U.S. DEPARTMENT OF
ENERGY
Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

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

Award: DE-EE0008223

DOE BTO Peer Review - May, 2018

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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: $131,289

- 27% of Total Federal Funds,
- 59% of BP1 Federal Funds

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

Foam Industry Support
Project progress is regularly consulted with two PIR manufactures 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?
2. At what cost?
3. Can new technologies replace the existing manufacturing methods?
4. What will be their market acceptance level?
5. What will be their environmental impact?

Problem Definition:

1. Very limited performance improvement potential with existing formulations and foam production methods and with currently-used blowing agents
2. Blowing agent problems (I) - Relatively expensive and troublesome production process for recent close–cell plastic foams:
   a. Currently-used close-cell plastic foams require a usage of expensive blowing agent technologies
   b. Some blowing agents are highly flammable and may cause explosion, which require an application of special safety measures
3. Foam aging - In sales/designing, it is challenging to accurately specify R-value of currently-used close-cell plastic foams, because they exhibit 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
4. Blowing agent problems (II) - 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
5. Blowing agent problems (III) - An application of blowing agent may often increase foam's environmental impact (low/zero environmental impact blowing agents are very expensive)

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

Technical Challenges and Market Competition:

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

4. Laboratory experiments demonstrated that nanoporous thermal insulations can reach R-value of R-12 per in.
   a) **Silica aerogles** are already used in different niche applications, including buildings and industry
   b) **Nano foam technologies** have already arrived on the international markets - newly-introduced plastic PU nano-foam (BASF) doesn't contain blowing agent and as a result does not exhibit foam aging
   c) Despite superiorly low thermal conductivity, nanoporous thermal insulations are still not really adopted by the building market, mostly due to high prices (due to an application of the supercritical CO_2 solvent drying)

5. 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?

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

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
2. **Keep production cost competitive**
   a. Produce foam without a need for costly blowing agent and use 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**

Proposed Solution – Approach and Expected Results:

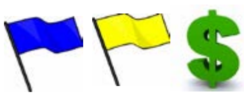
1. **Our major goal is the development of a nano-porous Super Insulation at Atmospheric Pressure (SIAP) that:**
   a. Can attain an thermal conductivity of 12×10^{-3} W/m/K (R-12 $hr \cdot ft^2 \cdot {}^\circ F/Btu \cdot in$)
   b. Is cost-competitive to the existing rigid close-cell foam board products (in cost per R-value comparisons)
2. **To keep the cost low, this novel nano-insulation will employ well-established polyisocyanurate (PIR) foam chemistry and the freeze drying process, instead of the prohibitively expensive supercritical CO_2 drying.**
3. **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
4. **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**

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

Technology Impact, Advantages, and Differentiation:

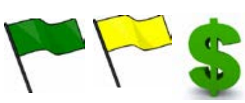
1. **Primary energy saving technical potential of PIR SIAP is about 0.7 quad** *(=20%*[2.5 quad for residential sector + 2 quad for commercial sector - BTO Market calculator and a conservative estimate of 20% reduction in energy consumption with the PIR SIAP were used, compared to PIR foam of the same thickness*)

2. **PIR SIAP will have the ability to improve the overall R-value of building envelopes between 30% to 50%,** without changing the dimensions of the structural components or insulating sheathing.

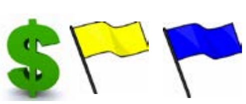


3. Proposed PIR SIAP uses well-established PIR chemistry, which will allow:
    1. Quick adoption of the new technology by industry and
    2. It's source materials will be less-costly

4. The proposed PIR SIAP, with target ~R-12.0 $hr\cdot ft^2\cdot {}^\circ F/Btu\cdot in$, will have almost double R-value, compared to the "in-service R-value" of today's PIR foams (which is only R-5.7)



5. The proposed PIR SIAP does not require a use of the blowing agent:
    1. It's chemistry will be less expensive and it will not show "thermal aging"
    2. It will have significantly lower environmental impact than today's plastic foam insulations



6. Because of a usage of a cost-effective freeze drying method, the price of the proposed PIR SIAP will be significantly lower comparing to other nanoporous insulations produced using supercritical CO_2 drying

Work Progress - Accomplishments & Milestone Update

- **Task 1: Analysis Supporting Technology to Market.**
- **Subtask 1.1**: Develop the IPMP.

  As required by the Milestone 1.1 the project team focused during Q1 on execution of an IPMP. We are starting to explore executing an Inter-Institutional Agreement to formalize Fraunhofer's role in commercializing any IP developed under this program.

- **Subtask 1.2**: Develop the Preliminary Cost-Performance Model (PCPM)

  During Q1 and Q2, the project team worked on the development 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 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:

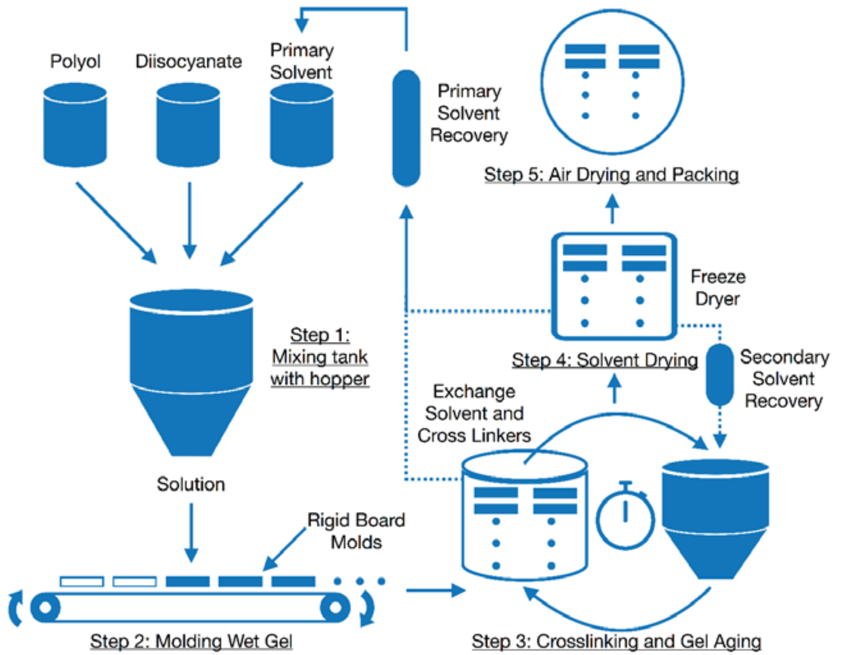
  1) mixing the chemical components,

  2) wet gel molding,

  3) crosslinking and gel aging,

  4) solvent drying, and

  5) air drying and packaging.



Work Progress - Accomplishments & Milestone Update

- **Development of Bill of Materials (BOM)**

Using the PFD described on previous page, the bill of materials for the PFD was developed. At this point in the analysis, it is not clear if a secondary solvent is needed, so only a single solvent (t-butanol) is used for the calculations. The four chemical silos are used to store the polyol, di-isocyanate, and the solvent(s).

- **Preliminary Cost Performance Model (PCPM)**

Using both the PFD and the BOM, the cost per board of the PIR-SIAP is being estimated for the PCPM. Using available literature, the production volume of a key contributor of PIR-SIAP to the U.S. polymer foam building and construction market is 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:

1. Financial fixed costs and sunk costs
2. Raw material costs
3. Energy costs
4. Labor costs

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.

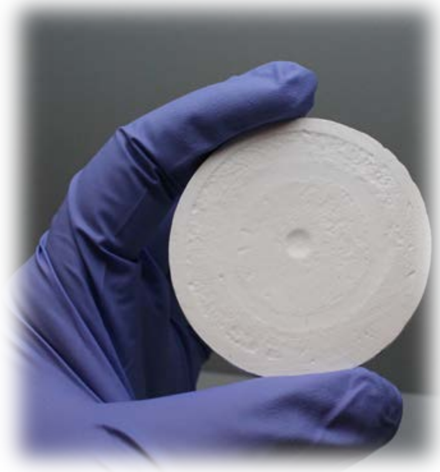
Standard, turn-key ready industrial freeze dryers have a typical capacity of 5,000 kg (sometimes even larger) [see for example: *http://www.esquirebiotech.com/industrial-freeze-dryer-1394480.html*] and many of them can be installed and operated by a same facility

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

Work Progress - Accomplishments & Milestone Update

- **Task 2: Laboratory-scale batch trials to produce PIR nanofoam using basic PIR precursors and employing freeze drying method.**

In this task, we initiated work focused on the effect of processing conditions on density, surface area, mean pore size, and most important of all, on thermal conductivity. We initially worked on polymeric aerogels formed from a trifunctional aromatic isocyanate and an aromatic triol (phloroglucinol). In this initial phase, we prepared aerogels following known, published recipes and dried them supercritically and by freeze drying. The recipe was the one originally developed by the Leventis group for polyurea, which is reported in Chem. Mater. 2010, 22, 6692–6710. In this recipe, the gelation solvent is acetonitrile.

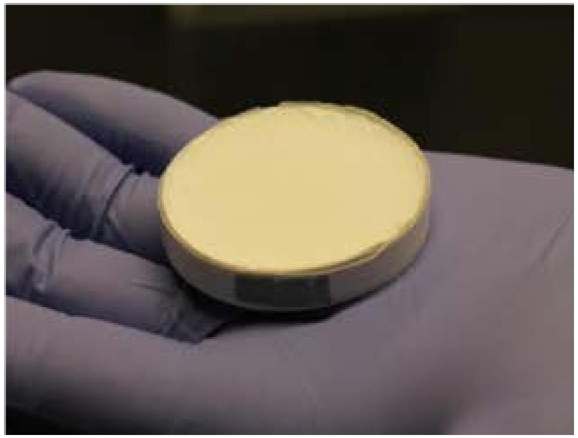


Work Progress - Accomplishments & Milestone Update

- **The first series of nano-foam samples fabricated during the project, the apparent thermal conductivity as measured by the HFMA was around 0.027 W/m-K, which is equivalent to thermal resistivity of about R-5.35 hr·ft2·°F/Btu·in.**

Measured thermal properties of the PIR nano-foam specimen

Description	Value	Units
Sample Density (geometric measurement)	167	kg/m^3
Thickness from HFMA	7.04	mm
Thermal conductivity	0.02701	W/m-K
Thermal conductance	3.834	$W/m^2 \cdot K$



Work Progress - Accomplishments & Milestone Update

- **Project team Q1 and Q2 target physical characteristics of PIR nano-foam samples:**
- **(I) pore radius around/below 100 nm**
- **(II) thermal conductivity between R-4.50 and 5.40 hr·ft2·°F/Btu·in**
- **Physical characteristics of Supercritically (SC) and Freeze dried (FD) samples confirmed that we can target performance of the best SC-dried technologies.**

Sample	Density [g/cm³]	Surface Area [m²/g]	BJH Pore Volume [cc/g]	Pore Radius [nm]	BET Surface Area [m²/g]	Young's Modulus [MPa]
1-SC	0.198	164.35	0.659	103.28	179.12	13.1
1-FD	0.148	143.23	0.809	103.89	152.65	14.3
2-SC	0.174	194.20	0.93	103.85	211.4	25.8
2-FD	0.192	171.47	0.977	104.22	169.1	22.7
3-SC	0.133	198.09	1.499	106.14	166.76	6.5
3-FD	0.157	130.81	0.718	53.24	134.12	7.5
4-SC	0.193	176.67	1.057	105.5	141.43	15.6
4-FD	0.221	114.40	0.593	105.77	113.85	13.9

Work Progress - Accomplishments & Milestone Update

- **Stakeholder Engagement**
  - This is a relatively early-stage project. We estimate project's TRL as between 2 and 4 with the end TRL target of TRL 4-5.
  - Our prior experiences (on different materials' R&D projects) has emphasized a need for close cooperation with industry and academia. In addition, we specifically appreciate the partners' commitments towards the technology development goals and alignment of interests, as the key determinants of collaborative success.
  - This part of the project's commercialization/IP protection work involves two crucial aspects of collaboration with industry: direct cooperation with selected company and coordination of inter-company technology development.
  - In this work, two key manufactures of the PIR foam and manufacturers' association have been already approached – with NDAs already signed.
  - To stimulate future R&D with these partners, we have already discussed alternative paths for our cooperation and possible project follow-on actions.
  - In future months, the project team will discuss with industry partners details of the technology scale-up stage, including industrial lab experiments and small scale field demonstrations. We will also focus our discussions on further patent developments and eventual IP licensing options.

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

Remaining Work:

1. **This is a pretty early stage of the two-year project - **Project team is currently finishing Q2

2. **Work target for Y1**
   a. Produce PIR nano foam with (R-6 hr·ft^2·°F/Btu·in)
   b. Produce PIR nano foam with pore sizes below 100 nm

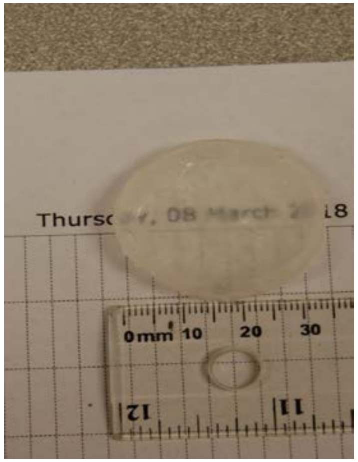
3. **Work Target for Y2**
   a. Attain an thermal conductivity of 12x10^{-3} W/m/K (R-12 hr·ft^2·°F/Btu·in)
   b. Scale up laboratory fabrication to 8x8-in.samples
   c. Develop formulation and fabrication method that will allow production of nano-foam which will be cost-competitive to the existing rigid close-cell foam board products (in cost per R-value comparisons)

4. **Commercialization Targets**
   a. Patent protection and eventual licensing
   b. 3-5 years of industrial scale laboratory trials and fabrication trials
   c. Field demonstrations
   d. Third party performance testing (fire, mechanical characteristics, long term durability, thermal and hygrothermal performance, etc.)
   e. Code approvals

Recent Fraunhofer CSE Progress in Fabrication of Other Polymeric Aerogels and Nanoporoous Composites

Hybrid and Transparent Crosslinked Aerogels.

•**Thermal conductivity 0.027 W/m*K. (R-5/inch)**
•Thermal conductivity (goal) R-8 to R-12.
•**Young's modulus 10 – 20 MPa.**
•Surface area 120 – 150 m^2/g.
•Density 0.15 – 0.3 g/cm^3.
•Mean pore radius 10 nm.
•Fire-resistant



Transparent Aerogel – ARPAe Project

Wood-polymeric aerogel composites by freeze drying.

•50% by weight wood.
•Thermal conductivity R-3 (goal).
•Young's modulus ~ 40 MPa.
•Surface area 20 – 30 m^2/g.
•Density ~ 0.4 g/cm^3.

Project proposal submitted to U.S.D.A.

Thank You!

Fraunhofer USA Center for
Sustainable Energy Systems (CSE),

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Director, Building Enclosures and
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Email: jkosny@cse.fraunhofer.org

REFERENCE SLIDES

Project Budget

Project Budget: $630,921 Total; $495,000 Federal and $135,921 Cost Share

Variances: We are working with the DOE Team (Samuel Petty, Antonio Ruiz and David Orens) to modify the VCU budget to transfer tuition to personnel costs. This will be a change in funding nor will it change the scope, objectives or milestones of this effort.

Cost to Date: $131,289 (27% of Total Federal Funds, 59% of BP1 Federal Funds)

Additional Funding: Fraunhofer expects to exceed our budgeted cost share contributions. Federal funding will remain as budgeted.

Budget History								
	October 1st – December 31st 2017 FY 2017 (past)		FY 2018 (current)		January 1st – November 30th 2019 FY 2019 (planned)		Totals	
	DOE	Cost-share	DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
Budget	47,315	12,265	196,336	51,529	251,349	72,127	495,000	135,921
Actual	66,790	13,358	64,499	13,409			131,289	26,767

Budget (back-up)

SUMMARY OF BUDGET CATEGORY COSTS PROPOSED					
Section A - Budget Summary					
		Federal	Cost Share	Total Costs	Cost Share %
	BP 1	$220,801	$57,237	$278,038	20.59%
	BP 2	$274,199	$78,684	$352,883	22.30%
	BP 3	$0	$0	$0	0.00%
	Total	$495,000	$135,921	$630,921	21.54%
Section B - Budget Categories					
CATEGORY	**Budget Period 1**	**Budget Period 2**	**Budget Period 3**	**Total Costs**	**% of Project**
a. Personnel	$23,145	$36,672	$0	$59,817	9.48%
b. Fringe Benefits	$13,424	$21,270	$0	$34,694	5.50%
c. Travel	$3,981	$1,460	$0	$5,441	0.86%
d. Equipment	$0	$0	$0	$0	0.00%
e. Supplies	$2,007	$2,003	$0	$4,010	0.64%
f. Contractual					
Sub-recipient	$104,916	$102,137	$0	$207,053	32.82%
Vendor	$30,000	$30,000	$0	$60,000	9.51%
FFRDC	$0	$0	$0	$0	0.00%
Total Contractual	$134,916	$132,137	$0	$267,053	42.33%
g. Construction	$0	$0	$0	$0	0.00%
h. Other Direct Costs	$0	$0	$0	$0	0.00%
Total Direct Costs	$177,473	$193,542	$0	$371,015	58.81%
i. Indirect Charges	$100,565	$159,341	$0	$259,906	41.19%
Total Costs	$278,038	$352,883	$0	$630,921	100.00%

Project Plan and Schedule

Milestone/ Go-No-Go Summary

Milestone 2.1: Fabricate 4x4 cm PIR nanofoam samples with pore size ~200–500nm using freeze drying method. (M9)
Go-NoGo Milestone 3.1: Fabricate 15x15 cm samples of PIR nanofoam samples with pore size ~100nm using freeze drying. (M12)
Milestone 3.1: Attain R-6 hr·ft2·° F/Btu·in for PIR nanofoam samples. (M12)
Milestone 4.1: Fabricate PIR nanofoam with pore size <50 nm using FD. (M18).
Go/No-Go Milestone 5.1: Fabricate 30x30 cm PIR nanofoam with pore size ~50 nm using FD, attain R-10 to R-12 hr·ft2·° F/Btu·in (M23)
Milestone 7.1: Cost analysis of selected PIR nanofoam formulations. (M24)

Project Tasks	Project Quarters							
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
1. Program Management & Reporting								
2. Laboratory-scale batch trials of production of PIR nanofoam using freeze drying								
3. Optimization of chemistry and processing conditions for PIR aerogel technology				G				
4. Reduction of pore size to 50 nm and increase of sample size to 15x15 cm								
5. Design of larger processing vacuum equipment and increase of sample size to 30x30 cm								G
6. Material characterization of PIR nanofoam								
7. Cost analysis of novel PIR SIAP								

Project time progress