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

Award: DE-EE0008223

DOE BTO Peer Review - April, 2019

Fraunhofer CSE, Virginia Commonwealth University (VCU)

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Project Summary

Timeline:

Start date: Nov. 2nd 2017

Planned end date: Oct. 31st 2019

Key Milestones

1. Initial Technology to Market Plan that outlines a roadmap for advancing BTO funded technology toward commercial viability and identifies key T2M factors for analysis. (M12)
2. Using freeze-drying method, fabricate 4x4 cm, 1/2-cm. thick PIR nano-foam of thermal conductivity < 0.24 (mW/m/K) (M12)
3. Using freeze-drying method, fabricate 28 cm, 2-cm. thick PIR nano-foam of thermal conductivity ~0.14 - 0.12 (mW/m/K) (M24)

Budget:

Total Project $ to Date: $299,816

- 42% of Total Federal Funds
- 47% of Total Project Budget,

Total Project $ 630,921

- DOE: $495,000
- Cost Share: $135,921

Key Partners:

Virginia Commonwealth University (VCU)	Prof. Massimo Bertino
Consultant	Prof. Nicholas Leventis

Project Outcome:

The project effort is a two-year development program focused on isocyanurate-base nanofoam for building and industrial applications. This is the early-stage innovation project.

The anticipated outcome is a new type of PIR aerogel-based super insulation at atmospheric pressure (SIAP) that :

1. Can attain an R-12 hr·ft2·° F/Btu·in (λ=12 mW/m·K) via creating nanoporous morphology,
2. Is mechanically robust, and
3. Is cost-competitive to the conventional rigid foam boards by employing a low-cost freeze drying method for pore solvent removal instead of the cost-prohibitive supercritical drying method.

DEVELOPMENT OF ISOCYANURATE-BASED SUPER INSULATION AT ATMOSPHERIC PRESSURE (SIAP)

Project Team:

Dr. Jan Kośny
Project PI
Fraunhofer CSE; 35 years of thermal insulations' and building materials' R&D experience; Recipient of the R&D100 Award

Prof. Massimo Bertino
Project Co-PI
Virginia Commonwealth Univ; Over 10 years of experience in aerogels' research; Mastered nano-insulation production with freeze drying

Prof. Nicholas Leventis
Project Co-PI
Missouri S&T; Pioneer in the field of polymeric aerogels; Inventor of polymer-crosslinked X-aerogels; Nano50 Award - 2 times recipients

Dr. Nitin Shukla
Project Co-PI
Fraunhofer CSE; 10 years of experience in the field of nano-technologies at the MIT's Nano-Engineering Group and Fraunhofer

Industry Support
Project progress is regularly consulted with two PIR manufactures, aerogel manufacturer, four producers of commercial freeze dryers and one industrial association

DEVELOPMENT OF ISOCYANURATE-BASED SUPER INSULATION AT ATMOSPHERIC PRESSURE (SIAP)

Key Questions?

1. Can thermal performance and durability of plastic foams be further improved and at what cost?
2. Can new technologies replace the existing manufacturing methods?
3. What will be the market acceptance level for a new type of nanoporous insulation?
4. What is the PIR foam improvement potential for new HFO blowing agents?

Problem Definition:

1. Very limited performance improvement potential with existing formulations and foam production methods and with currently-used blowing agents

2. Foam aging - time-dependent degradation of thermal characteristics
   a. Caused by escape of the blowing agent from the foam cells
   b. Caused by ingress of the water vapor into the foam cellular structure

3. Well-known blowing agent problems:
   a. Troublesome production process for recent close–cell plastic foams
   b. In low-temperature applications, some close-cell plastic foams may likely exhibit substantial degradation of thermal performance characteristics due to condensation of water vapor and sometimes blowing agent on the internal foam cell surfaces
   c. An application of blowing agent may often increase foam's environmental impact (low/zero environmental impact blowing agents are very expensive)

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Technical Challenges Associated with Conventional Foaming Methods:

1. Thermal aging process in close-cell foams can be reduced with new chemical formulations improving cellular structure and surface physics and through an application of nano-fillers – however this adds costs

2. A new generation of non-flammable, high-performance hydro-fluoro-olefin (HFO) blowing agents can bring R-value of the fresh foam to R-8 per in., but
    a) This will not eliminate the thermal aging effect
    b) Insufficient chemical stability is reported for HFOs in typical PIR foam formulations
    c) HFOs are quite expensive and
    d) They are still waiting for a wide-scale adoption by the foam insulation industry

3. Flammability, health and environmental impacts of plastic foams are still a challenge

Market Competition:

1. Laboratory experiments demonstrated that nanoporous insulations can reach R-value of R-10 to 12 per in.
    a) **Silica aerogles** are already used in different niche applications, including buildings and industry
    b) **First nano foam technology** has already arrived on the international markets – but, with only less than R-8 per in.
    c) **Nano foam technologies** don't contain blowing agent and as a result do not exhibit foam aging

2. Despite of a fast technology development (packaging materials and methods and improvements in durability, as well as, low-cost core materials) the question still exists: Can vacuum insulation be cost competitive, durable, and easy to apply in building conditions?

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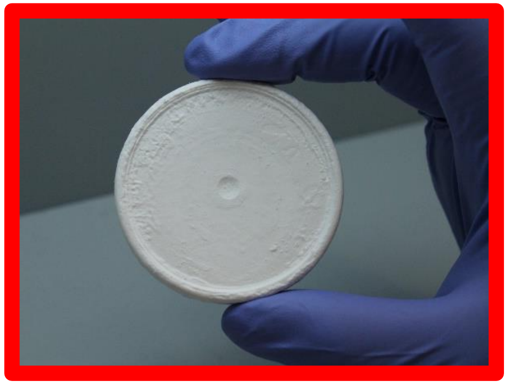
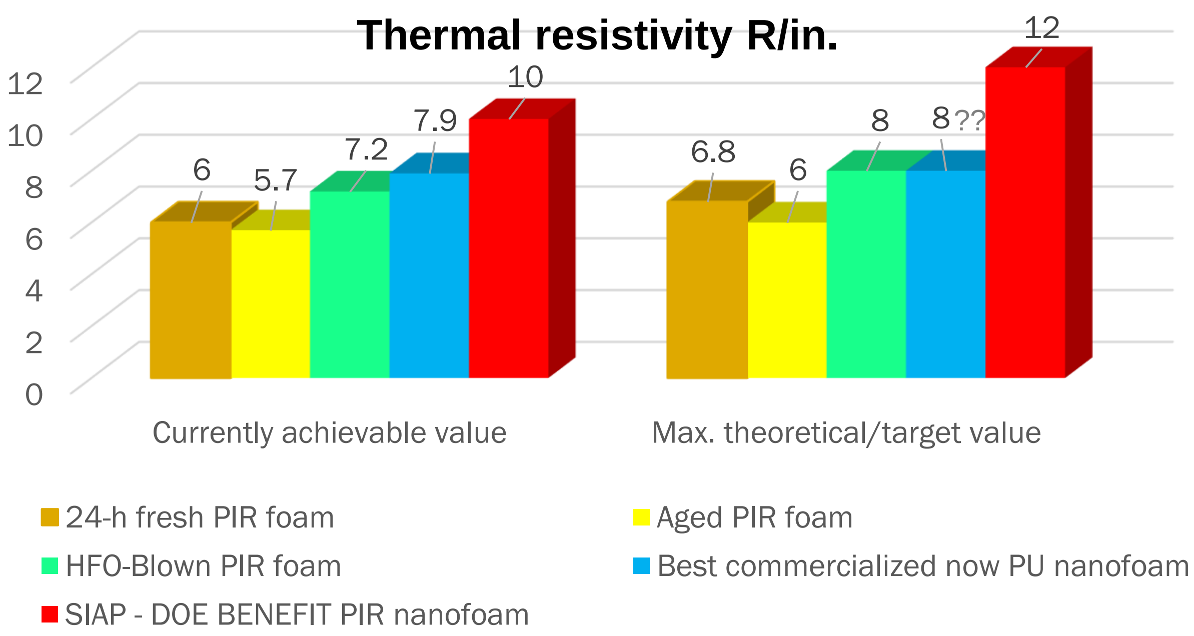
PIR Foam Performance Targets and Technology Development Reality:





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Proposed Solution - Theoretical Guidance:

1. **Increase foam R-value and eliminate foam aging effect**
   a. By reduction of the foam cell sizes below 70 nm, utilize the Knudsen Effect in the foam design; target surface area 300-400 m^2/g, density 0.1 to 0.3 g/cm^3
   b. Open-cell nanoporous foam will not require trapping blowing agent in close cells for attaining high R-value
   c. Lack of blowing agent will eliminate the foam aging process and reduce some material cost

2. **Keep production cost competitive**
   a. Produce foam without a need for costly blowing agent, but still use the well-established PIR chemistry
   b. Don’t use supercritical CO_2 drying in production of nano-foam. Instead utilize significantly less-costly freeze drying technology (lowers capex by ~10 times, and overall production cost reduced by 40%-65%)

3. **Utilize polymeric chemistry to improve mechanical strength comparing to silica aerogels**

Expected Benefits of PIR-Based SIAP:

1. **PIR-based SIAP will have several benefits over conventional foams:**
   a. Will show up to twice as low apparent thermal conductivity,
   b. Since, it will not require a use of blowing agent, it will not exhibit thermal aging, and
   c. Its thermal conductivity will not increase in low temperatures due to the blowing agent condensation

2. **When compared to the currently-produced non-reinforced silica aerogel products, the proposed PIR-based SIAP will be mechanically stronger, more elastic, significantly less expensive, and dust free**

Work Progress - Accomplishments & Milestone Update

- **Task 1: Analysis Supporting Technology to Market.**
- **Subtask 1.2**: Develop the Preliminary Cost-Performance Model (PCPM)

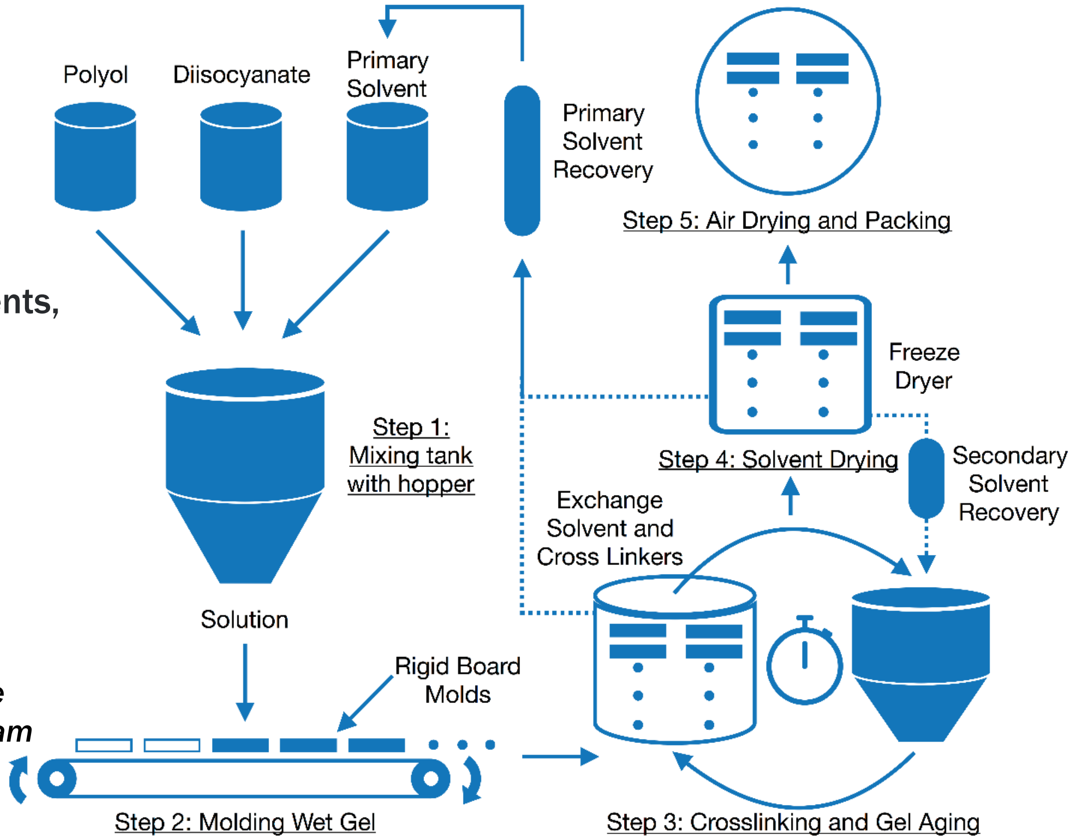
Project team worked with industry partners on update of the Cost-Performance Model with the main goal to identify the key cost drivers for the PIR-based nano-foam. The team has made a significant progress towards identifying the manufacturing process and the necessary materials and equipment for producing the freeze-dried PIR-SIAP.

A five step process has been identified.

The process includes:

1) mixing the chemical components,
2) wet gel molding,
3) crosslinking and gel aging,
4) solvent drying, and
5) air drying and packaging.

Four chemical silos are considered to store the polyol, di-isocyanate, and the solvent(s). At this point of work the team considers only a single solvent.



Work Progress - Accomplishments & Milestone Update

Estimate of the SIAP Plant Production Capacity

Large PIR foam plant capacity is about 200MM board feet/year. This is equivalent to about 15 MM kg of PIR foam/year.

For comparison, their annual production capacity of Aspen Aerogels (after recent additions of a new line) is now about 55 million square feet of aerogel blankets. Considering thickness of aerogel blankets of 10-mm and density 0.15 g/cm^3, this yields about 7.7 MM kg of aerogel product per year.

Standard, turn-key ready industrial freeze dryers have a typical capacity of 5,000 kg (sometimes even larger) [see for example: *http://www.esquirebiotech.com/industrial-freeze-dryer-1394480.html*] and many of them can be installed and operated by a same facility

Example of an industrial facility equipped with freeze dryers with a capacity of 1500 kg).

Work Progress - Accomplishments & Milestone Update

- **Task 1: Analysis Supporting Technology to Market.**
- **Subtask 1.2**: Develop the Preliminary Cost-Performance Model (PCPM)
  - The updated bill of materials was developed for production scale of 1 million ft^2 of PIR nanofoam boards/year. At this point in the analysis, only a single solvent is used for the calculations.
  - The cost per board of the PIR-SIAP was estimated for the PCPM. Using available literature, and consulting with PIR foam industry and aerogels manufacture, the potential production volume of a key contributor of PIR-SIAP to the U.S. polymer foam building and construction market was being estimated.
  - This capacity provides a production volume goal of the industrial scale facility. A preliminary cost of the PIR-SIAP per board is being decomposed into the following components:
    - Financial fixed costs and sunk costs
    - Raw material costs
    - Energy costs
    - Labor costs

Revised Bill of Materials (BOM) for production of 1 million ft^2 of PIR nanofoam boards

Item	Unit	Unit Price ($)	Total price ($)
Equipment			
Chemical storage tanks/silos	4	10,000	40,000
Mixer tank with hopper	1	40,000	40,000
Freeze dryer	3	250,000	3,000,000
Solvent recovery column	1	150,000	150,000
Belt conveyor	1	15,000	15,000
Pane packaging unit	1	20,000	20,000
Land and Plant Building			
Facility land + construction	30,000 ft^2	50/ft^2	1,500,000
Material			
PMDI	TBE*	2.0/kg - can be reduced up to 1.60/kg	
t-butanol	TBE	2.4/kg	
Base catalyst (amine based such as APTES or ammonium hydroxide)	TBE	0.5/kg	
Crosslinkers (diisocyanates, acrylics, etc.)	TBE	2.0/kg - can be reduced up to 1.60/kg	

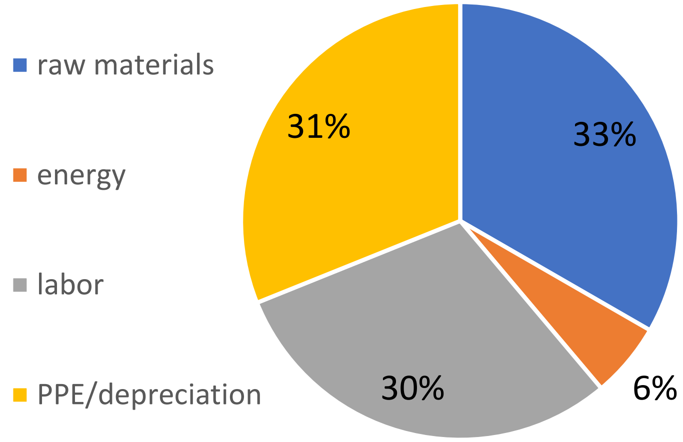
Work Progress - PIR Nano-Foam Production Cost Breakup

Cost Driver	Cost ($/ft^2)	Small-Scale Initial Cost Estimates	Industry-Suggested (Large-Scale) Cost Savings *	Cost ($/ft^2)
Raw material	**1.11**	Assumptions: 90% synthesis efficiency of pMDI; 10% solvent loss; 20% due to crosslinkers and other chemicals; board density = 0.1 g/cc; porosity = 92%; Per board: pMDI=0.236kg; solvent=1.68kg Per board cost =$ (0.236*2.0/0.9 + 1.756*2.4 x 0.1) *1.2	**50%–70%**	**0.33–0.55**
Energy	**0.18**	Panel frozen from 30^{o}C to -30^{o}C, and then heated back to RT Energy is needed to freeze solvent, condense vapors and solvent sublimation; Energy price =$0.12/kWh	**-**	**0.18**
Labor	**1**	1 production supervisor and 2.5 technicians Labor cost = $ (1*$60/hr + 2.5*$30/hr)*250days/yr*20hr/day*1.5(overhead)/(1M boards/yr)	**40%**	**0.6**
Financial	**1.04–1.24**	Equipment = $2.245M–2.815M; Auxiliary eqpt/piping = 50% of equipment cost; Hook-up and commissioning = 50% of equipment cost; Land&Building = $1.5M Capital =$5.59M–7.13M (=${2.245M–2.815M}*2+$1.5M); Eqpt Depreciation=7.5%/yr; Maintenance=10%/year of eqpt/facility Financial Cost = $ {5.59M–7.13M}*(7.5%/yr+10%/yr)/(1M boards/yr)	**50%–70%**	**0.31–0.62**
Cost Summary	**3.34–3.54**	**Mfg Cost at appropriate Large-scale Production**		**1.42–1.96**
	0.278–0.295	**Mfg cost/R-value – PIR SIAP (R-12/inch)**		**0.118–0.163**
	0.132	**Mfg Cost/R-value – PIR Foam (R-5.7/inch)**		**0.132**

** Consulting with industry indicated that both PMDI and crosslinkers can be purchased even 10% to 20% less costly in the large-scale industrial production environment. Other costs can be also significantly lower.*

Work Progress - PIR Nano-Foam Production Cost Breakup (cont.)

Total manufacturing of 1-inch thick PIR nanofoam	*Raw + Energy + Labor + Financial*	*$1.42–1.96/ft^2*

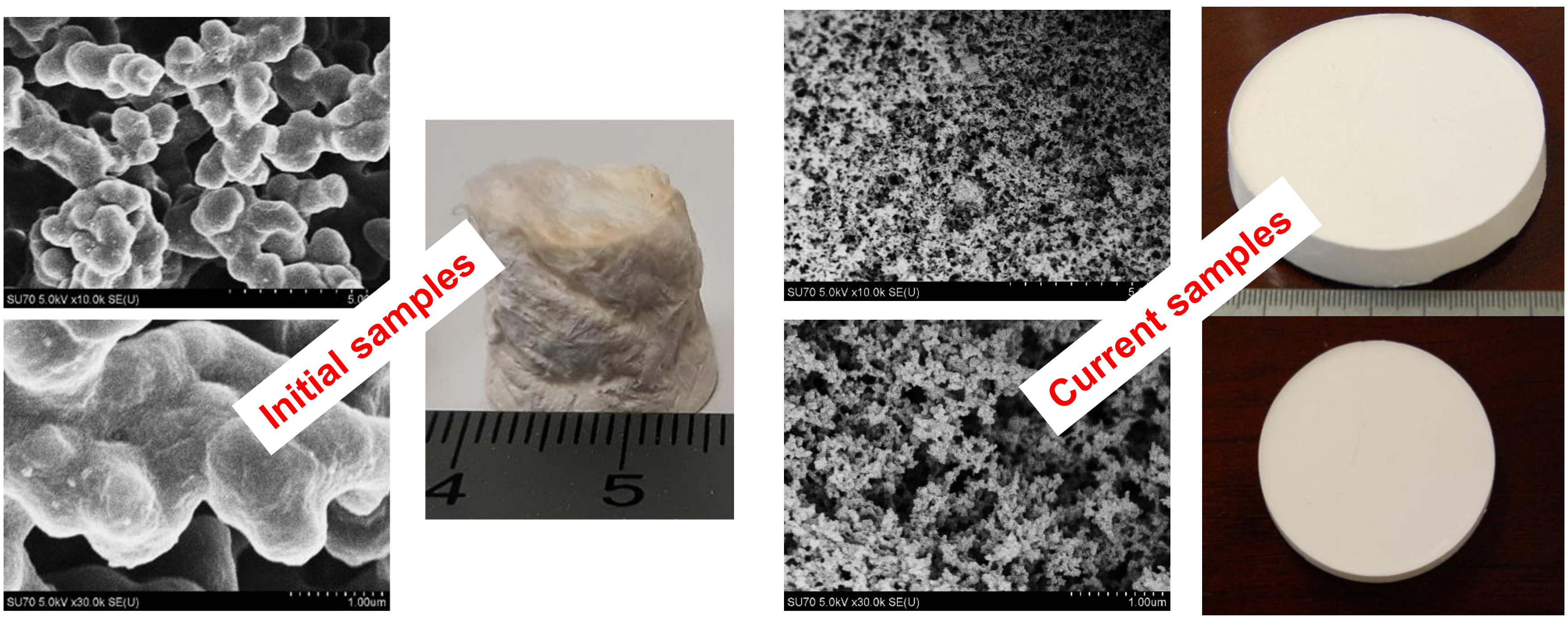


Example of commercial shelved freeze dryers

[1] RS Means Residential Cost Databook
PPE - Plant, Property & Equipment

Processing Improvement - Optimizing Freeze-Drying Conditions and New Solvents:

- In this subtask, we work on scaling up freeze drying process to allow fabrication of larger slabs of a PIR-based nano-porous material of acceptable quality (no cracks). This will allow us to fabricate sizes more relevant for building and industrial applications and it will permit hygrothermal and durability testing
- New samples of PIR nano-foam. Processing was improved to the point that samples are regularly fabricated without visual cracks no cracks

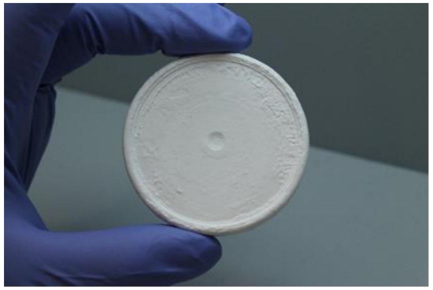


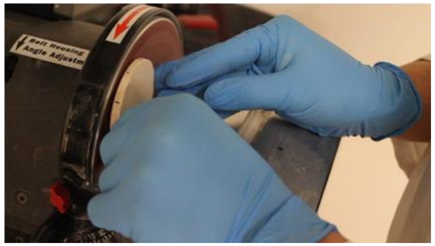
Recent Work Progress

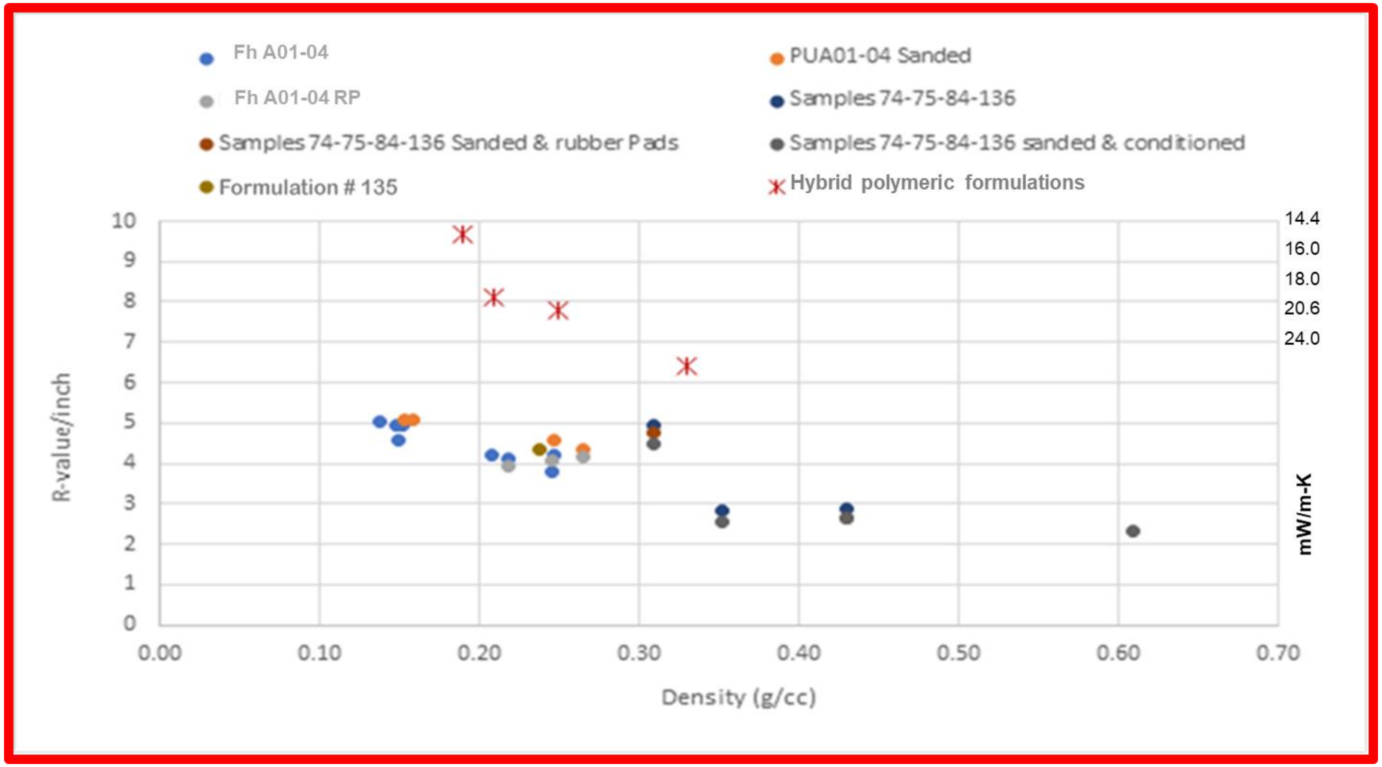
Experiments with New Freeze-Drying Equipment Allowing Production of Larger Samples

- Thanks to application of new solvents and new freeze dryer, the freeze drying conditions were notable improved
- Condenser work perimeters were optimized for operation with new organic solvents
- Freeze drying cycle was significantly shortened
- Thanks to this, processing was reduced to 8 hours drying time
- High temperature gradients lead to the sample cracking
- Thermal gradients were minimized by using metal, not glass, containers
- Large window also yields temperature gradients. So, now it is covered with a blanket during the testing

Recent Work Progress: Thermal Performance Results



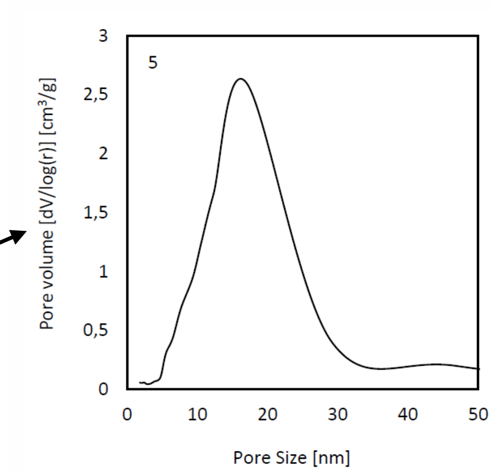


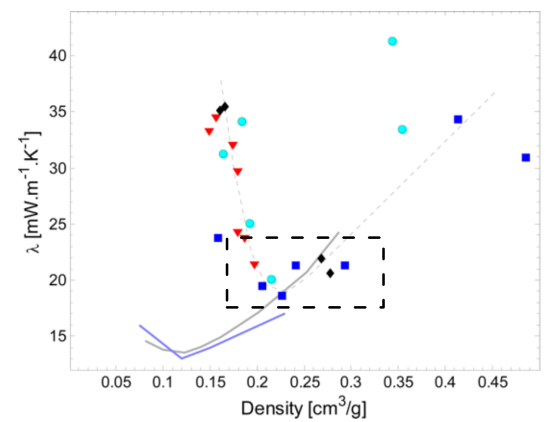


Y1 test data shows that hybrid SIAP formulations may reach R-10 per in.

Recent Work Progress: Laboratory-scale batch trials to produce PIR nanofoam using basic PIR precursors and employing freeze drying method – Recent Measurement Results

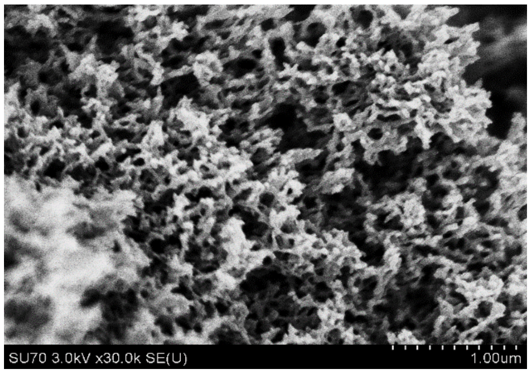
Properties:
Density: 0.18-0.5 g/cm^3
Surface Area: 80-200 m^2/g.
Modulus: 7-40 MPa.
Mean pore size ~ 15 nm.
Morphology NOT fibrillar





Reported densities, thermal conductivities of PIR-PUR aerogels

DOI: 10.1021/acsami.7b03344

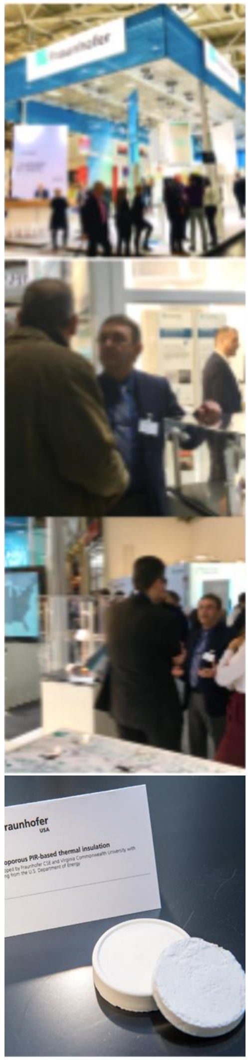


Moving forward:
- Master formulations, try hybrid formulations???
- Add silica components???
- Measure thermal conductivity.
- Make larger samples.
- Optimize conductivity (temperature, monomer).
- Optimize freeze drying (higher drying temperature)

Recent Work Progress: Technology Commercialization

Stakeholder Engagement - Improvements of Commercialization Pathway:

- To be able to penetrate into the PIR market and compete mainly on price will be difficult without economies of scale, which are only achievable with large chemical companies operating in different countries and on different continents.
- The project team has been regularly meeting with a number world's global manufacturers of plastic foam insulation, chemical suppliers, and silica aerogel company as well as producers of freeze-drying equipment. This includes:
  - 2 PIR foam companies and industry association from U.S., 2 from Europe, 1 from Golf Coast, 1 from Japan, and 1 U.S. aerogel company
  - 4 global chemical companies supplying PIR foam industry
  - 4 global freeze-drying equipment manufacturers
- Based on collaboration with the project team, one U.S. company is acquiring now a commercial pilot line for production of polymeric nanoporous materials



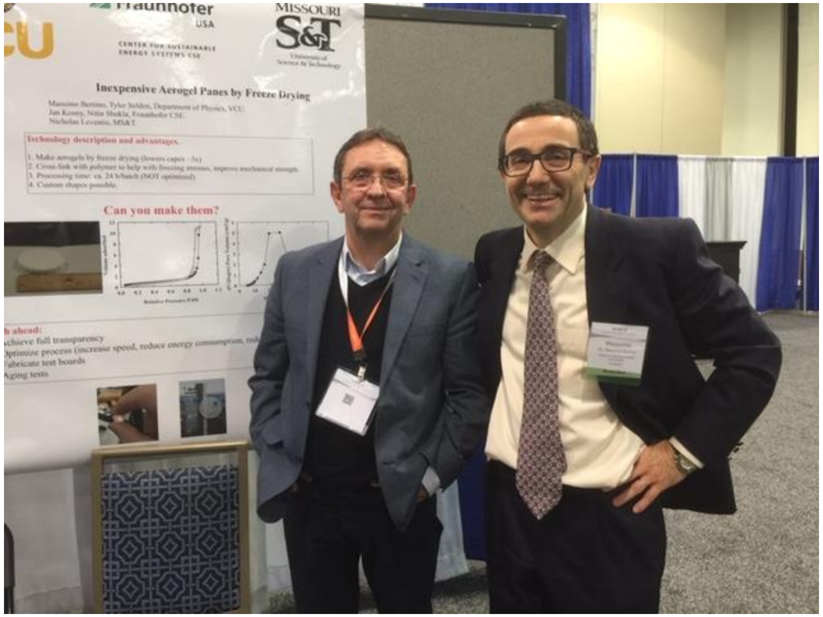
Conference Presentations and Exhibits:

- **Building Energy Boston 2018,** Mar. 7–9, 2018 – Westin, Boston Waterfront
- **2018 Material Research Society Meeting**, Nov. 25-30 2018, Boston, MA
- **ARPA-E SHIELD Annual Meeting** - Dec. 10th - 11th 1028 in Washington DC.
- During January 14th to 19th in Munich, Germany, Fraunhofer CSE was presenting recent developments in the area of insulation materials and nano-composites at the **BAU Munich 2019 -** We counted about 200 - 300 visitors per day were asking only about PIR nanofoam technology

Organization Changes, Issues, Risks, and Mitigation

- A need for organization changes within Fraunhofer USA
- Change of the project lead organization (transfer to VCU) and new project PI (prof. Massimo Bertino)
- Transition start date – March 15th 2019

- Newly-ordered freeze-drying equipment was delivered with several months delay. This made difficult to fully implement the sample preparation task targeting the addition of different amounts of silica to the aerogel formulation. Also, this fact affected the planned work on solvents
- At this moment, after successful installation of the new freeze-drying equipment and pilot fabrications trials, the planned work is realized with no further delays



Dr. Jan Kosny
Stepping Down Project PI (left)

Prof. Massimo Bertino
Coming Project - PI (right)
Virginia Commonwealth Univ. Over 10 years of experience in aerogels' research. Mastered nano-insulation production with freeze drying

Thank You!

Fraunhofer USA Center for
Sustainable Energy Systems (CSE),

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REFERENCE SLIDES

Project Budget

Project Budget: $630,921 Total; $495,000 Federal, $135,921 Cost Share
Variances: Due to a reorganization at Fraunhofer, it was decided to make VCU the prime and Fraunhofer a sub-recipient as of 2/28/2019. The novation for this change is underway
Cost to Date: 42% of Federal, and 47% of Total budget have been spent
Additional Funding: Fraunhofer Cost Share is expected to exceed contractual requirement (in form of direct labor and fringe)

Budget History					
12/1/2017 – FY 2018 (past)		FY 2019 to 11/30/2019 (current)		Total (planned)	
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
$195,183	$84,100	$299,816	$51,821	$495,000	$135,921