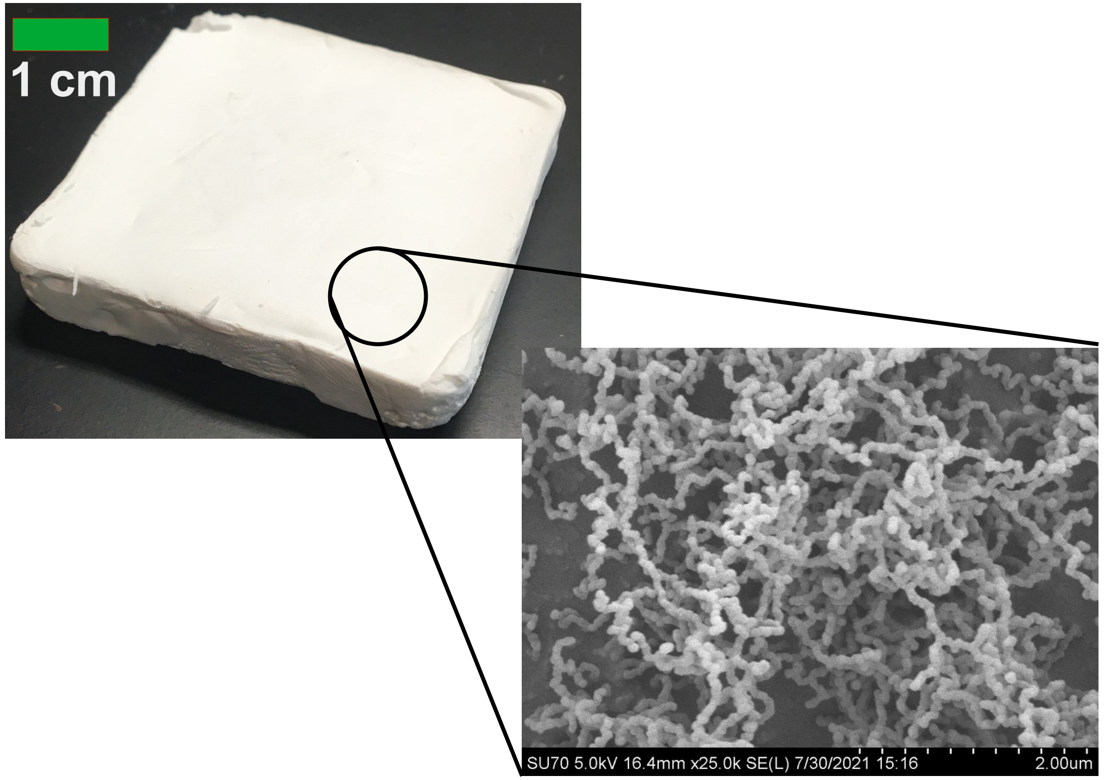
DEVELOPMENT OF ISOCYANURATE-BASED SUPER INSULATION AT ATMOSPHERIC PRESSURE (SIAP) WITH TARGET RESISTANCE OF R-12 HR·FT^2·°F/BTU·IN

Freeze drying...

Or ambient drying….



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Project Summary

Timeline:

Start date: 10/01/2017

Planned end date: 12/31/2021

Key Milestones

1. Fabrication of aerogels with thermal conductivity 0.027 W/mK by freeze drying attained 09/2018.
2. Fabrication of 6x6x1 cm aerogels with density < 0.1 g/cm3 without skeletal structure collapse and by ambient drying. 07/2021.

Budget:

Total Project $ to Date:

- DOE: $357,336
- Cost Share: $71,467

Total Project $:

- DOE: $495,000
- Cost Share: $120,866

Project Outcome:

The aim of the project is fabrication of PIR-PUR aerogels by freeze drying and with a thermal conductivity < 0.020 W/mK.

PIR-PUR chemistry improves fire resistance, while freeze drying reduces capital expenditures, and, therefore, cost.

Fabrication by freeze drying was achieved early on and has now been supplanted by a novel ambient drying technique that potentially allows for continuous processing.

Reaching low thermal conductivities has proven challenging, mostly due to collapse of the nanoporous structure. The collapse does not depend on the drying method, and is likely due to formation of hydorgen bonds between polymer strands. Shrinkage induced by collapse yields warped monoliths and increases their density. Strategies have been developed that prevent collapse and yield pristine monoliths with densities < 0.1 g/cm^3.

Team

- Original team: Fraunhofer CSE Boston (Jan Kosny) + VCU.
- Project novated to VCU in 2020 after CSE's demise in 2019.
- COVID halted work for good part of 2020.
- Bertino: ~20 years in aerogel fabrication, especially in processing.
- 3 patents adjudicated, 3 pending,[2-5] ca. 40 peer-reviewed publications in the field.
- 4 federal grants on aerogel technology (1 ArpaE, 2 DOE/BTO, 1 DoT).
- Director, Nanomaterials Characterization Core facility (13 state-of-the-art instruments). The facility has all characterization instrumentation needed for the project.
- Dr. Everett Carpenter, VCU. Professor of Chemistry, MBA. Advises on marketing strategy.
- Chris Ohlhaver, MS Chemistry, principal scientist, GSK. Advises on marketing strategy.

Challenge

Problem Definition:

1. Polymeric foams dominate the building insulation market.
2. Foams are typically produced by using a blowing agent that yields cells ~ 100 μm in size.
3. Blowing agents have disadvantages:
   - Ozone depleting.
   - Diffuse out of cells, degrading thermal insulation.
   - Can condense in cold climates.
4. Thermal conductivity of existing polymeric foams can be hardly decreased because of the large cell size.
5. Not surprisingly, progress in polymeric foams is slow and incremental.

Approach

1. Solution

- Freeze drying of organic aerogels (reduces capex).
- PIR-PUR chemistry to improve fire resistance.
- Target thermal conductivity: 0.016 W/mK

2. Advantages

- No Blowing agents
- Open cell, therefore no performance decay over time.
- Target thermal conductivity cannot be achieved by conventional foams.
- Polymer aerogels stronger than conventional (silica) aerogels.
- Aerogel materials not on the market because of cost,
- Freeze- or ambient-drying will reduce cost.

3. Challenges

- Chemistry: will established chemistry be sufficient? The goal is ambitious and most literature reports hover around 0.025-0.030 W/mK.
- Processing: freeze drying never demonstrated for samples > ~ 1x1x1 cm.
- Industry acceptance: radically different process than foam production.

4. Risk mitigation:

- Chemistry: thermal conductivity scales with density. Most formulations hover around 0.2 g/cm^3, there is room for improvement.
- Chemistry: follow conventional path, no major research effort.
- Chemistry: cross-linking and fillers will help strengthen materials.
- Processing: use experience gathered with ArpaE grant (also using freeze drying).
- Processing: several different solvents possible, lowering drying temperatures reduces cracking.
- Industry acceptance: keep process simple! Keep cost low!

Impact

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

- One subtopic of the 2020 BTO FOA focuses on “Development of low thermal conductivity (≥R10/inch), durable, opaque insulation materials at a comparable installed cost per square foot to conventional insulation materials such as aged polyisocyanurate with scalable fabrication processes.”.
- The 2020 BTO SBIR FOA requests “Development of durable aerogel insulation using continuous, high-throughput production methods (…) at atmospheric processing conditions (…).”

The achievements to date show that

1. Aerogels can now be processed at ambient 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. The drying is very gentle and it allows to dry samples with densities < 0.1 g/cm^3 with a modulus < 5 MPa. There is no process available on the market that allows anything like this.

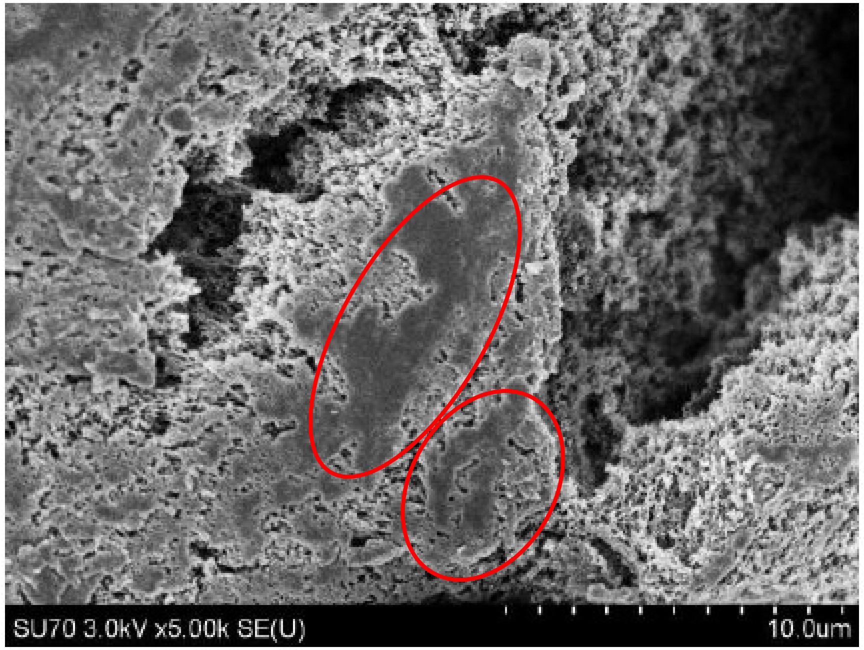
2. Due to the simplicity of the process, the cost estimate is xxxx

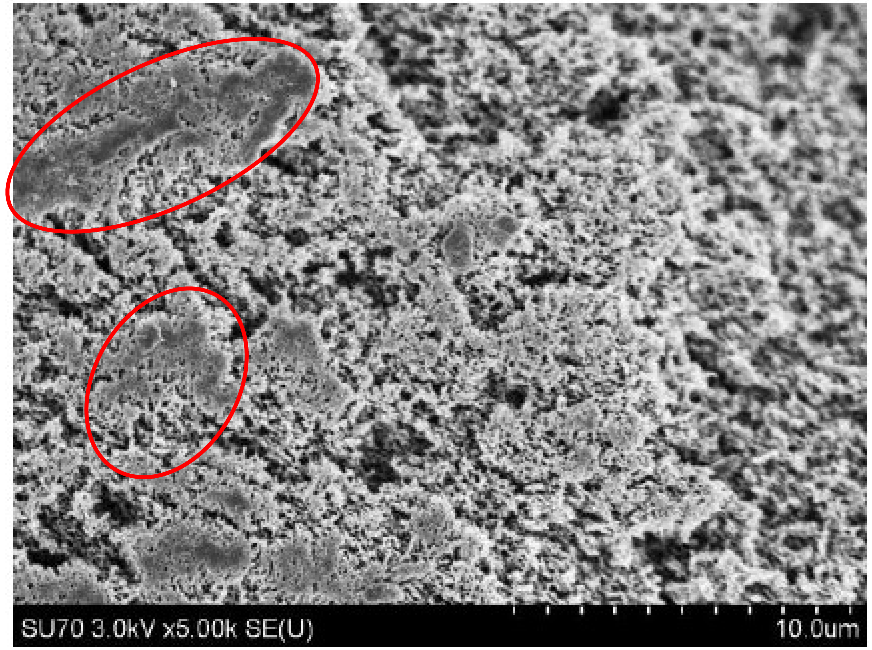
3. Strategies have also been validated that prevent collapse of the nanoporous structure. Moist literature on polymeric aerogel synthesis reports large shrinkage (> 20%) which leads to increased density, pore collapse and “welding” of the skeletal structure. Prevention of skeletal collapse is key to attaining low thermal conductivities.

Progress

Project is in late stage. In the initial stage, 1. we quickly established equivalence of supercritical and freeze drying

- Same surface area
- Same density, shrinkage
- Same morphology (granular with “flat” areas).

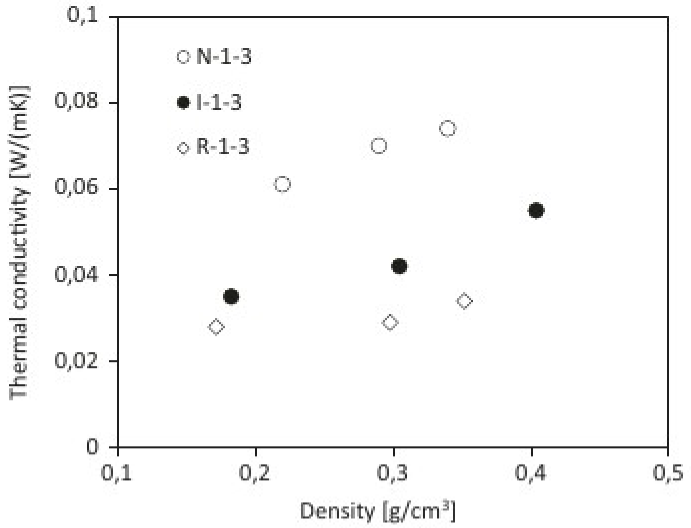




SEM of aerogels synthesizes using the same formulation. Left: supercritically dried. Right: freeze dried. Ovals indicate areas where the nanostructured skeleton collapsed, yielding flat regions. Collapse increases Thermal conductivity, and causes shrinkage and cracking of monoliths.[1]

Progress

Initial stage:
2. Identify monomers, catalyst, solvent, processing parameters.



From 1

Hence: decrease density.

It is paramount to work at densities < 0.2 g/cm^3,
Best < 0.1 g/cm^3.
Minor issue: new catalyst had to be identified.
Gelation did not occur at low monomer concentrations with original catalyst.

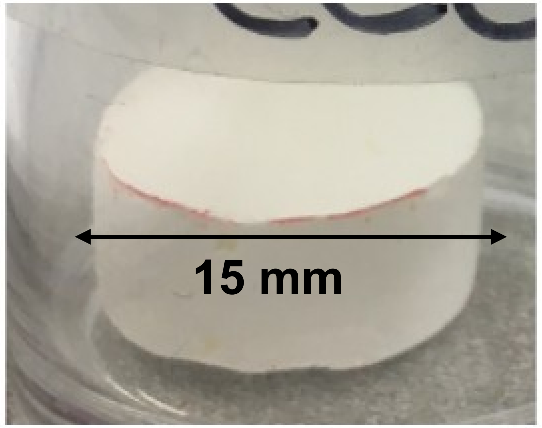
Most promising samples:
R-1-3, obtained with rigid monomers.
Note how thermal conductivity decreases with decreasing density.

Important independent discovery:
Ambient drying also possible.
Monoliths can be obtained.
Same density, other characteristics as those freeze dried.

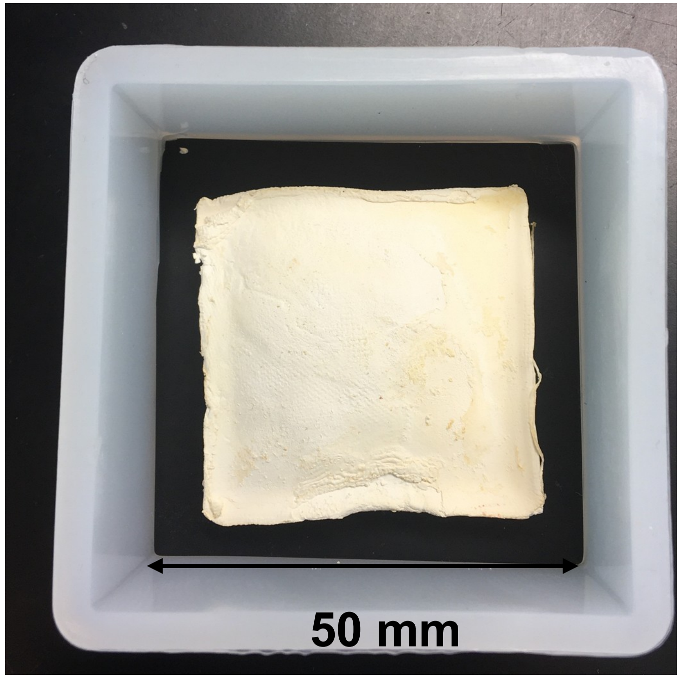
Progress

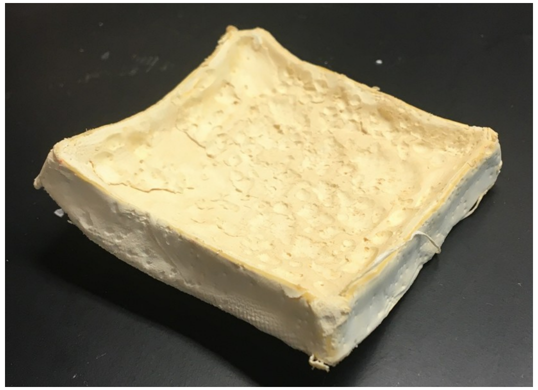
Major issue (solved July 2020)

- Low density monoliths with size > 20 mm warp and crack.
- For both freeze- and ambient- drying.
- Our supercritical dryer is not big enough so we could not compare.
- Literature typically reports samples < 20 mm in size, so comparison not possible.



Small sample:
~ 20% shrinkage,
no warping, no cracking.



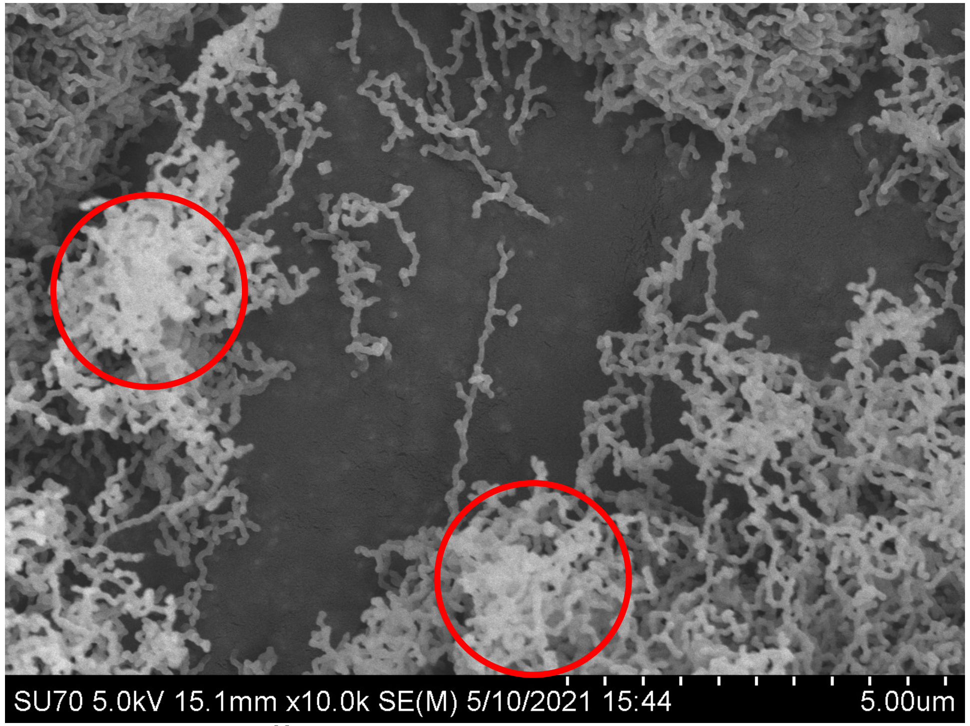


Larger sample, shown left with original mold:
~ 20% shrinkage, warping,
sometimes cracking.

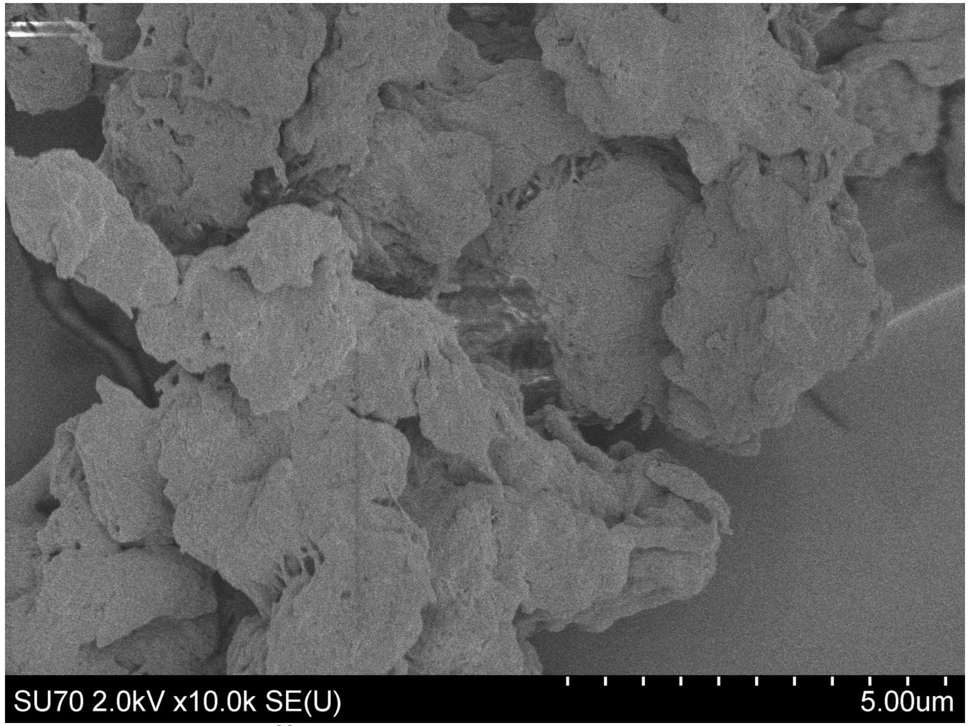
Progress

What is going on?

- Aerogel skeleton has fibrillar structure.
- Solvent fills the space between fibers.
- When the solvent is removed, fibers collapse due to high surface area, hydrogen bond formation between fibers.
- Low density formulations (=thinner fibers, less cross-linked) are more affected than others.



Formulation #1: some regions have collapsed.

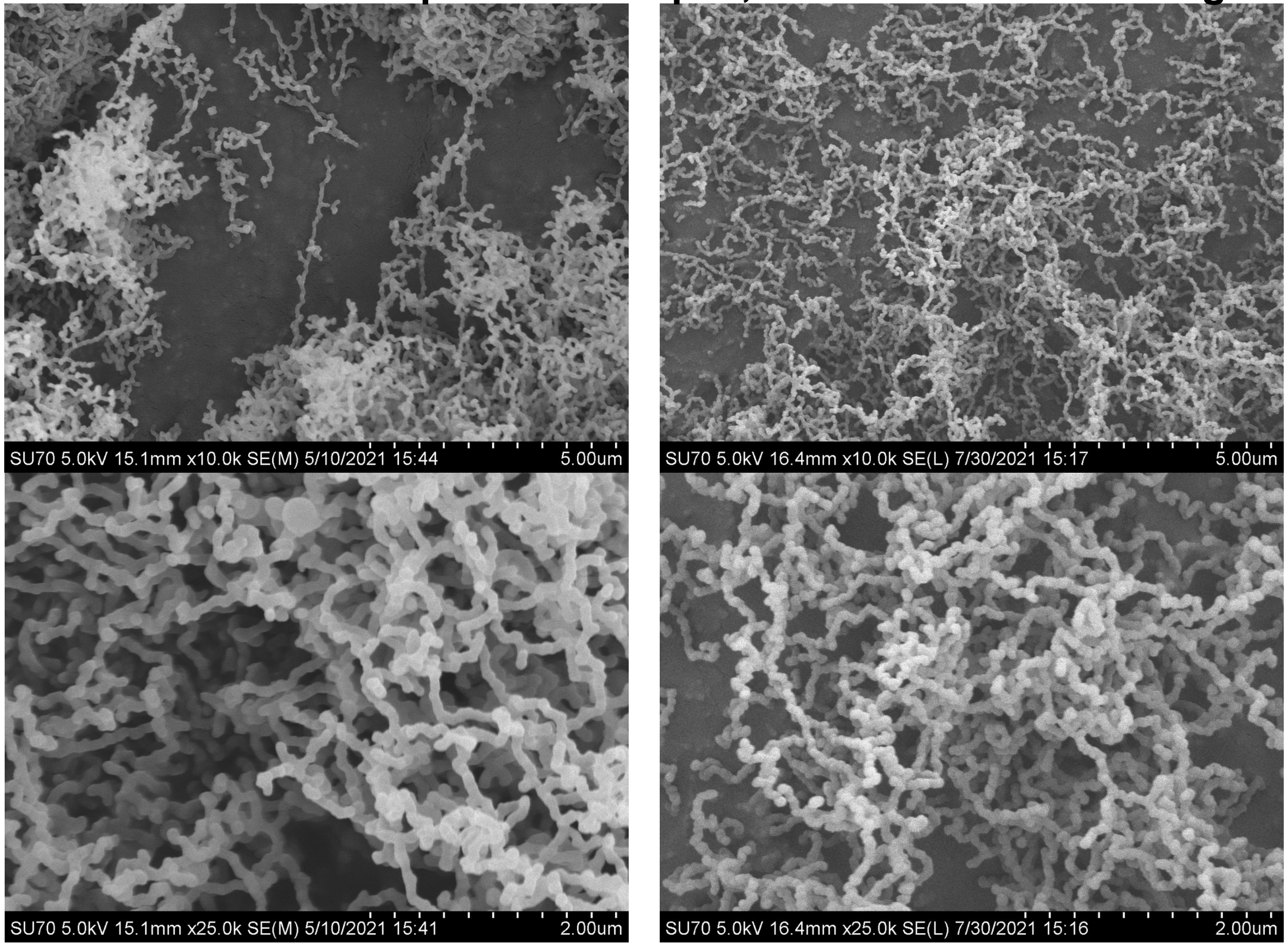


Formulation #2: general collapse.

Progress

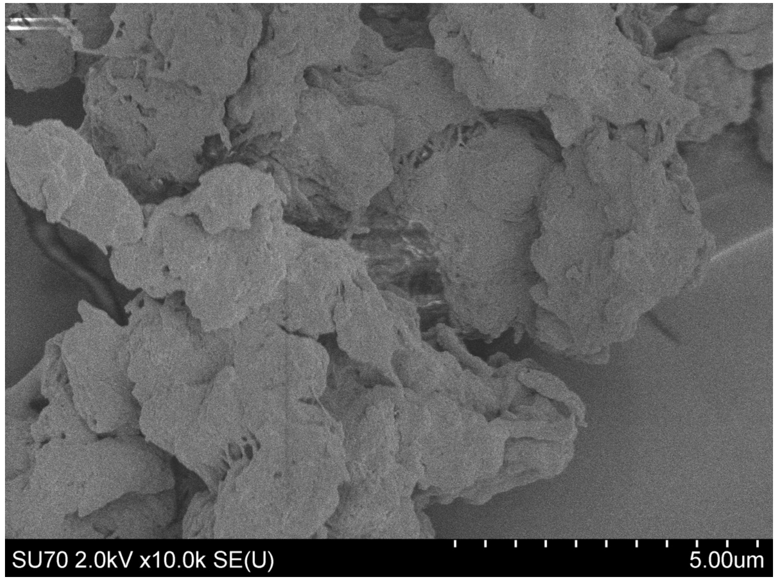
3 methods devised to prevent collapse, all of which are working.

Formulation 1, Collapsed

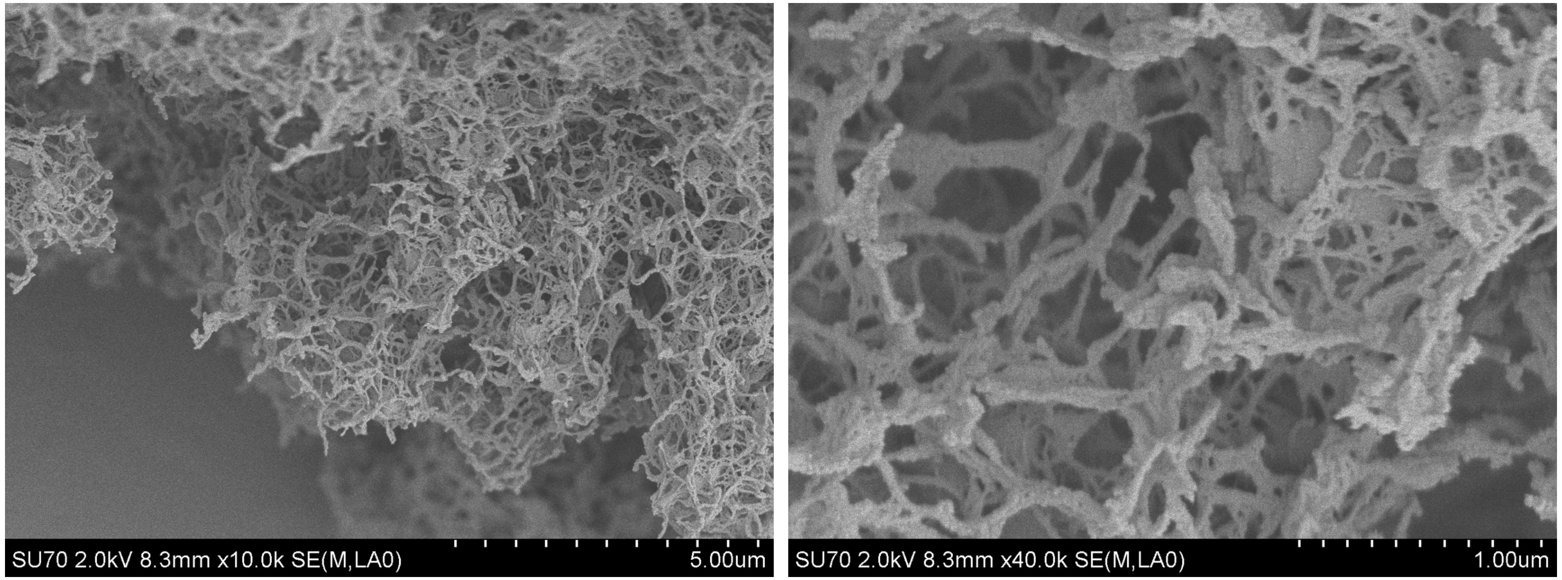


Formulation 1, Method #1, Not Collapsed

Progress



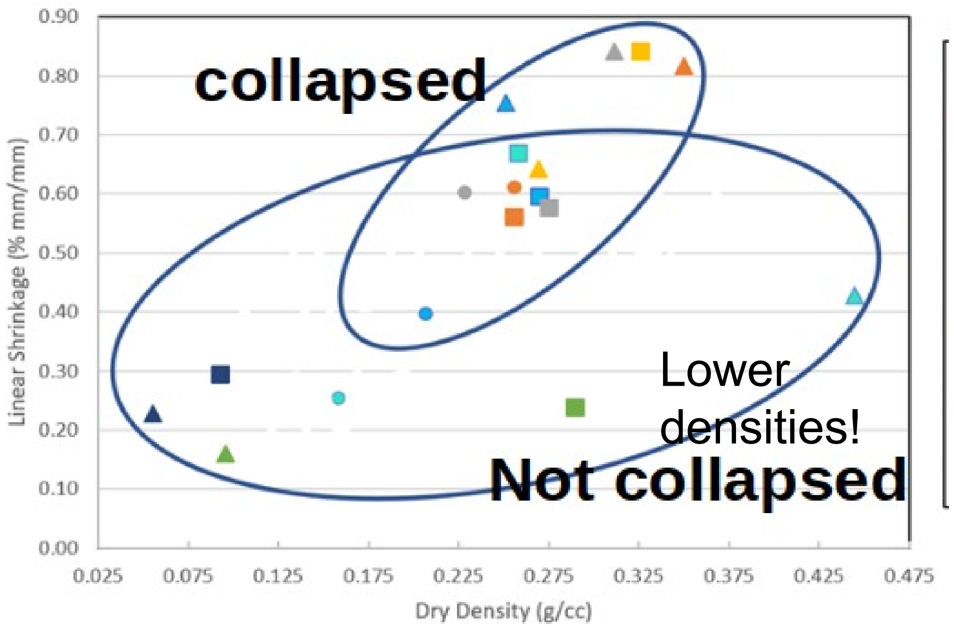
Formulation 2,
collapsed

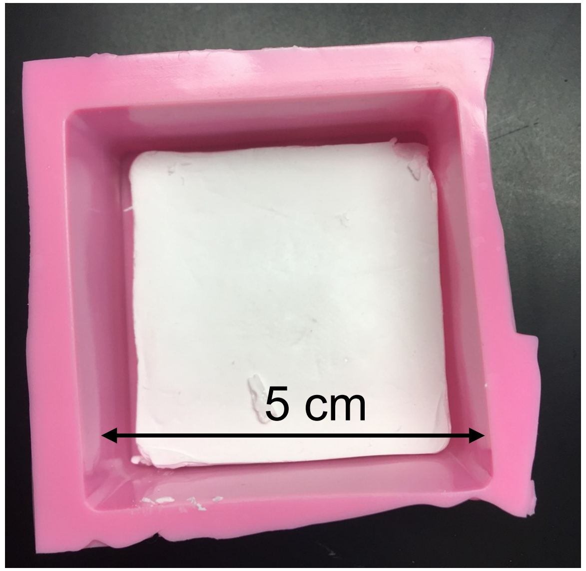


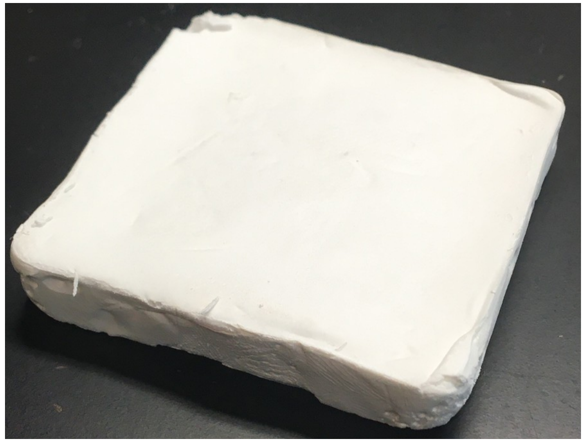
Formulation 2, methods #2 and #3.
some residual collapse, but great improvement.

Progress

Collapse prevention = low densities, low shrinkage, no cracking, monolithic parts.







Still an issue: Thermal conductivity of formulation 2 ~ 0.030 W/mK. Tbd for Formulation 1.
Why?
Some fibrils in Formulation 2 are still collapsing.
Solution: increase concentration of anti-collapsing agent, work on gelation solvents.

Progress

Cost estimate.

1. Assumed capacity: Pilot plant, 1 Million sq. ft/year, 1 inch thickness.
2. Based on current formulations:
   - Cost of monomers, catalyst: $471,000 (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: $0.90/$ft^2$ ($13.2/kg)
   - Cost/ft^2,(cost/kg) 97% solvent recovery: $1.33/$ft^2$ ($14.42/kg)

Stakeholder Engagement

Contacted or was contacted by companies in the construction materials arena.
Carlisle, Huber, Dow Corning, Aerogel Technologies plus 2 others that do not want to be mentioned.

Feedback:

1. Thermal conductivity <~ 0.02 W/mK if to replace current insulation technologies. **Working on it.**
2. Thermal conductivity <~ 0.03 W/mK if to be used as a structural element/part of a composite. **Done**.
3. Can it be integrated with wood-based materials? **Yes.**
4. Can you add fire-retardants, e.g., $Mg(OH)_2$? **Yes.**
5. Can you add PCMs? **Yes.**
6. Are the materials hydrophobic? **Yes** (more tests necessary, though)
7. Can you add an opacifier, possibly not carbon black? **Yes,** and yes.
8. Is the process continuous/not batch? **Yes.**
9. Does the process require specialized equipment/custom chemicals? **No**.

Contacts with industry not developed due to upscaling issues for the low density formulations.
Upscaling issues solved on Aug. 1, 2021.
Companies are being contacted, 3 conference calls planned in the next 2 weeks.

Remaining Project Work

In the ~ 3 months to the conclusion of the project:

1. Make larger monoliths. Paramount to demonstrate feasibility of ambient drying technology For low density materials. Target: 15x15x1 cm
2. Keep reducing fibril collapse. Achieved with Formulation 1, measurements being taken. Need additional work on Formulation 2.
3. Add opacifiers to formulations. Carbon Black, TiO_2.

Success criteria:
1. Demonstrate ambient drying technique.
2. Demonstrate that fibril collapse reduction leads to lower thermal conductivity.

Thank You

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REFERENCES

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Journal of Sol-Gel Science and Technology (2020) 93:149–167
2. M. F. Bertino, "Method for one-step synthesis, cross-linking and drying of aerogels", US Patent Number 10,414,894.
3. M.F. Bertino, L. S. White, T. Selden, "Method for rapid synthesis of aerogels", US patent 11,046,830. European Patent Application 17786738.9
4. M. F. Bertino, S. Czlonka, "Polymeric aerogel composite and synthesis by ambient and freeze-drying", PCT/US2019/034797, filed June 1, 2019.
5. 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: Project start: 10/2017. Project interrupted for good part of 2019 due to closing of Fraunhofer CSE (leading organization) and novation paperwork. Work stopped for several months in 2020 due to COVID.

Variances: No budget variances

Cost to Date: See below

Additional Funding: No additional funding sources.

Budget History					
10/01/2017-current (past)		FY 2021 (current)		FY 2022 – 12/31/2021 (planned)	
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
357,336	71,467	106,506	11,221	20,000	4,000

Project Plan and Schedule

- Project start: 10/17. See budget slide to understand history.
- Several months of interruption (COVID) in 2020.
- Disruption of supply chain (mostly reagent availability) still on-going.
- Overall, thermal insulation component delayed by technical difficulties, now solved. Fabrication part targets surpassed due to use of ambient drying. See table at the side with end-of-project goals.
- Project end: 12/2021.

Go-no-go decision points, achieved in February 2019.

- Fabrication of a phenolic aerogel board, 3 × 3 cm, 10 mm thick, with a modulus > 10 MPa, a thermal conductivity ≤ 30 mW/mK by freeze drying.

	Target	Status
Thermal conductivity	0.016 W/mK	Currently at 0.028 W/mK due to sintering, skeletal collapse.
Density (g/cm^3)	<0.2	Achieved: typically < 0.08
Board size	33x33x2.5 cm	Currently 5x5x1 cm, upscaling in progress.
Compressive strength (KPa)	>110	tbd