- Fibre size (Smaller diameter on fibres creates smaller pores)
- Density (More fibres, more compressed material, improves strength and reduce insulation)
- Glue (More glue filling the cavities improves strength and reduce insulation)

Mineral wool like Rockwool is produced in a very wide variety combining these properties ranging from a soft material with large fibres, low density and little glue to a material with high density and a lot of glue used for wall panels and roof tiles. Carbon powder can be added to reduce radiation transmission in the material.

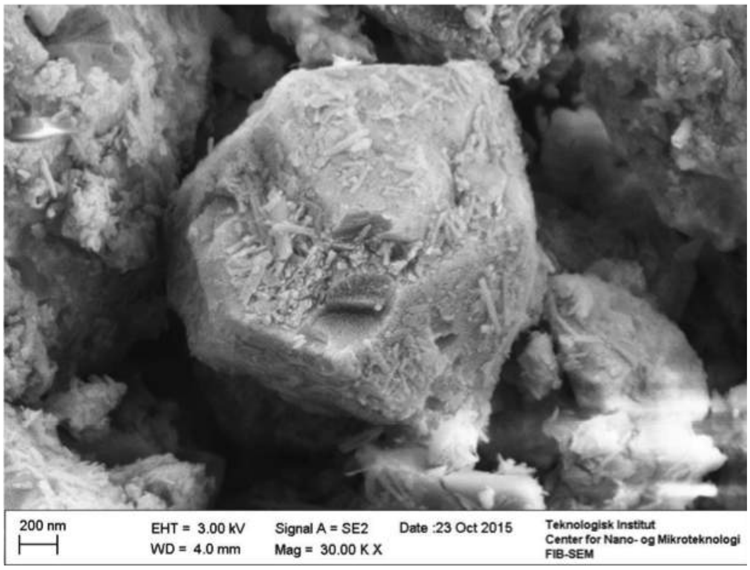
Fibres touch each another in a point contact like a Mikado play, and all these contacts points constitutes bottlenecks for the heat flow. These bottlenecks are an insulation advantage but it is also a mechanical disadvantage because all the fibres can move relative to each other. The penalty on improved mechanical strength with more glue is increased thermal conductivity.

Insulation fibres are usually inexpensive, average insulation performance, and soft. The stronger the material get, the less insulation.

The largest pores in composites made from fibres are proportional to the fibre size and could for practical purpose be considered equal to ten times the diameter of the fibres which is way too large for the coating to cover. Furthermore the fibres are not of uniform size

Fibrous materials are not a good material for the core of the cubes because the cavities are too big to be covered and the material is too soft to support the impermeable coating material. Fibre insulation is already a very common material (in fact the preferred) in the construction sector

Powder



Figur 7: SEM image of zeolite powder

This SEM is from Zeolite powder. A number of powder materials can be used for insulation

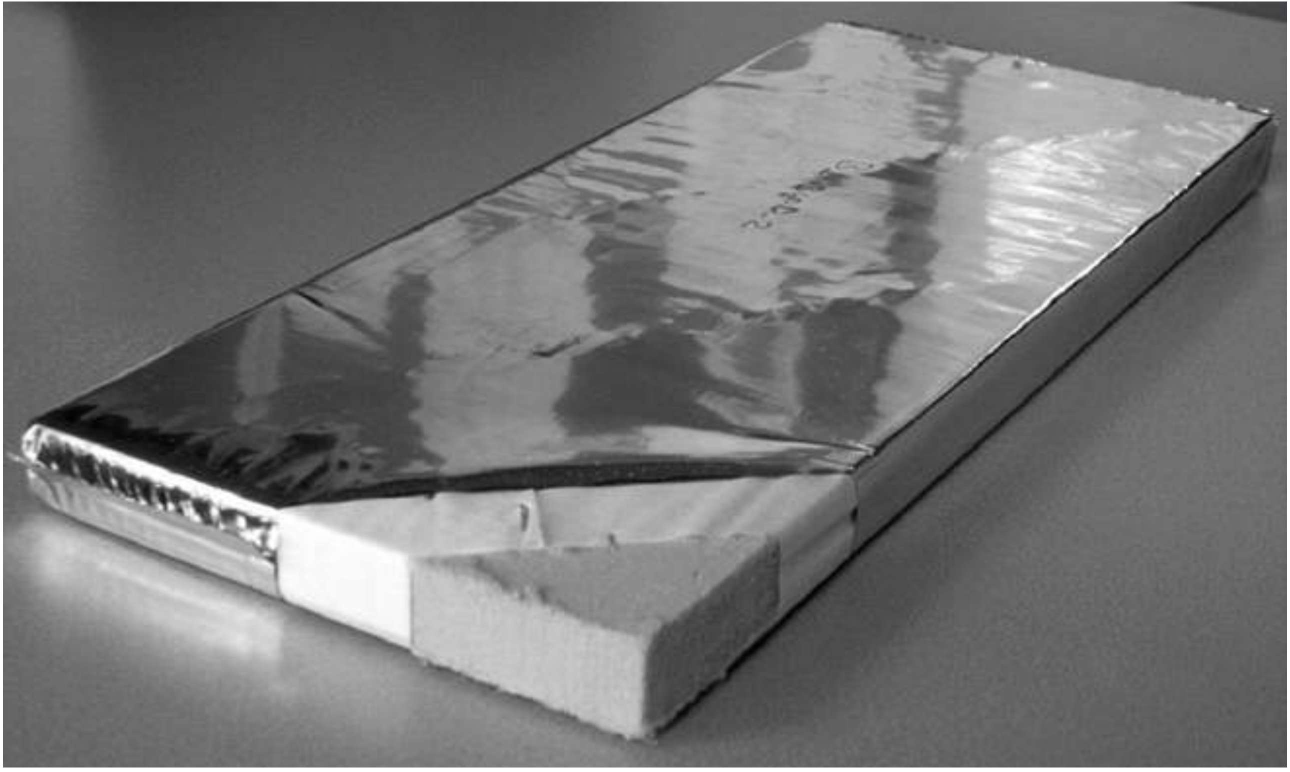
- Zeolite pellets are made from zeolite particles glued together with clay or glue, or fused together by melting.
- Perlite is a natural volcanic material that can be used for insulation
- Expanded perlite is a kind of pop-corn version of perlite.
- Fumed silica is a bi-product for production of silicon chips for computers. It became available when the chip producers were forced to filter the exhaust air from their factories.

Particles touch each another in a point contact and all these points constitute bottlenecks for the heat flow. This is good in terms of insulation but it is also a mechanical disadvantage because all the particles can move relative to each other. The penalty of more glue for improved mechanical strength is increased thermal conductivity across particles. Insulation powder is usually inexpensive.

- Zeolite has Knudsen regime pores and good strength but the material density is too high and the conductivity thus in the 0,6 W/mK range
- Metal Organic Framework has Knudsen regime pores and good strength but the density is too high and the conductivity is in the 0,32 W/mK range
- Expanded perlite is strong, but has macroscopic pores that cannot be coated, and conductivity is 0,029 W/mK in high vacuum (which cannot be maintained in the cubes). Perlite is used for cryogenic insulation and the very low conductivity is measured at extremely low temperatures where all insulation materials in general perform better
- Geopolymer can be foamed to a homogenous material in a mould, and has a thermal conductivity down to 0,058 W/mK, but the pores are too big to be coated. Geopolymer has performance similar to expanded perlite.
- Foam glass has relatively impermeable cell walls, a conductivity down to 0,035 W/mK and performance similar to geopolymer. Due to the closed cells it cannot be evacuated
- Fumed silica is soft because it is made from (nano-size) spheres. The conductivity is excellent at 0,020 W/mK and it is used in VIP with conductivity down to 0,006 W/mK in high vacuum
- MCM 41 has Knudsen regime pores and it is a getter The conductivity is excellent at 0,020 W/mK at ambient pressure

Powder is not a good material for the core of the cubes because is not sufficiently mechanically stable to support the impermeable coating. It cannot be used directly as a building material either.

Vacuum Insulation Panel (VIP)



Figur 8: VIP insulation with the different layers exposed

Vacuum Insulation Panels contain the above mentioned powders within a bag made from a vacuum proof membrane barrier. These bags have a centre thermal insulation value around 0,006 W/mK when new.

Thermal bridges in the barrier foil increases the conductivity to 0,009 W/mK. This performance is further degraded over time to 0,010 W/mK.

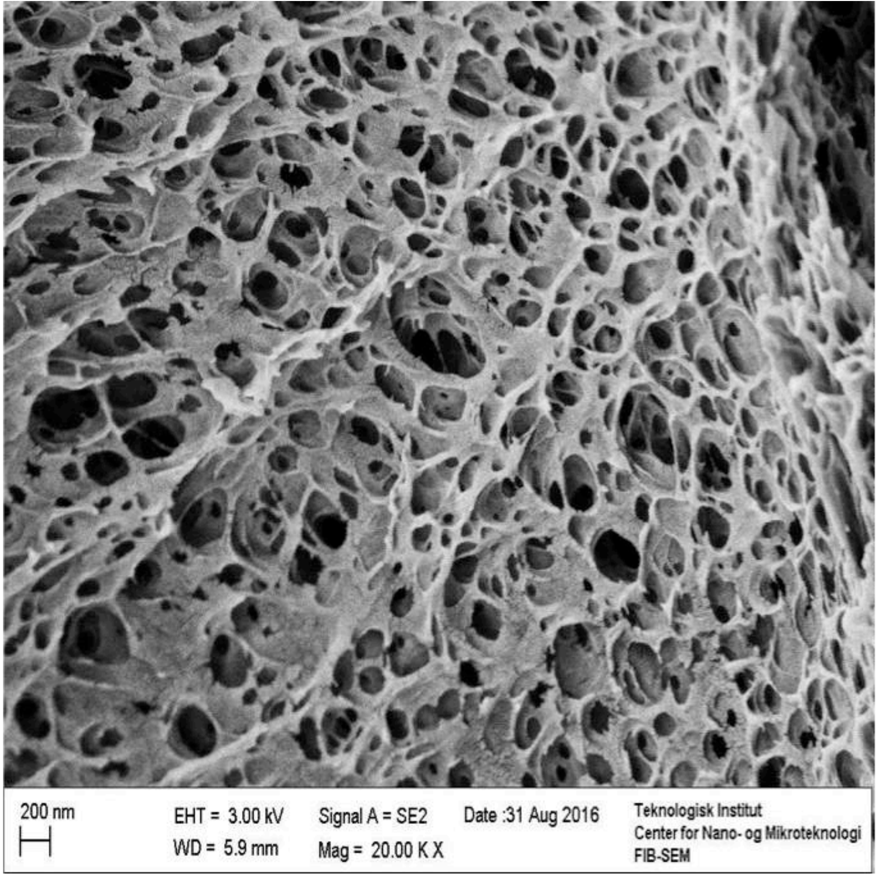
The edges of the VIP are slightly curved. If we assume a 1 mm distance between the panels the un-insulated area is 0,5% of the surface. The conductivity of this void is 3. W/mK or 300 times higher than the VIP. Hence, the heat loss through the 1 mm gap along a 60 x 60 cm panel is larger than heat loss through the entire VIP.

The membrane of the VIP is very vulnerable to puncture during the mounting process on construction site.

The VIP materials can be cast within a insulation foam solving some of the edge problems.

VIP serve as inspiration for the invention investigated in this project but the barrier foil is way too conductive to be the solution for the cubes, and the corners are too rounded. Containment film technology from VIP would add a devastating 0,032 W/mK to the conductivity of the invented insulation cubes

Materials made by the TIPS process



Figur 9 SEM image of a break edge of TIPS with nanoscopic pores in the 200-300 nm range

While foamed insulation material ideally is the skin of gas bubbles, the pores in Thermally Induced Phase Separation (TIPS) materials are motifs of droplets of solvents arising during the process. The end result may look rather similar, but the porous material tends to be more uniform and stronger. Additionally, the fabrication process is very different from gas-blowing leading to foams.

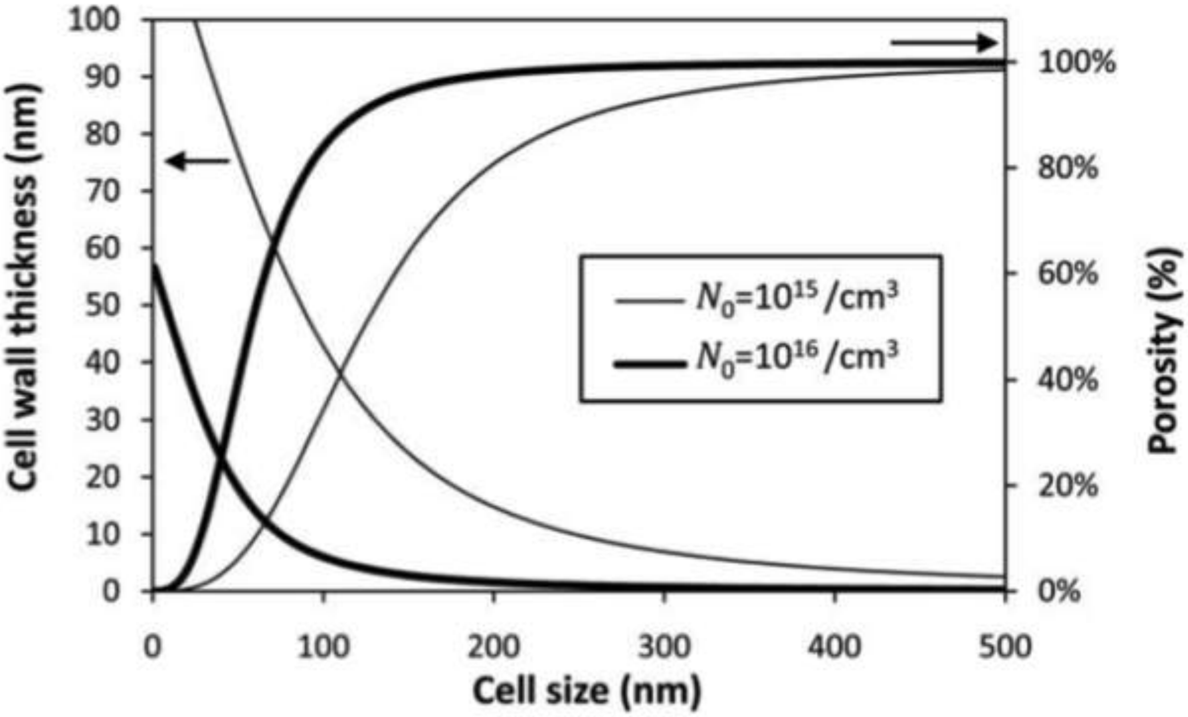
The TIPS material is made in a process where

1. Polymer like PMMA is dissolved in a particular mixture of a solvent and non-solvent under heating in a pressure vessel.
2. The resulting solution is left to cool during which process a reticulous network forms
3. The PMMA network matures to form a porous matrix fully containing the reaction mixture
4. A porous material is isolated after certain washing and drying steps.

Pore size in nano scale TIPS is far from uniform and it can be difficult to assess. The maximum size of interconnected pores can be quite large. The maximum pores size in the surface of the same material depends on whether the surface is cast or cut. Cutting the surfaces expose interconnected pores which in unfortunate cases will run parallel with the cut. With 100 billion pores in the surface of one cm^3 cube the risk is large that at least some pores are being interconnected in the cut surface. However cutting with a heated wire tend to close the pores in the surface we have found.

TIP materials are good candidates to the core of the cubes, as they are good insulation materials, open pore structures and mechanically sufficiently strong to support a vacuum barrier.

Conductivity of the material vs its porosity, κM



Figur 10: Conductivity of PMMA foam expanded with CO2 depending af pore size, porosity and cell wall thickness

The conductivity of the solid material is reversely proportional to relative density (100% - porosity %).

- Solid PMMA has a conductivity of 0,17 W/mK.
- With 90% porosity is has a conductivity of 0,17 (100-90)/100 =0,017 W/mK.

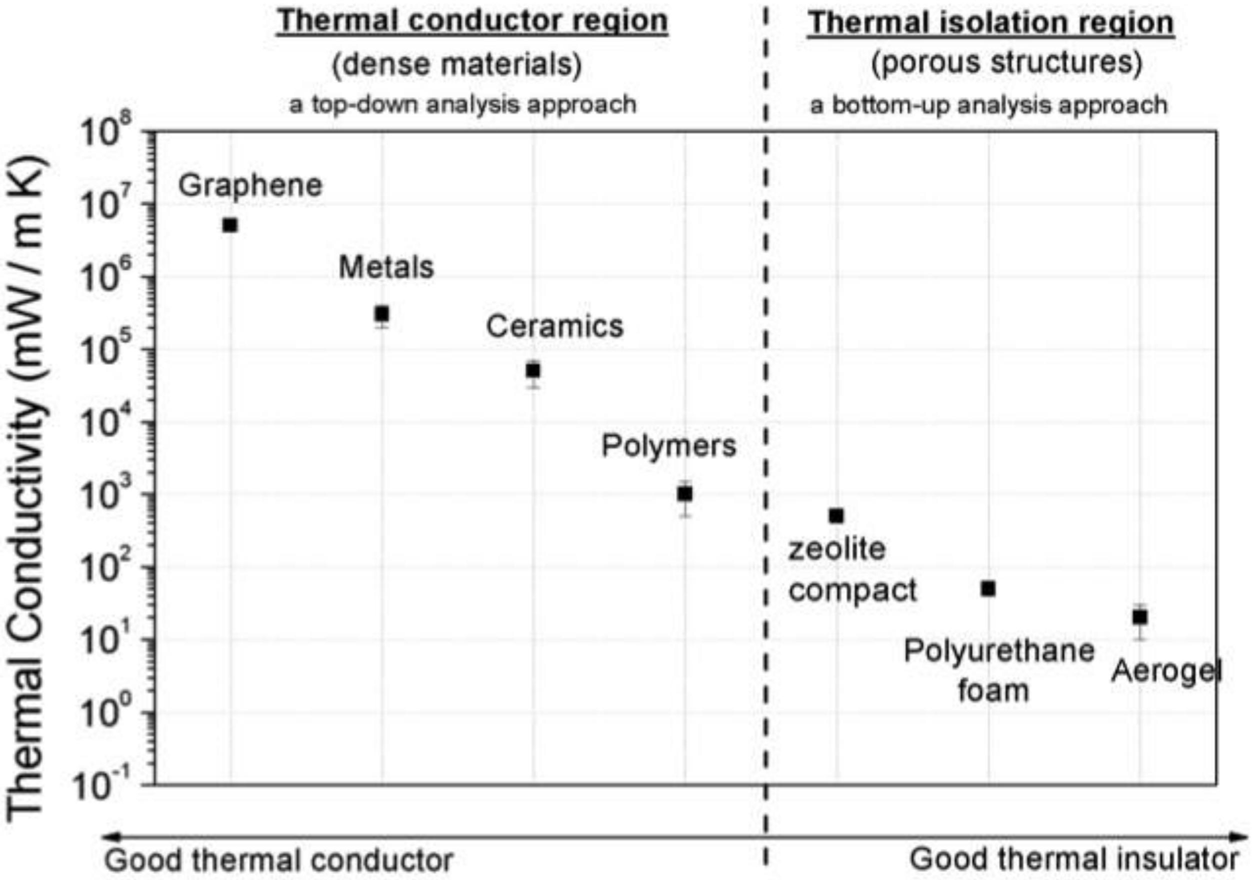
If the base material has ten times larger conductivity the porosity has to increase too in order to maintain a low conductivity.

- Silica has a dense conductivity of 1,38 W/mK
- A 99% porosity silica aerogel reach 1,38 (100-99)/100 =0,0138 W/mK

Figure 10 illustrates the trade off between pore size and porosity in CO_2 blown PMMA with a wall thickness of 75 nm. If the cell size is reduced to around 100 nm the porosity drops below 80% and at 30 nm the porosity is below 30%. The material becomes all walls. If the wall thickness is reduced this balance moves along, but it is still a limitation on pores in the Knudsen effect regime that smaller pores reduce porosity and increase the conductivity in the material proportionally. Even with vacuum and radiation blockers you cannot achieve a thermal conductivity lower than the conductivity of the material.

TIPS is more like a lattice than like bubbles. Lattices have a much smaller cross section than bubble walls, so TIPS tend to move the curves in the figure above to the left

Density



Figur 11: Dense materials left are conductors while porous material right are insulators

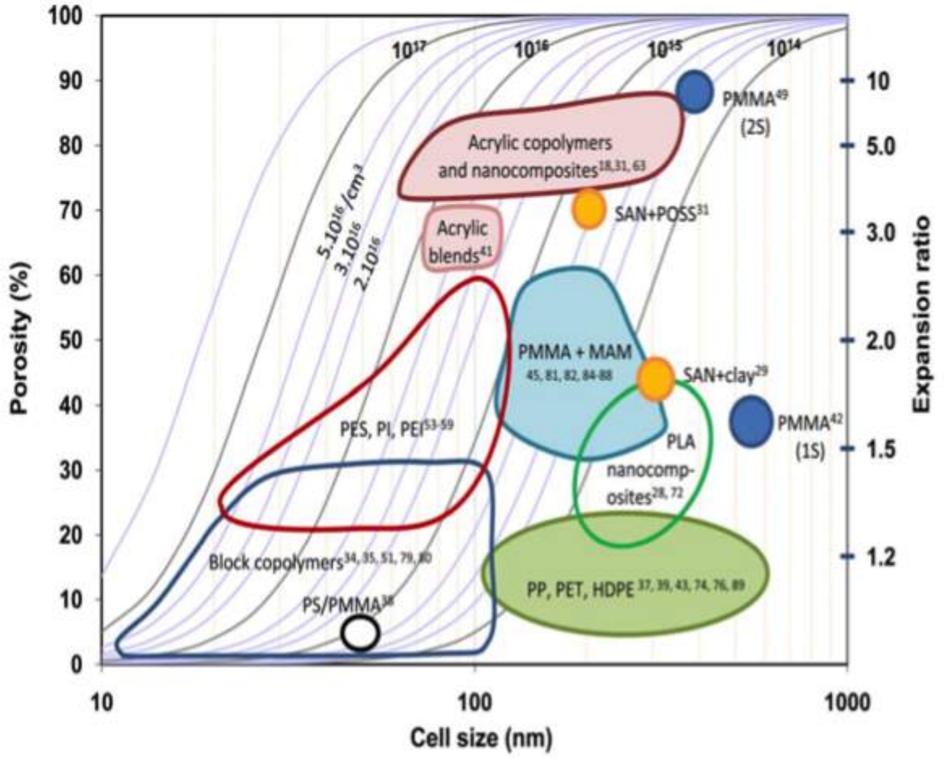
The thermal conductivity of dense materials is usually above 1 W/mK. Their thermal conductivity can be divided into two parts:

1. Lattice thermal conductivity, in which the heat is carried by phonons, or vibration of the lattice. This conductivity is proportional to specific density.
2. Electron thermal conductivity, in which heat is carried by electrons. Electron thermal conductivity is proportional to electrical conductivity by Wiedemann–Franz law. This is the reason why metals and graphene has higher thermal conductivity than would be expected from their specific density.

The extremely high thermal conductivity of graphene is only valid in extremely thin 5nm layers. The smooth structure of graphene is free of boundary effect for its phonons along the plane. The graphene oxide we proposed for barrier membrane has a thermal conductivity in the same range as metals

PMMA has a thermal conductivity of 0,17 W/mK. So even as a massive material it is an insulation material

Polymers have lower conductivity



Figur 12: We want a material in the upper left corner with high posity and small cells

In order to reduce the lattice thermal conductivity, 'chaos' is preferred, which means random atom positions (amorphous), mass fluctuation, and thin structures (diameter effect). This is why the complex polymers have a lower thermal conductivity than ceramics.

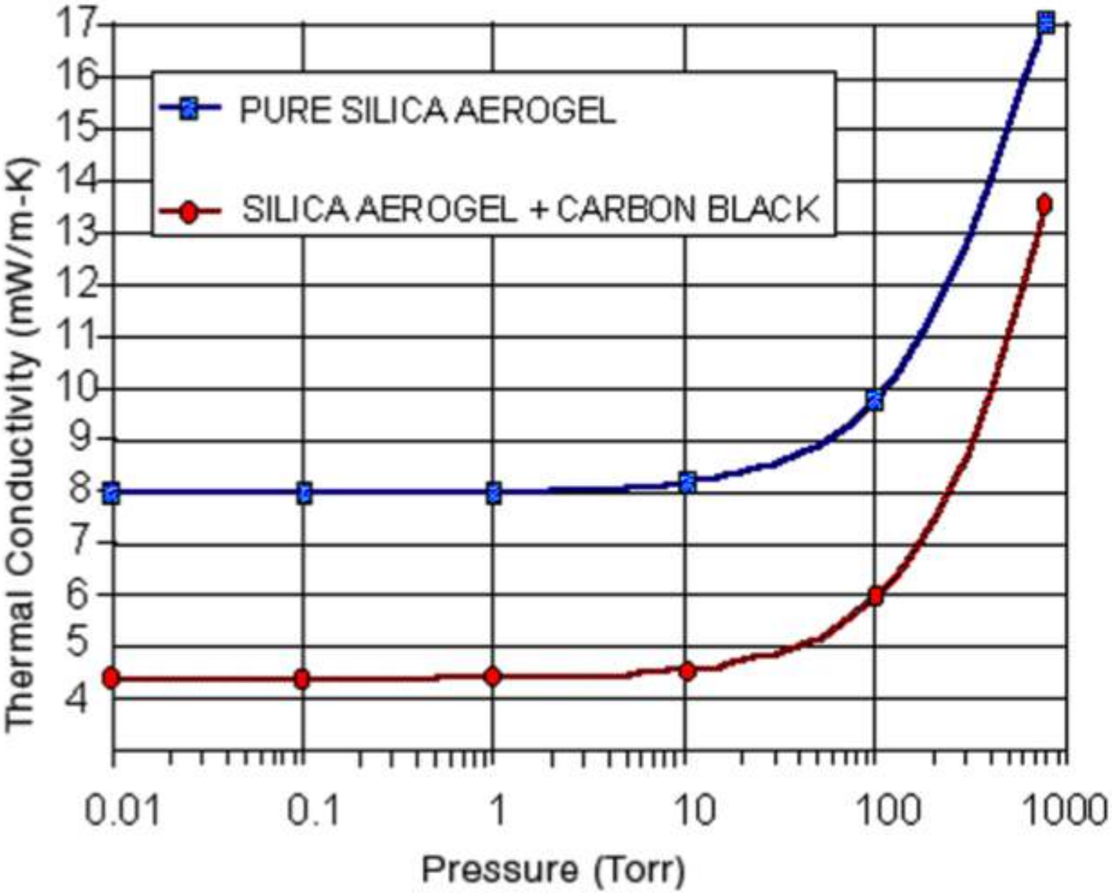
The lattice thermal conductivity is proportional to the combined relaxation time of phonons, τc, which follows the equation:

τc-1=τpd-1+τN-1+τB-1
τpd is the point defect scattering,
τN is the normal phonon-phonon scattering,
τB is the diameter effect scattering.
L is the diameter, size, or boundary distance.
v is average speed of sound
τB-1=v/L , suggests the smaller L, the smaller τc. This relationship applies to any material including air and other gases.

The effect of the boundary distance is particularly interesting in porous materials with walls around 1 nm thickness (L=1 nm) like aerogel, MCM 41, and acrylic nano foam. The very thin dimensions means an extra second order reduction

TIPS materials made from PMMA which has a low thermal conductivity as a massive material and it can be made with around 85-90% porosity. The conductivity in TIPS excluding gas conductivity and radiation is around 0,017 W/mK

Radiation trough the material, κR



Figur 13: Thermal conductivity as a function of vacuum and cell size with and without carbon black blocking radiation

Radiation can be stopped by:

1. Metalized surfaces
2. Multiple layers of opaque material
3. Carbon black / Graphite

or any combination

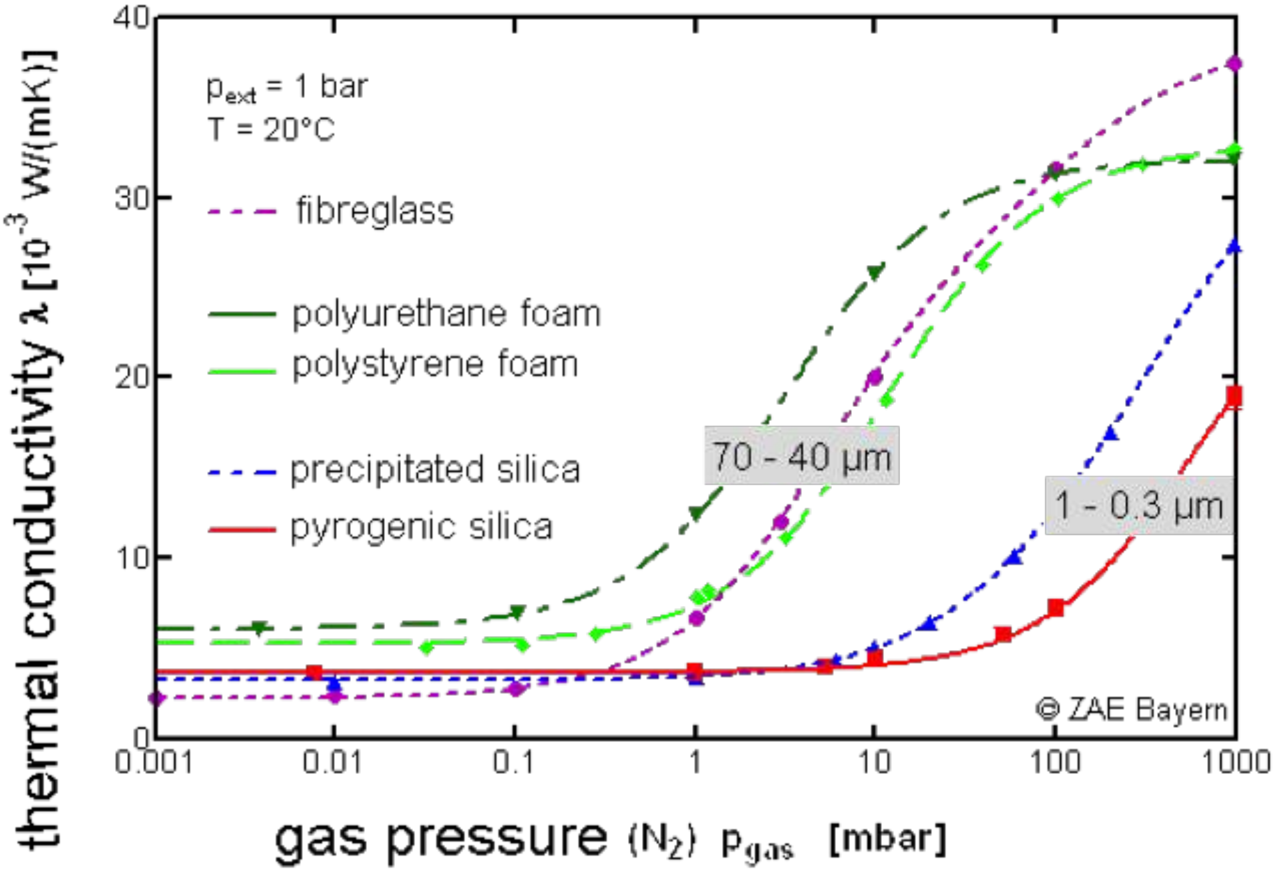
Nano porous insulation materials cannot be metalized inside the pores because metal is a very good conductor and will ruin insulation performance, even if applied as a single atomic layer. However, finely dispersed opaque materials may be added to foams and aerogels without penalty of increased material conductivity.

Graphite is already added to EPS insulation to make Neopor and improves the insulation performance by approximately 0,0035 mW/mK. Similar performance improvement has been measured in silica aerogel as shown in Figure 13. A similar effect will be achieved in other translucent insulation materials.

Adding infrared blocking materials improves the fire retarding performance. The polymer is still melting but the fire is not propagating.

Black material blocking radiation is particularly important in translucent materials like PMMA and silica aerogel. I will most likely also work well in TIPS

Conductivity in gas in vacuum, κG



Figur 14: Materials with nano size pores only need a moderate vaccum

Conductivity in the gas is proportional to

- A material constant for the gas (only in gas within large pores)
- Pressure
- Pore size

Gasses like argon, krypton, CO2, sulfur hexafluoride (SF6), freon has 2-4 times lower thermal conductivity than air in large pores.

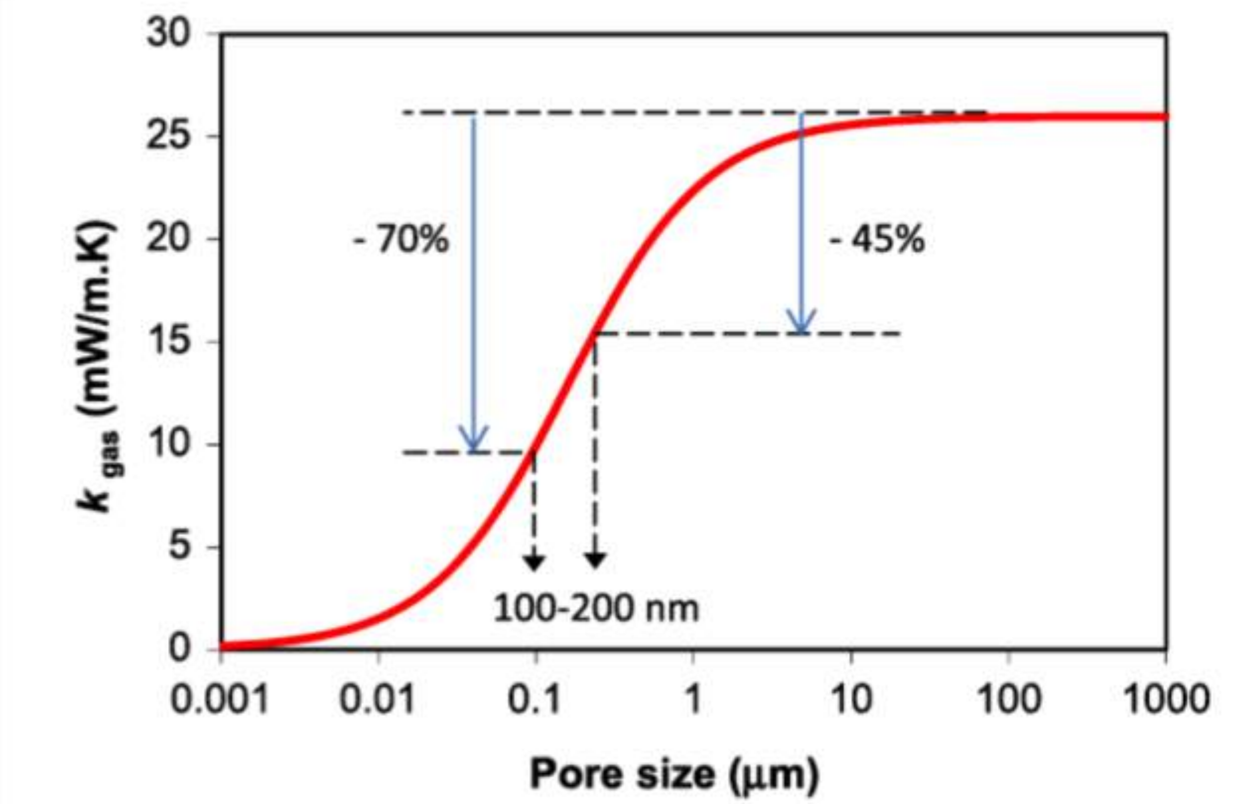
Reducing the pressure to vacuum removes the gas conductivity

A moderate vacuum can reduce the mean free path enough to move pores of 300-1000 nm into the Knudsen regime.

Vacuum degrades over time. The best containments degrade insulation performance around 1% a year.

Initially we wanted vacuum in the cubes but enlightened by the trouble of securing vacuum within an impermeable barrier we have fallen back to a material at ambient pressure of air and with pores in the 100 nm Knudsen effect range

Knudsen effect



Figur 15: The Knudsen effect kicks in with 45% at 200 nm and 70% at 100 nm

The Knudsen effect reduce thermal conductivity in gases when the size of the cavity encompassing the gas becomes comparable to the mean free path. The cavity restricts the movement of the gas particles = heat transfer. For example, thermal conductivity of air is 25 mW/m·K, but decreases to 5 mW/m·K in a 60 nanometer pore

The table show the mean free path for different gasses. That translates into a

Gas	Mean free path = Max pore size
Hydrogen	115
Nitrogen	59
Oxygen	65
Helium	175
Argon	64
Air	67
Krypton	49
Xenon	36
Water vapor	68
Carbon dioxide	40

We have succeeded in getting the pore size of TIPS down from 200 micrometer to 200 nanometer and can most likely get it further down to a hundred or even 60 nm.

Conductivity through membrane, κB

Vacuum need to be contained and any surrounding containment is a thermal bridge

It is not a coincidence that impermeable barriers are made from extremely heat conducting materials. The density and structure of the material blocking permeability has a higher conductivity. The relevant materials are.

- Aluminium (200 W/mK) 10.000 times larger than the super insulation
- Silicium carbide (120 W/mK)
- Graphene (10 W/mK)
- Stainless steel (7 W/mK)
- Glass (1 W/mK) (Glass need mm range thickness to be impermeable due to micro cracks)

often in a combination with polymer film (0,2 W/mK).

We faced quite a few problems with the impermeable coating

- We assume from macroscopic test that the impermeable containment needs to be 5 times thicker than the pore diameter. For a 200 nm pore size that means 1000 nm
- The flexibility of the coating must be larger than the flexibility of the core material or the coating will crack. Ceramic coatings are commercially available. They are impermeable but they are applied in layers of 5-10 micrometer and they need a very stable core or they will crack. Coatings from brittle materials like glass and Silicon Carbide are particularly vulnerable
- Yttria-stabilized zirconia is applied by 700°C chemical vapor deposition to create a cost-effective, robust thermal barrier coating that can be applied to complex-shaped components. Zirconia also need a very stable core or it will crack
- Glass could also be melted and sprayed but again the layers are in the mm range rather than the micrometer range. It will also crack on soft or fragile cores.
- In an open pore material even small pin holes in the coating will destroy the vacuum. VIP handles this problem by using a film with up to 5 different layers of metal applied one by one. Statistically the pinhole will not be on top op each other in many layers of film. But we can not be sure that pin holes will not be the same place if we coat a cube instead of using film because the edges and corners are more likely to cause problems that he flat areas.

Reduced graphene oxide r(GO) is the most impermeable material available. A thickness of 100 nm is enough. Graphite-oxide is produced by exposing graphite to strong oxidisers like sulphuric acid. These oxidisers work by reacting with the graphite and removing an electron in the chemical reaction. This reaction is known as a redox. In order to turn graphite oxide into graphene oxide, a few methods are possible. The most common techniques are using sonication, stirring, or a combination of the two. Reduced graphene oxide (rGO) is produced from GO (Graphene Oxide) by:

- Treating GO with hydrazine hydrate and maintaining the solution for 24 hours
- Exposing GO to hydrogen plasma for a few seconds
- Exposing GO to another form of strong pulse light, such as those produced by xenon flashtubes

I the laboratory r(GO) could be the finished surface but in the construction industry and on the wall of a house the 1000 nm (=0,001 mm) r(GO) coating needs protection. We have for practical reasons assumed that painting on industrial objects are a measure for minimum thickness of a durable, scratch resistant surface. Industrial painting is minimum 10 micrometre (0,01 mm). That is a rather optimistic evaluation. The r(GO) can be modified with plasma treatment at the surface in order to be stronger without painting the surface. Most scratch resistant surfaces are 10.000-50.000 nm thick
Graphene Oxide r(GO) has to be protected from water because it is made from flakes and the flakes separate in water.

r(GO) came out as the only viable solution due to the extreme impermeability of even thin layers. The minimum thickness for impermeable containments is

- 10 micrometer for aluminium, silicium carbide, stainless steel and glass
- 0,1 micrometer for r(GO)

The impermeability over time depends on:

- The thickness of the impermeable material
- The material (metal, ceramics, grapheme)
- The likelihood of pinholes
- The number of layers (as more layers reduces the risk of pinholes being exactly the same place)
- Number of gas-barrier-gas transmissions
- The time to degrade a vacuum further depends of:
- The volume of vacuum to be filled related to the surface of diffusion

Aging is a trade off between thermal bridge in the containment and permeability over a longer time span of years. The durable containment is made from metal foil, but it adds a larger thermal bridge while the metalized polymer adds less thermal bridge and has a shorter life span.

The aging effect of leaks is 10.000 times larger in the individual cube than in a 1 m^2 VIP panel

Assuming that we could produce the cubes with:

- Super efficient TIPS
- 5 layers of graphene oxide coating
- 1 layer of scratch resistant paint
- Evacuation of the aerogel

And assuming that this product would be durable we still have a major problem:

r(GO) coating is expensive and 5 layers are 5 times more expensive.
Coating in vacuum is making it even more expensive

Our research narrowed the options down to

- **1 micrometer graphene covered by**
- **10 micrometer waterproof polymer paint.**

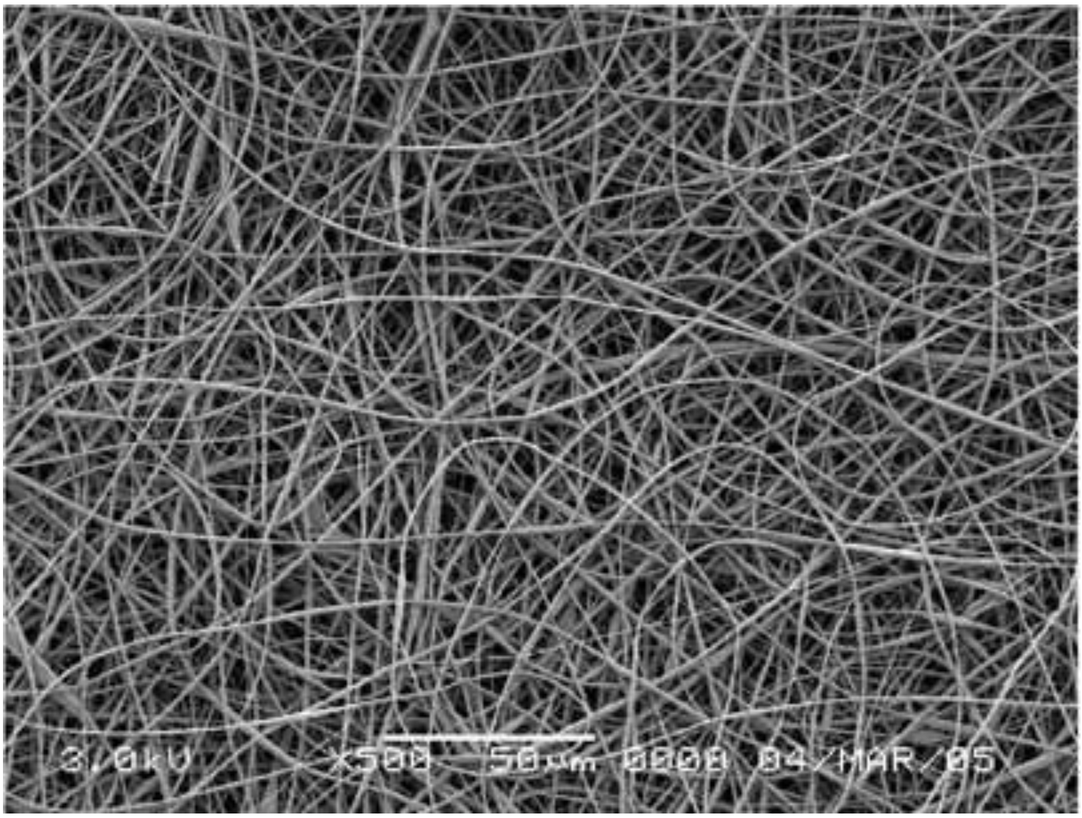
It could add as little as 0,007 W/mK to the heat flow in the cubes. That is unfortunately almost as much as the 0,009 W/mK benefit from vacuum.

We found a solution, but it was not worthwhile going through several coatings and evacuation to achieve a benefit of 0,002 W/mK

Wild card technologies

We wanted to make sure that we have tried out all possible alternative so we also looked into

Electrospinning



Figur 16: SEM image of electro spun polymer

Electrospinning is a fibre production method, which use electric force to draw charged threads of polymer solutions or polymer melts up to fiber diameters in the order of some ten nanometres. Electrospinning shares characteristics of both electrospraying and conventional solution dry spinning of fibers. The process does not require the use of coagulation chemistry or high temperatures to produce solid threads from solution. This makes the process particularly suited to the production of fibres using large and complex molecules. Electrospinning from molten precursors is also practiced; this method ensures that no solvent can be carried over into the final product. The material looks like mineral wool with woven structures and the insulation is most likely similar.

The electro spun material has large pores and poor structural stability

3D printing

Figur 17: 3D printed statue walking on a hair

The step from electrospinning to 3d print is that 3D printers can control the exact geometry. It is possible to 3D print in the micrometer range. With a 3D printing technology you could optimize the geometry and make the surface without cavities and the core almost without material. But 3D printing is a very slow process. Normally a 3D printer is printing layers of 0,3 mm. If the layers are down to 300 nm, the print time grows by 1000 x 1000 x 1000 = billion times. Printing one m^2 in 25 mm thickness with 90% porosity takes about 100 hours on a FDM 3D printer and the material cost is 500 DKK. 3D Printing it in nano scale would take 100 billion hours or 11 million years. Nano scale 3D printing is not feasible for insulation material.

Vacuum by condensation

Instead of evacuating the cubes we considered creating the vacuum within the cubes. That would make it much easier to coat the cubes with impermeable coating. The vacuum in the closed cells could alternatively be produced from heating and evaporation of a fluid and subsequent cooling and condensation. Liquids are for instance

- Water and water solutions,
- Hydrocarbons (highly flameable),
- Acids
- Bases (highly reactive and degrading)

They all have a condensation point well below indoor temperature

So far so good, but the droplets containing the fluid for a 100 nm pore should be 10 nm diameter and that is quite small

The specific density of water is 1000 kg/m3 and for water vapour it is 0,6 kg/m3 so condensation can theoretically create a 0,017 mBar pressure. The partial pressure of water is however 22 mBar= 1/50 atm.

Vacuum by chemical processes

Sodium bicarbonate (known from baking) releases CO^2. Above 50 °C, sodium bicarbonate gradually decomposes into sodium carbonate, water and carbon dioxide. The conversion is fast at 200 °C:

$2\ NaHCO_3 \rightarrow Na2CO_3 + H_2O + CO_2$

Most bicarbonates undergo this dehydration reaction. Further heating converts the carbonate into the oxide (at over 850 °C)

$Na_2CO_3 \rightarrow Na_2O + CO_2$

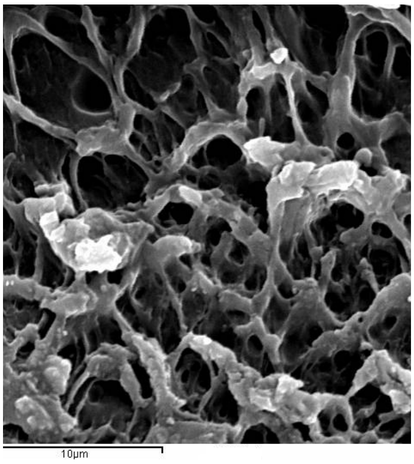
This process is however not reversible.

Can we find a reversible chemical process, -an equilibrium-, creating gas when heated?
Boudouard reaction $2\ CO \rightleftharpoons CO_2 + C$ is an example.
The reversible reaction of nitrogen gas with hydrogen gas to form ammonia:
$N_2\ (g) + 3\ H_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$

Vacuum from hydrogen diffusion

Hydrogen will diffuse through almost any thin material. The partial pressure of hydrogen in the atmosphere is negligible. If we foam the insulation material with hydrogen the hydrogen will disappear even through closed cells and even through billions of cells. Titanium hydride and zirconia hydride can produce hydrogen inside the cells

Vacuum by absorption



Figur 18: SEM image of superaborbent polymers

Superabsorbent polymers (SAPs) are polymers that can absorb and retain extremely large amounts of a liquid relative to their own mass. They are used for baby diapers and sanitary napkins

Water-absorbing polymers, which are classified as hydrogels when cross-linked, absorb aqueous solutions through hydrogen bonding with water molecules. A SAP's ability to absorb water is related to the ionic concentration of the aqueous solution. In deionized and distilled water, a SAP may absorb 300 times its weight (from 30 to 60 times its own volume) and can become up to 99.9% liquid, but when put into a 0.9% saline solution, the absorbency drops to maybe 50 times its weight. The presence of valence cations in the solution impedes the polymer's ability to bond with the water molecule.

We did not test this alternative

Vacuum by getter adsorption

The vacuum can be produced within the pores by a nano porous getter material like MCM 41, activated charcoal, or zeolite through a cycle where

- The getter is mixed into the PUR or acrylic resin,
- The CO2 is desorbed from the getter by microwaves creating bubbles in the resin,
- The resin settles to a foam,
- CO2 is re-adsorbed in the getter creating a vacuum within the bubbles.

Adsorption and desorption is fully reversible.

Activated carbon nano spheres http://pubs.acs.org/doi/abs/10.1021/am400112m?journalCode=aamick can adsorb 8 mmol/g = 0,35 g CO2 pr. g activated coal = 0,175 g /cm3 = 175 kg/m3 at 1 atm and 25 C. Desorbed the density is 2 kg/m3 expanding approximately 90 times. Or counted the other way around crating a vacuum of 0,011 atm.

Nitrogen-containing ordered mesoporous carbon (MCM 41). We have tested MCM 41 and our test results show thermal conductivity better than fumed silica. The density of MCM is larger than that of fumed silica but the reduced gas conductivity of MCM 41 makes it better. MCM 41 is a better getter but also a very expensive alternative to activated coal.

Impermeable foam

The principal barrier for the solutions above is that the cells in the insulation material are not impermeable

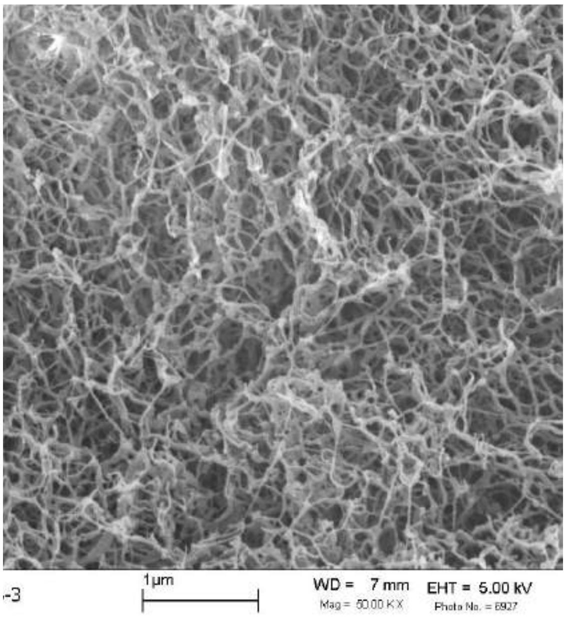
Platelet-like nanoparticles slow down the desorption of CO^2 out of nanocomposites by means of a physical barrier effect, enabling a higher concentration of CO^2 to remain in the polymer. As a consequence of the higher amount of CO^2 retained in the polymer and the cell nucleation effect promoted by the nanoparticles, polymer nanocomposite foams presented finer microcellular structures, in the case of PMMA even submicrocellular, and higher specific moduli and electrical conductivities when compared to their pure counterparts.This kind of particles is used in lubrication oil and in medical application and has names like IF-WS2 IF-MoS2 or Sm2O3

Multilayered

So far we have imagined that the solution is some kind of extrusion or batch production like most other insulation manufacturing processes. What if we are producing this insulation material as a film and glue the layers of films together like plywood? Thermal bridges perpendicular to the heat flow is a smaller problem

- It is much faster to produce films than to produce by extrusion or batch
- It is easier to load PMMA with CO2 if the film is thin
- It is easier to control dispersed materials in this layers without stratification

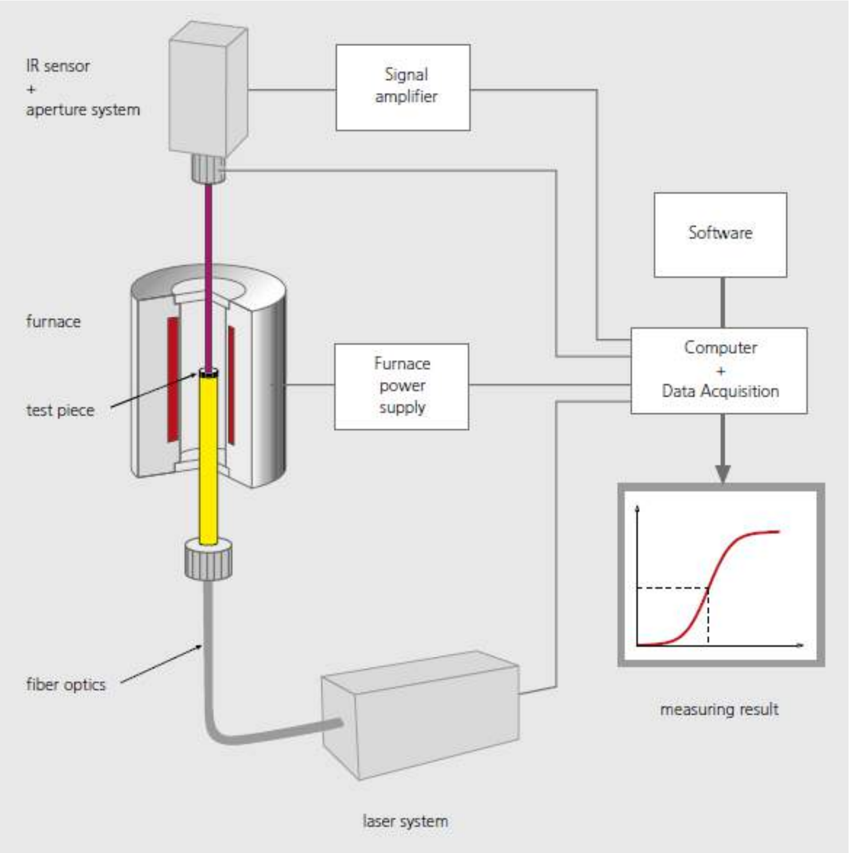
PAN semi crystaline nano foam



Figur 19: SEM image of polyacrylonitrile (PAN) material

Crystaline, semo cystaline and liquid crystaline materials are almost impermeable and would be much better as vacuum containment. Compare to the previous page the crystaline structures have no holes for the transportation of gas through the polymer. Polyacrylonitrile (PAN), also known as Creslan 61, is a synthetic, semicrystalline organic polymer resin, with the linear formula (C3H3N)n. Almost all Polyacrylonitrile resins are copolymers made from mixtures of monomers with acrylonitrile as the main component.

Laser measurements



Figur 20: Laser flash for fst and convinient measurement of thermal conductivity

DTU has a Laser Flash measuring device, which can make fast measurements of thermal conductivity in super insulation materials. The laser flash analysis or laser flash method is used to measure thermal diffusivity of a multiplicity of different materials. An laser energy pulse heats one side of a plane-parallel sample. The temperature rise on the backside due to the energy input. The higher the thermal diffusivity of the sample, the faster the energy reaches the backside. A state-of-the-art laser flash apparatus (LFA) is able to measure thermal diffusivity over a broad temperature range, is shown on the right hand side. The key advantage is that this instrument can be used on small samples .

In a one-dimensional, adiabatic case the thermal diffusivity a is calculated from this temperature rise as follows:

$$a = 0.1388 \cdot \frac{d^2}{t_{1/2}}$$

Where

a is the thermal diffusivity

d is the thickness of the sample

t1/2 is the time to the half maximum

Experiments with TIPS

The term "Thermally Induced Phase Separation" tells the story. Well it should have been "Cooling phase separation" as the exiting thing happens during the cooling and separation process

1. First the PMMA is fully dissolved in a combined water and ethanol solution when heated to a temperature well above 100ºC in an autoclave or pressure cooker. The PMMA/water/ethanol becomes a transparent clear fluid.
2. When the PMMA is fully dissolved, the fluid can return to ambient pressure and embark on a cooling process.
3. When the temperature is reduced well below the boiling point of the ethanol the fluid separates in PMMA, and ethanol/water.
4. The ethanol/water become nano size droplets and the PMMA fills the gap between the droplets.
5. Eventually the ethanol/water leaves the PMMA and the PMMA transit from a glassy phase to a solid phase.
6. The remaining ethanol is washed away with water and the water is dried from the cavities of the material.

The principle is simple, but the material is very sensitive to:

- The relation between water, ethanol and PMMA
- The cooling gradient, particularly during the phase separation process

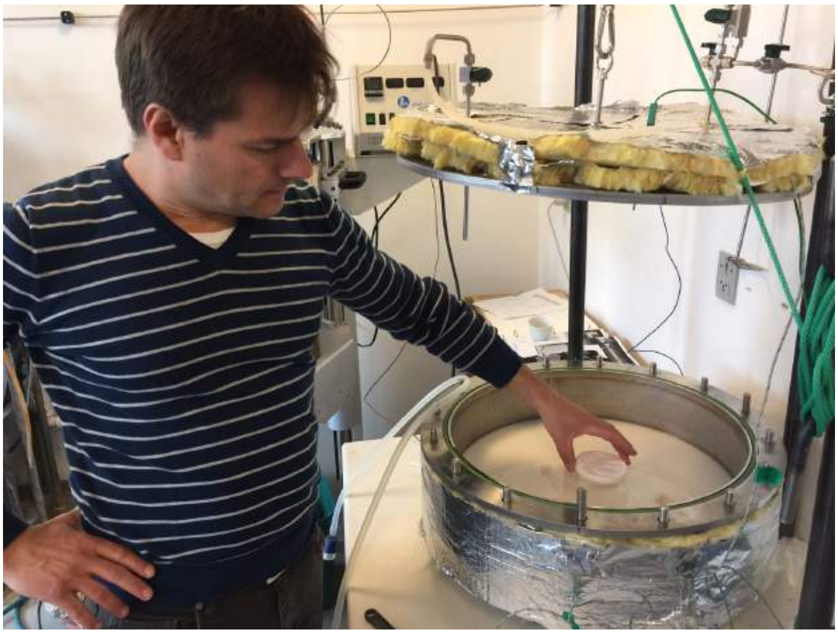
Minor tweeks of the same materials and almost the same process can result in very different materials

- Densities between 15 and 25%
- Pore sizes from 200 to 10.000 nanometers
- Almost closed pores to very open lattice
- Flexible or stiff product

DTI has done more than 40 samples from the autoclave and hundreds of test samples cut from the "Camembert" segments. The experiments systematically changing parameters and can now repeat experiments and get the expected performance of a sample.

A few month ago DTI got a transparent glass autoclave where it is possible to watch the transmission from the clear fluid to the white camembert cheese like samples.

In a new and much larger autoclave the first 46 cm large samples has been produced.



Figur 21 Kristian pointing to the 46 cm diamter TIPS material

Figur 22: Martin holding the 46 cm diameter TIPS sample

Business plan: Thinsu

We have named the TIPS insulation material Thinsu = Thin insulation

The unique selling point for Thinsu is a unique combination of:

- Good insulation like mineral wool and foam Reduce conductivity 72% from 0,14 W/mK in wood to 0,04 W/mK in the TIPS material
- Mechanical properties like wood
- Can be cast in any shape and profile
- Hydrophobic
- Completely inorganic, corrosion free and naturally white without painting
- Finished smooth durable surface.

Thinsu is not like other types of insulation filled into a cavity in the construction, it is the construction

The advantage of the thin insulation is:

- It provides space for interior insulation
- Easy installation and minimal repair work
- It provides more net area of the building than conventional insulation
- It provides "floor heating" effect when it is integrated into flooring with a thin surface.
- Prevents condensation and indoor air problems
- Is completely hydrophobic

The business idea is to produce a thin super insulation Thinsu as a board that combines:

- Available ready to mount on the wall
- Available to industries who want to upgrade their current products like click flooring, window frames, door frames and sills, ceramic tiles, refrigerators with super insulation performance

The market for products that will benefit from Thinsu insulation inside are gross about 6 billion m^2 so even a small market share can provide the volume needed for large-scale production

Products

Thinsu basic product is:

- A super insulating board you can cut, drill, and build with just like wood and woodboard.
- Hard boards coloured straight through
- Supplied in floor to ceiling height as plasterboard and in smaller formats customers can pick up at an outlet and take home in the trunk
- Thinsu can be cast as click flooring with its own colored durable and smooth surface and sold through building markets and on the Web in competition with laminate flooring
- Thinsu brings this product to the market through the wood floor manufacturers
- Thinsu can be glued to the back side of the tiles or thin gorilla glass, which can then be bonded with mortar. This product Thinsu bring to the market through tile manufacturers.
- Window frames, window sills and linings can be made directly from Thinsu eliminating the thermal bridge in window constructions and thus ensure their isolation and their energy approval. This product Thinsu bring to the market through window manufacturers
- Refrigerators can be produced directly from Thinsu, cold storage modules, including refrigerated container and refrigerated trucks. This product Thinsu bring to market through manufacturers
- Thinsu can be cast in molds used for internal lining of ceilings, dashboard, doors, etc. in cars. This product Thinsu bring to the market through automakers. It will particularly of electric cars will be interesting with good insulation properties.
- Thinsu can be cast in profiles for glass roofs
- Thinsu can be cast as insulated pipes for HVAC, both for water and for air

- Thinsu can be cast as bottles and transport containers for medicine

Value proposition and market

Indoor retrofit insulation

The price of a construction with super insulating Thinsu should be compared to the cost of mounting wood structure, mineral wool insulation, vapour barrier, drywall, linings and moving the radiator and electrical switches. Improved comfort and cleaner CO2 conscience are added values

Retrofit floors

Thin insulation is essential when insulating a floor. There may be room for a click-floor of 14-16 mm, but slightly thicker insulation will force the door to be lifted and then it becomes really expensive

Insulation of wooden floors has a corresponding savings as calculated above for walls. Heat loss of floors is slightly smaller, but many floors are also even less isolated, especially on the ground floor in older apartment buildings where they only consist of wood on the floor and plaster on the roof below. Insulated wooden floors will be warmer to your feet because the heat from the feet cannot be transmitted through Thinsu insulation. The super-insulating Thinsu floor is thus a very inexpensive alternative to under floor heating.

Windows

Many window manufacturers have trouble with regulatory requirements for insulation in the Scandinavian countries and zero-energy requirements in other countries. They have now developed profiles with PUR foam to break the thermal bridges.

The area of the wooden part of the VELUX skylight is quite large because the window is elevated significantly above the roof insulation. VELUX manufactures already linings to fit the windows and if these panels were constructed in Thinsu the entire skylight would reach a completely different energy class. Presumably, the heat loss could be halved depending of size.

Heat loss is often only calculated perpendicular to the roof surface. The profiles are designed with drainage channels located underneath the insulation thermal bridge-break and therefore transferring heat from the outside into these channels. The channels are open at the bottom end and unfortunately often also at the top end. It is therefore possible to circulate the cold outdoor air through these channels. Profiles are not insulated at the ends providing heat flow parallel to the roof. Aluminium is an exceptionally thermally conductor and all in all it means problems with increased heat loss and condensation.

Glass room profiles

The amazing potential of Thinsu made from TIPS is that TIPS can be casted in profiles witch are:

- Shaped with drain channels like aluminium profiles
- Completely without thermal bridges
- Self supporting

Cold storage and refrigerated containers

Trucks and refrigerated containers are a core market for vacuum insulation panels (VIP).

Thinsu has the advantage that it has a finished surface and strength to be the wall surface instead of being within the wall. Extra thin insulation will provide more space inside the truck or container. Euro pallets are 120 x 80 cm and the maximum width of trucks is 250 cm. If mounting rails in the floor, it will probably be possible to run two euro pallets onto a width within the truck and still have 30 mm insulation

Market potential

In contrast to conventional insulation produced and distributed within a radius of a few hundred kilometers Thinsu can reach a global market because the thickness is reduced. Half of the global consumption of building materials is in Southeast Asia and particularly in China. Factoris in China, Europe and USA could deliver to the entire world.

A 40 'container can hold approximately 60 m3 = 3000 m2 Thinsu of 2 cm thickness. Transport from China to Europe costs 16 500 DKK and thus constitute less than 6 DKK /m2 Thinsu insulation.

It is estimated that several hundred billion m2 building envelope need insulation or extra insulation. It is both beneficial to insulate this building envelope in cold countries where it saves heating and in hot countries where it saves cooling. Cooling is about 3 times more energy-consuming than heating so the savings are greater by insulating buildings with air-condition

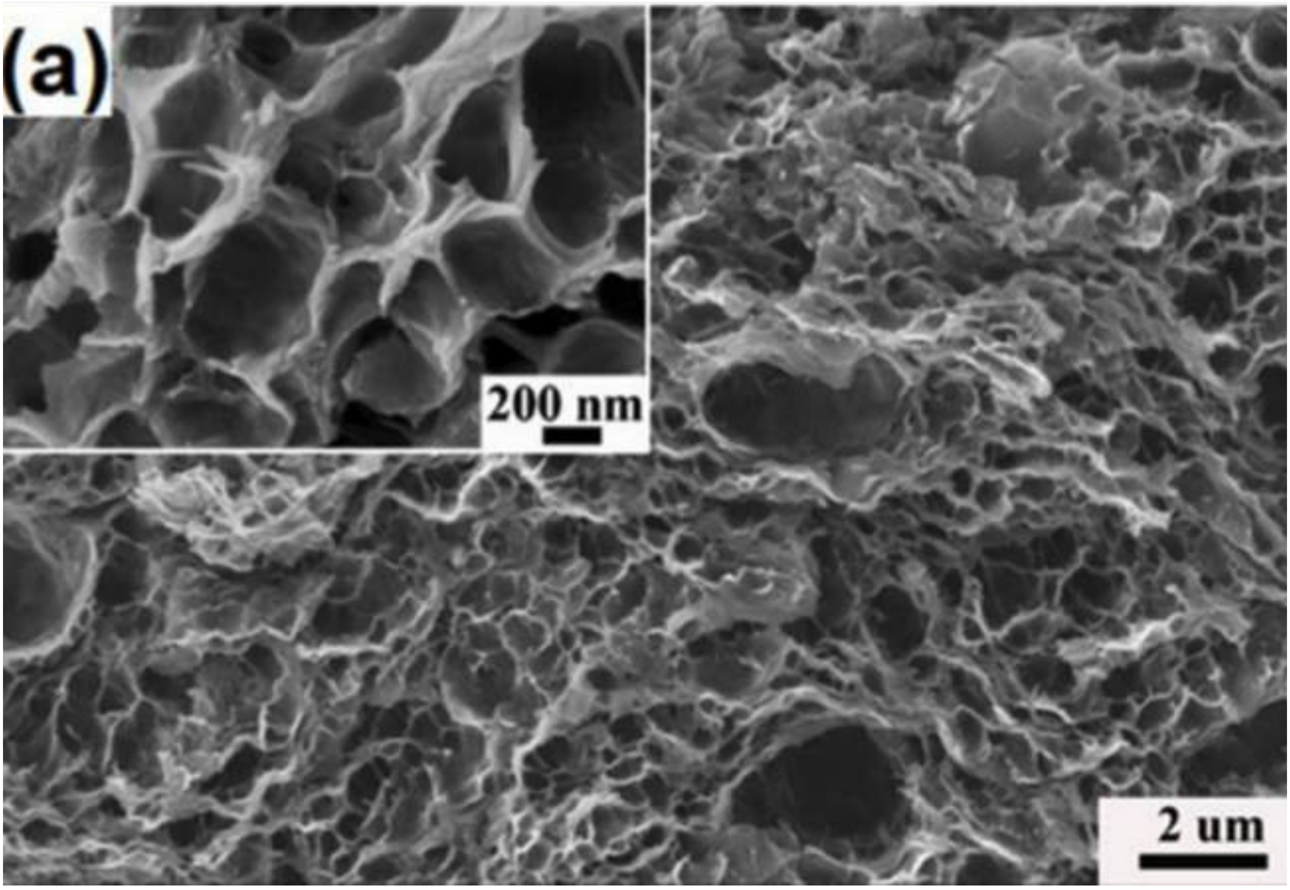
An estimated 2 billion m2 of plasterboard are mounted in isolated constructions

- Global sales of wood flooring is about 1 billion m2 and here be an estimated 0.5 billion m2 on ground floors and in one-storey houses.
- Global sales of ceramic tiles is about 12 billion m2 annually. It is estimated that 6 billion are floor tiles and it is estimated that about 3 billion m2 are insulated floors or insulated outer walls.
- Global sales of windows and glass facades is about 2 billion m2 of which window frames, window sills and linings constitute about 10% or 0.2 billion m2.
- Approximately 100 million m2 cold storage elements are produced annually. The figure is uncertain because the same product can also be used for other purposes, for example. Industrial buildings.
- Gross market for these products are about 5.8 billion m2. A market share of one per thousand amounts to 5.8 million m2 annually.

Competition

Mainly 4 kind of insulation is competing with Thinsu:

- Mineral wool for example. Rockwool or glass wool
- Expanded polystyrene (EPS) for example. Sundolitt and Flamingo
- Polyurethane foam (PUR)
- Slentite (not yet commercially on the market)

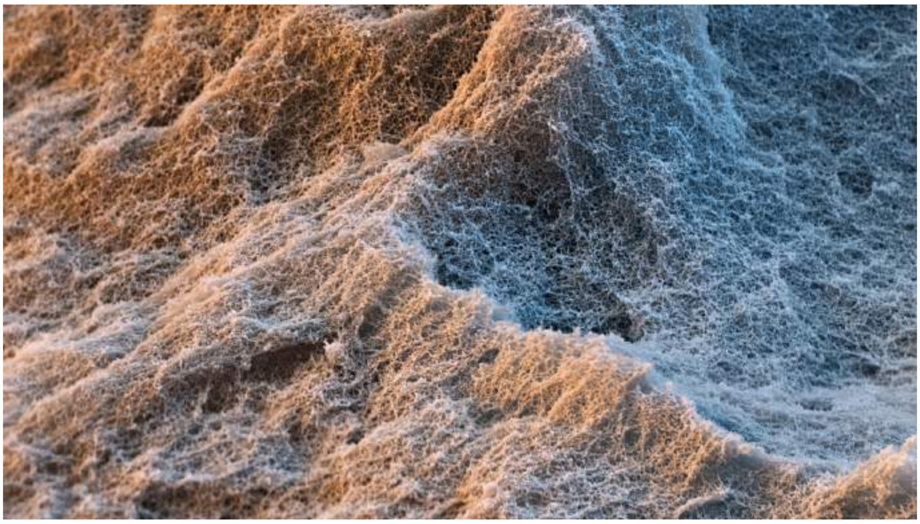


Figur 23: SEM image of Slentite

Slentite

BASF has developed a new insulation material Slentite improving the existing PUR/PIR foam as described in patent PCT/EP2013/061349.They have built a factory and Slentite is expected on the market within a year.

The Slentite invention relates to a composite material containing nanoporous aerogel particles and at least one binder made of at least one isocyanate and at least one polymer P selected from the group consisting of polyvinylamine, poly(meth)acrylic acid or ester, polyvinyl alcohol, polyvinyl thiol, and mixtures thereof, wherein the at least one binder is used in a quantity of 0.1 to 20 wt.% based on the quantity of nanoporous particles. The invention also relates to a composition for producing such a composite material, as moulded bodies containing the composite material, and to the use of the composite material for thermal and/or sound insulation. Aerogel is first made hydrophobic and then mixed into an aquarius solution of the polymer in the process.

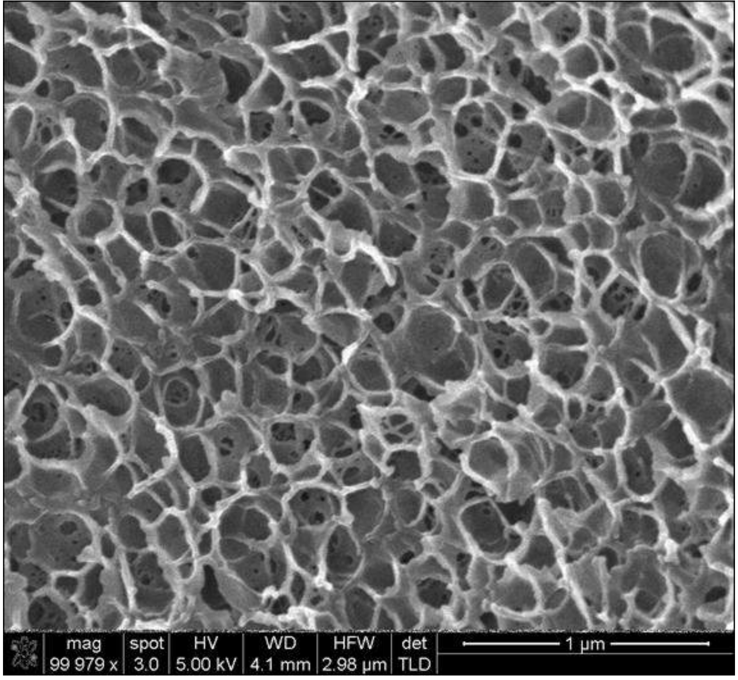


Figur 24: SEM image of Slentite

Dow PMMA foam

PMMA (acrylic) nanocellular foams are broadly defined as having pore size below one micron. However, it is only when pore size reaches the Knudsen effect region below 100 nm, that super low thermal conductivity is reached due to gas confinement in the cells and polymer confinement in the cell walls. Producing such materials with low density by physical foaming with CO^2 requires the controlled nucleation and growth of 10^{15} to 10^{16} cells/cm^3. This is a formidable challenge that necessitates new foaming strategies. Low density nanofoams and nanostructured polymers is produced in a process in which nucleation can be precisely controlled

Stephane Costeux from Dow has made a PMMA foam with thermal conductivity of 0,014 W/mK
Nano porous acrylic foam is as strong as massive acrylic. The small closed regular shaped pores create mechanically strong 3D structures.



Figur 25: DOWs PMMA foam with CO2

Conventional insulation

The global market for mineral wool is annually about 66 billion DKK. Approximately 20% is technical insulation and an additional 20% sound absorbing products. Building insulation makes up 40 billion DKK /

year. Converted to an insulating effect comparable with Thinsu cost of 95 mm thick Rockwool is about 20 DKK / m2 in the store and we assume here a price of 10 DKK /m2 factory. It is thus similar to some 4 billion m2 building insulation annually.

Thinsu is also competitive in the technical insulation and sound absorbing market
The global market for EPS is 16 billion$. A significant part of this market is packaging. Based on the same assumptions as above, the production volume is assumed to be around 6 billion m^2 building insulation annually.

The global market for PUR insulation is virtually the same size

These figures indicate that the gross market insulation is about 16 billion m^2 or twice as large as assumed in the market section above. This is due to our market figures above do not include constructions with insulated concrete elements, aerated concrete, brick walls with cavity insulation etc..

Vacuuminsulation

The world market for Vacuum Insulation Panels (VIP) with an insulation performance comparable to Thinsu are globally about 3 million m^2 / year, or 0.02% of the total insulation market.

Among the competing companies are:

- va-Q-tec
- Doe Corning
- EVONIK AEROSIL
- LG HAUSYS
- OCI
- Panasonic
- ThermoCor
- Porextherm
- Microtherm
- Marley Eternit
- Suzhou Wei Yipu New Materials Co., Ltd.
- Creek
- Super Tech
- Yinxing Electric
- Changzhou Sanyou Dior Insulation Materials MFG Co., Ltd
- Shanxi Jiudi Energy Saving Technology Company

:
http://www.prnewswire.com/news-releases/global-vacuum-insulation-panel-vip-industry-report-2014-2019-with-focus-on-the-chinese-industry-258606571.html

Cost of consumables

	DKK/m^2 (2 cm thickness)	%
PMMA	36,0	72
Water	0,2	1
Ethanol	13,6	27
Consumeables total	49,8	100

The potential for recycling of PMMA for Thinsu is is examined. Initial studies indicate that

- Powder is better than solid material
- PMMA with long molecular chains are better than PMMA with short molecule chains.
- It is not clear how the recycled material should be sorted and what difference molecular size make.

PMMA costs as new material about 10 DKK/kg. and having a density of 1.18, it is approximately 11.8 DKK/l. With a porosity of 85% it cost 1,8 DKK/l. PMMA for a 2 cm thick plate cost 36 k/m2

Water costs about 50 DKK for 1000 litre so 4 litre cost 0,2 DKK

Ethanol costs about 8 DKK/ l . With 85% porosity and 80% ethanol in the ethanol / water mixture consumption is 13,6 liters for a square meter or about 109 DKK ethanol pr m2. Part of this ethanol can, however be recovered. It costs about 0.5 kWh. liter or 6.8 kWh = 13,6 DKK per. m2 plate of 2 cm thickness. Distillation can use excess heat from power stations or industrial processes and in that case energy consumption is considerably smaller and cheaper.

Investments

The following is calculated based on an annual depreciation and interest of 20%, production is distributed over 200 days and 7,500 m^2 boards are produced every day. In the first years a 50% load factor is more likely so we adjust til figures to a 50% loadfactor

	Investment (1000 DKK)	%	Pr m^2 board
Autoclave	1.800	2,1	0,24
Heated piping	100	0,1	0,01
Moulds	37.500	43,7	5,00
Cooling tank	10.000	11,6	1,33
Robots	1.500	1,7	0,20
Rinsing tank	10.000	11,6	1,33
Ethanol recovery destillery	5.000	5,8	0,67
Factory	20.000	23,3	2,67
Total investment	85.900	100,0	11,45

The processes are:

- Heating under 5 atmospheres pressure and a temperature of 150 degrees for 8 hours. An autoclave with capacity of 5000 tons per year including PMMA, water and ethanol, costs 300,000 DKK. 7500m2 board a day 200 days a year is 1.500.000 m^2 = 30.000 m3 = 6 such autoclaves
- Liquid PMMA solution is transported as a fluid I pipes heated to 70 °C
- The TIPS material is cooling of the moulds for a day. We will need 7500 moulds to reach 7,500 sheets per day. The one m^2 moulds will probably cost 5,000 DKK each.
- They can be placed in a 10 x 25 x 1 m cooling tank accommodating 7,500 boards in a pool of costing 10 million DKK.
- 6 robot costing 250,000 DKK each a taking the material out of the moulds and transporting them to the rinsing tank
- Rinsing with water in the basin requires processes for about a day, A 10 x 25 x 1 m cooling tank accommodating 7,500 boards in a pool of costing 10 million DKK.
- Distillation of ethanol from water is a relatively expensive facility for 3-5 million DKK, for the 250,000 liters per day
- Buildings for factory assumed to cost 20 million

https://www.alibaba.com/product-detail/ethanol-distillation-plant-95-99-9-_1206693196.html?s=p

Staff cost

If it is assumed that 10 employees can run the plant. With an average salary of 500,000 DKK /year the payroll costs is 5 million DKK / year which spread over 1.5 million m2 is about 3,33 DKK/m^2. During the first years a 50% load factor is more likely so we adjust the figures to a 50% loadfactor

Total cost

	DKK/m^2 (2 cm thickness)	%
Consumables	49,8	77
Investment pr. m2	22,9	35
Staff pr m2	6,66	10
Total production cost	**79,36**	
Profit 10%	7,94	
Markering & Sale 30% B2B	26,19	
MOMS (WAT 25%)	28,37	
Price	**141,86**	

SWOT

Strengths

The unique selling point for Thinsu is a unique combination of:

- Good insulation like mineral wool and foam Reduce conductivity 72% from 0,14 W/mK in wood to 0,04 W/mK in the TIPS material
- Mechanical properties like wood
- Can be cast in any shape and profile
- Hydrophobic
- Completely inorganic, corrosion free and naturally white without painting
- Finished smooth durable surface.

Thinsu is not filled into a cavity in the construction, it is the construction

Weaknesses

- New unknown product that requires effective marketing
- Required substantial production from day 1
- We must have orders for a product that exists only as prototypes

Opportunities

- We focus only on a very small market share in a gigantic market
- Growing recognition of the need for CO^2 reduction and energy savings

Threats

- Exclusive agreements between retailers and manufacturers
- Technical barriers to trade like fire test that favours mineral wool in Denmark
- Discounts to construction businesses invisible to the end customer
- No patent protection
- Slentite is 5 years ahead in development

Patent

A patent was filed in Denmark before the project started.
A PCT patent was filed during the project period.
Both Danish and PCT patent authorities came independently back with the same message:
It is possible to get a patent on the vacuum insulated cubes.
The patent was made public April 28 th 2016
Create.dk, holder of the patent has decided not to continue the patent, as this invention is not economically viable.

We have not applied patents on the TIPS technology. We have made a comprehensive survey of TIPS patents and TIPS literature and se a potential for a patent when we know exactly how to control the process.

Litterature

Barrier coatings

rGO
Functionalization of graphene surfaces with downstream plasma treatments
Niall McEvoy, Hugo Nolan, Ashok Kumar Nanjundan, Toby Hallam, Georg S. Duesberg
Impermeable barrier films and protective coatings based on reduced graphene oxide
Y. Su, V.G. Kravets, S.L. Wong, J. Waters, A.K. Geim & R.R. Nair
Thermal properties of graphene and multilayer graphene: Applications in thermal interface materials
Khan M.F.Shahil 1, AlexanderA.Balandi
Preparation of reduced graphene oxide films by dip coating technique and their electrical conductivity
H. B. Suna, J. Yang*a, Y. Z. Zhoua, N. Zhaoa & D. Lia
Impermeability of graphene and its applications
Vikas Berry

Other barrier coatings

Stacks on Flexible Polymer Substrates High-Performance Transparent Barrier Films of SiO x SiN x
T. N. Chen, D. S. Wuu, C. C. Wu, C. C. Chiang, Y. P. Chen and R. H. Horng
Thermal Sprayed Coatings Used Against Corrosion and Corrosive Wear
P. Fauchais and A. Vardelle
Polysiloxane Super-toughening of Silica Gas Barrier Coatings on Polymer Substrates
P. Fayet, G. Rochat, Y. Leterrier, B. Singh, J. Bouchet, J.-A.E. Månson
Titanium oxide thin film deposition by pulsed arc vacuum plasma
I S Zhirkov*, C Paternoster, M P Delplancke-Ogletree
New vacuum equipment for multilayer coating deposition on large area glass
V. Kozlov, E. Yadin, G. Taiminsh, and V. Fomin
Graphene Oxide Thin Films: A Simple Profilometer for Film Thickness Measurement
Satish bykkam, K.Venkateswara Rao, Ch.Shilpa Chakra, V.Rajendar, Rotte Naresh kumar, J.Ananthaiah

Calculation tools

Study on the Characteristics of Gas Molecular Mean Free Path in Nanopores by Molecular Dynamics Simulations
Qixin Liu 1,* and Zhiyong Cai 2
Opacified silica aerogel powder insulation
E. Hummer, Th. RettelbacXh., Lu, J. Fricke
Thermal Insulation
Axel Berge, Pär Johansson
Pore-size dependence of the thermal conductivity of porous silicon: A phonon hydrodynamic approach
F. X. Alvarez, D. Jou and A. Sellitto

Nanofoams

Polymer Nanofoams
Bernd Krause
Continuous extrusion of nanocellular foam
Stephane Costeux
CO2-Blown Nanocellular Foams
Stephane Costeux
Low density thermoplastic nanofoams nucleated by nanoparticles
Stéphane Costeux*, Lingbo Zhu
Ultrasonic formation of nanobubbles and their zeta-potentials in aqueous electrolyte and surfactant solutions
Sung-Ho Choa, Jong-Yun Kimb, Jae-Ho Chuna, Jong-Duk Kima
Temperature influence and CO2 transport in foaming processes of poly(methyl methacrylate)–block copolymer nanocellular and microcellular foams
Javier Pintoa,b,∗, José A. Reglero-Ruizb, Michel Dumonb, Miguel A. Rodriguez-Pereza,∗∗
Porous Inorganic Materials

Xiqing Wang Xianhui Bu& Pingyun Feng
Polymer nano-foams for insulating applications prepared from CO2 foamingC.
Foresta, P. Chaumonta, P. Cassagnaua,∗, B. Swobodab, P. SonntagbalMP
On thermal conductivity of micro- and nanocellular polymer foams
Sriharsha S. Sundarram andWei Li

Generating vacuum in closed cells

Supercritical carbon dioxide-soluble polyhedral oligomeric silsesquioxan (POSS) nanocages and polymer surface modification
Cerag Dilek,
Adsorption ofCO2 from dry gases on MCM 41silica at ambient temperature and high pressure:Pure CO2 adsorption
Youssef Belmabkhout, RodrigoSerna-Guerrero, AbdelhamidSayari
Determination of the MCM-41 wall mean densities from sorption capacity and neutron diffraction measurements.
N. Floquet', J.P. Coulomb', S. Giorgio', Y. Grillet b and P.L. Llewellyn
Polymerization time for a microwave-cured acrylic resin with multiple flasks
Daniela Maffei Botega, Tatiana de Souza Machado, José Antônio Nunes de Mello, Renata Cunha ,
Matheus Rodrigues Garcia, Altair Antoninha Del Bel Cury
CapturingCO2 fromambientairusingapolyethyleneimine–silica adsorbent in fluidized beds
WenbinZhang,HaoLiu n, ChenggongSun,TrevorC.Drage,ColinE.Snape
CO2 adsorption kinetics on mesoporous silica under wide range of pressure and temperature
Sravanthi Loganathan, Mayur Tikmani, Satyannarayana Edubilli, Aakanksha Mishra,Aloke Kumar Ghoshal
Modified Atmosphere Insulation - Scoping Study for Next Generation Building Envelope Materials
Kaushik Biswas

Aging and diffusion

Formulas for diffusion through membranes
file:///Users/Create/Downloads/chapter4.pdf
Nano-Structured, Semicrystalline Polymer Foams
C. Beaucage, J. H. Aubert, R. R. Lacasse, D. W. Schaefer, T. P. Rieker, P. Erlich, R. S. Stein,S. Kulkarni And P. D. Whaley3
Synthesis of stabilized semi-crystalline polymer foam
Robert Silberman and June Silberman
Crystallizable diluent-templated polyacrylonitrile foams for macroporous carbon monoliths
Qing-Yun Wu, Ling-Shu Wan, Zhi-Kang Xu
Controlled foaming of polymer films through restricted surface diffusion and the addition of nanosilica particles or co2-philic surfactants
Srinivas Siripurapu,Joseph M. DeSimone, Saad A. Khan, and Richard J. Spontak
A new view of diffusion in nanoporous materials
Christian Chmelik, Lars Heinke, Rustem Valiullin und Jörg Kärger
Aging of Polyurethane Foam Insulation in Simulated Refrigerator Panels — Two-Year
Kenneth E. Wilkes, W. Alex Gabbard, Fred J. Weaver
Closed Cell Foam Insulation: A Reviewof Long Term Thermal Performance
Therese Stovall
Diffusion and permeability in polymer
Paula M Wood-Adams

Ceramic Aerogel

Preparation of silica aerogels with improved mechanical properties and extremely low thermal conductivities through modified sol-gel process
Zuo, Yanjia
Beyond Vacuum Insulation Panels - How May It Be Achieved?
Bjørn Petter Jelleab, Arild Gustavsenc and Ruben Baetensd
Chemistry of Aerogels and Their Applications
Alain C. Pierre† and Ge´rard M. Pajonk*,‡
Ultra-thin Aerogel Films
Kimberly A.D. Obrey and Roland K. Schulze
Synthesis of flexible silica aerogels using methyltrimethoxysilane (MTMS) precursor

A. Venkateswara Rao a,∗, Sharad D. Bhagat a, Hiroshi Hirashima b, G.M. Pajonkc
A tour-de-force in polymer crosslinked aerogels
Sudhir Mulik
Highly compressible 3D periodic graphene aerogel microlattices
Cheng Zhu, T. Yong-Jin Han, Eric B. Duoss, Alexandra M. Golobic, Joshua D. Kuntz1, Christopher M. Spadaccini1 & Marcus A. Worsley
International symposium on Superinsulating materials

Organic aerogel

Natural Aerogels Production by Supercritical Gel Drying
Lucia Baldino, Stefano Cardea*, Ernesto Reverchon
Polymer/Carbon-Based Hybrid Aerogels: Preparation,Properties and Applications
Lizeng Zuo ,Youfang Zhang, Longsheng Zhang, Yue-E Miao,Wei Fan 2 and Tianxi Liu
Aerogel-based Composite/Hybrid Nanomaterials for Cost-effective Building Superinsulation systems
Eunate Goiti
Multi-scale cellulose based new bio-aerogel composites with thermal super-insulating and tunable mechanical properties
Bastien Seantier, Yves Grohens, Hamid Kaddami
Ultra-light nanocomposite aerogels of bacterial cellulose and reduced graphene oxide for specific absorption and separation of organic liquids†
Yonggui Wang, Sandeep Yadav, Thorsten Heinlein, Valentino Konjik, Hergen Breitzke, Gerd Buntkowsky Jörg J. Schneider and Kai Zhang
A Novel Method to Manufacture Superhydrophobic and Insulating Polyester Nanofibers via a Meso-Porous Aerogel Powder
Z. Mazrouei-Sebdani, A. Khoddami, H. Hadadzadeh, M. Zarrebini
New tannin–lignin aerogels
L.I. Grishechkoa,b, G. AmaralLabata, A. Szczureka, V. Fierroa, B.N. Kuznetsovb, A. Pizzi c, A. Celzarda
Multifunctional Polyurea Aerogels from Isocyanates and Water. A Structure–Property Case Study
Nicholas Leventis, Chariklia Sotiriou-Leventis, Naveen Chandrasekara, Sudhir Mulik, Zachary J. Larimor, Hongbing Lu, Gitogo Churu, and Joseph T. Mang

MFO,

Effective Thermal Conductivity of MOF-5 Powder under a Hydrogen Atmosphere
Hui Wang, Zhiguo Qu, Wen Zhang, Wenquan Tao

Geopolymer,

Thermal insulating foamy geopolymers from perlite
V. Vaou, D. Panias Marcelo Strozi Cillaa,b,n, Paolo Colombob,c, Márcio Raymundo MorelliaGeopolymers – State of the art : COIN Project report 37 – 2011
Klaartje De Weerdt
30 Years of Successes and Failures in Geopolymer applications, market trends and potential breakthroughs.
Joseph Davidovits

Foam glass

Water and waterglass mixtures for foam glass production
Daniela Heskya,n, ChristosG.Anezirisa, UlrichGroßb, AnjaHornb
High Strength Borosilicate Foams by Expansion of Ar-Filled Pores and Release of Dissolved Ar Gas Bo Wang, Koji Matsumaru, Jianfeng Yang and Kozo Ishizaki
Fabrication of highly insulating foam glass made from CRT panelglass
Jakob Königa,b,1, RasmusR.Petersena, YuanzhengYuea

Zeolite

Thermal conductivity of pure silica MEL and MFI zeolite thin films
Thomas Coquil,1 Christopher M. Lew,2 Yushan Yan,2,a and Laurent Pilon1
Microporous Mixed Matrix (ZeoTIPS) Membranes
Caleb Vincent Funk, B.S.
Aluminosilicate and aluminosilicate based polymer composites: Present status, applicationsand future trends
A.C. Lopes 1, P. Martins 1, S. Lanceros-Mendez ⇑

Commercial insulation and IP

Thermal insulation materials made of rigid polyurethane foam (PUR/PIR)
Federation of European Ridid Polyurethane Foam Associations 2006
http://www.excellence-in-insulation.eu/site/fileadmin/user_upload/PDF/Thermal_insulation_materials_made_of_rigid_polyurethane_foam.pdf
Closed Cell Foam Insulation: A Review of Long Term Thermal Performance Research
Therese Stovall http://info.ornl.gov/sites/publications/files/Pub40530.pdf

Patents

NANOPOROUS POLYMER FOAMS
US 2011/0287260 A1
May 20, 2011
AEROGEL-CONTAINING POLYURETHANE COMPOSITE MATERIAL
WO 2013/182506
VACUUM ASSISTED PROCESS TO MAKE CLOSED CELL RIGID POLYURETHANE FOAMS USING MIXED BLOWING AGENTS
WO 2015042300 A1
METHOD OF FORMING IMPERMEABLE CARBIDE COATS ON GRAPHITE
US 3778300 A

Product brochures
Pyrogel 20mW/mK (aerogel)
http://www.aerogel.com/_resources/common/userfiles/file/Data%20Sheets/Pyrogel_XT_DS.pdf
Slentite: 17 mW/mK (aerogel)
http://www.polyurethanes.basf.de/pu/solutions/en/content/group/innovation/products/slentite/intro

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