Thermal conductivity and mechanical properties of polymeric aerogels for cryogenic insulation applications

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Abstract. Non-vacuum insulation systems are frequently applied in the thermal management of low temperature systems as well as for the use and storage of cryogens. Aerogels are known for their low density, high mesoporosity, high surface areas, low thermal conductivity and high acoustic impedance. This study focuses on polymeric aerogels that can be mass produced as large monoliths while maintaining the low thermal conductivity over a wide temperature range. The manufacturing flexibility of polymeric aerogels allows fabrication of monolithic blocks and sheets that can be applied in various configurations to insulate cryogenic and superconducting devices. To measure the thermal conductivity, an immersion calorimeter was developed and has been operated at different cold boundary temperatures. The calorimeter heats a hollow cylinder of insulating material on the inside surface and the surrounding bath maintains a cold boundary. This calorimeter was used to measure the thermal conductivity of commercially available FoamGlass and a hollow cylinder of a polymeric aerogel machined from a cast cylinder. The thermal conductivity of the FoamGlass and the polymeric aerogel are compared at room temperature (290 K), ice bath (273 K), and at liquid nitrogen (80 K) cold boundary temperatures. Room temperature measurements of the modulus of elasticity and yield strength using an optical technique are also reported for flat specimens of the aerogel made from the same stock as the cylindrical specimens tested for thermal conductivity. Mechanical properties of aerogels are also reported under compression and both at room temperature and at cryogenic temperature (Liquid nitrogen).

1. Introduction

Thermal insulation systems are used to control heat leak into low temperature spaces. A variety of insulating materials and systems of materials are available, and new materials are constantly under development to provide different functionality. It is generally accepted that the highest performance (lowest effective thermal conductivity) is obtained using vacuum insulation systems such as multi-layer superinsulation. Rigid foams such as polyurethane [1] have been successfully applied in many applications such as refrigerated vehicles, pipelines, and liquid gas tanks for LPG and LNG.

Aerogels are a class of materials that are renowned for their low thermal conductivity. Traditional aerogels made of silica and other metal alkoxides are mesoporous materials that have good thermal insulations, but their fragility and manufacturing difficulties makes their use untenable. For this study, we explore organic based polymeric aerogels as alternatives to traditional aerogels. Polymeric aerogels of this study can be cast as flat sheets of various thicknesses, cylinders, and other shapes as required since molds of any shape and size can be used. For this study the materials were made following a modified process similar to that described by Leventis et al [2]. The resulting materials are mechanically robust monolithic aerogels that can be mass produced. Figure 1 shows flat specimens of different thicknesses (a) and (b), a cast solid cylinder, and a hollow cylinder (c) which was machined from a solid piece.

Figure 1. Organic aerogel (a) 1-inch-thick disk stack of thin disks, (b) series of thin disks, and (c) cylinder as cast and after machining into a hollow cylinder.

One of the Achilles heels of the aerogel materials is their fragility. Traditional silica aerogels are weak, mesoporous materials that cannot support any appreciable load. Most applications for silica aerogels and other metal alkoxide aerogels are limited to uses in space exploration where expensive equipment are needed to produce aerogels of any appreciable size. This is because traditional aerogels are prepared using the sol-gel process that requires the use of an autoclave to remove the processing fluids through the supercritical fluid extraction. The aerogels of this study however were processed using low-vapor fluids such as pentane that can be extracted at room temperature and pressure. The process eliminates the need for expensive and time-consuming supercritical extraction. In addition, it allows the ability to produce aerogel materials of any shape and size since we are no longer confined to using a size and shape limiting autoclave that is traditionally used for supercritical fluid extraction.
The morphology of the aerogels of this study shows a nanofibrous open structures that are filled with air. Figure 2 below shows the Scanning electron microscopy (SEM) of such materials. A wave travelling through such a material would encounter multiple interfaces and voids filled with low thermal conducting air that would impede its forward progress. This torturous path results in the material's low thermal conductivity.

2. Thermal conductivity measurements

The thermal conductivity of the aerogel was measured and compared against a commercially available cellular glass material, FoamGlas [3]. The thermal conductivity of a cylindrical or pipe type geometry was measured using an immersion calorimeter developed at LeTourneau University. Previously measured flat sample measurements using a boil-off calorimeter are also presented [3,4]. Many applications at liquid nitrogen temperatures and above do not use vacuum insulation systems for cost or reliability reasons. The objective of this study was to determine the performance of the aerogel for thermal insulation without vacuum.

2.1 Immersion calorimeter description and operation

The immersion calorimeter consists of a heated core which is surrounded by the insulation test specimen. Platinum resistance thermometers (the red dots on figure 3(b)) were placed at locations as shown. The heater was a nichrome wire wrapped around a G-10 core. The thermometers were Minco S651PD platinum resistor thermal ribbon thermometers (PRT) with 100 ohms nominal resistance at 0°C. The thermometers were supplied a 10 milli-amp current from a Lakeshore model 121 current source.

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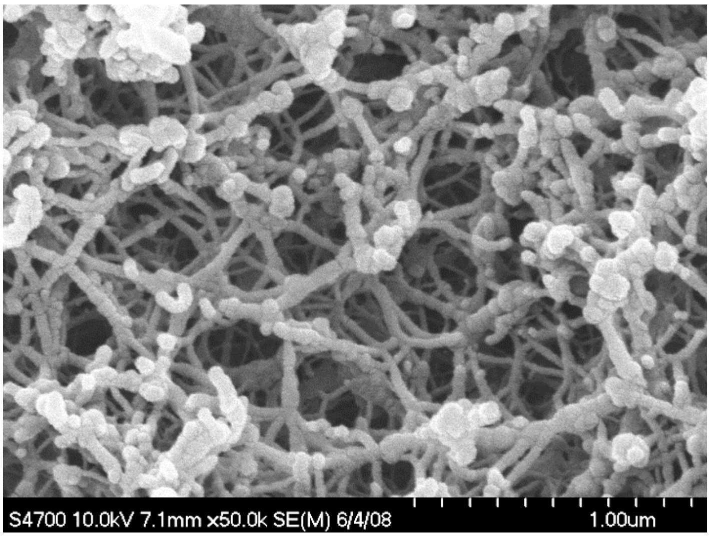
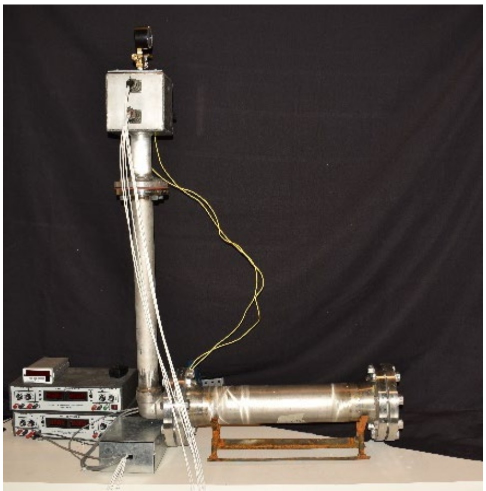
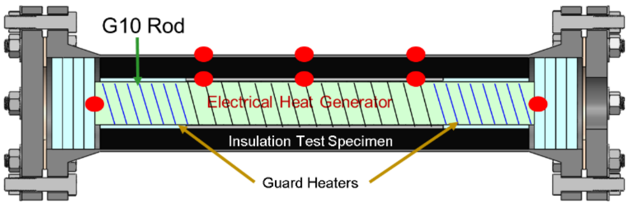


Figure 2. SEM of polyurea Aerogels (PUA) aerogel showing the fibrous open morphology of PUA aerogels of this study.



(a)



(b)

Figure 3. Immersion calorimeter (a) fully assembled and (b) details of test section construction. The insulation test specimen had an inner dimension of 60.3 mm, an outer diameter of 110 mm and length of 304 mm.

The voltage across the test heater and the current applied to the heater were measured to determine the heater power, Q, in Watts. Nichrome wire guard heaters are present at each end of the G-10 core to limit the heat transfer out from the ends. The warm boundary temperature (WBT), T_w, was measured at the central thermometer of the heater and the cold boundary temperature (CBT), T_c, was measured at the middle of the outer surface of the sample. The thermal conductivity can be calculated from these measurements from the heat conduction equation in cylindrical form as:

$$k = \frac{Q \ln(D_{out}/D_{in})}{2\pi(T_w - T_c)} \quad (1)$$

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The chamber was not vacuum tight, so when the calorimeter was immersed in liquid nitrogen, a helium gas purge of up to 30 kPa was applied to both the FoamGlas and the aerogel. This was done to prevent the potential for drawing in moisture during ice bath measurements and to prevent the potential for condensing air inside the device when testing in a liquid nitrogen bath.

2.2 Boil-off calorimeter description and operation

The thermal conductivity was measured for flat samples using boil-off calorimetry in a NASA cryostat-400. The procedure has been discussed in [5]. It is suitable for testing rigid, flat disk type materials in an ambient pressure environment. Figure 4 shows the schematic of the cryostat-400 and the components that were used to take measurements. The temperature distribution can also be measured through the thickness of the sample by installing thermocouples through the thickness. Once the temperature profile is obtained, it is a simple matter to determine the thermal conductivity as a function of temperature. The conduction heat transfer is analysed assuming Fourier's law for heat conduction:

$$k = \frac{Q \times t}{A(T_w - T_c)} \tag{2}$$

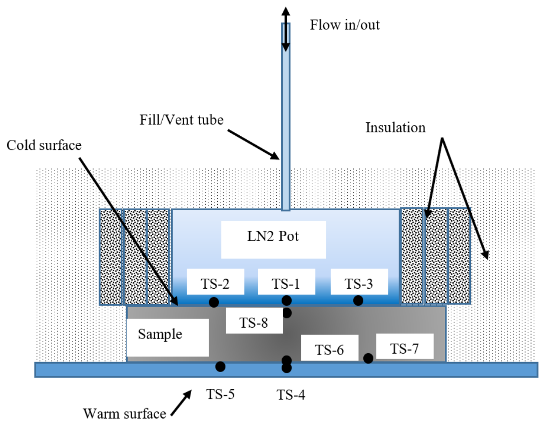

Figure 4. Test configuration for flat samples. The diameter of LN2 pot was 150mm, while the samples had a thickness of 25 mm, and a 200 mm diameter.

The heat load, Q, was determined directly from the experiment. The area of the specimen, A, the thickness, t, CBT, T_c, and WBT, T_w, are all measured. The heat load across the sample was determined from the boil-off measurement [5].

2.3 Thermal conductivity results

Thermal conductivity measurements that were taken using the immersion test apparatus are presented in Figure 5 as a function of the average temperature. The average temperature is simply the average of the cold boundary temperature and the warm boundary temperature. These values are presented in Table 1 as well.

Comparison of the thermal conductivity results are presented in Figure 5 for the immersion calorimeter. The dashed line represents the thermal conductivity of helium gas and the solid line is for air both at ambient atmospheric pressure (101 kPa) as functions of temperature [5].

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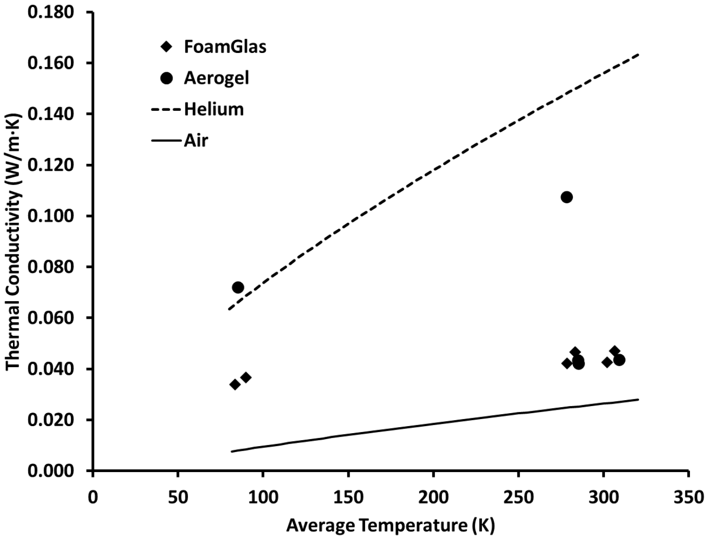

Figure 5. Thermal conductivity measurements of FoamGlas and Aerogel using the immersion calorimeter.

The measurements indicate a slight decrease in the thermal conductivity for the FoamGlas as the temperature decreases. The thermal conductivity results for the aerogel were comparable to FoamGlas for room temperature and the ice bath with CBT of 0°C. It was expected that the aerogel would continue the trend and demonstrate thermal conductivity in the liquid nitrogen bath similar to FoamGlas, but this was not the case. FoamGlas is a closed cell foam whereas the aerogel has an open microporosity. When helium was applied to the aerogel, the thermal conductivity of the helium gas overwhelmed the measurement, and the thermal conductivity was very close to that of helium. Helium has a higher thermal conductivity than air as shown in figure 5. To determine whether this was the case, the aerogel was measured under a helium gas purge in the ice bath, but the helium gas pressure was limited to around 15 kPa. As seen in Figure 5 the measured thermal conductivity of aerogel was approaching that of helium. Table 1 summarizes the results of all the immersion calorimeter tests and provides a result for a solid flat sample. Results from the boil-off calorimeter are for temperatures between liquid nitrogen and room temperature. This test was conducted in a slight nitrogen purge but at ambient pressure. The FoamGlas results are consistent with previous measurements.

3. Mechanical Property Measurement

Aerogels are known for their fragility that makes them unusable for load bearing applications. The organic aerogels developed by this team are robust and can carry loads even at cryogenic temperatures. Tensile tests were carried out according to ASTM D638 standard. However, due to the fragility of the samples, two-dimensional digital image correlation method (2-D DIC) was used for strain measurements and the data collated to stress data obtained from an Instron mechanical test system. DIC effectively is a measurement technique that captures and compares images of shapes, motion, and deformations of solids. The benefit of the method is that it provides the ability to take strain measurements without any need for contact with the sample. Inherently, when an observed object is in contact with the measurement device, the measurement tool will induce some type of stress on the sample. This would significantly alter the results of fragile aerogel materials. DIC avoids this altogether. In principle, the measurement technique is simple. As the region of interest (ROI) of the object under observation deforms, a camera captures images of the deformed region over time. The derived strain data can then be extracted from the changes between each of the images by tracking the movement at the pixel level as the material is deformed. Figure 6 below shows the sample before the test and at the end of the test when it had experienced brittle failure. A tensile stress-strain graph of the room temperature tests is shown in figure 6 (C) for various low-density aerogels.

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Table 1. Measured values of thermal conductivity.

Test Method	Material	CBT (K)	WBT (K)	Average T (K)	k (W/m K)
Immersion calorimeter	Aerogel	79.4	90.8	85.1	0.0721
Immersion calorimeter	Aerogel	301.6	316.1	308.9	0.0436
Immersion calorimeter	Aerogel	276.8	293.7	285.3	0.0421
Immersion calorimeter	Aerogel	275.1	281.4	278.3	0.1075
Immersion calorimeter	Aerogel	276.9	292.9	284.9	0.0434
Boil-off calorimeter	Aerogel	81.3	275.7	178.5	0.0518
Immersion calorimeter	FoamGlas	274.4	282.3	278.4	0.0421
Immersion calorimeter	FoamGlas	274.7	292.0	283.4	0.0467
Immersion calorimeter	FoamGlas	297.5	306.3	301.9	0.0427
Immersion calorimeter	FoamGlas	298.1	314.9	306.5	0.0470

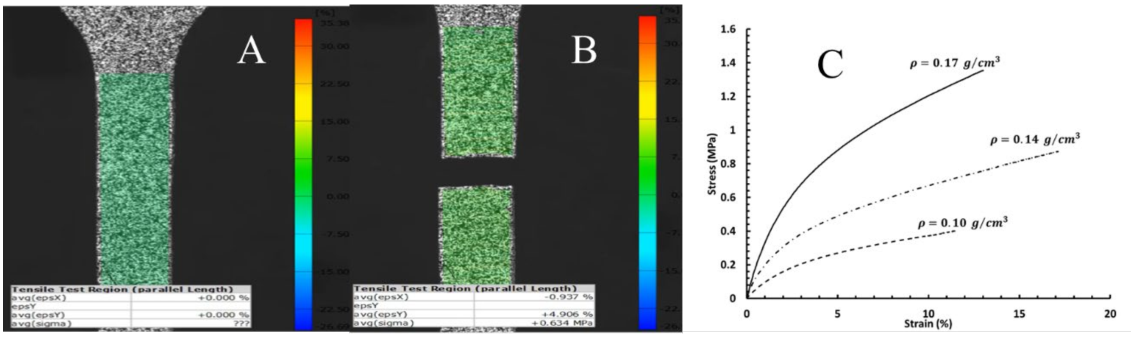

Figure 6. Speckle pattern on test specimen used for DIC showing the samples before (A) and after tensile test (B). figure C shows the stress v/s strain graph for various densities of aerogels.

Results of compression tests at room temperature and after soaking in liquid nitrogen are shown in Figure 7. These were done following ASTM D695 for rigid plastics. It should be noted that no standard test protocols are available for testing aerogel, but the above test standards were chosen after carefully observing the physical properties of aerogels of this study and the need to produce data that can be replicated. Samples for low temperature tests were immersed in liquid nitrogen for eight hours before being quickly tested following the relevant ASTM standards. Some samples were also soaked in oil to elucidate the effects of such environmental conditions on mechanical properties.

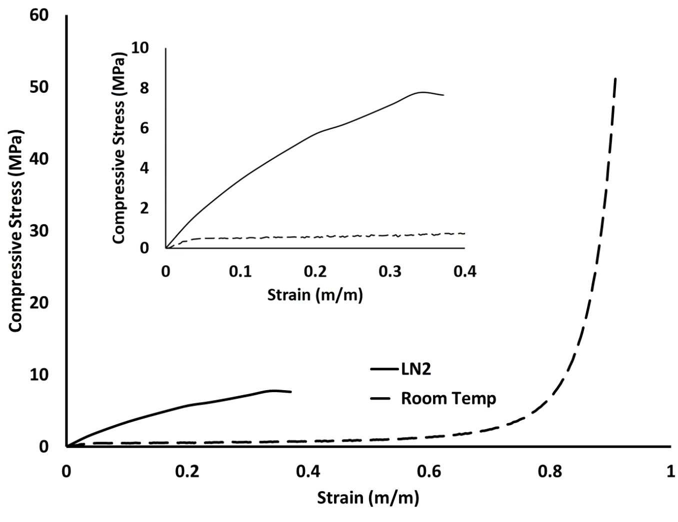

Figure 7. Compression Stress-strain curves for low density aerogels (ρ = 0.11g/cc) at room temperature (dashed line) and at liquid nitrogen (solid line).

The modulus of elasticity and Poisson's ratio were measured in tensile test using 2-D DIC [6]. The x- and y- strains were both measured experimentally to calculate the elastic modulus and Poisson's ratio

as shown in Table 2. In total, the experiment design tested two factors, bulk density and oil soak, at three levels. Not only were the properties reported, but conclusions made about the data set which included general tends that could be both interpolated and extrapolated for other academic or industrial applications. The results were also compared to a similar test of the same PUA aerogel material [3].
The mechanical properties of PUA aerogels using 2-D digital image correlation (DIC) were investigated to give engineers a baseline of mechanical properties and investigate how they are affected by density and environment. This study investigated the tensile properties of PUA aerogel with densities of 0.10, 0.14, and 0.17 g/cm^3 in different environments including oil and water soaked, in oil and water for five weeks. Elastic modulus values of 12, 23, and 44 MPa and Poisson ratios of 0.23, 0.23, and 0.26 for the 0.10, 0.14, and 0.17 g/cc, respectively. Figure 6 (C) shows that the mechanical strength depends on the density of the materials. The mechanical properties were found to depend on the density as well the environmental conditions that the materials were exposed to. This insight will aid materials scientists in designing material recipes that can be tailored to specific applications as well as predict their behaviour once in service in different environments [3].

Table 2. Summary of tensile test data

Sample Density (g/cm^3)	Poisson's Ratio	Modulus (MPa)	Stress at break (MPa)	Strain at break (%)
0.10	0.225	12.14	0.32	12
0.14	0.23	23.5	0.8	17.5
0.17	0.258	44.65	1.3	13

4. Summary and conclusions
The thermal conductivity and mechanical properties of PUA aerogels were measured for cryogenic applications. PUA materials of this study had open mesoporous so that gas which was contained in the pores significantly affect the thermal performance. In addition, aerogels have other desirable properties such as high acoustic impedance, mechanical strength and the ability to tailor them to different applications as needed. Thermal conductivity was found to decrease with decrease in density of aerogels. For future work, the team would like to process aerogel materials with much lower bulk densities and test them under cryogenic temperatures. Such passive insulators which have robust mechanical properties while retaining the low thermal conductivity values even at cryogenic temperatures would also be applicable in space explorations where they would serve a host of purposes as structural members as well as acoustic and thermal insulation.

A future improvement to the immersion calorimeter includes modifications to test under vacuum or slight overpressure.

5. References

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