Advanced Insulation for High Performance Cost-Effective Wall, Roof, and Foundation Systems

Final Non-Proprietary Report

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Executive Summary

The objective of this project conducted by The Dow Chemical Company (referred to as "Dow" in the report) was to explore and potentially develop high performing insulation with increased R/inch and low impact on climate change that would help design highly insulating building envelope systems with more durable performance and lower overall system cost than envelopes with equivalent performance made with materials available today. The proposed technical approach relied on insulation foams with nanoscale pores (about 100 nm in size) in which heat transfer will be decreased.

Through the development of new foaming methods, of new polymer formulations and new analytical techniques, and by advancing the understanding of how cells nucleate, expand and stabilize at the nanoscale, Dow successfully invented and developed methods to produce foams with 100 nm cells and 80% porosity by batch foaming at the laboratory scale. Measurements of the gas conductivity on small nanofoam specimen confirmed quantitatively the benefit of nanoscale cells (Knudsen effect) to increase insulation value, which was the key technical hypothesis of the program.

In order to bring this technology closer to a viable semi-continuous/continuous process, the project team modified an existing continuous extrusion foaming process as well as designed and built a custom system to produce 6"x6" foam panels. Dow demonstrated for the first time that nanofoams can be produced in a both processes. However, due to technical delays, foam characteristics achieved at the end of the project fall short of the 100 nm / 80% porosity targets set for optimal insulation foams.

In parallel with the technology development, effort was directed to the determination of most promising applications for nanocellular insulation foam. Voice of Customer (VOC) exercise confirmed that demand for high-R value product will rise due to building code increased requirements in the near future, but that acceptance for novel products by building industry may be slow. Partnerships with green builders, initial launches in smaller markets, and efforts to drive cost down will help acceptance in residential and commercial retrofit and new construction.

The work from this program resulted in 5 patent applications filed, 9 publications and 11 technical presentations at scientific conferences, with 2 best paper awards.

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Program Objectives

Background and Technical Hypothesis

The development of nano-cellular insulation foams using CO_2 as an environmentally friendly blowing agent (no ozone depletion potential, global warming potential of 1 compared to 1000 or more for typical extruded insulation foams) is a significant technical challenge, which requires the production of cell size of the order of 0.1 microns (100 nm) to benefit from the Knudsen effect (reduced gas conduction), with low enough densities (void volume of about 90%) to minimize heat conduction through the solid material in the foam. While some examples of nano cellular foams were found in the literature prior to the start of the project, the cells size was too large (500nm or more) and the void volume (or porosity) far too low (20% or less). Most of these examples were thin films. A new strategy, proposed by The Dow Chemical Company ("Dow"), produced unique foam structures with cell size close to 200 nm and porosity of about 70% at the time of the initial proposal. The technical objective of the project was set towards improving this technology to obtain a further two-fold decrease in cell size, two-fold decrease in density (porosity of at least 80%) and increase size about ten-fold in each dimensions.

To pursue this ambitious goal, a technical project plan in three phases was proposed, as illustrated in Figure 1: Proof of concept, Concept validation and Feasibility of continuous production. During the first phase, the goal was to produce and test samples at a small batch scale to identify possible solutions and key performance requirements were identified by marketing. During concept validation the goal was to build and evaluate a miniplant scale continuous foaming process. The third phase aimed at producing larger prototype by a continuous or semi continuous process. In parallel, assessment of the market opportunity and risks were to be conducted. The desired outcome of the project is a plan for scale-up and commercialization of the technology in selected markets.

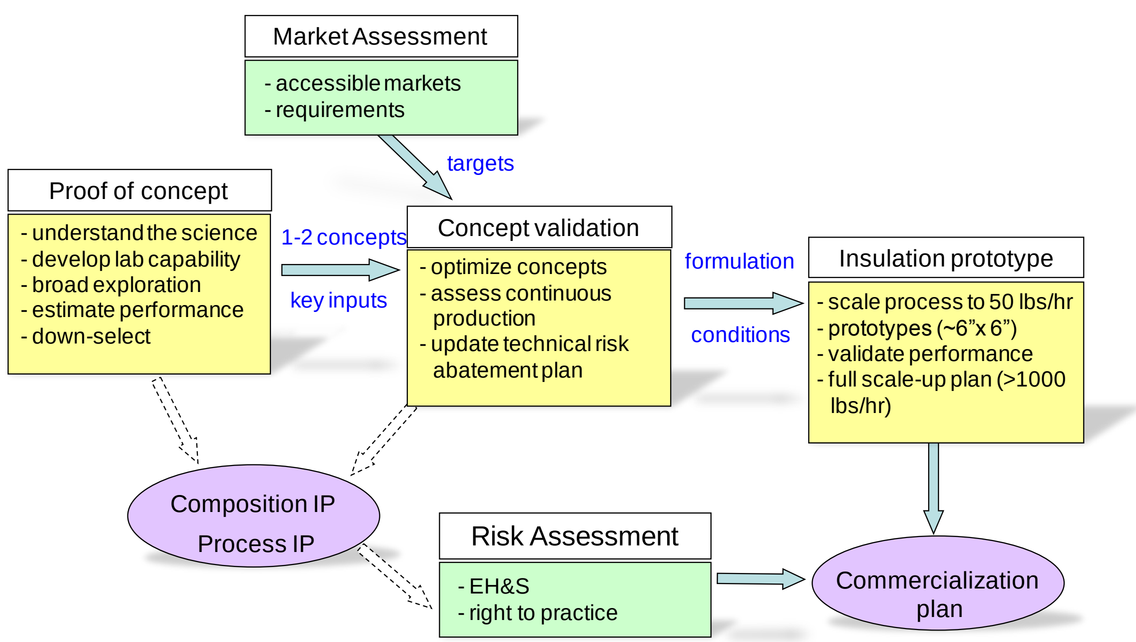


Figure 1. Project organization in three phases, with parallel activities

Work organization

The project work was organized in the following tasks:

Task 1- Project Management Plan
Task 2 - Proof of Concept
- *Subtask 2.1* R&D Scoping
- *Subtask 2.2* Market research

Task 3 – Concept Validation
- *Subtask 3.1* Material science and formulation
- *Subtask 3.2* Design options for continuous process
- *Subtask 3.3* Risk assessment
- *Subtask 3.4* Intellectual property

Task 4 – Feasibility of Continuous Production
- *Subtask 4.1* Build continuous process
- *Subtask 4.2* Produce and test small prototype
- *Subtask 4.3* Commercialization strategy
- *Subtask 4.4* Design options for large scale continuous process

Project Milestones and Program Accomplishments

The accomplishments with respect to the initial milestones are listed in Table 1 below. Dow was able to successfully complete the proof of concept phase and the concept validation, by optimizing formulations and process conditions to produce nanofoams at a small scale with desired attributes (cell size ~ 100 nm, porosity ~ 80% or more). This constitutes significant advances in foam science and technology that have resulted in several patent applications and publications, and two awards.

The third phase has not been fully successful. It involved the scale up of nanofoam technology into large prototypes, which turned out to be a far more difficult challenge than anticipated. Panels of acceptable dimensions could only be produced with cell size 5 times as high as the target, and with densities 20% too high. The insulation value for such panels is similar to XPS, despite a density 8 times as high, due to the benefit of the Knudsen effect. However, such a high density is cost-prohibitive, and such panels are not acceptable for insulation. Thus we failed to deliver the adequate performance, and as a result the commercialization plan was postponed. Additional experimentation would be needed to overcome the remaining technical challenges

Table 1. Delivery on Project Milestones

Project Milestones	Project Accomplishment	Actual Completion Date
I- Project Management Plan completed	Completed and modified during program as necessary	**Completed** 10-18-2010
II- Produce a small batch-scale nanofoam meeting minimum requirement for insulation performance target (100nm/80% or R/7.5)	Demonstrated batch scale foaming of a commercial acrylic polymer; cell size ~90 nm, porosity ~80%	**Completed** 6-30-2011
III- External validation of market opportunity and identification of additional nanofoam physical properties critical to product success	External company (Baverstam) completed VOC activities that identified potential market opportunities	**Completed** 6-17-2011
IV- Produce a continuous/semi continuous nanofoam meeting minimum requirement for insulation performance target (100nm/80% or R/7.5), validated at the miniplant scale (< 5 lbs/hr)	Produced continuous and semi-continuous foam with 300 nm, 75% porosity at miniplant scale.	**Quantitative target not fully reached in time.** 6/31/2013
V- Demonstrate that the nanoporous insulation materials meet key code requirements based on 4” to 6” prototypes	Produced prototypes of acceptable dimension (6” x 6”). Cell size/porosity did not meet target.	**Completion of this milestone requires further progress on Milestone IV** 8/31/2013
VI- Final technology and commercialization plan	Not completed due to un-met technical targets	Postponed

Detailed Summary of Project Activities

Task 1: Project Management Plan

The Project Management Plan was initially completed in October 2010, and further modified during the progress on the program evolved.

Task 2: Proof of Concept

The objective of the proof-of-concept phase is 1- to demonstrate the feasibility of a nanoporous material with high insulation performance, and 2- to identify the combination of attributes and property targets that the insulation product will have to possess to meet key customer requirements.

Subtask 2.1 – R&D Scoping

Goal: The primary objective of this task was to advance the understanding of foaming science to the point where we could identify most promising polymer systems and best conditions for the production of nanocellular foams with smaller cell size and higher porosity than ever reported.

Original hypotheses: Gas foaming remains the most attractive method to produce porous materials at relatively low cost. Microcellular foams can be produced relatively easily in batch process, and it has been documented in open literature that a significant effort has devoted to the development of continuous processes in the industry. Such foams have cell densities (number of cells produced in one cm^3 of polymer material) of about 10^{12} cm^{-3}. Yet the benefit for insulation is rather insignificant when cells remain larger than a micron. However, the theoretical gas contribution to thermal conductivity could be reduced by 70% if the cell size could be made close to 100 nm (Knudsen effect) while lowering the foam density to minimize heat conduction through the solid phase. This requires achieving much higher cell densities (10^{16} cm^{-3} or more) than had been achieved at the start of the project (~ 10^{14} cm^{-3}) in industry or academia. We hypothesized that by the proper choice of polymer and foaming conditions, it should be possible to generate by batch foaming the adequate number of cells, potentially with the help of a cell nucleating agent. We further hypothesize that it is possible to expand all these cells to minimize density, without destroying the cell structure.

Fundamentals and theory

State of the art review — An extensive literature search (articles and patents) was completed to obtain the most recent picture of the relevant state of the art in the experimental and theoretical domains. Despite an increasing activity in the nanofoam area, no high porosity (>50%) nanofoams with homogeneous cells smaller than about 300 nm have been reported by either academic or industrial groups.[1] This is illustrated in Figure 2 (open symbols). The limitations of the approaches followed by other groups, in particular in terms of equipment design, polymer choice, foaming protocol and conditions, have been for the most part identified. Information from open literature and past foaming results were reviewed with several Dow chemistry and materials science experts to identify opportunities for improvement. An ideation session was conducted to list copolymer and blends of interest to produce nanofoams from cost-effective raw materials. We used the team's

[1] H. Ruckdäschel *et al.*, *Adv. Polym. Sci.*, **227**, 199-252 (2010).

expertise in materials science, chemistry and engineering to hypothesize solutions for the production of nanofoams, in terms of polymer properties required (gas solubility, viscosity etc.) and process conditions.

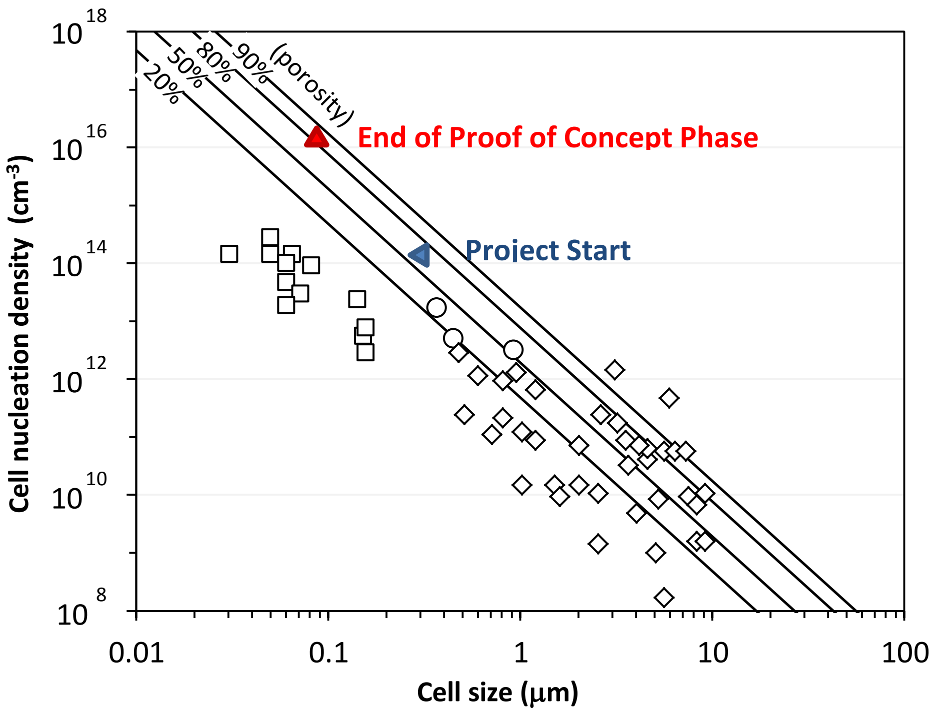


Figure 2. Comparison of foam characteristics collected from the literature at the onset of the project (open symbols). Triangles indicate cell size/ porosity performance achieved by Dow at the start and at the end of the proof of concept phase.

Foaming science — Significant progress was made towards understanding phenomena involved in generating nanocellular structures: generation of the nascent cells (nucleation), growth of the cells (expansion) and freezing of the structure (stabilization). In particular, the team formed the hypothesis that nanoparticles could be used to promote nucleation at the nanoscale under specific conditions.[2] This was validated experimentally both for acrylic and styrenic polymers,[3] which resulted in the improvement in cell size and cell nucleation density shown in Figure 2.

Several models were developed and refined during this program that enabled further fundamental understanding of the phenomena involved in generating nanocellular structures. A proprietary theoretical model of the foaming process was developed and implemented. The model accounts for the dissolution of the foaming gas into the polymer under high pressure, the formation of nascent bubbles when the pressure is decreased (cell nucleation), the growth of the bubbles (cell expansion, which depends on gas diffusion and viscosity of the gas-saturated polymer) and the stabilization of the foam.[4] An algorithm of the model is shown in Figure 3.

[2] S. Costeux and L. Zhu, "Thermoplastic nanocellular foams with low relative density using CO_2 as the blowing agent", proceedings of the SPE FOAMS 2011 Conference (Iselin, NJ).

[3] S. Costeux and L. Zhu, *Polymer*, **54**, 2785-2795 (2013).

[4] I. Khan, "Numerical Modeling of Nanocellular Foams Using Classical Nucleation Theory and Influence Volume Approach", 65th American Physical Society DFD Meeting, 2012 (San Diego, CA)

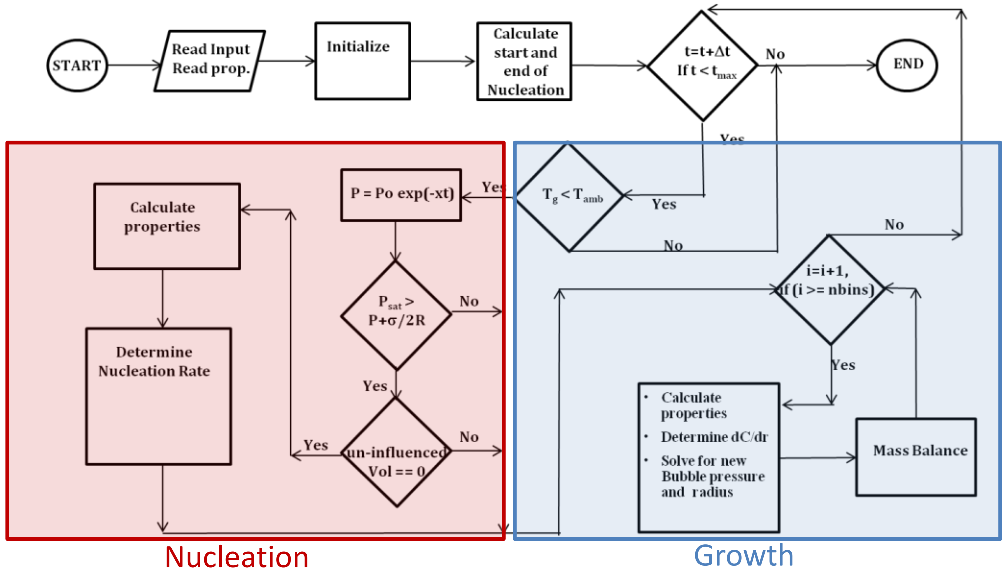


Figure 3. Overview of algorithm for the foaming model combining cell nucleation and growth.

All inputs for the model (polymer characteristics, properties in the presence of CO_2, experimental conditions) can be determined experimentally, except for one constant parameter related to cell nucleation rate for a given polymer. Once this parameter is identified, the proprietary foaming model can predict the evolution of cell size and porosity of the foam during its expansion. This provides insight into the effect of independent parameters on final foam characteristics. The trends predicted by the model were validated by comparison with a series of experiments,[5,6] as exemplified in Figure 4.

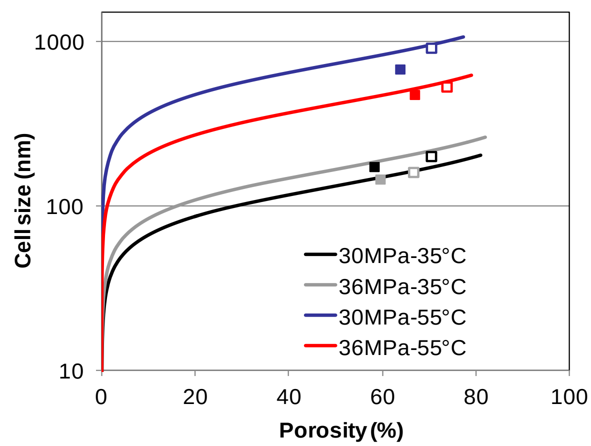


Figure 4. Prediction of foaming model

Dow collaborated with VLXE ApS (Denmark) to develop a thermodynamic model able to predict gas solubility and interfacial tension for polymeric blends saturated with a high pressure gas such as carbon dioxide. Maps of gas solubility, interfacial tension, and viscosity were developed on a wide range of temperatures and pressures and subsequently used in the foaming model to guide the choice of experimental foaming conditions.

[5] I. Khan, S. Costeux *et al*., "Numerical Studies of Nucleation and Bubble Growth in Thermoplastic Foams at high Nucleation Rates", proceedings of SPE FOAMS 2013 Conference (Seattle, WA)

[6] I. Khan, D. Adrian and S. Costeux. "A model to predict the cell density and cell size distribution in nano-cellular foams", submitted to Chemical Engineering Science journal, Mar. 2015

Predicting foam properties — In addition, a model was developed to estimate thermal conductivity based on solid, gas and radiation components was completed. Comparison of this model with thermal conductivity data on foams with sub-micron cells has confirmed the existence of the Knudsen effect in these foams by showing a reduction of gas thermal conductivity with reduced foam cell size. As the knowledge of nanoscale heat transfer progressed, the model was regularly updated to improve the prediction of the conductivity through the solid polymer matrix defining the cells of the foam.

Knudsen effect confirmed

Dow's measurements on nanofoam gas conductivity confirmed quantitatively the benefit of nanoscale cells (Knudsen effect) to increase insulation value. Dow's collaborators at the University of Valladolid (Spain) independently confirmed these results. This validates one of the key original hypotheses.

Screening experiments

Designs of experiments were conducted to screen the effect of formulation and foaming conditions on foam cell size and porosity. Foams with smaller pores and higher porosities than reported in the literature were achieved.

Small scale batch foaming — A schematic of the principle of a batch foaming experiment is shown in Figure 5. A small polymer sample is placed into an autoclave maintained to a temperature *T*; CO_2 is introduced in the autoclave and maintained at a pressure *P*. After several hours of equilibration, the autoclave is depressurized quickly and the foam is retrieved. Optional post-foaming treatment by immersion in a heated water bath allows for completion of the foam expansion. For a given polymer systems, conditions are selected to maximize foam expansion and cell nucleation density.

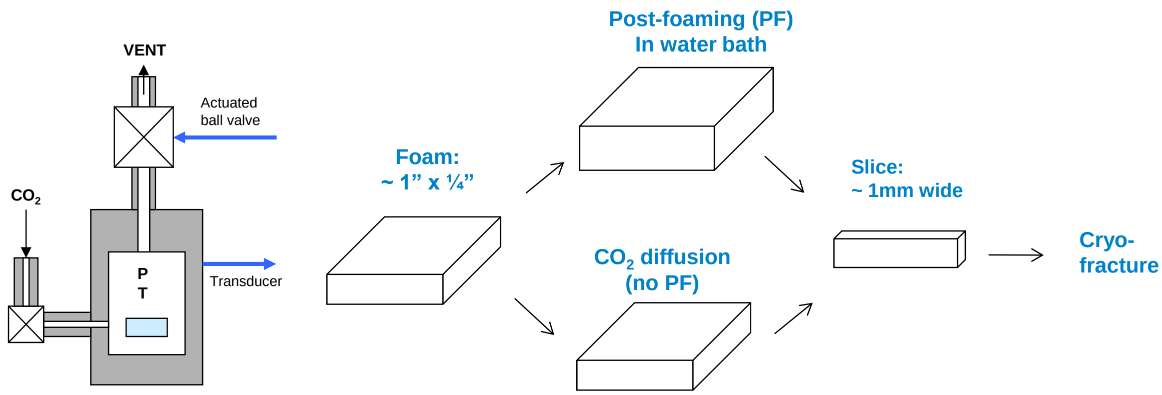


Figure 5. Schematic of a batch foaming experiment, and subsequent treatment of the foam.

During the duration of the project, over 2000 batch foaming experiments were conducted to screen effect of pressure, temperature and other process variables on the foam structure (cell size and porosity). Batch foaming equipment was built in three locations to allow for parallel work. Foam dimensions from this equipment are typically less than 1". Experiments were conducted to study the interplay of polymer structure, nucleators and process conditions on cell size and porosity. The results demonstrated the reproducibility of the foaming experiments, and support the fundamental understanding of the nanofoam formation process. A family of polymer was identified that readily produces sub-micron cell foams under appropriate conditions.[7] Some additives were shown to improve the balance of cell size and porosity. Blends from commercially available polymers were also identified that readily produce sub-micron cell foams under appropriate conditions. These foams were tested by the analytical methods previously below. A patent application that covers nanofoams produced by blends of commercially available polymers was filed in October 2011. Two additional patent applications were filed on the additive work in 2012.

Analytical method developments

Several analytical techniques were developed in this program to measure key properties of high pressure polymer/gas systems, as well as characterize foams on the nanoscale and measurement of the thermal conductivity. This information was essential to analyze experimental foaming data.

High pressure polymer/gas testing — Measurement techniques for the physical properties (solubility, diffusion, glass transition temperatures, viscosity) of polymers under high gas pressure were developed. The measurement technique for gas solubility at high pressures (up to 5000 psi) using a magnetic suspension balance was improved, resulting in a ten-fold increase in precision and a 3-fold reduction in measurement time. A new high pressure visualization cell was developed to measure the swelling of polymers. In addition, a SFT phase monitor was installed to monitor the phase behavior of a polymer formulation in the presence of high pressure gas (see Figure 6). A Quartz Crystal Microbalance (QCM) was modified to measure glass transition properties of polymers saturated with gas. In collaboration with McGill University (Montreal, Canada) a method to measure the high pressure viscosity of polymers saturated with a foaming gas was developed using their High Pressure Sliding Plate Rheometer.[8]

Figure 6. Measurements techniques for phase behavior and CO_2 solubility. Left: SFT Phase Monitor II; Right: Magnetic suspension balance

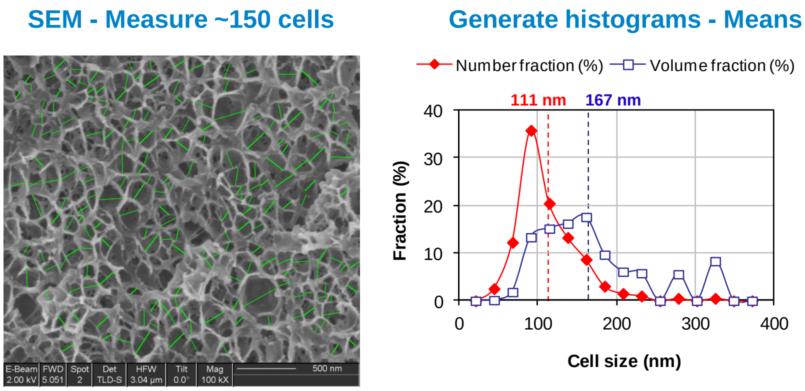
[7] S. Costeux, H. Jeon *et al.*, "Nanocellular foams from acrylic polymers: Experiments and modeling", proceedings of the SPE FOAMS 2012 Conference (Barcelona, Spain).

[8] H. E. Park, J. M. Dealy, *Macromolecules*,**39**, 5438–5452 (2006)

Foams characterization — A reliable method to characterize pore size by Scanning Electron Microscopy (SEM) was developed for sub-micron foams. Several techniques were evaluated to produce foam fracture surfaces that reflect the internal structure of the foam without significant damage. A high resolution microscope was used to acquire images containing several hundred cells. Image analysis and a statistical method were applied to determine the average cell size and cell size distribution. An example of foam analysis is shown in Figure 7.

> **Successful Proof of Concept**
>
> Dow developed new analytical techniques and advanced the understanding of how cells nucleate, expand and stabilize at the nanoscale. We increased cell densities hundred-fold, and showed that optimum batch foaming can produce foams with 100 nm cells and 80% porosity. Dow filed patents to protect this leading nanofoam technology.

Thermal conductivity testing — A new hot-wire apparatus to measure thermal conductivity of materials in the range of 0.015 W/m-K - 1 W/m-K was implemented. Its design is identical to that used in Lawrence Livermore National Laboratory for the characterization of aerogels. For such materials, the unit accurately measures thermal diffusivity of materials. It requires samples with dimensions of about 2”. The mode of operation is different than standard heat flow methods, for which the heat required to maintain a given temperature difference across the thickness of the sample is measured. In situations where the surface of the samples has higher thermal diffusivity than the core, the hotwire technique may give erroneous results. For samples of dimensions close to 4”, existing heat flow equipment used for R-value measurements by ASTM C 518 was retrofitted. Both devices can operate under vacuum, and thus provide access to the gas contribution to thermal conductivity.



Average cell size

ϕ

Voids volume fraction

$$p = 1 - \frac{\rho_{foam}}{\rho_{pol}}$$

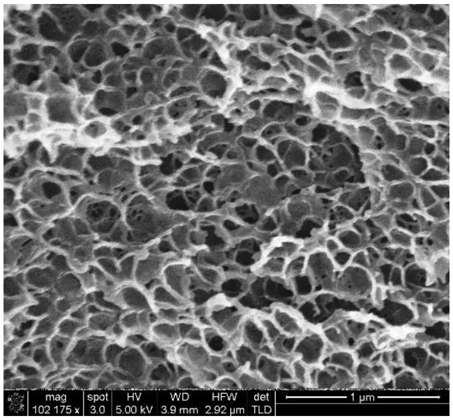
Cell density (/cm³ of polymer)

$$N_C = \frac{p}{\pi\phi^3/6}\frac{1}{1-p}$$

Figure 7. Foam structure analysis: determination of cell size distribution and cell nucleation density

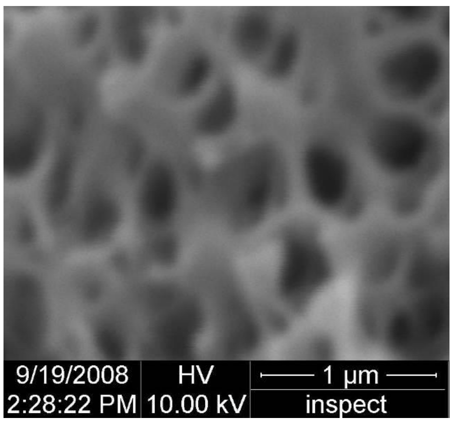
Outcome of the Proof of Concept phase

Despite the uncertainty regarding the feasibility of the low density nanofoam concept, the first phase proceeded as planned. Foams that achieve the targets defined by Milestone (II) listed in Table 1 were produced by June 2011. The scanning electron micrograph (Figure 8, upper image) shows a foam with a cell size of ~90 nm and a porosity of ~ 80%. This material is an acrylic polymer with small molecule additives that enhance gas solubility and reduce interfacial tension. For comparison purpose, a representative image of foams made at the time the project proposal was written is also shown (Figure 8, lower image) at the same scale. Note the improvement in cell size and porosity, but also in the image quality due to improvement in sample preparation and characterization techniques during the Proof of Concept phase.



Milestone II – New foam
Example of an acrylic foam made from a commercial polymer by batch foaming.

Cell size average: ~ 90nm
Porosity: ~ 80%



Baseline performance
Foam made from acrylic polymer at the time the project was proposed

Cell size average: ~ 250nm
Porosity: ~ 60%

Same scale as above.

Source: Dow Proposal No. 09081739

Figure 8. Illustration of progress towards decreasing cell size and increasing porosity since initial project submission

A paper entitled "Nanocellular Foams from Acrylic Polymers - Experiments and Modeling" was presented at FOAMS 2012 (Barcelona, Spain), the premier international conference sponsored by the Society of Plastic Engineers, to an audience of 140 academic and industrial participants. This contribution, which highlights some of the copolymer and foam modeling work generated during Task 2, received the "**FOAMS 2012 Best Paper Award**" by the conference technical committee.

Subtask 2.2 – Market Research

Goal: In parallel with the technical work, some effort was directed to the determination of most promising applications for nanocellular insulation foam (NIF).

Original hypothesis: Nanocellular insulation will provide insulation value up to R-7.5 per inch at a cost per unit of R-value similar to existing materials (phenolic foams, XPS), but with beneficial attribute (environmentally more friendly, stable insulation performance). The main market should be continuous insulation sheathing for residential and commercial building, in particular for retrofit where space is limited and thinner products are advantaged.

Voice of Customer (VOC)

Internal discussions and a review of existing VOC data for insulation materials were conducted. Most of the information readily available pertains to well established materials such as XPS and EPS, or thermoset foams such as polyisocyanurate foam boards or spray insulation. This confirmed the need for more specific data collection targeted towards sustainable, high performance superinsulation with stable R-value. Because Dow is well established in the insulation market with connections a number of customers and builders, conducting the VOC using Dow personnel and usual counterparts being in commercial relationship with Dow may not allow Dow to obtain truly objective feedback. To obtain unbiased data, the choice was made to engage an external consulting company to conduct the VOC study. Baverstam Associates Inc. (Boston, MA, http://www.baverstam.com/) submitted a suitable proposal and was selected. The agreed-upon data collection process comprised 2 phases:

> **Market opportunities identified**
>
> Voice of Customer confirmed that demand for high-R value product will rise due to building code increased requirements in the future.
>
> Despite the need, acceptance may be slow due to building industry being very conservative and often reluctant to adopt novel products.
>
> Partnership with green builders, launch in niche markets initially, and efforts to drive cost down will help acceptance in residential and commercial retrofit and new construction.

I. Broad base consultation with insulation manufacturers, builders, architects, building science consultant but also building codes, government and national association representatives.

II. Select main (3-5) applications, and identify competition, potential partners, and business models. Identification of potential markets size, acceptance rate, specific requirements.

Phase I was conducted in February-April 2011. A dozen potential applications were identified by asking interviewees to list applications most suitable for a Nanocellular Insulation Foam (NIF) with a long-term R-value close to 8 at competitive cost. A mid-study review of the initial findings of the VOC was held on April 18th which completed Phase I. Dow Building Solutions (DBS) Marketing and R&D condensed this list to 6 applications of interest to Dow Building solutions.

Phase II was conducted in May-June 2011 to identify factors that would support or hinder commercial success of a nanoporous insulation foam in the applications selected by DBS. In collaboration with DBS personnel, key competitors were identified. Phase II ended on 6/17/2011, which completed Milestone (III), as shown in Table 1.

Outcome of the Market Research

The executive summary of the outcome of the Baverstam study are listed in Figure 9. The key potential markets for a sustainable, high performance insulation with a stable R-value recommended are:

- Green building (zero-energy homes)
- Continuous insulation (residential and commercial), Structural insulated panels, retrofit wall systems.
- Walk-in coolers and refrigerated trucks could constitute non-building envelope applications with a lower barrier to entry in the market, until costs are reduced sufficiently to meet targets for B&C

Dow Building Solutions marketing is rather familiar with most of these applications, and will be able to provide CTQ (critical to customer) requirements on prototypes are available for testing.

Executive Summary

Opportunity for NIF in residential and commercial markets (as of June 2011)

- A Nanocellular Insulation Foam product with higher R-value will have a large market in building insulation when federal regulations on energy efficiency take effect.
- The adoption of the 2012 IECC building code for residential construction and the ASHRAE 90.1 2010 code for commercial construction both will open up opportunities for the rigid foam material, although the price will have to be competitive.
- The market is not very strong today because most states are still building to old codes which do not require high insulation value. The adoption of the new codes is expected to take 3-5 years, which is roughly the time line for product development of the NIF material also. Therefore, the timing of the market demand might coincide with the product being ready.
- However, future building codes are going to be more stringent in terms of insulation values, so the industry will be forced to adopt high R-value materials despite higher initial costs. This presents an opportunity for the NIF material.
- Most builders and design professionals agree that the codes will begin to have an impact within the next 5-7 years, requiring the industry to seek higher R-value materials to simply build to code.
    - Most builders are only interested in building to the minimum code; however, there is a growing number of "green" builders who are building above code. This presents opportunities even today, but it is very small and niche. Cost is again the critical factor in material selection.
- In particular, continuous insulation on the exterior of a building (both residential and commercial) will be an attractive potential market. Other niche applications such as spandrel panels and SIPS.
- Availability of a material also influences the codes to a certain extent, so sourcing from multiple distributors and/or licensing to other companies will enable faster acceptance of the material in the building and construction industry.

Initial markets

- While waiting for the building industry to become ready for the new material, Dow can begin the commercialization process for the NIF insulation by entering other selected markets where there is a demand for the material today, and where market penetration will be easier and faster.
- We have identified walk-in coolers and commercial freezers as the most attractive market for the NIF in the short term. The demand for high R-value which is stable over long periods of time, makes it attractive for this application. It is somewhat similar to the building construction market, because federally established codes have mandated the use of higher R-value materials.
- Refrigerated trucks have similar requirements, so would be a natural extension of the above market; however, the established manufacturing practice of foamed in place panels will present a challenge to the NIF rigid foam. If the material can be available in spray foam form, it would open up more opportunities.
- Similarly, packaging containers that are undergoing a transition to new materials for better insulating performance, present an attractive short term opportunity for NIF.

Baverstam Associates, Inc.
Boston San Francisco Geneva Stockholm
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Figure 9. Summary of Baverstam's Conclusions on Market Opportunities for Nanocellular Insulation Foams (NIF)

Task 3: Concept Validation

Goal: The objective of the concept validation phase was to assess the feasibility of a small scale continuous process to fabricate specimen suitable for testing of foam performance. This represent another significant challenge, due to the fact pressure and temperature conditions used in lab batch foaming are such that the polymer is solid under these conditions, unlike in a typical XPS foaming process. This is the reason that no continuous process for foams with cells smaller than a few microns has ever been reported in the literature.

Original hypothesis: In a continuous foaming process, gas is added to the molten polymer, and the mixture is cooled before being either extruded or injected into a mold. We hypothesize that by a proper choice of conditions, a sufficient amount of gas can be added to match the gas solubility in the batch foaming process, and that equipment redesign should allow temperature and pressure to be controlled to approach conditions needed to nucleate very high cell densities. We also expect that by further optimizing polymer or blend properties and additives, it may be possible to reduce the need for such low temperatures or high CO_2 concentrations. This justifies the need to pursue materials science effort in parallel with foam extrusion experiments.

Subtask 3.1 – Materials Science and formulation

Structure-property relationships — Experiments were conducted to identify and optimize additives to enhance nanofoam properties, by increasing porosity while maintaining a cell size below 100 nm. It has been found that the successful choice of molecular additives depends on their solubility parameters and on the specific polymer structure. Establishing this structure-property relationship has enabled new additives and new blends to be identified. A very interesting example of synergy between blend components is shown in Figure 10: very homogeneous nanofoams, with average cell size of 100 nm or less and very narrow cell distribution can be produced in cases where neither blend component can produce such foams by itself.[9] Such systems constitute good candidates for continuous extrusion studies as they do not require a nanoscale nucleator. Three patents on additives and blends were filed in 2011-12.

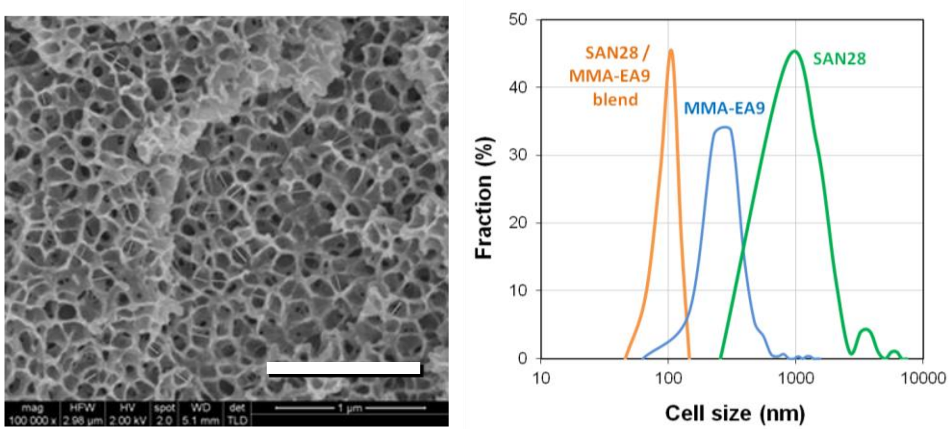
(a)  (b)

Figure 10. Example of nanofoam from blend of styrene-acrylonitrile and an acrylic copolymer (MMA-EA9), showing smaller cells and narrower cell distribution for the blend.

[9] S. Costeux *et al*., "Homogeneous nanocellular foams from styrenic-acrylic polymer blends ", *J. Materials Research*, **28**, 2351-2365 (2013).

Synthesis capability — During Phase 1, the choice of polymer materials was limited to commercial polymers. This did not allow for systematic investigation of microstructure effect on bulk properties such as thermal conductivity, fire performance etc. A one gallon emulsion reactor system was implemented, which enabled the production of larger quantities of new polymers for systematic evaluation and study.

Low thermal conductivity copolymers for nanofoams — In addition, two routes to lower thermal conductivity polymers, which can ultimately contribute to lowering the thermal conductivity of nanocellular foam were evaluated.

- Acrylic copolymers were synthesized with a number of comonomers thought to provide a benefit for thermal conductivity compared to commercial Polymethylmethacrylate (PMMA). Most promising comonomers resulted in 15% lower thermal conductivity for the copolymer compared to standard acrylic copolymers, while maintain high gas solubility. Batch foaming of these materials has found that there are viable routes to producing foams with the appropriate cell size/porosity balance with lower thermal conductivity compared to PMMA. However, some of these variations are brittle and require a rubber modifier to improve mechanical properties. Commercially available rubber modifiers have been identified as candidates to use in this application.
- Because polystyrene has low thermal conductivity but also low CO_2 solubility compared to PMMA, styrenic copolymers were also developed to further improve CO_2 affinity. The polymers have approximately 15% lower thermal conductivity solid compared to PMMA, with about 20% higher gas solubility compared to polystyrene. These materials resulted in high porosity foams, but with cell size higher than the 100 nm target.

Acrylic copolymers with improved fire performance — Imparting flame retardancy to nanofoams represents a significant challenge because of the balance of gas solubility, diffusivity, interfacial tension and the nucleation phenomena. Several effective non-halogenated flame retardants, both small molecule and polymeric, were identified for the polymer resins evaluated. Polymeric flame retardants proved to be easier to incorporate into the foam system while maintaining the nanostructure. Specific acrylic copolymers were shown to provide fire retardancy improvement to commercial acrylic polymers. A patent application that covers this approach was filed in December 2013.

Outcome of the Materials Science effort

The work uncovered unique foaming behavior of polymer blends, and provided polymer options from which we can choose depending on specific requirements for processing (CO_2 solubility, viscosity) or for final performance (e.g. fire retardancy).

External recognition

A paper entitled "Homogeneous nanofoams from synergistic blends", which highlights some of the work on polymer blends studied in Task 3, was presented at the SPE FOAMS 2013 conference (Seattle, WA) to an audience of 150 participants.
This contribution selected as the "**FOAMS 2013 Best Paper Award**". It was the second consecutive recognition for the joint Dow / U.S. DOE project at this premier conference.

Subtask 3.2 – Design options for continuous process

Foams with the finest cell morphology made by a continuous process have cell larger than 1 micron. The state-of-the-art is the MuCell™ process, invented at MIT in the 1990's and commercialized by Trexel Inc., which is able to make foams with cells as small as 5-10 micron cell with various polymers and CO_2 (e.g. PS and 1-5% CO_2). However, this process works best for injection molding (i.e. very high pressure) and produces high densities foams (porosity lower than 50%, often lower than 20%).

In comparison, continuous foaming of nanocellular foams requires to further reduce the size of the cells between 20 and 100 times, which means producing foams with cell densities 10^4 to 10^5 times as high as these microcellular foams. It is well accepted that meeting this objective would constitute a major breakthrough, especially if lower density foams can be made (about 80% porosity).

Continuous foaming at the miniplant scale

A miniplant foaming line ("Line 6") operating at 2-5 lbs/hr is available in Dow Building Solutions' facility in Midland, MI. The advantage of an extrusion line at this scale is its rating for very high pressures, which provides a safety factor beyond the pressures that were needed in batch foaming to produce nanofoams. This is essential for the development of an unknown foaming process with potentially very high levels of CO_2.

Preliminary assessment — Initial evaluation of the line prior to the official start of the DOE program showed that it did not have the capability to feed enough CO_2 and cool the mixture efficiently enough to make homogeneous foams with submicron cells. This resulted in the foam structures shown in Figure 11. The cell distribution is bimodal, with submicron cells in the interstices between cells that are 5 to 10 microns in size. The presence of large cells points to an issue with gas dissolution, and to the need for equipment modification. However, the presence of the submicron cells establishes that it is possible to achieve high nucleation density with our system.

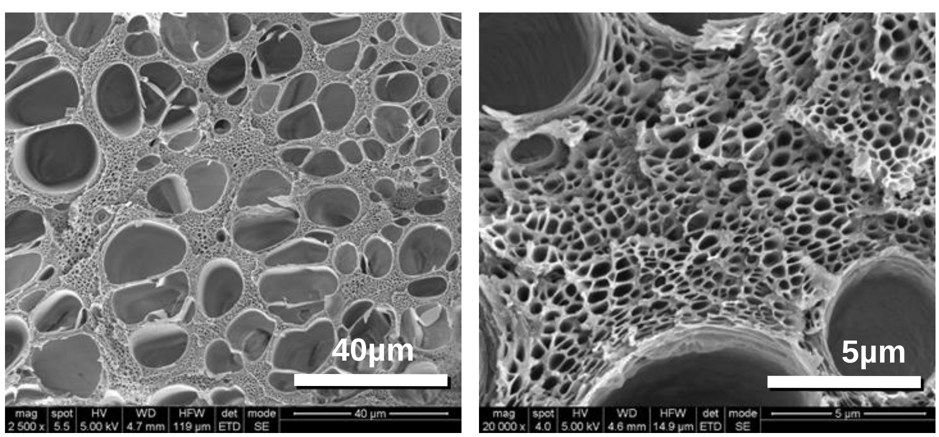
a)  b)

Figure 11. SEM images at 2 different scales of continuous foams made at miniplant scale prior to any modification. Nanocells are present, but cell morphology is very inhomogeneous.

Dow then made modifications to the miniplant equipment to improve gas feeding at high rate and high pressure. Further modifications allowed for better cooling and improved dissolution of the gas before the extrusion die.[10] Subsequent foam extrusion miniplant trials with an acrylic copolymer, showed the ability to produce continuous foams with submicron cells. The pressure-temperature maps, similar to those developed during Phase 1 for the modeling effort, provided direction to further decrease cell size, to achieve continuously extruded homogeneous foams[11] with about 300 nm cells and porosity of 75%, as shown in Figure 12.

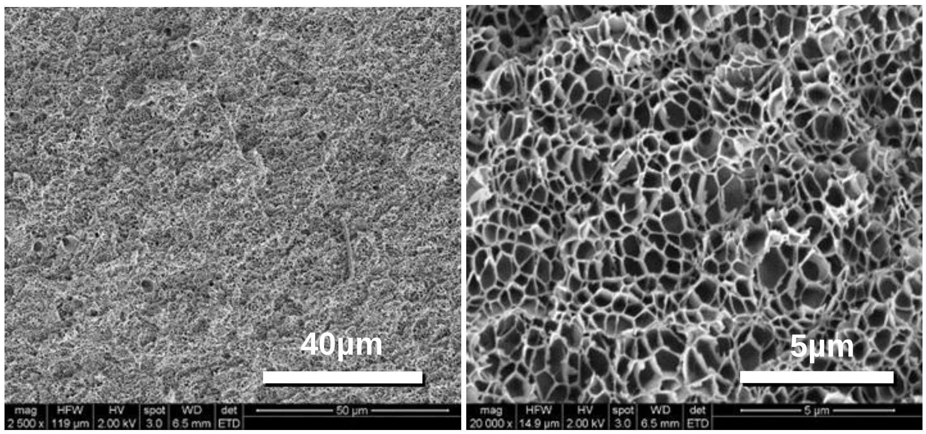
a)  b)

Figure 12. Foams produced after miniplant modification with an acrylic copolymer. Cells are homogeneous, with average size of 300 nm.

Further efforts to reduce cell size — During this phase of the program, additional trials were conducted with polymer blends of various compositions and under different operating conditions to further reduce cell size. The conclusion of this effort was that at the production rate of the miniplant, pressure control was insufficient to further increase the nucleation density without having to excessively reduce the die opening. This would be unsuitable for the production of increased size samples.

Process and economic modeling — Excessive production cost can prove to be a show-stopper for any new product development. This task aims at determining whether any cost related to process or material could be prohibitive, and thus be a factor in the risk assessment that follows in Task 3.3. Detailed cost analysis results, however, will have to remain proprietary to Dow as they directly impact our competitive advantage.
The experimentation at the pilot scale provided useful information on the minimum requirements of a continuous process for nanocellular foams. A first-pass cost estimate of large scale continuous foaming equipment was calculated, assuming

- scale-up of the extruders/mixers to a production rate to 2000 lbs/hr, with high loading of CO_2 (up to 35wt%)
- stringent engineering needs to handle high pressure throughout the line, and to ensure gas dissolution. No need, however, for corrosion resistance or handling of flammable gases.
- standard cost for die and thickness calibration devices
- standard equipment to cut/finish/package the foams

[10] Note: all costs associated with the engineering design and construction of miniplant-related equipment have been paid with funds other than those received from DOE and are not part of Dow's Cost Share.
[11] S. Costeux, D. Foether, "Continuous extrusion of nanocellular foams", 12^{th} International FOAMS Conference proceedings (2014)

- standard overheads for piping, installations etc.

The outcome pointed to a capital cost for a new foam line that is similar (within 40%) to a new extruded polystyrene foam line. The decision was made not to look for a more accurate estimate at this stage, due to uncertainty with the process. Economic modeling of the product cost was found to be mostly dependent upon polymer cost, which directly relates to porosity. Approaching porosities of 90% or higher would provide a very interesting cost position.

First extruded nanofoams

Dow demonstrated for the first time that nanofoams can be produced in a continuous extrusion process. The homogeneous foams have 300nm cells and 75% porosity. A patent was filed to protect this process.
However, this is still short of the 100 nm target set for optimal insulation foams.

Outcome of the Miniplant experimentation

The positive outcome is that for the first time, nanocellular foams were produced by continuous foam extrusion. The foams made have about 75% porosity, which is remarkable, and have homogeneous cells around 300 nm. While this is a significant breakthrough, it does not yet meet the product requirements for insulation. Furthermore, foam cross-sections are very small (around 1 cm^2 or less), thus unsuitable for any property testing.

The initial plan was to scale-up the approach to 50 lbs/hr. As a result of the difficulties in reducing cell size, a change of strategy was needed. The review of various options was carried out as part of the Risk Assessment review (Task 3.3).

Subtask 3.3 – Risk assessment

Updated technical risk assessment

Based on the previous results, a review of the technical risks and abatement plans with Dow Building Solutions technical management and staff was completed.

Environmental / health — No significant risk was uncovered. The product is expected to be environmentally friendly, recyclable and overall reduce CO_2 emissions. The use of CO2 in the process is a negligible contributor to global warming, compared to standard blowing agents. CO2 could be recaptured, if needed. In case nanoparticles are needed as nucleators, they would be fully embedded in the polymer structure, and thus pose little risk compared to materials such as aerogels where free nanoparticles can be present.

Material performance — Conceptually, nanofoam can be produced with a range of styrenic copolymers and blends. We have demonstrated the ability to use lower thermal conductivity polymers and polymer formulations with adequate fire resistance. No show-stopper is expected, although achieving higher porosities may further increase chances of success from a cost and thermal insulation perspective.

Viable production process — Preliminary results of the continuous foaming work on the miniplant point to a potential risk that extrusion foaming may not be able to provide a pathway to produce large boards or panels with thick cross-section and optimum cell size. Yet, the evaluation done at the miniplant may be misleading due to low output rates, which result in lower pressure drop rate in the die. This risk was considered high enough to justify not building the new pilot plant dedicated to nanofoam production before ensuring that meeting the target cell size was possible by direct extrusion foaming.

The following abatement plan was put in place:

- Instead of building a new pilot line at 50-100 lbs/hr, Dow would retrofit an existing pilot line able to produce XPS at 30-50 lbs/hr. The cost is a fraction of that for a new line, and would help determine whether higher output rates can resolve the cell size/cross section issue.
- Since Task 4 will require prototypes for property testing, the decision was made to design a semi-continuous process, consisting in a foam molding system to be added at the end of either the miniplant or the pilot plant. This equipment will be fed with the polymer-gas mixture from the foam line, the mixture will fill a mold in which it will be conditioned. Foaming will be controlled by parameters such as the mold opening speed, in order to make foam panel prototypes of minimal dimensions for property testing.

Design teams were assigned the task to engineer both the retrofit equipment for the pilot line, and the panel molding equipment. Dow decided to support all the engineering design and construction costs outside of the funding assigned to the project. Evaluation of the equipment will be part of Task 4, where feasibility of a viable continuous or semi-continuous production process will be studied.

Market risk assessment

An objective for this task is to assess the attractiveness of key applications identified during the VOC exercise, and to determine which business strategy offers the best chance of commercial success.

The “Real-Win-Worth” methodology, which is used within Dow to assess new product opportunity. It was applied to the following potential markets for a sustainable, high performance insulation with a stable R-value, previously identified in Subtask 2.2.

- Green building (zero-energy homes): niche market today, growing number of builders looking for materials going beyond current code requirements. Dow is building relationship with these builders to identify potential future partners.
- Continuous insulation (residential and commercial), structural insulated panels, retrofit wall systems. Successful commercialization of these markets will require adoption of 2012 IECC building code for residential construction and the ASHRAE 90.1 2010 code for commercial construction.
- Walk-in coolers and refrigerated trucks, This non-building envelope applications has a lower barrier to entry in the market and will accept higher price than residential and commercial construction due to the need for higher insulation in a reduced space. This would allow Dow to start paying for the R&D investment, to work toward assessing long-term performance & durability of nanofoams while reducing costs sufficiently to meet construction targets.

A new market segment, EIFS (Exterior Insulation and Finish System), was identified by our marketing partners as a growing market segment which could become the greatest potential for a high R-value insulation product. The current US EIFS market segment is valued at approximately $212MM and 200 MM sq ft of product with 6% average annual growth. Dow already has experience with this technology in Europe.

- Mechanical and physical property requirements for the insulation component as well as the final EIFS product have been identified. Key additional requirements for these products besides thermal performance and cost are mechanical strength (vertical compressive strength), resistance to moisture, water-vapor transmission rate and fire performance.
- A channel to market analysis was completed. Dow has existing ties to top EIFS manufacturers, which can be leveraged to market a higher R-value insulation product for their EIFS. Dow's reputation for being a building science leader can also be used to influence leading architects who ultimately make decisions on product choices in their building designs.

Leading application identified

Dow Building Solutions marketing experts recommended EIFS as a primary construction market to launch a future nanofoam product. This is a growing market where the compressive strength of nanofoam will be an advantage.

The adoption of the 2012 IECC building code will mandate the use of a continuous insulation with an increase in building efficiency of 30%. Products such as EIFS, with the dual functionalities of providing insulation and aesthetics, will strongly benefit from the 2012 code update. However, code changes have not been able to capture property owner's attention as architects/consultants are the main group following code changes and their implications for construction. Initiatives from the U.S. DOE to accelerate code adoption will support the commercialization of superior technologies.

Outcome of the Risk assessment

Initial assumptions are for the most part still valid, and do not require a major change in the program strategy.

Market attractiveness and commercialization success are very dependent on global economics, and adoption in the building sector is generally slow, but the current softness in the B&C sector together with the imminence of new regulations may actually help trigger a mindset change that could benefit sustainable high-performance insulation products.

Nanofoam technology development still has to overcome significant challenges, in particular the scale-up to large panel production. Abatement plans are in place to enable success while managing research expenses.

Subtask 3.4 – Intellectual property

The objective of this task is to generate an IP landscape for the technologies used in this project. An extensive patent search on micro- and nanocellular foam composition and processes was conducted. Over 2000 patents were screened and a list of the 50 most relevant patents was established. No blocking prior art was identified thus far. We subscribed to a monthly patent digest dedicated to foam technologies to stay abreast of competitive activity in the future. Patent watches were also put in place to monitor progress towards grant of competitive patent applications most closely related to our technology. This IP landscape was continually monitored for new patents in this technology space.

Task 4: Feasibility of (Semi-)Continuous Production

Goal: The first objective of this task was to develop a pilot process to make insulation prototypes on which foam properties can be tested and compared with requirements for the most promising applications. The second objective was to analyze all the lessons learned during the program and propose a strategy to bring nanocellular insulation form technology to market.

Original hypotheses: during project planning, the expectation was that continuous production of 100 nm cell foams would have been proven at the miniplant scale, and that this last phase would focus on the scale-up to new dedicated pilot line capable of producing foam at 50-100 lbs/hr with a process that could ultimately be scaled-up to commercial scale (>1,000 lbs/hr).[12] The properties of the prototypes from the pilot scale would then be used to decide how to commercialize the technology in the future.

Subtask 4.1 – Build (semi-)continuous process

As explained in Section 3.3, the decision was made to assess two processes in parallel.

Continuous pilot process

The team elected not to invest initially in a new dedicated pilot line capable of producing foam at 50-100 lbs/hr based on the results of miniplant experimentation, which only demonstrated 300 nm cell foams (vs the 100 nm target for insulation). However, an existing line (30-50 lbs/hr) became available for modification, which significantly reduces risk and capital investment. The decision was made to focus the engineering design task on modifying this pilot extrusion foaming line, to demonstrate scalability of the process at about 50lbs/hr (from 2-5 lbs/hr for the current miniplant experimentation).

Experimentation on the modified miniplant highlighted the need to improve CO_2 feed system to allow higher gas loadings, to improve the cooling capability and the ability to dissolve the gas. Additionally, the existing pilot line does not have sufficient downstream pressure rating to handle the full range of pressures observed in the miniplant during start-up and shutdown. These modifications need to be made without permanently affecting the ability of the pilot line to produce standard XPS foams, as it is shared with other Dow researchers.

The most effective way to retrofit the existing pilot line was a parallel design, shown in Figure 13. A divert valve was added to the existing line, allowing to select flow toward the "old" line, or towards the new downstream section designed specifically for nanofoam production. This new section has its independent temperature control and pressure monitoring. The CO_2 feed system was also modified with a pressure booster, allowing introduction of CO_2 at high loading even when the pressure in the line is increased in its "nanofoam configuration". The die can be shared between the 2 downstream branches.

[12] Note that because of time, cost and EH&S requirements, the scale-up to commercial size was beyond the initial scope of the proposed project.

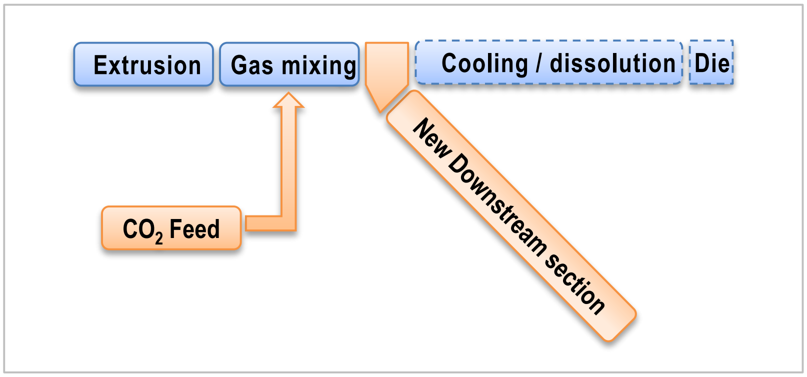


Figure 13. Modified pilot line to evaluate nanofoam production, including divert valve, a side-arm downstream section, and a continuous CO_2 feed system.

Semi-continuous process

The design team for a semi-continuous, mold injection foaming process consulted with external vendors to select the optimum technology that will meet the high pressure and fast mold opening requirements for nanofoam panel production. The selected design was based on a custom press, with a thru-way for the polymer/CO_2 mixture produced by the foam line and an elaborate hydraulic system allowing very fast opening of the mold and activation of valves directing the flow toward the mold. Due to very high pressures (up to 5000 psi) and the need to produce 6”x6”panels, equipment had to be sized to withstand forces in excess of 250,000 lbf. A sophisticated computer-controlled programming scheme actuates all the valves, controls all displacement and monitors speed, pressures and temperatures. The equipment, shown in Figure 14, was built, delivered and installed at the end of 2012.

Figure 14. Picture of the “Mold-Press”, designed for foam panel production. The hydraulic system is shown on the left, and the mechanical molding system on the right. The equipment is 12 feet high.

Several months were necessary for the vendor to optimize the programming of the Mold-Press and allow for smooth operation, before attempting to produce foam panels nanofoam panels. Because of the radical new design of this equipment and the forces involved during operation, several equipment modifications were required to improve performance and part reliability. Overall, implementation occurred 6-months later than initially planned. Most of these delays were anticipated in time to request modification of the project management plan, and manage timeline for milestones accordingly.

After the completion of these modifications, the first large panels (6x6") were produced in March 2013, thus completing the implementation phase for the Mold-Press. Although these panels met the minimum dimensions required for mechanical and thermal testing, they had irregular shape and were not uniformly flat, as shown on the left in Figure 15.

Since sample flatness is an absolute requirement for accurate property testing, in particular for R-value, optimization work continued through the remainder of the program to optimize process conditions to improve the sample quality as part of Subtask 4.2.

Subtask 4.2 – Produce and test small prototypes

Initial evaluation of the continuous process indicated that the cooler design would need to be further modified to improve the residence time. The focus was placed on prototype production with the Mold Press and investigation determined that uneven flow and issues with pressure control were causing sample distortion. This required a complete redesign of the mold filling gate and significant modification of the hydraulic control system. This was completed within two months.

Significant progress was made in making improved samples, despite difficulties with equipment operation. Changes in the control system allowed new molding protocols that made it possible to constrain the foam during expansion. Resulting foams were significantly improved over what was achieved initially. Figure 15 (on the right) shows the latest 6" panels with controlled dimensions and parallel surfaces.

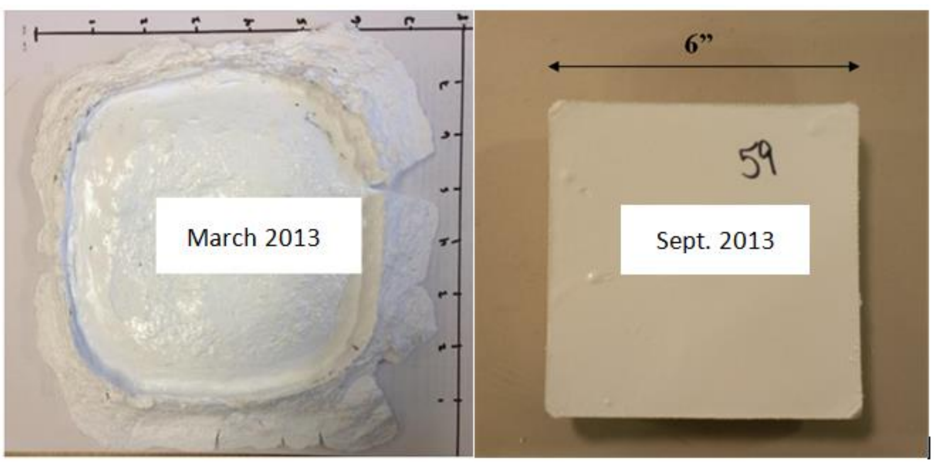


Figure 15. Panel produced by semi-continuous process prior to modification (left) and after modification (right)

Outcome of the Prototype production work

Optimization work was carried out before the end of the program (Sept 30th, 3013) to attempt to meet the criteria of Milestone IV. In that limited time, foams with up to 75% porosity and cell size as low as 500 nm were produced.

The concept of the Mold-Press is valuable, considering the recent commercialization by equipment manufacturers of injection molding machine with sufficient clamping to withstand forces needed to make similar foam panels. Such a process would avoid foreseen issues with continuous nanofoam extrusion, namely the difficulty to make large cross-sections. Dow plans on completing the optimization work in the future, and gather data necessary to file a patent[13] and attempt to match the target foam cell size and porosity, as was achieved by batch foaming.

Subtask 4.3 – Commercialization strategy

Marketing strategy

Dow's Marketing strategy cannot be made public at this time.

Manufacturing strategy

Dow's Manufacturing strategy cannot be made public at this time.

IP strategy

The competitive patent landscape has continuously been monitored throughout the project. Six patent applications have been filed by Dow as part of this DOE funded project, in addition to the three applications filed before the project starting date. Three patent applications were published in 2013-14. Three applications are anticipated to be published in 2015.

We also determined that the cell size/porosity targets needed to be validated for various polymer materials and foam cell structures in order to achieve the insulation performance. Through a relationship with the University of Valladolid (Spain), who has unique capabilities to characterize foam structure and analyze heat transfer mechanisms, a number of materials and foams were tested to assess the suitability of the techniques for nanofoams. The work was completed, and the main outcome was the confirmation of the Knudsen effect in nanocellular foams.

SubTask 4.4 – Design options for large scale continuous process

Dow's plan for the scale-up of the continuous or semi-continuous process for nanofoams cannot be made public at this time.

[13] Note: a patent was filed in May 2014

Documentation, Partnerships and Technologies Developed under the Award

During the course of the project, Dow has ensured intellectual property was protected by filing patents whenever possible. Once patent applications were published, the results were shared with broader scientific audiences through publications and conference presentations. This in turn triggered exchanges and collaborations with academic group or institutes with knowledge or capabilities that may help Dow continue towards commercialization of the technology in the future.

Inventions/Patent Applications:

- WO 2013048761 - Polymeric nanofoam from polymer blends (filed Sept 2011)
- WO 2014052032A1 – Additives for nanocellular thermoplastic foam and method for making the same (filed Sept 2012)
- WO 2014078215 - Polyhedral oligomeric silsequioxane grafted polymer in nanofoam (filed Nov 2012)
- 75491 - Flame-retardant copolymers and polymer foams made therefrom (filed Dec 2013)
- 76092 - Nanocellular foam with solid flame retardant (filed Mar 2014)
- 76114 - Mold process for making nanofoam (filed May 2014)

Publications:

- I. Khan, D. Adrian and S. Costeux. “A model to predict the cell density and cell size distribution in nano-cellular foams”, submitted to *Chemical Engineering Science* journal, Mar. 2015
- S. Costeux and D. Foether, “Continuous Extrusion of Nanocellular Foams”, *SPE ANTEC Conference proceedings* (2015)
- K. A. Patankar et al., “Evaluation of Nitrogen as a Co-Blowing Agent in Nanocellular Foam”, *SPE ANTEC Conference proceedings* (2015)
- S. Costeux and D. Foether, “Continuous extrusion of nanocellular foams”, *12th International FOAMS Conference proceedings* (2014)
- S. Costeux, I. Khan et al. “Experimental study and modeling of nanofoams formation from single phase acrylic copolymers “, *J. Cellular Plastics*, **51**, 197-221 (2015)
- S. Costeux, S. Bunker and H. Jeon, "Homogeneous nanocellular foams from styrenic-acrylic polymer blends ", *J. Materials Research*, **28**, 2351-2365 (2013).
- S. Costeux, S. Bunker, H. Jeon, “Homogeneous nanofoams from synergistic blends”, *11th International FOAMS Conference proceedings* (2013)
- Khan, S. Costeux *et al*., “Numerical Studies of Nucleation and Bubble Growth in Thermoplastic Foams at high Nucleation Rates”, *11th International FOAMS Conference proceedings* (2013)
- S. Costeux, H. Jeon, *et al*., “Nanocellular Foams From Acrylic Polymers: Experiments And Modeling”, *10th International FOAMS Conference proceedings* (2012)

Presentations:

- S. Costeux, “Continuous Extrusion of Nanocellular Foams”, Society of Plastic Engineers ANTEC Conference, Mar. 22-25 2015 (Orlando, FL).
- K. A. Patankar et al., “Evaluation of Nitrogen as a Co-Blowing Agent in Nanocellular Foam”, Society of Plastic Engineers ANTEC Conference, Mar. 22-25 2015 (Orlando, FL).

- S. Costeux, "Continuous extrusion of nanocellular foams", FOAMS 2014 Conference, Sept. 11-12 2014 (Iselin, NJ).
- S. Costeux, "Nanocellular Foams", Invited Webinar, Society of Plastics Engineers, Aug. 12, 2014.
- S. Costeux, "Polymeric nanocellular foams for thermal insulation – Challenges and Promises", Invited Presentation, TechConnect World Innovation Conference & Expo, June 15-19 2014 (Washington DC)
- S. Costeux, "Homogeneous nanofoams from synergistic blends", FOAMS 2013 Conference, Sept. 11-12 2013 (Seattle, WA). [Best Paper Award]
- I. Khan, "Numerical Studies of Nucleation and Bubble Growth in Thermoplastic Foams at high Nucleation Rates", FOAMS 2013 Conference, Sept. 11-12 2013 (Seattle, WA)
- J. Moore, "Evaluating Nitrogen As a Co-Blowing Agent for CO_2-Blown Polymeric Nanofoams", AIChE Annual Meeting, Nov. 6 2013 (San Francisco, CA)
- I. Khan, "Using Improved Equation of State to Model Simultaneous Nucleation and Bubble Growth in Thermoplastic Foams", 66th American Physical Society DFD Meeting, Nov. 24-26 2013 (Pittsburgh, PA)
- S. Costeux, "Nanocellular Foams From Acrylic Polymers: Experiments And Modeling", FOAMS 2013 Conference, Sept. 10-11 2012 (Barcelona, Spain) [Best Paper Award]
- I. Khan, "Numerical Modeling of Nanocellular Foams Using Classical Nucleation Theory and Influence Volume Approach", 65th American Physical Society DFD Meeting, Nov. 18–20 2012 (San Diego, CA)

Networks or collaborations fostered:

- Collaboration with University of Valladolid (Spain): during FOAMS 2012 conference, early results on nanocellular foams were presented by Dow. The group of Prof. Rodriguez-Perez at U. Valladolid also presented results on high density nano-cellular foams. Discussion led to a collaboration to assess techniques to characterize energy transfer in nanocellular foams.
- Baverstam Inc. in Boston, MA was selected to provide an early market study on applications for nanocellular foams.
- An update on the progress of the government-funded program was presented to personnel of Oak Ridge National Lab during a visit to Dow. Discussions are on-going regarding collaboration on foam process development.

Technologies/Techniques developed:

Several new proprietary techniques were developed by Dow for :

- the production and testing of nanocellular foams. This includes the design of a continuous extrusion line, a semi-continuous injection-molding system.
- the characterization of properties of polymer/CO_2 systems. This includes a high pressure Quartz Crystal Microbalance for solubility and glass transition temperature measurements, and an Infrared technique to measure CO_2 diffusion in polymers.
- The project partly funded the development of a model to predict the thermodynamic properties of polymer blends with CO_2. This was integrated in the commercial package VLXE-Blend, commercialized by VLXE ApS in Denmark.

Other products, such as data or databases, physical collections, audio or video, software

Non applicable

Conclusions

The objective of this project was to explore and potentially develop high performing insulation with increased R/inch and low impact on climate change that would help design highly insulating building envelope systems with more durable performance and lower overall system cost than envelopes with equivalent performance made with materials available today. The proposed technical approach relied on insulation foams with nanoscale pores in which heat transfer will be decreased.

To this end, Dow successfully invented and developed methods and formulations to produce foams with 100 nm cells and 80% porosity by batch foaming at the laboratory scale. This involved the development of new analytical techniques, and contributed to advancing the understanding of how cells nucleate, expand and stabilize at the nanoscale. Lab capability to make measurements of the gas conductivity on small nanofoam specimen confirmed quantitatively the benefit of nanoscale cells (Knudsen effect) to increase insulation value. Dow's collaborators at the University of Valladolid (Spain) independently confirmed these results. This validates one of the key original hypotheses of the program.

In order to bring this technology closer to a viable semi-continuous/continuous process, the project team modified an existing continuous extrusion foaming process as well as designed and built a custom system to produce 6"x6" foam panels. Dow demonstrated for the first time that nanofoams can be produced in a continuous extrusion process. The homogeneous foams have 300 nm cells and 75% porosity and a patent was filed to protect this process. The semi-continuous process produced 6"x 6" foam panels with sub-micron cells and similar porosity; yet further optimization would be needed to achieve smaller cell size with this technology.

In parallel with the technology development, effort was directed to the determination of most promising applications for nanocellular insulation foam. An external company conducted a Voice of Customer (VOC) and confirmed that demand for high-R value product will rise due to building code increased requirements in the near future. Despite this need, acceptance may be slow due to building industry being very conservative and often reluctant towards adopting novel products. Partnerships with green builders, initial launches in niche markets, and efforts to drive cost down will help acceptance in residential and commercial retrofit and new construction.

During the course of the project, Dow has ensured intellectual property was protected by filing patents whenever possible. Once patent applications were published, the results were shared with broader scientific audiences through publications and conference presentations. This in turn triggered exchanges and collaborations with academic group or institutes with knowledge or capabilities that may help Dow continue towards commercialization of the technology in the future. The work from this program resulted in 6 patent applications filed, 9 publications and 11 technical presentations at scientific conferences, and won 2 best paper awards.