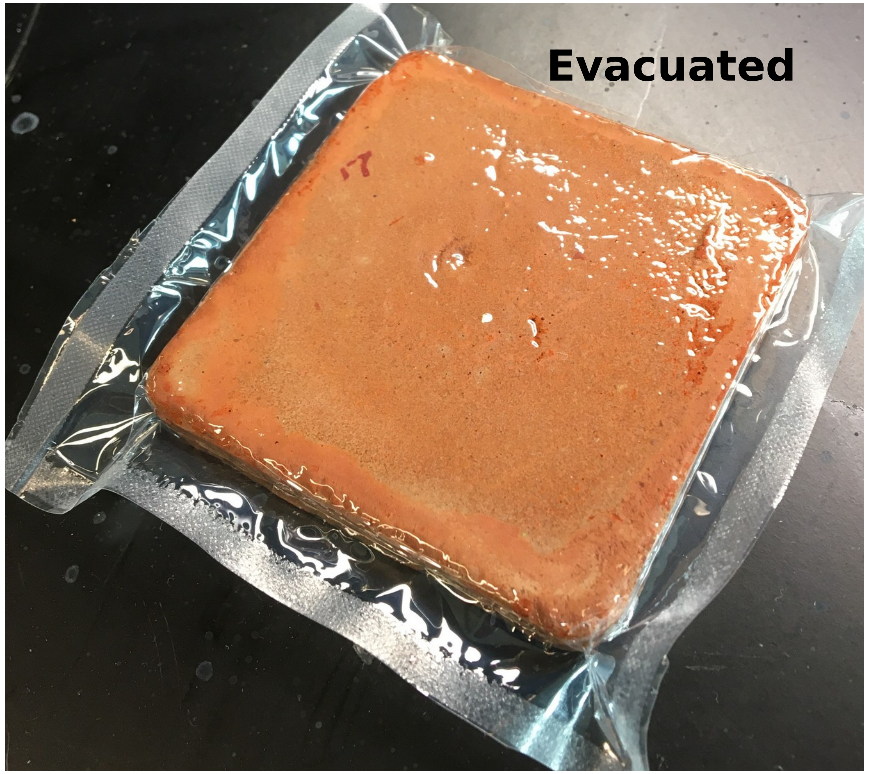
Inexpensive and durable aerogel-based VIP cores



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Project Summary

Timeline:

Start date: 06/01/2019

Planned end date: 5/31/2022

Key Milestones

1) Fabrication of phenolic aerogel monoliths by ambient drying. Achieved 02/2020.
2) Fabrication of aerogel monoliths not collapsing when used as VIP cores. Achieved 11/2020.
3) Validation of aerogels as VIP cores (thermal conductivity, outgassing, mechanical strength). In progress.
4) Minimization of thermal conductivity of aerogel cores, target 0.020 W/mK. In progress.

Budget:

Total Project $ to Date:

- DOE: $251,726
- Cost Share: $51,635

Total Project $:

- DOE: $493,470
- Cost Share: $123,394

Project Outcome:

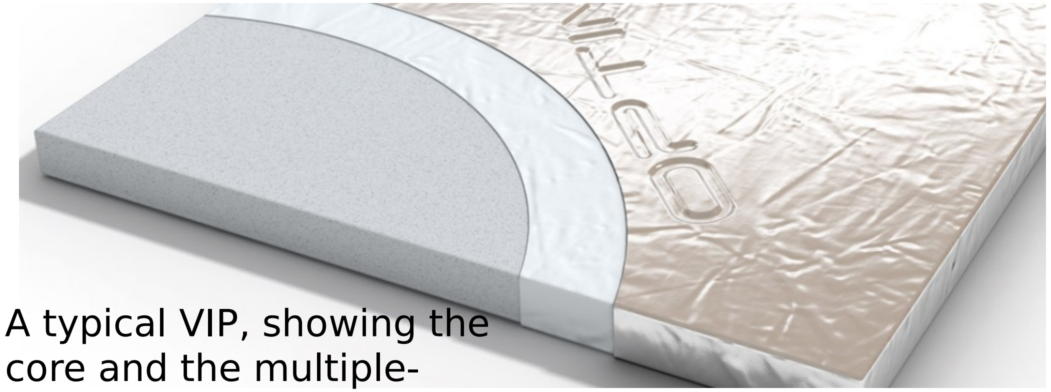
The aim of the project is fabrication of low cost phenolic aerogel cores to be used as VIP cores. The project has several ambitious goals, which have never been systematically attained before, much less in a combination.

- To minimize cost, fabrication will be carried out at ambient conditions.
- To withstand atmospheric pressure, the cores will have to be mechanically strong.
- To ensure thermal resistance in case of envelope failure, the cores will have to have a thermal conductivity $\lambda \sim 0.020$ W/mK.
- To alleviate vacuum issues, the cores will have to be nanoporous, and attain a $\lambda = 0.005$ W/mK at 100 mbar.

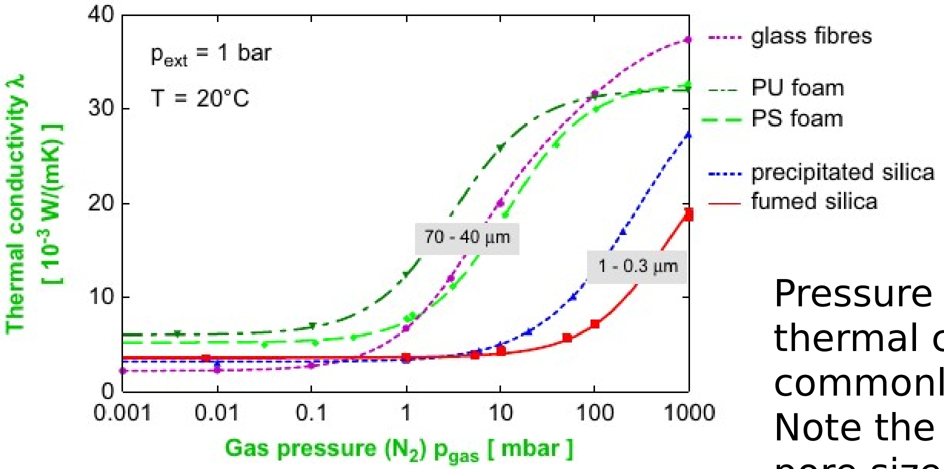
Challenge

Problem Definition:

1. Vacuum Insulated Panels (VIP) are the best thermal insulators available on the market. Their thermal conductivity (T.C.) is ~ 0.005 W/mK, or > R-28/inch.
2. But, the core of conventional VIPs is too expensive.
   - Example. Fumed silica: ~ \$3/kg. Typical core density: 150-200 kg/m^3. Cost of a panel 1ft^2, 1 inch thick --- \$1-1.5 **CORE ONLY.** Kingspan appears to price their VIPs at ~\$20/ft^2.
3. Most cores have comparatively large pores (100s of nm) --- Need pressures < 10 mbar (typically 1 mbar) to be in the Knudsen regime (mean free path of air molecules > pore size).
4. Low pressures mean longer pumping times, require metallized envelopes to act as getters and as vapor barriers --- increase cost, increase the thermal conductivity of the envelope, introduce edge effects, decrease lifetime.
5. Many cores are in powder form --- envelope failure can result in dispersion of the powder inside the building.
6.



A typical VIP, showing the core and the multiple-layered envelope. From Kinsgpan website.[2]



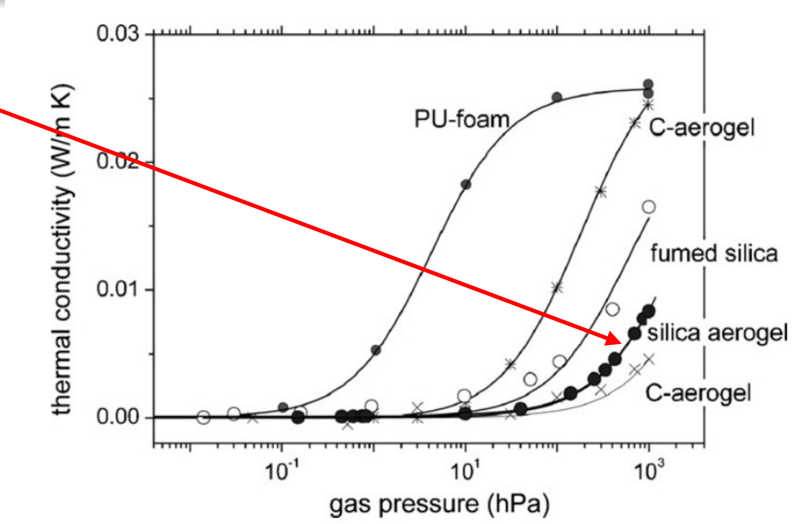
Pressure dependence of thermal conductivity for commonly used VIP cores.[1] Note the dependence on pore size (in gray).

Approach

Solution:

Make nanoporous monolithic aerogels.

- Nanoporous, therefore reach low thermal conductivity at higher pressures than conventional cores.
- No need to compact/press materials.
- Materials are monolithic, no powder dispersion if envelope fails.
- Aerogels are good insulators to begin with, so lower heat resistance loss if envelope fails.



To-do list:

- Aerogels must be robust, to withstand evacuation.
- Cost must be low: ambient drying is a must. Also: simple processing, common chemicals.
- Phenolic chemistry to improve fire resistance.

Challenges:

- Chemistry: will established chemistry be sufficient? Or new chemistry will have to be developed?We need to combine low thermal conductivity with mechanical strength, which is a tall order.
- Processing: Another tall order. Ambient drying seldom demonstrated for samples > few cm in size.
- Outgassing? Materials must not outgas.
- Industry acceptance: radically different process.

Risk mitigation:

- Chemistry: several different pathways available, yielding materials with varying strength, thermal conductivity.
- Chemistry: fillers will help strengthen materials.
- Processing: several different solvents, drying temperatures can be used to prevent cracking.
- Processing: use experience gathered with ArpaE grant, also focusing on non-supercritical drying techniques.
- Industry acceptance: keep process simple! Keep cost low! Overall, VIP industry is more accustomed to experimentation than most construction materials industries. This can be leveraged.

Impact

The project aligns with past and current DOE-BTO targets.

- The 2022 BTO FOA and SBIR FOA both include subtopics asking for cost-effective, durable VIPs.
- The 2022 BTO SBIR FOA has a subtopic requesting “Development of durable aerogel insulation using continuous, high-throughput production methods (…) at atmospheric processing conditions”.

The **milestones reached to date** fit well into these programmatic goals.

1. We have shown that aerogels can be processed at ambient conditions in monolithic form and large sizes. The process is simple, continuous (as opposed to batch), it does not require any specialized equipment (e.g., autoclaves, or freeze dryers) and it uses commonly available chemicals. There is no process that allows anything like this.

2. The aerogels can withstand atmospheric pressure after evacuation of the envelope without cracking or pancaking. This is another relevant achievement. Cores of VIPs are typically in powder form and need to be compacted before evacuation.

3. The aerogel mean pore size is < 50 nm, which likely allow to attain a low thermal conductivity at a modest level of evacuation (> 10 hPa--- 10 mbar).

Impact.

Cost estimate.

1. Assumed capacity: Pilot plant, 1 Million sq. ft/year, 1 inch thickness.
2. Based on current formulations:
   - Cost of monomers, catalyst: \$802,000 (Prices: internet, and in part wholesale suppliers).
   - Cost of solvents, 99.7% recovery (industry standard): \$12,000.
   - Cost of solvents, 97% recovery (realistic for pilot plants): \$126,000.
   - Personnel (4 technicians, \$20/hour): \$266,000.
   - Instrumentation cost: \$137,000 (internet prices for mixers, conveyor belts, etc.).
   - Installation cost: 5x instrumentation cost (industry standard).
   - Interest on loan for instrument: 12% of instrumentation+installation cost.
   - Rent for a 10,000 sq. ft. facility: \$60,000/year (mean US rental prices).
   - Density of materials: 0.18 g/cm^3
   - Cost/ft^2,(cost/kg) 99.7% solvent recovery: \$1.01ft^2 (\$6.02/kg)
   - Cost/ft^2,(cost/kg) 97% solvent recovery: \$0.90/ft^2 (\$5.34/kg)

Cost/ft^2 is lower than that of fumed silica cores.

Team

- Original team: VCU lead + Fraunhofer CSE Boston/Kosny.
- Project awarded in its entirety to VCU after CSE’s closure.
- COVID halted work for good part of 2020.
- Bertino: PI, ~20 years in aerogel fabrication, especially in aerogel processing.
- 3 patents adjudicated[3-6], 3 pending, ca. 40 peer-reviewed publications in the field of aerogels.
- 4 recent (3 active) federal grants on aerogel technology (1 ArpaE, 2 DOE/BTO, 1 DoT).
- Director, Nanomaterials Characterization Core facility (13 state-of-the-art instruments) which contains all necessary characterization tools.
- Dr. Everett Carpenter, VCU. Professor of Chemistry, MBA. Advises on marketing strategy.
- Chris Ohlhaver, MS Chemistry, principal scientist, GSK. Advises on marketing strategy.

Progress

Project stage: mid-stage

- Processing: straighforward, no major difficulties encountered.
- Chemistry: some difficulties related to catalyst, striking a compromise between thermal conductivity and strength. Led to catalyst screening, Design of Experiments.

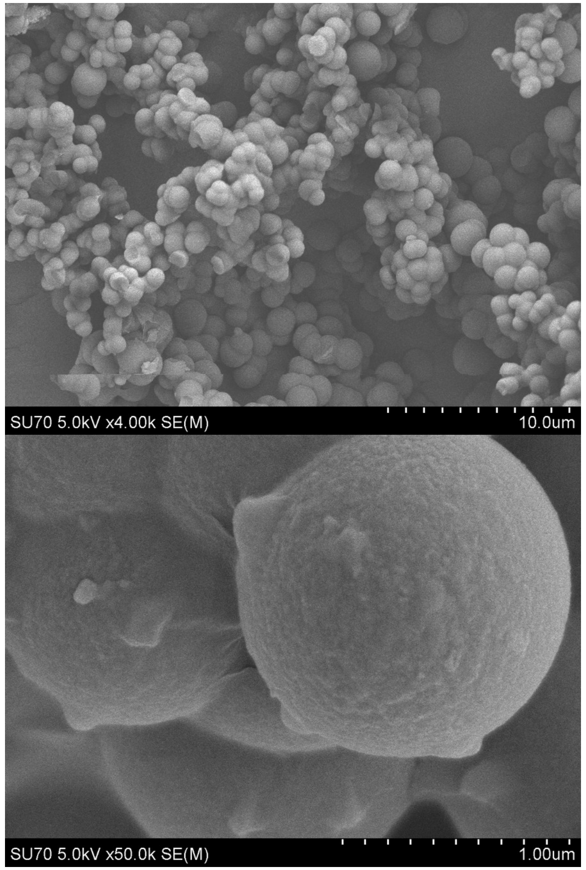
Catalyst Choice is paramount.

- “Conventional” catalyst: weak materials that pancake, crack under vacuum.
- Catalyst screening led to a catalyst yielding strong materials that do not crack/shrink during drying and do not collapse under evacuation. Sizes of 10x10x1.25cm (4”x4”x1/2”) have been attained.

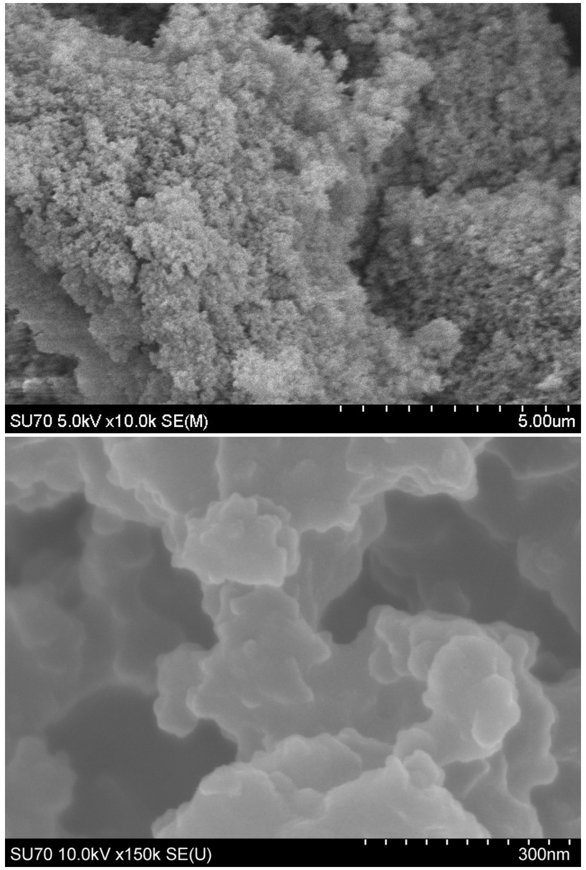
Progress

Design of Experiments (D.o.E.)

- Concentrations of Monomers 1 and 2 ([M1],[M2]) and catalyst [CAT] varied systematically.
- Two solvents used: a “good” solvent where the polymer is highly soluble (data in **red**) and a “bad” solvent (**blue**).
- Good solvent yields large particles, large pores and a robust skeletal structure.
- Bad Solvent yields smaller particles, smaller pores, but a weaker structure. Fillers (2-4% wt/wt) are required to reinforce the skeleton.



“Good” solvent:
Large particles.

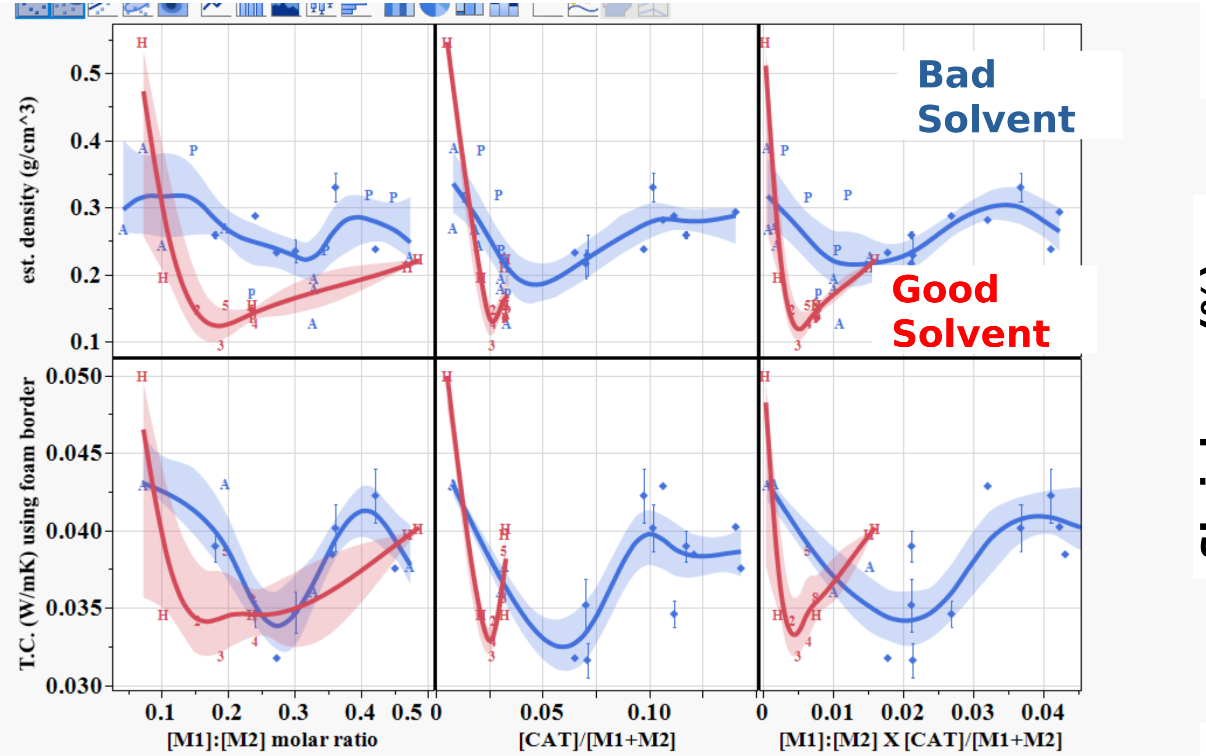


“Bad” solvent:
Small particles.

Progress

Design of Experiments (D.o.E.)

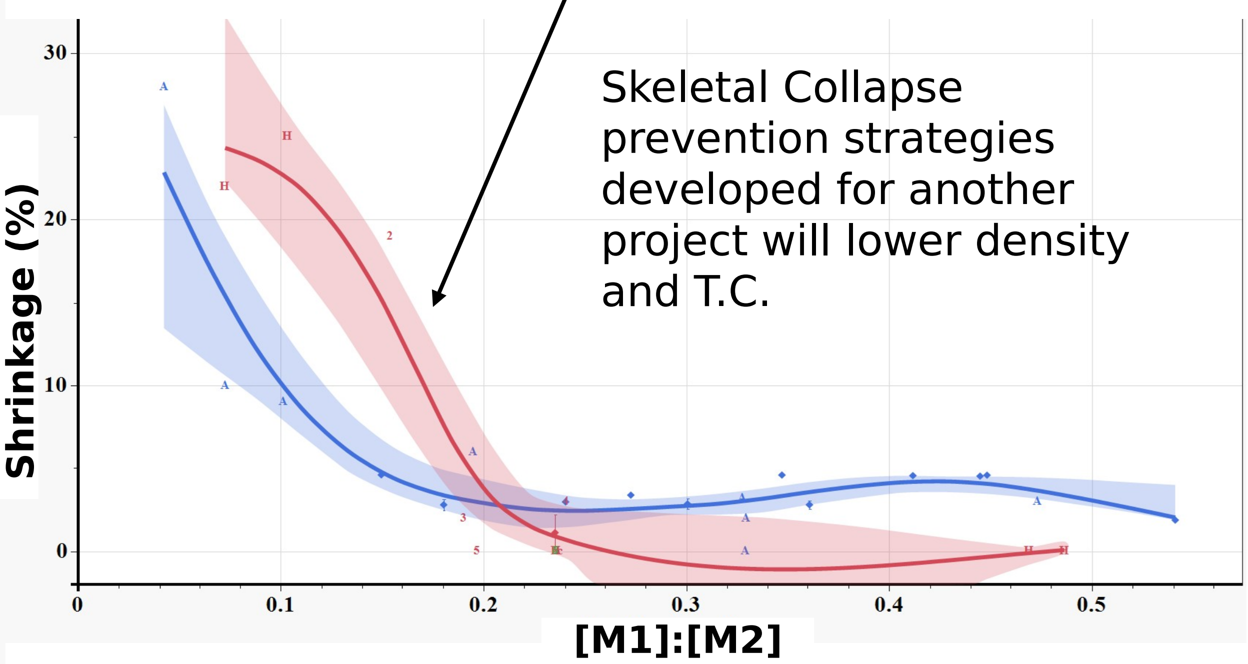
- Note how thermal conductivity (T.C.) scales with density. Most evident in rightmost panels.
- Several dependencies analyzed. Density and T.C. correlate with monomer mole ratio ([M1]:[M2]), CAT to total monomer concentration ([CAT]/[M1+M2]), and [M1]:[M2]x[CAT]/([M1] + [M2])



Bad Solvent

Good Solvent

NOTE: at low [M1]:[M2], density increase could be related to larger shrinkage.



Skeletal Collapse prevention strategies developed for another project will lower density and T.C.

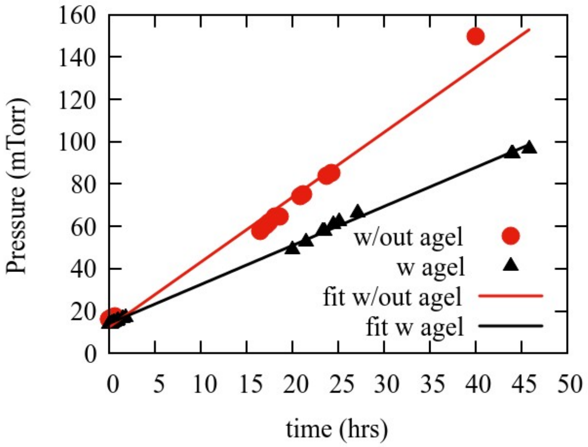
Progress

VIP fabrication

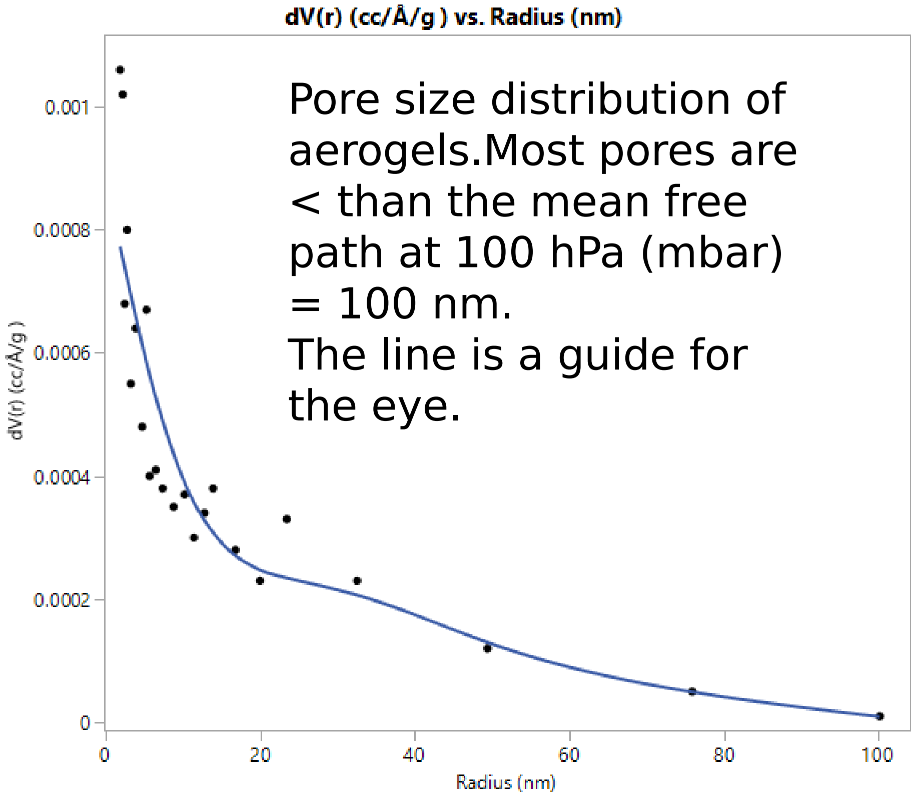
Aerogels:

- Can be placed in a vacuum bag and can withstand evacuation.
- Act as **getters** if properly degassed prior to evacuation.
- Have pores with radius <50 nm, on target.
- Can be made hydrophobic, current contact angle ~ 110°.

Aerogel in vacuum bag; Dimensional change < 5%.



Pressure increase in a vacuum chamber after closing the valve to the pump. Note how the presence of an aerogel slows the pressure rise.



Pore size distribution of aerogels.Most pores are < than the mean free path at 100 hPa (mbar) = 100 nm.

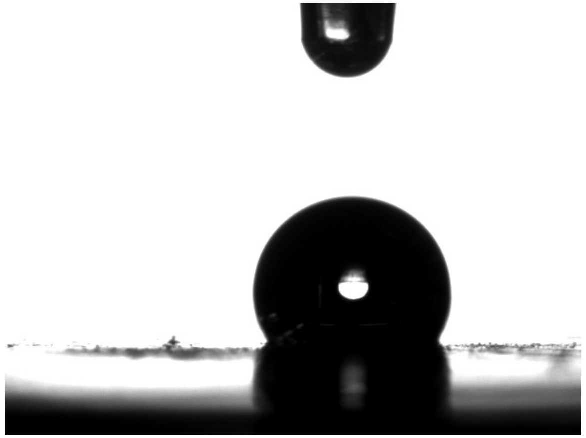
The line is a guide for the eye.

Stakeholder Engagement

Contacted Kevotherm (manufacturer of VIPs) and Kuraray (manufacturer of VIP envelopes).
Both companies are **willing to manufacture VIPs using aerogel cores** and validate our materials.
We have also gotten the following feedback.

1. Pore size < 100 nm for operation at 1 hPa (= 1 mbar). **Check.**
2. Important that it is a monolith, most manufacturers compact powders. **Check.**
3. Degassing must be low. Many materials fail there. **Check.**
4. Are the materials hydrophobic? **Check.** (more tests necessary, though)
5. Is the process continuous/not batch? **Check.**
6. Does the process require specialized equipment/custom chemicals? **Check.**
7. Flammability? Cone calorimetry tests 4th September week.
8. Minimum sample size for validation: 150x150x12.5 mm (6x6x1/2”).
Currently at 100x100x12.5 mm (4x4x1/2”), working on larger sizes.

Samples will be sent to the companies for validation after pore size, density optimization.



Contact angle ~ 110°. Additional tests (aging, humidity cycles) being planned.

Relevant information tidbit:
An award has been granted by Department of Transportation
To use the same materials, loaded with PCMs, to prevent thermal runaway of battery packs.

Remaining Project Work

In the ~ 10 months remaining for this project, we intend to:

1. Optimize the formulation to minimize thermal conductivity at ambient. Target: 0.020 W/mK, currently 0.028 W/mK (at the start: 0.040 W/mK).
2. Optimize pore size distribution to attain conductivity < 0.005 at 10 hPa.
3. Make large monoliths for validation by industrial partners. Target: 15x15x2.5 cm
4. Characterize aging and mechanical properties of the materials using the appropriate ASTM tests.
5. Use cheaper monomers, solvents to further reduce cost.

Success criteria:
1. Attain target thermal conductivity at target pressure.
2. Validate outgassing and durability of the cores.
3. Attain cost targets.

Thank You

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Colloids and Surfaces A: Physicochem. Eng. Aspects 300 (2007) 204–210
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3. M. F. Bertino, "Method for one-step synthesis, cross-linking and drying of aerogels", US Patent Number 10,414,894.
4. M.F. Bertino, L. S. White, T. Selden, "Method for rapid synthesis of aerogels", US patent 11,046,830. European Patent Application 17786738.9
5. M. F. Bertino, S. Czlonka, "Polymeric aerogel composite and synthesis by ambient and freeze-drying", PCT/US2019/034797, filed June 1, 2019.
6. M. F. Bertino and T. Selden, "Fabrication of Aerogels and Aerogel Composites by Ambient Pressure Sublimation of Frozen Solvents", PCT/US20/39485, filed June 25, 2020.

Project Budget

Project Budget: Expenditures have been on track with the proposed budget, COVID interruption notwithstanding.
Variances: No budget variances
Cost to Date: see table below.
Additional Funding: No additional funding sources.

Budget History							
06/01/2019-FY 2018 (past)		Expenditures to date		FY2021		FY 2022 – 5/31/2022 (planned)	
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
493,470	123,394	251,726	51,635	62,585	12,517	70,000	14,000

Project Plan and Schedule

- Project start: 06/19.
- Several months of interruption (COVID) in 2020.
- Disruption of supply chain (mostly reagent availability) still on-going.
- Overall, project on target, see table with end-of-project goals.
- Project end: 05/2022.

Go-no-go decision points, due Nov. 2020.

- Fabrication of a phenolic aerogel board, 3 × 3 cm, 12 mm thick, with a modulus > 10 MPa, a thermal conductivity ≤ 30 mW/mK and capable of resisting evacuation. Board to be produced by ambient drying. **Achieved 09/2020**
- Credible path to low VIP cost, $0.85/sqft. **Achieved.**

	Target	• **Status**
Core cost	\$5/kg	• See TEA above
Thermal insulation	R-20 @ 100 mbar	• Work in progress; need to send to stakeholders for VIP manufacture, validation.
Density (g/cm^3)	<0.3	Achieved: typically < 0.2
Porosity (%)	>80	Achieved; typically > 85%
Compression Modulus (MPa)	>10	Achieved; typically 10-12 MPa.
Max. degas.	$<1.1*10^2 cm^3(STP)/(m^2*day)$	Achieved, but more tests needed.
Thermal conductivity at ambient	0.020 W/mK	Project start: 0.040. Currently: 0.028. D.o.E. in progress to minimize T.C. at ambient.