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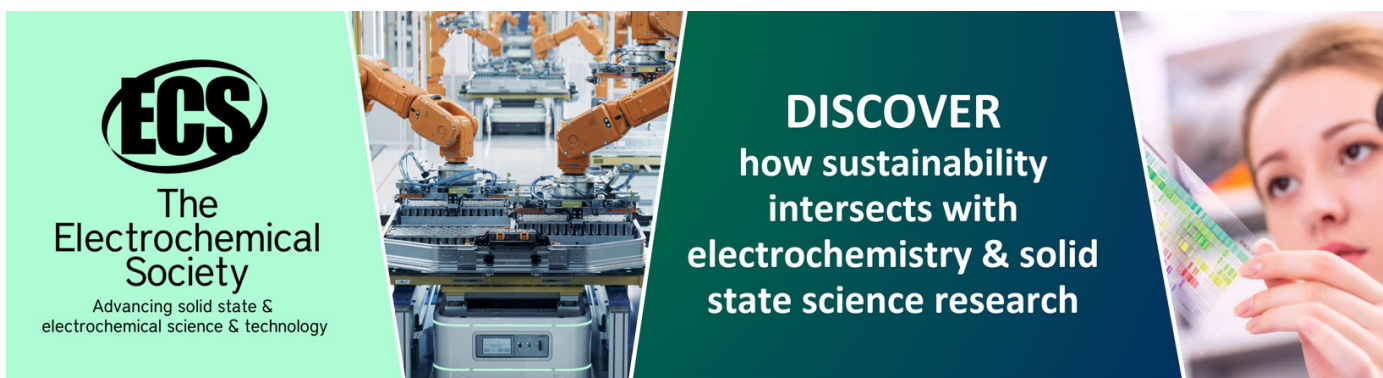
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Thermal and Electrical Properties of Isocyanate Derived Organic Aerogels for Cryogenic Insulation Applications

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Abstract. The use and storage of cryogenics such as liquefied nitrogen, helium, hydrogen among others requires reliable and efficient thermal insulation systems. Passive insulation from high performance materials that are well-known for their inherent low thermal conductivity would reduce the overall costs involved in design, manufacture and maintenance of such systems. One such class of materials are referred to as aerogels. These materials are known for their low density, high mesoporosity, high surface areas, low thermal conductivity and high acoustic impedance. Aerogels were invented by S.S. Kistler in 1931 and the most common type are those made of silica. However, the inherent fragility of silica aerogels makes them hard to mass produce, and therefore applications have been limited. A major breakthrough was introduced by our team almost 20 years ago with the invention of polymer crosslinked silica aerogels. Those materials shifted attention to all-polymer aerogels that have overcome all fragility issues associated with their inorganic counterparts. This study focuses on such polymeric aerogels that can be mass produced as large monoliths while maintaining the low thermal conductivity of traditional silica aerogels over a wide temperature range. Manufacturing flexibility of polymeric aerogels allows fabrication of blocks and sheets that can be applied in various configurations to insulate cryogenic and superconducting devices. The thermal conductivity with 80 K and room temperature boundary are reported as well as other properties (electrical), that need to be considered when designing devices for cryogenic applications.

1 Introduction

For effective control and to maintain the optimal cryogenic temperatures, high performance or low thermal conductivity insulation is needed to prevent heat transfer into the cryogenic piping and other reservoirs used to contain such fluids. Currently, multilayer and vacuum insulations [4] are widely used but the need to maintain vacuum in most cases adds another layer of complexity when designing and maintaining such systems. Aerogels [1-3] are being used in many space applications [5]. The current state of the art is to use silica aerogel embedded in loose fibers to form aerogel blankets [6]. This method is not very efficient since you still need a thick layer of insulation to increase Δx , the insulation thickness or, the distance the heat has to travel before it comes into contact with the cold surface. The use of such fibers also increases the effective thermal conductivity of the resulting materials, making them less effective than what would be expected if pure aerogels were used.



According to Grand View research Inc. [7] market research on aerogels, the aerogel market size is expected to grow to over \$3.2 billion by the year 2025. This is mainly driven by the demand from the oil and gas industry. Companies that do subsea oil and gas exploration and in the polar regions especially need to insulate pipelines so that they can maintain the viscosity needed to keep the oil flowing when the surrounding temperatures are very low. Most oil companies such as British Petroleum (BP) and Exxon Mobil [8] use aerogel blankets consisting of fibers impregnated with silica aerogel powders. This is not ideal since the full potential of aerogels as an insulator is not utilized; the presence of other fibers increases thermal conductivity of the overall structure.

In most thermal insulation applications, silica aerogels are used either as powders entrapped inside blanket type materials as described above. Rarely are monoliths used because they are very hard to manufacture and to mass produce [9]. Silica aerogel monolithic materials are brittle and have very poor mechanical properties. In addition, they require supercritical drying to get the optimal properties. As such, the size that can be obtained is restricted to the size of the autoclave of the supercritical dryer, which further increases the cost of production. The fact that they also use chemicals that have high toxicity such as Tetraethylorthosilicate (TEOS) and tetramethyl-orthosilicate (TMOS) as the basic precursors makes mass production much more challenging [10].

2 Organic aerogel description

Two types of aerogels have been widely synthesized and studied. The first type consists of inorganic aerogels that are synthesized from transition metals and semimetal alkoxide. They include metal oxides aerogels such as TiO_2 , Al_2O_3 among others, as well as binary systems of metal oxides that form more complex systems like $\text{Al}_2\text{O}_3/\text{CuO}$ aerogel [11]. Ternary aerogel systems that consist of more than two metal oxides such as $\text{ZrO}_2/\text{CuO}/\text{ZnO}$ etc have been synthesized [8] and used in catalytic converters in automobile exhaust systems to control emissions. Considering the large number of transition metals as well as many possible combinations that can form binary as well as ternary systems of oxides and semimetal alkoxides, the list of possible aerogels is large. This observation was first made by S. S. Kistler, concluding in his first paper on the subject that the “list can be extended indefinitely”, meaning the list of possible aerogels that can be fabricated is theoretically endless [3]. The process also gives us room to incorporate aerogels in areas such as in catalysis where nanoparticles can be assembled to maximize the contact surface area and improve catalytic efficiency compared to more compact arrangements.

The second type, organic aerogels [11], which are the focus of this work, are derivatives of polymeric systems and other natural organic products like cellulose, polyurethane, polyurea among others [12]. The work of R. Pekala initially involved synthesis and characterization of resorcinol-formaldehyde (RF) phenolic type organic aerogels. The aerogels of this study were made using a sol-gel process similar to one used by Leventis et al [12-14]. Isocyanate was reacted with water in presence of a triethylamine catalyst. Various densities were made by varying the concentration of the isocyanate in acetone that was used as the primary solvent. The density ranged from 0.075 g/cm^3 on the lower density end to 0.16 g/cm^3 . The materials were allowed to gel and age in mold and later washed in acetone to remove the reaction products which mainly consisted of water and carbonic acid. The materials were then washed in pentane and dried in ambient conditions [14].

The organic aerogel has been made in various shapes such as thick (25.4 mm) and thin (6 mm) sheets and also in cylindrical shape as shown in Figures 1a, 1b, and 1c. The discs shown are the samples tested in this study and were cut from larger sheets. Shown in figure 1c is a solid cylinder and on top a hollow cylinder machined from a solid cylinder. This organic aerogel can be cast in different shapes provided a pattern for the mold is provided. Both the flat samples and the hollow cylinder of pipe were tested and results presented in this paper.

3 Flat sample thermal conductivity measurement

The thermal conductivity was measured for flat samples using boil-off calorimetry in a NASA cryostat-400. The procedure has been discussed in [13-16]. The samples are flat discs with a diameter of 203 mm and 25.4 mm thickness or stacks of four-layer samples that have the same total thickness. The pot shown in the figures is filled with liquid nitrogen to produce a temperature gradient across the sample. The boil-off is measured and is related to the heat transfer across the sample. The temperatures at the warm and cold boundaries are measured as shown in Figures 2a and 2b. For the four-layer tests, measurements of temperatures in between the layers was also performed for one test run.



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

Knowing the size of the sample, the heat load, and temperature difference across the sample, the thermal conductivity can be calculated from the one-dimensional heat conduction equation as:

$$Q_{meas} = k_{meas} A_{eff} \frac{(T_{meas,warm} - T_{meas,cold})}{Thickness} \quad (1)$$

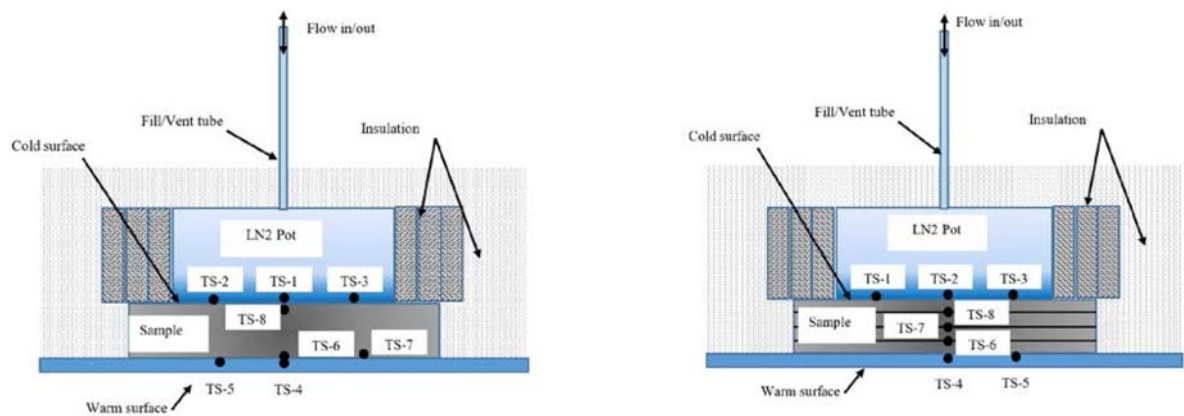


Figure 2. Test configuration for flat (a) solid and (b) the four-layer samples. The diameter of LN2 pot was 150mm, while the samples had a thickness of 25 mm, and a 200 mm diameter.

The Cryostat-400 is a comparative measurement and provides a reasonable estimate of the thermal conductivity. Most significant for this work is the relative comparison of the magnitude of the thermal conductivity of the materials measured. A summary of the measurements of two commercial insulations, Foamglass [18], and Aspen aerogel [19], along with the measurement of the organic aerogel are provided

in Table 1. The thermal conductivity of the organic aerogel is seen to be slightly less than measurements of the Foamglass, but higher than the Aspen material. In general, the organic aerogel is comparable to these commercial materials. When making the organic aerogel, there is the possibility of controlling the density which tends to decrease the thermal conductivity as the density decreases.

Table 1. Summary of test results for the thermal conductivity, k , of organic aerogels compared to measurements on foam glass and three layers of an Aspen aerogel blanket. The sample boundaries were at a warm boundary temperature (WBT) and a cold boundary temperature (CBT).

Sample	WBT(K)	CBT(K)	k (mW/m-K)
Foamglass	293.0	82.0	64.7
Organic aerogel high density	280.1	82.0	53.9
Organic aerogel low density	292.2	81.9	49.0
Org-Solid-Sample-3	275.7	83.6	50.9
Organic aerogel 4 layer, (thermocouples between layers)	282.1	81.8	56.9
Organic aerogel 4 layer	274.3	81.3	55.8
Organic aerogel 4 layer	273.4	80.9	57.8
Three-layer Aspen aerogel blanket	278.7	82.3	48.0

4 Pipe shape insulation test results

A hollow cylinder or pipe shape sample was also tested in a device shown in Figure 3. The test apparatus is designed to do an absolute thermal conductivity measurement and was part of a two-year development as a Senior Design class project on the “Standardized Testing of Low Temperature Insulation” or STOLI [17]. The STOLI test section is shown in Figure 3b indicating the locations of temperature sensors. A test sample is placed over a heater as shown in the figure. The ends are insulated and there are guard heaters at each end to maintain a constant temperature along the length of the sample. An electrical measurement of the heat applied to the test section and the warm and cold surface temperatures are measured along the sample. Knowing the length of test section, $L = 0.3048\text{ m}$, the inner diameter of the sample corresponds to the outer diameter of a standard 2-inch pipe, $D_i = 0.06033\text{ m}$, and the outer diameter corresponds to the inside diameter of $D_o = 0.110\text{ m}$. The thermal conductivity is determined from the one-dimensional heat conduction equation in a cylinder given by:

$$Q = \frac{2\pi L k_{meas} (T_{Hot,meas} - T_{Cold,meas})}{\ln(D_o/D_i)} \quad (2)$$

In order to validate the results obtained in the STOLI apparatus, measurements were performed on commercially available materials including Foam-glass [18], and Aspen aerogel [19]. Table 2 shows the results of the known materials as well as the measurement of the organic aerogel material discussed in this paper.

5 Electrical Breakdown Characterization

Electrical breakdown characterization of Isocyanate Derived Organic Aerogels was performed at 77 K and room temperature as an initial screening to determine the functional limit of this insulation. Two aerogel insulation samples were provided, GC 7.75 and GC 11, and had average thickness of 0.187 mm and 0.197 mm respectively. For 77 K characterizations, 5-cm squares were placed between two rounded flat plate electrodes and immersed in liquid nitrogen (Fig. 4). AC voltage was applied across the electrodes using a

100 kV ac source that was ramped at a rate of 1 kV/min ramp rate. Two aerogel sample types were assessed, and their average breakdown strength were 15.1 kV/mm (GC 11) and 17.0 kV/mm (GC 7.75). Weibull distributions for each sample (Fig. 5) for each breakdown measured showed comparable uniformities with respect to the slopes of the failure probabilities with the performance of the GC 7.75 showing slightly higher performance.

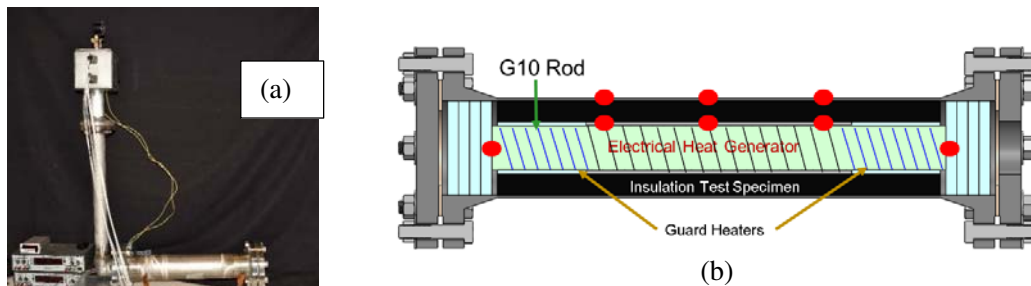


Figure 3. Pipe test apparatus (STOLI) (a) fully assembled and (b) details of test section. The insulation test specimen had an inner dimension of 60.3 mm, an outer diameter of 110 mm and length of 304 mm.

Table 2. Comparison of measured results and reported data for Foamglass, Aspen aerogel and organic aerogel.

Material	WBT (K)	CBT(K)	k (mW/m-k) measured	k (mW/m-K) Reported data
Foamglass [16]	335	309	42.1	40 – 42
Foamglass [16]	310	279	40.2	36 – 40
Aspen Aerogel [17]	335	275	17.9	12 – 18
Organic aerogel	324	298	51.8	N/A



Fig. 4. Electrode and sample configuration for ac electrical breakdown measurement of aerogel insulations at 77 K.

For measurements at room temperature, the difference in the average breakdown strength and functional dependence of the breakdown strength grew between the two sample aerogel sample types. At room temperature, aerogel samples were immersed in Exxon Univolt transformer oil and placed in a Type TC/IEC test cell with adjustable, 36-mm diameter spherical dome electrodes to minimize possible flashover and to localize the electrical field across the sample (Fig. 6). AC voltage was applied to the electrodes using a 60 kV ac source with a 0.5 kV/min ramp rate. The average breakdown strengths for the two sample types, GC 11 and GC 7.75, were 11.9 kV/mm and 17.0 kV/mm respectively. Weibull distributions for each sample (Fig. 7) for each breakdown showed that the differences between the two samples was consistent of the samples measured and not from sample defects that could have impacted the failure distribution and average electrical breakdown strength. When compared to electrical breakdown strength for the Exxon Univolt

measured with a fixed electrode separation comparable to the aerogel insulation thickness, a measurable improvement in electrical breakdown strength from the aerogel is demonstrated. However, this improvement lags behind when compared to other dielectrics like polyimides and cross-linked polyethylene that have dielectric breakdown strengths closer to 100 kV/mm. This difference is not surprising given the known porosity of the aerogels, but knowledge of the dielectric breakdown strength could be beneficial to applications where the functional use of the aerogel has to serve thermal and electrical isolation. Additional systematic investigation and refinement that cover topics ranging from the influence of the aerogel structure on interfaces that could result in partial discharge to dimensional measurement of electrical properties to screen for volumetric scaling and defects could be beneficial.

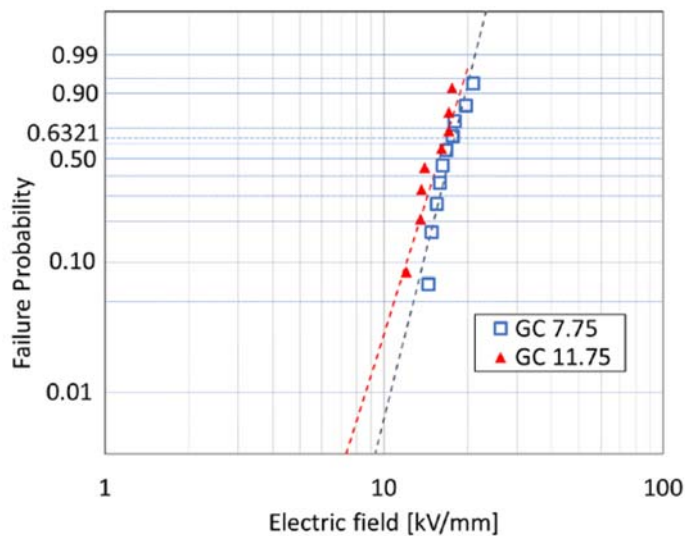


Fig. 5. Weibull distribution for ac electrical breakdown measurements at 77 K for two aerogel samples.

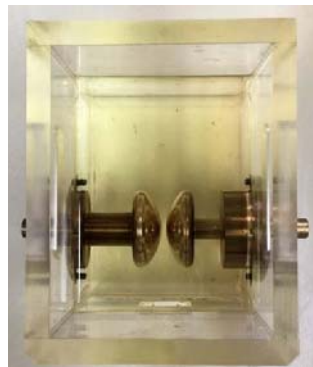


Fig. 6. Electrode and sample configuration for ac electrical breakdown measurement of aerogel insulations at room temperature.

6 Summary, Conclusions and Recommendations for Future Work

An organic aerogel has been developed and measurements of the dielectric strength and thermal conductivity have been measured for applications at liquid nitrogen temperatures. The data was obtained over a limited temperature range for the flat plate tests. The main conclusion from these tests is that the thermal performance for this material is comparable to other insulations. The material can be processed into different shapes such as plates, and cylinders depending on the mold used. Testing was performed on these

two common shapes which showed that the thermal performance is not significantly affected by the manufactured shape.

There was a correlation between the thermal and dielectric constant with density, with lower density materials showing a lot of promise. More research on production of such materials is warranted and ongoing. Other recommendation is to conduct additional tests in the STOLI apparatus to obtain low temperature thermal conductivity data. Future plans are to also conduct mechanical property measurements of tensile and compressive strength under different static and cyclic loading conditions.

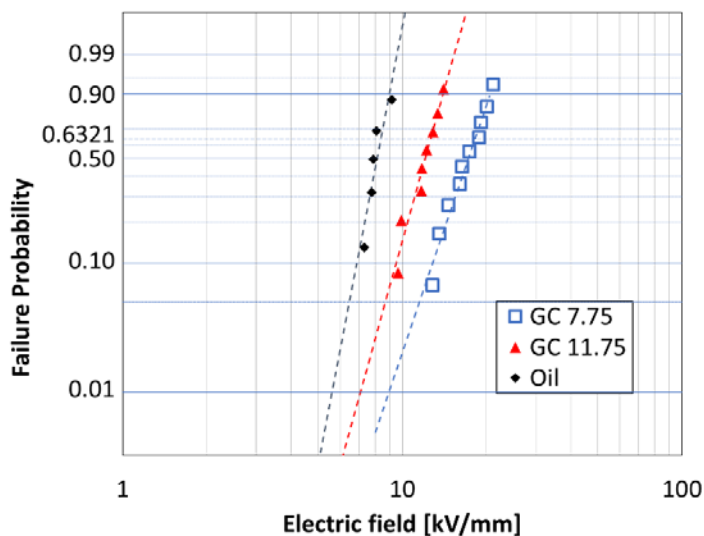


Fig. 7. Weibull distribution for ac electrical breakdown measurements at room temperature for two aerogel samples.

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