

Polymer-Reinforced, Nonbrittle, Lightweight, Cryogenic Insulation for Reduced Life-Cycle Costs

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InnoSense LLC has developed a cryogenic insulation (CryoPore™) for use in NASA fuel storage applications. Our project entailed the incorporation of aerogel additives into polyurethane base foams. Aerogels offer much improved insulative properties that, in turn, reduce the boil off rate of expensive NASA fuels. The highly porous structure of aerogels results in significantly lower thermal conductivity. Therefore, incorporating a material of such low thermal conductivity into polyurethane foams will result in a volumetric reduction of thermal conductivity. To compensate for a variety of foaming variations due to additive incorporation, we integrated green blowing agents to improve foam expansion which ultimately led to improved aerogel distribution. The cure and rise time of the foam were modulated by these additives to generate low density foams with a fine cell structure. Such finer cell structures further improved the overall thermal and mechanical properties of the system. We have developed a pour system that can easily be integrated into a wide variety of insulation applications including fuel tanks and refrigeration. Here we present the ability to control cell size, and improved insulation properties through the addition of aerogel additives and additional blowing agents. Our CryoPore™ insulation has been formulated for large-scale industrial spray and pour applications. This project was performed with support from the NASA SBIR program (Contract number NNX11CB53C).

Nomenclature

<i>CIEMS</i>	=	California Institute of Electronics and Materials Science
<i>CryoPore™</i>	=	InnoSense LLC's cryogenic insulation
<i>ET</i>	=	External fuel tanks
<i>ISL</i>	=	InnoSense LLC
<i>MA&I</i>	=	Maleic anhydride and 1-methylimidazole
<i>Nanogel</i>	=	Cabot Corporation P100 Nanogel
<i>Part A</i>	=	diisocyanate mixture
<i>Part B</i>	=	polyol blend
<i>SOFI</i>	=	Spray-on foam insulation
<i>X-30</i>	=	Tap Plastics' two-part rigid polyurethane foam

A. Introduction

NASA has identified passive insulation as a high priority. The main purpose of passive insulation is to prevent the excessive loss of valuable fuel due to boil-off while the spacecraft is at the launch site and/or in flight. We have previously demonstrated to NASA the use of aerogels to decrease the thermal conductivity of existing closed- and open-cell polyurethane foams by at least 10%. Processing conditions for this insulating foam need to be refined to achieve our goals of cost-effective manufacturing.

Since NASA missions are expanding to further reaches of space including Mars and other destinations, increased quantities of cryogenic propellants will be needed. However, cryogenic propellants (e.g., liquid hydrogen and oxygen) currently comprise up to one half of the total weight of an earth-launched spacecraft. Thus, to maintain the fuel quantities needed for survival without exceeding safe storage/weight parameters, alternative approaches to fuel storage will be required. One feasible approach to achieving long duration missions is space-based refueling.

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This approach will require stable technologies to maintain suitable storage environments and minimize evaporative losses. The insulating ability to transition from a variety of diverse environments is also an important requirement. As the space-based fuel tank travels through various planetary and space environments, improved insulation must be able to withstand the rigors of varying temperatures and pressures.¹

For NASA component acceptance, the insulation must at a minimum exhibit excellent insulative properties (low k-value or high R-value, and low density), and meet standards for mechanical robustness in extreme temperatures and environments. An immediate use for a spray-on foam insulation (SOFI) is to insulate external fuel tanks (ET). These tanks carry massive amounts of liquid hydrogen (LH₂) to fuel the spacecraft. Although current SOFI options insulate the ET well, they do not transition well to low pressure environments. Many SOFIs are polyurethane-based foams that have a tendency to absorb water vapor, which adds unwanted weight to the spacecraft during liftoff. This moisture intake can improve the thermal resistance of the polymer foam, and reduce charring from the extreme heat produced during launch; however, the added weight increases fuel requirements for liftoff. Moreover, these insulations must also adhere to fuel tanks and be able to withstand stresses induced by refueling and mission operation. As with many polyurethanes, these foams tend to degrade with prolonged exposure to UV radiation.^{2,3,4,5}

This paper discusses the results of a study conducted under NASA Contract #NNX11CB53C in which InnoSense LLC (ISL) researched the use of hydrophobic aerogels as additives to standard polyurethane insulation. The resulting polyurethane foam will intrinsically provide a heat conduction barrier because its high closed cell content inhibits conductive heat transfer by limiting convection to the individual cells and other voids formed within the foam structure itself. With the addition of aerogels, the closed cell structure becomes finer (due to the nanoscopic pores present in the aerogel itself) and thus provides better insulation performance. Aerogels have been developed for, and subsequently demonstrated, low thermal conductivity (k-value).^{6,7,8} By incorporating a low k-value material in a bulk polyurethane foam, we have demonstrated enhanced insulating properties. Thus, volumetrically, the addition of aerogels into a foam network will decrease the thermal conductivity. The thermal conductivity of composite foam would be expected to be a volume average of aerogel materials and foams.

The use of hydrophobically functionalized aerogels reduces the inherent water ingress into the foam materials via a reduction in wetting that minimizes the capillary action of moisture ingress. This is ultimately expected to aid in the reduction of both vapor and liquid water in the foam system. Further investigation into this effect will be investigated.

Foam brittleness can be modulated by controlling the polymeric rheology. The formation of a flexible network may also be possible through the use of addition materials. Early results have indicated some improvement of material flexibility using a three-point bend test.

A variety of blowing agents have been added to polyurethane foams. The Department of Energy has patented a method to generate epoxy foams using the reaction of maleic anhydride and 1-methylimidazole (MA&I) to generate carbon dioxide as a blowing agent.⁹ By integrating these reactants into an existing two-part polyurethane foam, it is possible to generate a low density closed cell foam. This foam also exhibits lower k-values than base polyurethane foams using traditional blowing agents. Moreover, greener blowing agents are attractive because they limit the environmental impact of large scale foam insulation application.

B. Experimental Formulation

1. X-30 Polyurethane with Silica Aerogel Formulation

Silicate aerogel-impregnated polyurethane foams were fabricated by mixing silicate aerogels directly into the polymer matrix. In our research, we formulated a two-part polyurethane system that modifies commercially available polyurethane foam and aerogels: X-30 two-part rigid polyurethane foam (TAP Plastics)¹⁰ and P100 Nanogel (Cabot Corporation). X-30 is a pourable formulation similar to existing spray-on ET polyurethane foam insulation. Cabot Nanogels are currently used by NASA for various forms of insulation including extrudable plastic “foam” structures.

Two-part polyurethane foams consist of a diisocyanate mixture (Part A) and a polyol blend (Part B). For TAP Plastics X-30, the two parts are mixed in a 1:1 ratio to generate a rigid, rapid rise foam commonly used as Energy Star appliance insulation. For our formulation, Cabot Nanogel P100 aerogel particles (diameter ~2 mm)¹¹ were folded into Part B at mass ratios of 1:20 and 1:10 (aerogel:Part B) with a commercial Sunbeam Mixmaster. This blend was then gently mixed together for up to 20 seconds with the Sunbeam Mixmaster at a low speed setting (few hundred rpm) to ensure the distribution of aerogels throughout the liquid Part B phase. Low rpm mixing allows both the aerogel and the polyol to mix while preventing the aerogel from breaking. Part A was then added and gently mixed in the Mixmaster for an additional 30 seconds.

Once mixed, the polyurethane formulation was poured into a custom made 12 in. × 12 in. high-density polyethylene mold lined with wax paper. In this configuration, the polyurethane mixture rose and cured; it was then

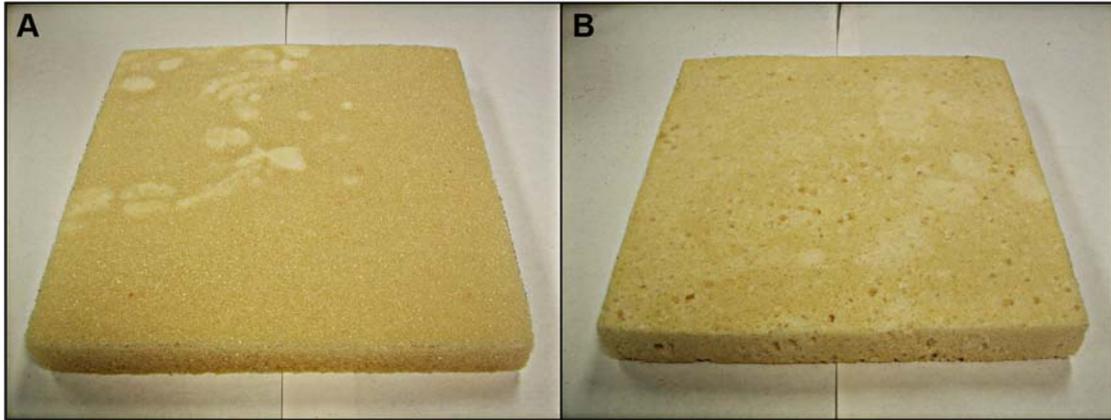


Figure 1. 8 in. x 8 in. samples. A) Bare X-30 and B) 1:20 X-30.

allowed to fully cure for 24 hours before cutting blocks for testing. Images of the 8 in. × 8 in. samples are shown in Fig. 1. The resulting structure shows a predominantly closed cell foam with a finer cell structure than foams without aerogel additives. Pock marks are observed in the aerogel sample. This could be due to the foaming process. Efforts to mitigate will be investigated. The foaming formulation will require further refinement to reduce the occurrence of these pock marks. Refinements will be focused on the use of flow modifiers to control the overall material rheology.

2. Maleic Anhydride X-30 Polyurethane with Silica Aerogel Formulations

A method used to improve the rise characteristics of the aerogel-polyurethane foam had maleic anhydride and 1-methylimidazole (MA&I) introduced into the X-30 polyurethane matrix. The resulting foam exhibited a much lower density than the base X-30 foams. Using this method, which was reported at Sandia National Laboratory in US

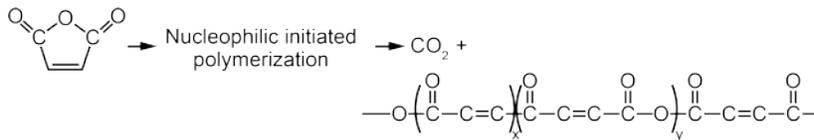


Figure 2. Schematic for the production of epoxy resins.

Patent # US 8,003,730 B1, we manipulated the reaction of maleic anhydride combined with a 1-methylimidazole catalyst to generate carbon dioxide as a blowing agent for foam. Originally derived for epoxy foams, the reaction scheme in Fig. 2 shows how an epoxide precursor reacts to form epoxy foam. We used two-part X-30 polyurethane foam kits.⁹ We are currently investigating the possible chemical mechanisms for the imidazole reaction. In our case, the maleic anhydride-imidazole reaction generated carbon dioxide to form a closed cell rigid polyurethane foam exhibiting lower density and ultimately improved thermal properties. In our formulation, the 1-methylimidazole is added to Part A, and the maleic anhydride is added to Part B. **The production of carbon dioxide resulted in reduced density by expanding the foam and thus “lifting” the aerogel during the foaming process.**

A small amount of silicone surfactant, Shin-Etsu KF-105, was introduced to Part B and mixed for 30 seconds. These silicone-based surfactants are used to help stabilize the foam cell structure. Therefore, well-defined cell structures may be fabricated. MA&I X-30 sample processing was very similar to X-30 sample processing. Modifications were introduced to the previously described process in order to ensure the uniformity and reactivity of the added blowing agents. The 1-methylimidazole was added into Part A and hand stirred until completely dissolved. The powder form of maleic anhydride was melted on a 70 °C hot plate controlled with an electric thermostat. Next, the maleic anhydride was added into Part B following the addition of aerogels and the KF-105. The Part A and Part B mixtures were mixed using the Sunbeam mixer for 20 seconds. After sufficient mixing, the foam was poured into the high density polyethylene mold and immediately placed in a 70 °C oven at ambient pressure for three hours. Maleic anhydride and 1-methylimidazole thermally activated to generate carbon dioxide, which ultimately decreased the density of the polyurethane network. After the samples were removed from the oven, they were cooled and aged at room temperature for 24 hours before being cut into test samples. Figure 3 shows the cut 8 in. x 8 in. MA&I X-30 samples.

In contrast to the bare X-30 samples, MA&I polyurethane foams are red in color, exhibit lower densities and high closed cell content. The images in Fig. 3 show the visible difference in foam cell size and texture between the bare X-30 and MA&I 1:20 X-30 samples. The introduction of aerogel particles again provides a nucleation point

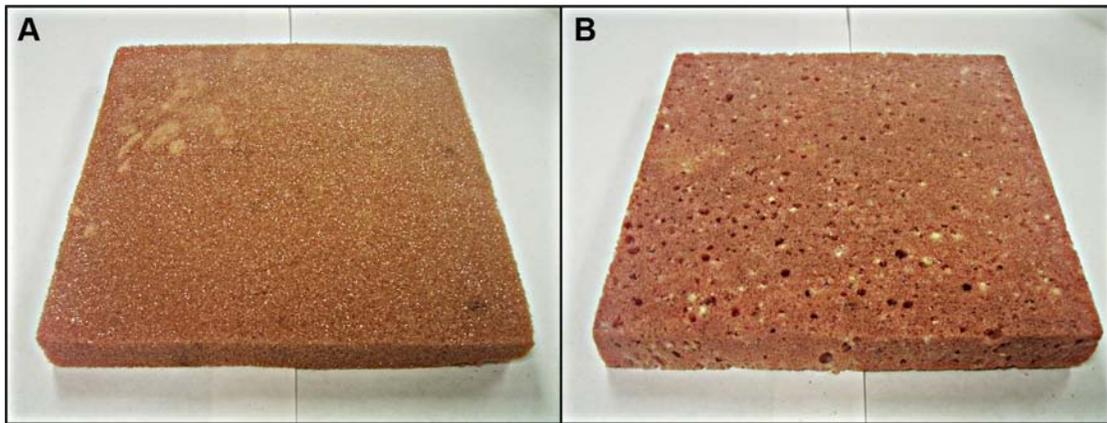


Figure 3. 8 in. x 8 in. samples. A) Bare X-30 and B) 1:20 X-30 with MA&I.

Table 1. Viscosity of Precursor Material Averaged for Five Samples

Sample	Viscosity (cP)	Std Dev (cP)
Part A	362	9
Part B	469	4
Part B with 1:20 Aerogel	2920	102

that disrupts foam generating behavior. Aerogels are distributed throughout the foam as seen in the right hand side image of Fig. 3. The use of the MA&I additive provides a method to distribute aerogels throughout the foam

while reducing the foam density. Some pock marks are observable. Efforts of mitigation will be investigated. In particular, further refinements are required to develop even rise time and foaming rheology.

For spray applications, the viscosity of the foam must be taken into account in order to prevent spray equipment from becoming clogged and/or inoperable. Viscosity measurements of the independent Part A and Part B of X-30 polyurethane were obtained using a Brookfield HB series viscometer at 100 rpm. The viscosity of the Part B with added Cabot Nanogel P100 for a 1:20 foam sample was measured in the same fashion. Table 1 shows the average results obtained from five measurements for each sample. When aerogels are added to Part B, the viscosity increases. Through discussions and subsequent feasibility testing at a spray facility (Diamond Liners of Santa Fe Springs, CA) using a Graco foam sprayer, we concluded that the viscous aerogel-Part B formulations are within range of use for the spray equipment. Foams with low density and fine structure were formed using the spray unit with both the base X-30 and MA&I formulations. Structurally, samples with aerogels exhibited slightly smaller cell size, while the MA&I samples exhibited lower density.

C. Sample Evaluation

1. Density

The density of the foam samples was measured using foam 1 in. x 1 in. cubes. The dimensions were precisely measured using a pair of digital calipers. Samples were measured at least three times for statistical relevance. Each sample was then weighed on a Denver Instrument precision balance. The apparent volumetric density was then calculated. In general, the density is increased with aerogel additives; however, when **MA&I is added, the density of aerogel-containing foam samples is comparable to the standard bare X-30 samples.**

The effect of including aerogel only in the polyurethane matrix was compared to the effect of the addition of aerogel and the MA&I blowing agent on the density of the sample. Figure 4 shows the effect of aerogel on the density of X-30 samples and MA&I X-30 samples respectively. All the data were gathered from three cube samples taken from multiple batches to ensure a representative data set.

Although the addition of aerogel increased the density of the polyurethane matrix, density was markedly decreased when MA&I was also added. The MA&I X-30 foam exhibited a lower density increase than the regular X-30 samples when aerogels are incorporated into the polyurethane matrix. The X-30 samples show more than a 50% density increase from the bare to the 1:10 aerogel loading. In comparison, the MA&I X-30 samples exhibit only a 20% increase. **The results showed that density is successfully controlled using the MA&I blowing agent system.**

The MA&I system offers a method for improved rise and foam stabilization. The addition of aerogels affects the rise of the foam itself, as evident from volumetric density measurements. Therefore, a more effective blowing agent

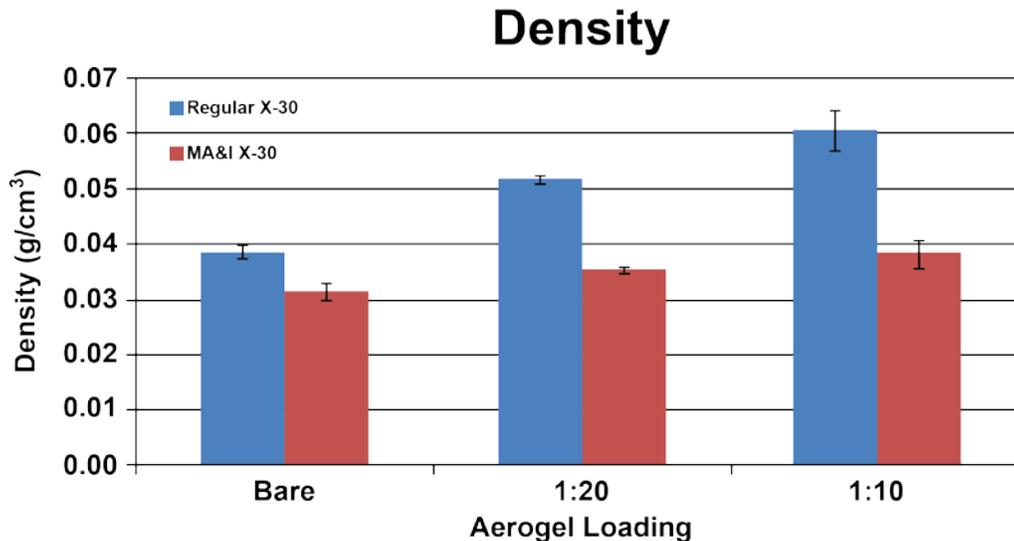


Figure 4. Density comparison of regular X-30 with MA&I X-30 polyurethane cubes.

is required to generate a low density foam. It should be noted that a silicone-based surfactant (Shin-Etsu KF-105) was added to the MA&I reaction mixture to stabilize the foam cellular structure. The resulting foam contains a closed cell structure that is excellent for insulation.

2. Cell Size Distribution

The cell size of the two-part polyurethane foams was reduced by introducing aerogel additives when samples were processed under identical conditions. The distribution shows the range of cell sizes for each type of sample and indicates the size distribution dependence on additives. The fine closed cells are expected to further reduce convective heat transfer, introduce void space, and improve insulating properties.

Optical microscopy indicated the production of finer cell structures with the addition of aerogels. In order to quantify these results, thin slices of the aerogel-polyurethane foam composite samples were cut using a sharp razor blade. Slices were taken from various samples and regions within each independent sample to eliminate experimental bias. Sliced foam cell samples were then imaged with an optical microscope at 40x. Images were uploaded to the ImageJ program for image processing. Using the ImageJ software, a scale was set on the images and precise distance measurements were made. Five distinct cells were measured from each image. The diameter of these cells was measured several times at different orientations and averaged for statistical relevance. Measurements were multiplied by a correction factor of 1.273 to account for the 3D size distribution of spheres in the 2D image.

Figure 5 shows the reduction of cell size in response to the addition of aerogel to the X-30 polyurethane matrix. The cells present in Bare X-30 are significantly larger than those present in the 1:20 X-30 when produced using identical processing methods. The cell size distribution data in Fig. 6 shows that the cell size of samples with aerogel

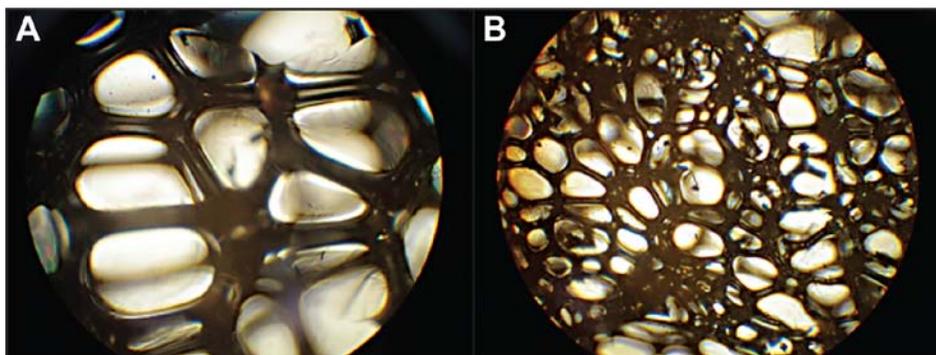


Figure 5. Cell size images of regular A) Bare X-30 and B) 1:20 X-30 at 40x magnification.

is narrower and peaks at a smaller cell size. The averages showed an approximate 30% decrease in cell size. **The inclusion of aerogel produced a finer cell structure for the foam insulation. This, combined with the nano-scale pore size of the aerogel will improve the insulation characteristics of the foam.**

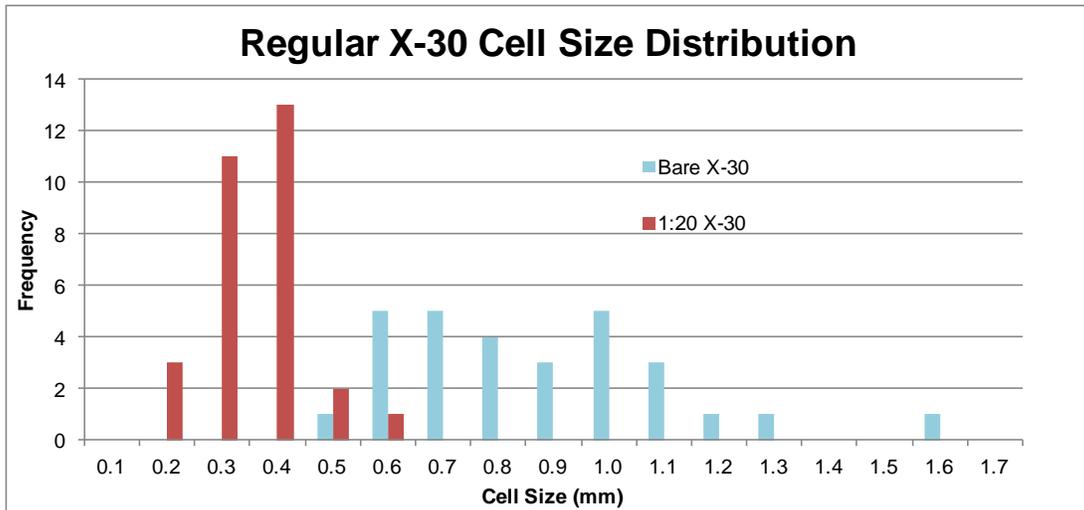


Figure 6. Cell size distribution of regular Bare X-30 and 1:20 X-30.

The cell size distribution data is shown in Fig. 6. As the foam is formed, nucleation occurs at the aerogel interface, thus a finer cell structure can be formed. It should also be noted that the apparent distribution of cell size is narrower for the aerogel-added sample. Foams with a narrow size distribution will provide improved insulation and a more even structure.

The cell size distributions for the MA&I X-30 foams were also analyzed following the same protocol as previously described. Figure 7 shows the optical microscope images of these samples at 40x. Here one can visibly observe the difference in cell size with the addition of aerogel. The cell-size distribution is shown in Fig. 8. The same protocol that was used for the bare X-30 samples was followed to analyze the MA&I samples. The observed images and distribution chart were similar to those obtained with the regular X-30 samples. Cell sizes measured for the MA&I foams were comparable to the regular X-30 samples. Figure 8 illustrates similar narrowing of the cell size distribution with the addition of aerogels to the polyurethane foam matrix.

Figures 5 and 7 show the formation of a fine cell structure, the result of the addition of aerogels. Moreover, the polymer filaments generating the foam exhibit a much finer diameter. These attributes may be a result of a controlled reaction through the addition of the aerogel. The heat of generation from the foaming process was also reduced with the addition of aerogel particles. This is an indication of reaction control due to the addition of fine particles to the two part reaction system.

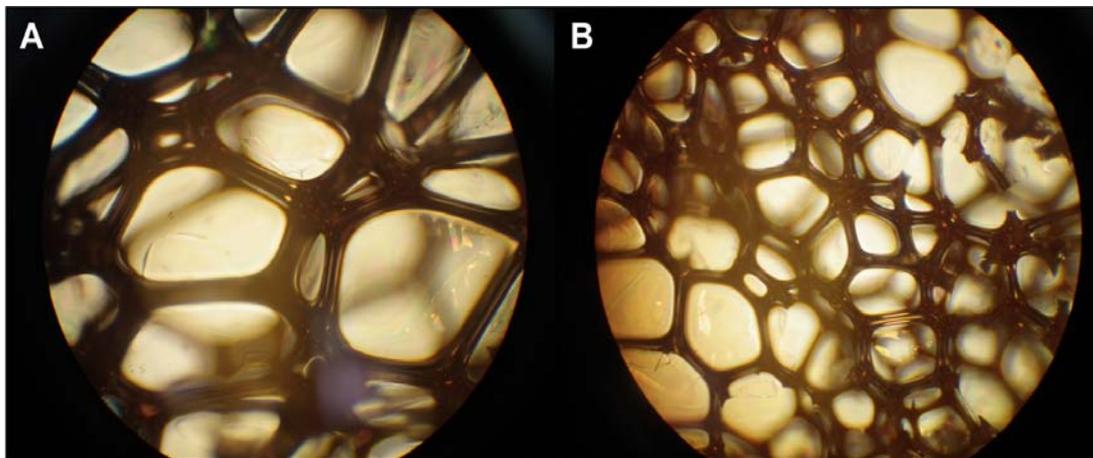


Figure 7. Cell size images of A) MA&I KF-105 Bare X-30 and B) 1:20 X-30 at 40x magnification.

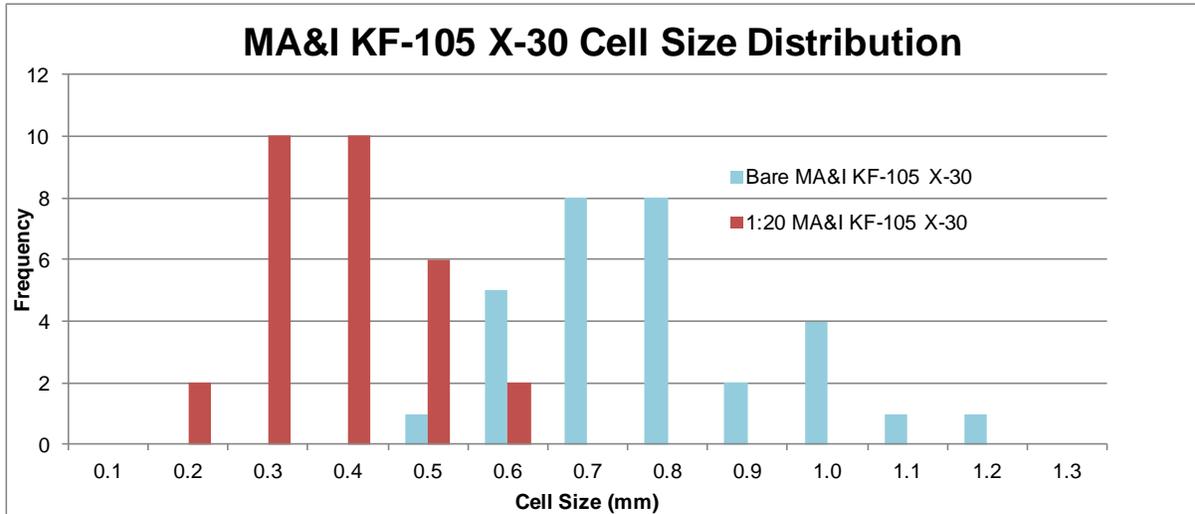


Figure 8. Cell size distribution of MA&I KF-105 Bare X-30 and 1:20 X-30.

3. Thermal Properties

A series of screening tests were performed to qualitatively identify the enhancement of insulation with the addition of aerogel particles. In-house testing was based on part of ASTM C177 for a guarded hot plate test. These screening tests were used to measure differences that could then be further refined and measured through the use of more accurate ASTM testing at external facilities.

The hot plate was used to test foam performance when measured in the same environment. For this test, 4 in. x 2.5 in. x 1 in. foam samples were placed in direct contact on top of an aluminum plate. The aluminum plate was fitted with two 1-ohm Vishay-Dale resistors to provide a constant resistance that would heat the block; this was the source heat for the screening test. The experimental resistor was supplied with 1 ampere of current to provide 2 watts of power radiating from the aluminum plate. An adhesive thermocouple with a contact area of 1 cm² was attached at the top of the aluminum plate to monitor the heat source-foam interface temperature. A second thermocouple was attached to the surface of the sample to monitor the temperature of the ambient room environment. All temperature data was gathered using an Omega Data Logger Thermometer. The sample was allowed to equilibrate to a steady state temperature. By reaching a steady state temperature, time dependence is removed from the experiment, simplifying it to a spatial gradient problem.

Our system exhibited large variations due to losses experienced within the system. However, the relative test

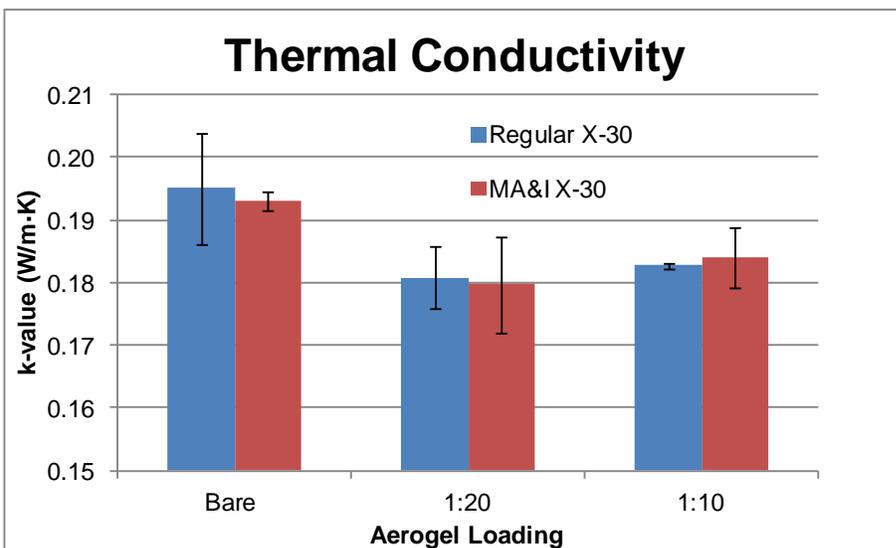


Figure 9. Thermal conductivity of regular and MA&I X-30 samples.

environment remained constant between samples, so the trends presented here are believed to be representative of the insulation samples. Figure 9 shows the relative trend for the addition of aerogel to the X-30 and MA&I insulation foams. Based on this data, the k-value decreases with the inclusion of aerogel additives.

Cryogenic testing was performed at the Boeing Chemistry Group Facility in Huntington Beach, CA. Samples were loaded into a cryobox, part of an Ilikon vacuum chamber.

The cryobox chamber environment is maintained through the use of a helium cryopump that generates a vacuum of 5×10^{-6} torr. The lower limit of this cryobox is 6K (-267 °C). Inside the test chamber a testing apparatus was constructed with a one cubic foot copper box. A second helium cryopump was attached to this box for further cooling. The box was shielded from thermal radiation present within the chamber with a liquid nitrogen cooled thermal shroud. Contact between the copper box and the cryobox was formed by a thin layer of silver epoxy. Outer copper plates were maintained at 20K while two insulation samples (1.0 in. x 5.5 in. x 5.5 in.) were set between the outer plates. Between the two insulation specimens, a 0.125 in. thick copper plate was placed and heated by a silicone rubber heater. Two T-type thermocouples were used to monitor the temperature of the inner plate, and three T-type thermocouples were used on the outer plate. A germanium thermometer was also attached to the outer plate for temperature measurement. The input from the thermocouples was recorded by a 34970A data collector with a 34902A collection card that was controlled by an Agilent Datalogger program. This system collects temperature data down to 73 K (-200 °C). Temperatures below the operating range of the collection device were collected from the thermocouples and converted to temperatures using data acquired from the germanium thermometer attached to the outer copper plate. The heater power was approximately 0.37 W. From this data, the k-values for a limited test set were obtained. Figure 10 shows the experimental setup used for low temperature k-value testing at the Boeing Facility.



Figure 10. Cryobox and copper holder.

In both the X-30 and the MA&I X-30 samples, the inclusion of aerogel decreased overall cell size and narrowed the breadth of the distribution. A reduction in density may also contribute to improved insulation properties. Here we see the addition of inexpensive blowing agents reduce density and reduce the thermal conductivity. Here, the thermal conductivity of the standard (bare X-30 sample) was calculated at 0.00380 W per meter per degree K (W/m-K), and the MA&I sample was calculated at 0.00175 W/m-K. It should be noted that these results are from samples measured under a vacuum environment and 20 K. Here we clearly see that our formulation additives improve the thermal conductivity of the base polyurethane insulation. Converting these values to English units gives:

- Bare X-30 sample: 0.0038 W/m-K = 0.00220 BTU in/hr ft² F
- Bare MA&I X-30 sample: 0.00175 W/m-K = 0.00102 BTU in/hr ft² F

Further refinements are needed. However, the results were promising for the proposed insulating materials. As a comparative baseline, the Boeing Company has tested bare X-30 and MA&I samples only. Follow-on funding is being sought for expanded testing and comparison to existing materials.

Samples that were sent to Boeing included bare X-30 and MA&I blown X-30 and were supported by independent third party testing at room temperature at California Institute of Electronics and Materials Science (CIEMS). Table 2 summarizes the thermal conductivity data obtained by CIEMS. This testing was performed at ambient conditions.

Table 2. Summary of k-value measurements X-30 Polyurethane Foam using ASTM C-177 at ambient conditions

Sample	Surface Density (mg/cm ²)	Volume Density (mg/cm ³)	Thickness (mm)	Thermal Conductivity (W/m K)
Bare X-30	113.6	38.9	25.9	0.0264
Bare MA&I X-30	82.9	32.9	25.2	0.0227

III. Conclusion

Over the course of this project, we have demonstrated that the use of aerogels and the reaction between maleic anhydride and 1-methylimidazole (MA&I) resulted in finer cell size and lower density that in turn reduced the

thermal conductivity of the base polyurethane foam. This was screened at the ISL facility where trends indicated that **these additives are directly responsible for the decrease in thermal conductivity.**

The use of aerogels led to a 20 to 30% reduction in cell size. This is potentially due to the introduction of nucleation sites that alter the foaming rheology at reaction. MA&I further reduced the densities of the foams, making them comparable to X-30 base foams.

The use of the relatively inexpensive MA&I system reduces the density of an X-30 polyurethane foam. MA&I (including those with aerogel additives) samples exhibited significantly lower density (up to 30% reduction) over the base X-30 polyurethane foam. When stabilized with a silicone surfactant (KF-105), the density of the foam and cell size decreased leading to a decrease in overall k-value. **Samples were tested under vacuum and at 20 K at Boeing in Huntington Beach, CA. Results indicate that our MA&I treated samples have significantly lower k-value than base foam.**

ISL's CryoPore insulation can potentially reduce the required amount of material to efficiently insulate a variety of NASA-specific applications. The enhanced insulation properties per unit thickness will lead to thinner insulation, thus reducing the insulation weight load on the spacecraft. By reducing the weight load, it may be possible to maximize fuel economy. Combining improved economy with a reduction in fuel losses, our insulation can aid NASA in making long distance space travel possible.

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