ABSTRACT

Title of Document: DESIGN AND FABRICATION OF A JOULE HEATED FIBER-REINFORCED CARBON AEROGEL FOR INSULATION IN THERMALLY HOSTILE ENVIRONMENTS

Stephen Barbagallo, Ellen Cesewski, Naveed Chowdhury,
Joseph Langreo, Colin Qualters, and Nathaniel Schreiber

Submitted: ENMA490: Materials Design - Capstone Project
Department of Materials Science and Engineering
A. James Clark School of Engineering
University of Maryland

May 12, 2015

In this report we investigate carbon fiber-reinforced carbon aerogels for Joule heated thermal insulation applications - particularly as a lightweight cold weather insulation layer in clothing. We consider microstructural, thermal, and electrical properties in our design of the composite. Our main design components are carbon fiber fraction content, porosity of the carbon aerogel, and effective product thickness. Our models indicate encouraging thermal insulation at a reasonable aerogel thickness, and provide electrical conductivity on the order of 10^3 S/cm, but our current design geometry is ineffective for Joule heating as a bulk fabric. Lack of appropriate equipment prevented completion of successful prototyping. We suggest further research in investigating this material for Joule heated thermal insulation applications either as strips in composite wearable devices or for other military, aerospace, or outdoors applications.

DESIGN AND FABRICATION OF A JOULE HEATED FIBER-REINFORCED CARBON AEROGEL FOR INSULATION IN THERMALLY HOSTILE ENVIRONMENTS

By

Stephen Barbagallo, Ellen Cesewski, Naveed Chowdhury, Joseph Langreo,
Colin Qualters, and Nathaniel Schreiber

Acknowledgements

We would like to thank Dr. Raymond Phaneuf for the support and guidance of this project. We would also like to thank Dr. Yifei Mo for his collaboration and feedback on the technical approach of our models, Dr. Robert Bonenberger for his support in the Modern Engineering and Materials Instructional Laboratory, and Dr. Liangbing Hu and Doug Henderson of the Energy Research Center. This research was funded by the Department of Materials Science and Engineering of the A. James Clark School of Engineering at the University of Maryland.

Table of Contents

Chapter 1: Motivation

1.1 Introduction

Current high-performance clothing systems that are designed to assist the wearer in combatting extremely cold weather situations rely heavily on the concept of layering in order to protect and insulate. The Army's Extended Climate Warfighter Clothing System (ECWCS)[1], for example, contains 7 different layers of varying fabric components in order to insulate a soldier from temperatures as low as -60 °F (-51 °C). While systems like these have been undoubtedly formulated for great performance, further efforts can still be made to improve the thermal insulating efficiency, weight, and overall capability. **We plan to design and fabricate a carbon fiber-reinforced carbon aerogel fabric component that exhibits comparable thermal insulation to current cold-weather technologies, while also having the ability to Joule heat, and thus warm the wearer.**

A carbon-based aerogel fabric component could feasibly provide a solution to many of these goals. Carbon aerogel is an ultra-low density, highly porous material made up of a fibrous carbon network. This material has been shown to exhibit a vast number of interesting properties dependent on its processing- namely low thermal conductivity, good electrical conductivity, and mechanical durability.[2] We seek to take advantage of these material characteristics to create a fabric component that not only performs well as a thermal insulator, but allows for improved cold-weather performance via the ability to Joule heat.

In order to make carbon aerogel feasible to act as a component, we will reinforce it with polyacrylonitrile (PAN) fibers, which carbonize in the composite synthesis process. We add the PAN fiber because carbon aerogels have a few intrinsic disadvantages: they are brittle, carbonization can lead to cracking, and they are not mechanically durable. Previous work has suggested that adding PAN fibers may address all three of these issues and make aerogel composites a viable candidate for use in fabric components.[3]

1.2 Material Science and Engineering Aspects

This project is reliant on knowledge and skills acquired throughout our education in the Department of Materials Science and Engineering, as it lies on the interface of physics, chemistry, and engineering. A key component to the success of our capstone project is the use of modeling and simulations to apply fundamental scientific knowledge and theories to practical applications. In particular, we utilize our knowledge of electrical and thermal mobility from solid state physics, and our understanding of electron transport dimensionality and scattering from our electronic materials class to describe, model, and predict the behavior of our composite. The concept of tunneling was covered extensively in our nanocharacterization course, and we will also apply this to our model. Upon acquiring a qualitative understanding of the underlying scientific concepts, we will use our knowledge of computational modeling to quantify the material properties over a variety of conditions and time periods.

A crucial part of our material science education has also been the practical application of material and product synthesis techniques. Organic chemistry and polymer science are both extremely relevant to our project in designing and fabricating an organic aerogel composite. Polymer Physics offered us insight into how to manipulate polymeric materials to obtain a desired performance. Specifically, the course covered the importance of cross-linking polymers and how that introduces structural robustness. Cross-linking is significant in the synthesis of aerogels because a cross-linking process ensures the formation of the aerogel's structural framework. Since an aerogel is synthesized by utilizing indirect phase boundaries, we must utilize our knowledge of thermodynamics. Our studies in Thermodynamics of Materials and Materials for Emerging Technologies taught us the basic principles behind a material's phase diagram as well as methods to control material properties via a phase diagram.

Characterization of our prototype also relies heavily on material science and engineering aspects. Not only must we know how to operate characterization tools, it is essential that we understand the basis of the technique and how to analyze the results correctly. We have learned about SEM, neutron scattering, mechanical characterization, and thermal and electrical investigation in classes, such as Mechanical Properties of Materials in addition to our characterization laboratory classes and device classes. We particularly seek to utilize our knowledge of SEM, bending tests, the 4-point probe test, and the hot plate technique to characterize our samples in this project.

1.3 Intellectual Merit

Over the course of the semester, we have learned far more about the applicability of carbon aerogels for our intended application. Our original proposal was the development of a carbon aerogel without any reinforcement. However, upon reviewing the literature, we learned that just a carbon aerogel would not be sufficiently flexible or mechanically durable to be used as a fabric component. Therefore, we justified the addition of PAN fibers, which will carbonize and become carbon fibers upon carbonization.[3] PAN fibers have been added to carbon aerogels before, and the thermal properties have been investigated. The novelty of this project is the study of the electrical properties and its relationship with carbon fiber content which to our knowledge has not been done before. Furthermore, there has not been much research reported on the Joule-heating capability of carbon aerogels, but we would be the first to study the Joule-heating capability of carbon fiber-reinforced aerogels.

Previously studied carbon fiber-reinforced aerogels required a supercritical dryer for extended amounts of time which we currently do not have access to, and thus additional alternatives must be explored. Resorcinol-formaldehyde (RF) carbon aerogels have been successfully made via ambient drying methods[4–6]. However, only Schwan reports on making flexible RF aerogels. We would like to explore the possibility of making carbon fiber-reinforced aerogels via ambient drying from the method reported by Schwan, in addition to a freeze drying method.

Overall, our design caters to a carbon aerogel reinforced by carbon fibers in order to increase durability, flexibility, and electrical conductivity, with the hope of remaining thermally insulative. We have done a design of experiments (shown in Chapter 3: Technical Approach) in order to weigh the processing parameter effects and to find the optimal parameter combination to synthesize the aerogels. We hope to learn what R/W ratios and what fiber fraction to use in order to optimize electrical conductivity, thermal conductivity, and flexibility.

Goal:

We hope to contribute to the field of lightweight Joule heated materials by investigating the processing parameter effects and capability to resistively heat a carbon fiber-reinforced carbon aerogel (CFCA). Other groups may be able to make use of our work and a favorable combination of the aforementioned thermal conductivity, electrical conductivity, and hydrophobicity when designing materials in the future.

Research Questions:

(i) Will carbon fiber-reinforced carbon aerogel (CFCA) thermally perform as well as industrial synthetic down with marginal heat generation from Joule heating?

(ii) Which variation in processing parameters will yield an aerogel with minimum thermal conductivity for a practical electrical conductivity for Joule heating potential?

Chapter 2: Literature Review

*2.1 Current Standard Wearable Insulator*s

Common insulators currently utilized in wearable thermal insulation applications include air, cotton, goose down, and synthetic down. Goose down has excellent thermal insulation due to its unusually effective thermal barrier and its high mechanical resilience to deformation.[7] However, natural down is expensive and difficult to obtain. This has led to the development of synthetic down, which seeks to mimic natural down properties using polyester fibers.[8] This is one of the current state-of-the art technologies in wearable insulators. This material has a density P_F from 3.20 kg/m^3 to 9.21kg/m^3 and an apparent thermal conductivity measured by the plate-to-plate method with heat flow of less than 0.0702 W/m-K (cite patent here). Although synthetic down is lightweight and thermally insulative, these fibers cannot be actively heated, meaning that heat must be generated by the body or with a heating element, most of which are far heavier than the down.

2.2 Aerogels for Thermal Insulation

Aerogels were first introduced by Dr. Samuel Kistler in 1932, when he replaced the liquid in a gel with gas without collapsing the gel solid network.[9] Kistler achieved this by supercritically drying the gel- heating the sample in an autoclave until the pressure and temperature exceeded the critical temperature T_c and pressure P_c of the liquid in the gel pores, effectively evacuating the liquid.[10] This process is diagrammed in **Figure 2.1** as the green arrow**.** Supercritical drying utilizes the critical point of the material to avoid crossing a phase boundary. This way, the densities of the liquid and vapor phases are equal. Unlike ordinary drying, there is no capillary pressure, so the liquid does not pull on any solid structures when it is removed.[11] Freeze drying can also be used to avoid the direct liquid-gas phase boundary, although going through the solid-gas boundary can also cause cracks and collapse.[11]

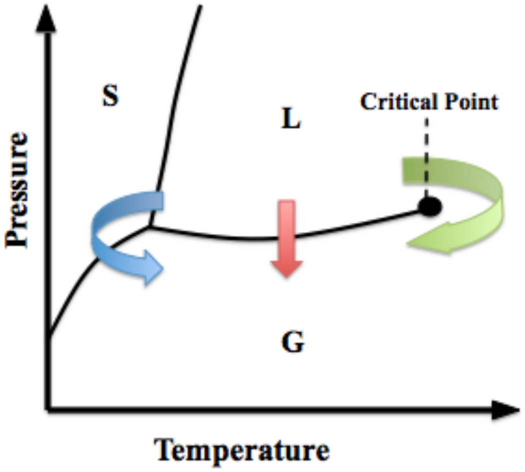


Figure 2.1. Three drying processes- ordinary drying (red arrow), freeze-drying (blue arrow), and supercritical drying (green arrow)

This processing technique resulted in a product with unprecedented thermal insulative and mechanically strong properties for an ultra-low density solid. Aerogels exhibit high relative or specific pore volume- the pore volume fraction is typically on the order of 90%[10], although silica aerogels, for example, have been synthesized to a pore volume fraction up to 99.8%.[12] Aerogels exhibit low thermal conductivity because their structure and composition inhibit heat transfer mechanisms. The high pore fraction limits conductive and convective heat transfer because gas is a poor conductor, and the structure prevents circulation through the aerogel.[10] The radiative heat transfer is highly dependent on composition. The addition of carbon to a silica aerogel has been shown to decrease radiative heat transfer since carbon acts as an IR absorber.[13] Aerogels of all types have been used in thermal insulation applications for both cryogenic and high temperature conditions. Devices, pipes, and appliances are very commonly insulated with aerogels.[14] The insulative properties of aerogels along with their low density have led to widespread usage, but they have not been thoroughly investigated in wearable applications in terms of thermal insulation, nor in any actively heated applications.

2.3 Joule Heating

Joule heating, also known as active or resistive heating, is an effect caused by current particle interactions and the transfer of kinetic energy into heat. When a current is run through a conductor, charged particles collide with ions, resulting in ionic kinetic or vibrational energy, which often manifests into heat.[15] This effect can be detrimental to some devices due to unwanted temperature increase and current loss, but it can be used advantageously in other applications. Joule heating has been investigated and controlled for carbon fiber polymer composite applications successfully, so it is justifiable to research the potential to Joule heat a carbon fiber-reinforced carbon aerogel, especially because a pure carbon aerogel is electrically conductive.[16]

2.4 Carbon Aerogels

There are several types of aerogels with varying compositions and microstructures based on the materials used in the gel formation as well as the solvents, and even the process used to dry the gel. Carbon aerogel is an ultra-low density, highly porous material made up of a fibrous carbon network. **Figure 2.2** shows an electron micrograph of this material.[17] The material has recently been shown to exhibit a vast number of interesting properties, namely low thermal conductivity, good electrical conductivity, and mechanical durability. Carbon aerogels are made by carbonizing organic resorcinol-formaldehyde (RF) aerogels in an inert gas.[18]

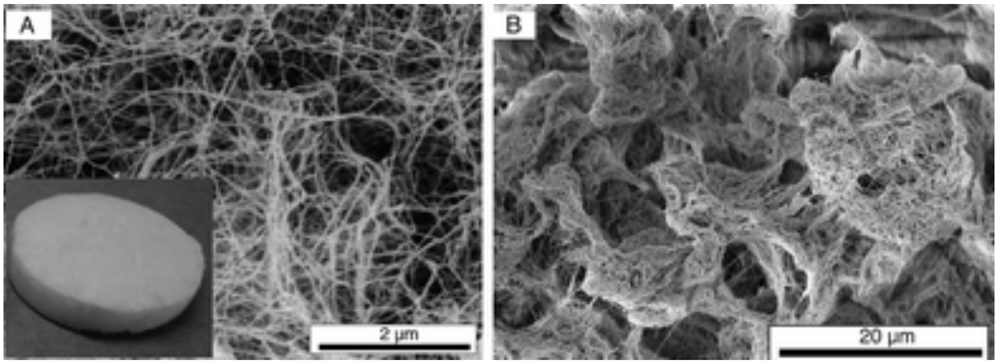


Figure 2.2.[17] SEM micrograph of carbon aerogel.

Carbon aerogels have very large surface areas for double layer charge separation.[19] Since carbon aerogels are electrical conductors, they have been investigated for fuel cell and capacitor electrode applications.[20] In current research, carbon aerogels are usually investigated for thermal and electrical properties separately, although they are highly interconnected. We seek to take advantage of both the electrical conductivity and low thermal conductivity to create a fabric component that not only performs well as a thermal insulator, but allows for improved cold-weather performance via the ability to Joule heat.

2.5 Carbon Fibers and CF-Reinforced Aerogels

Some drawbacks to carbon aerogels in terms of our intended application include brittleness and shrinkage during fabrication. In attempts to combat this issue, it has been shown that carbon aerogels can be reinforced with carbon fibers to decrease shrinkage and increase flexibility. These reinforced aerogels can be made by impregnating the RF solution with carbon fibers and supercritically drying the gel.

One previous study done by Feng et al. showed promising thermal conductivity and produced crack-free samples. This study, however, did not thoroughly examine or characterize the thermal and electrical properties, nor make an attempt to optimize the process parameters or morphology of the composite to target any certain application. One study done by Drach et al. characterized and modeled thermal conductivity across the anisotropic directions of their samples dependent on the orientation of the nanofiber felt sheets, but did not examine electrical conductivity or the concept of Joule heating their samples.[21] We hope to use the information from these studies to extend the application of these composites and examine the potential to joule heat the samples at minimum power and maintain maximum useful thermal conductivity as well as mechanical durability/usability in a fabric.

2.6 Aerogel Synthesis Review

There are numerous types of aerogels that have been researched and developed, however our focus is on the synthesis of the resorcinol-formaldehyde (RF) carbon aerogel. There is a significant amount of research that has been done on RF carbon aerogels that presents them as promising light-weight thermal insulators as well as a possibility to be Joule-heated due to its ability to be electrically conductive.[10] There are 2 main stages of synthesis of the RF aerogel: the first stage involves preparation of the sol mixture and gelation and curing of the gel while second stage is associated with the drying of the wet gel. Once the RF aerogel is created, it is carbonized in order to transform it to a carbon aerogel.[18]

When first synthesizing the RF carbon aerogel, the resorcinol and formaldehyde are mixed at a certain molar ratio in the presence of a basic catalyst and water, many times being sodium carbonate, which is also added at a certain molar ratio. Heat is then applied to the solution to form a cross-linked gel, usually at around 80 degrees Celsius. The polymerization that occurs is shown in **Figure 2.4**.[2] Once the gel is formed, it must undergo solvent exchange with a pure solvent, usually acetone. Solvent exchange is performed in order to gradually transition from a water-based gel (which experiences destructive capillary forces when the water evaporates), to a gel submersed in a non-destructive liquid (i.e. a liquid that does not exert large capillary forces). Next, the gel has to be dried in order to create the RF aerogel. Ideally, the gel will be supercritically dried in order to keep the gel's framework and to avoid large amounts of shrinkage that occurs when ambient drying is done. Lastly, the RF aerogel is carbonized at high temperatures to convert the organic material into a carbon aerogel.

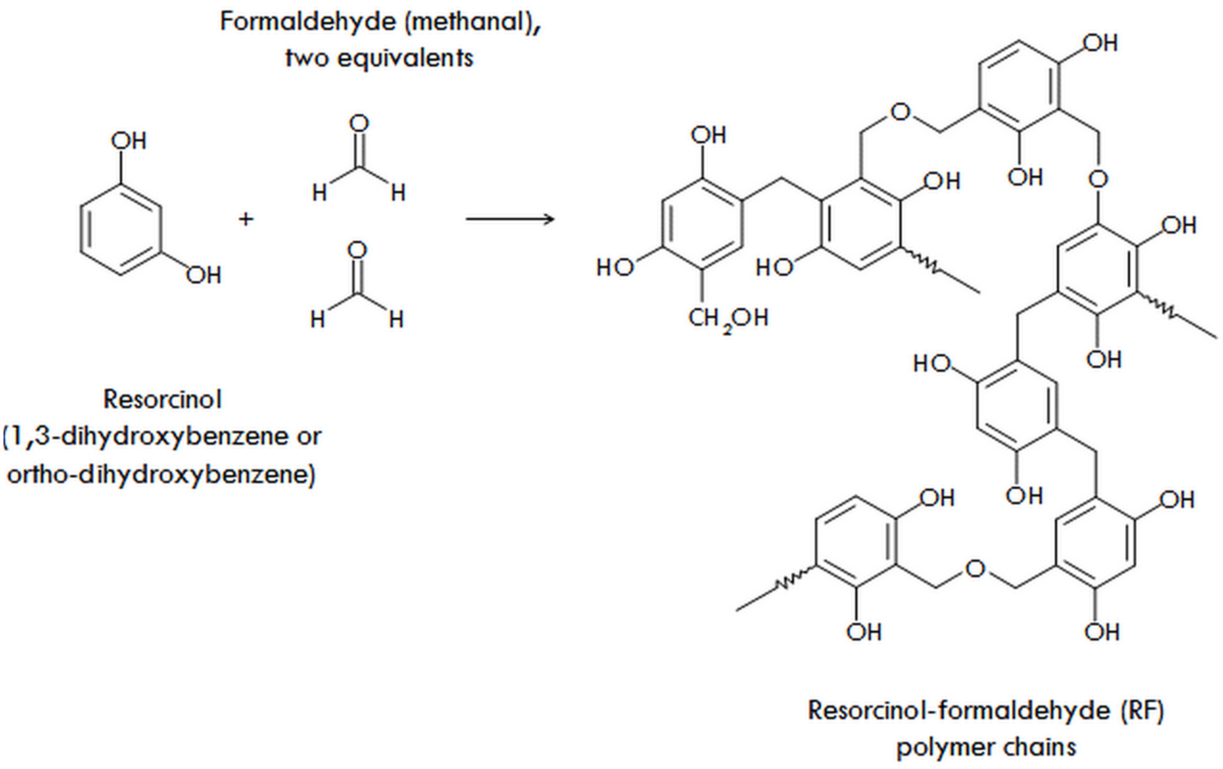


Figure 2.4.[2] Resorcinol-formaldehyde polymerization

A drawback to the method of making flexible aerogels via adding PAN fibers proposed by Feng is that one needs access to a supercritical dryer. An alternative method is presented by Schwan et al.- the method presented in this paper claims to produce RF aerogels that are flexible and ambiently dried.[4] These new types of RF aerogels are elastically deformable by more than 40% in an almost reversible manner. Schwan explored the effects of various sol–gel parameters on the flexibility, such as resorcinol to water and catalyst molar ratio and the pH of the initial solution. They kept R/F ratio at 0.5 to have uniform gelation rates and R/C ratio at 50 in order to try to get similar pore sizes for their various samples. pH was varied via the addition of nitric acid to the solution, as well as by varying the R/W ratio. They found that by keeping the R/W ratio between 0.006 and 0.01, and adjusting the pH to 5.0-5.6, that they were able to produce flexible RF aerogels. We could expand upon this method by adding PAN fibers to the RF gel and pyrolyzing into a carbon aerogel that would hopefully still result in a flexible material. We plan to investigate variations on this technique in our technical approach to our product. Our design considerations and approach are detailed in Chapter 3: Technical Approach.

<u>Chapter 3: Technical Approach</u>

3.1 Project Design Goals

We propose the design of a carbon fiber-reinforced aerogel fabric component with insulating properties that performs as well as top of the line commercially available insulating fabrics with the added novelty of active heating. Below in **Figure 3.1** we present the trade off in the properties between possible aerogel designs of consideration.

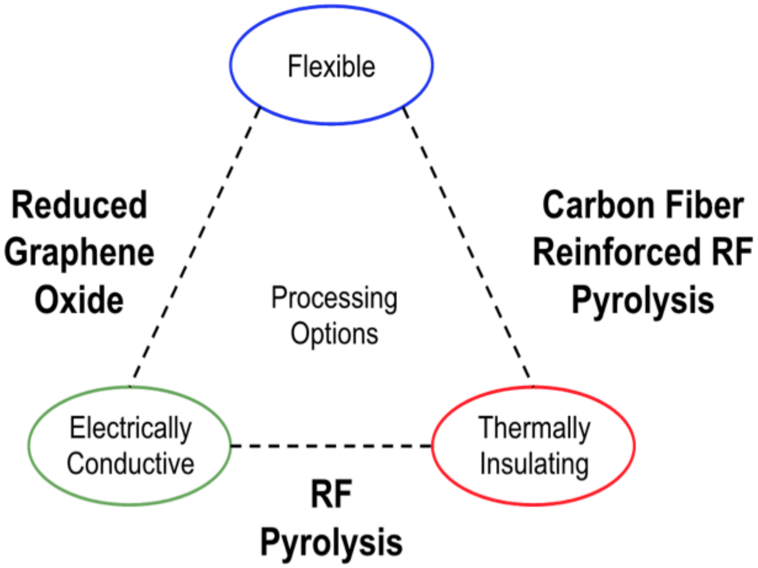


Figure 3.1. Material property tradeoffs associated with various processing options.

Reduced graphene oxide carbon aerogel has been studied in terms of its electrical conductivity and flexibility, but it has a high thermal conductivity, failing to serve as a thermal insulator.[22] RF aerogels have been shown to be thermally insulating and electrically conducting, but their brittleness make them poor candidates for a fabric component. A CFCA may have the desired thermal, electrical, and mechanical properties. The thermal properties have been thoroughly studied and the composites have been shown to be flexible due to the addition of PAN fiber, but the electrical behavior has not been thoroughly investigated, especially in relation to the thermal insulation. Carbon fibers are conductive, so we hypothesize that there is a trade-off interface that will allow for a thermally insulative aerogel composite with sufficient electrical conductivity to Joule heat while remaining flexible.

Our design will be constrained by the environmental parameters in which high-end fabric components are currently used. Many camping and hiking applications require insulation for environments as low as -20 °F; therefore, we will use this environment to quantify material performance. The design of this fabric component will be mediated by three numerical and one empirically-based model. These models, which we will detail later, assess the intrinsic thermal properties, extrinsic electrothermal behavior, and fit-for-use mechanical reliability of our idealized fabric component. The goal of the project is to develop an optimal fabric component that will perform as well, or better, than industry standard fabric components of comparable weight based on the aerogel density, and the weight of any power supplies necessary for active heating. Additionally, the idealized fabric component should also display excellent fatigue strength when cyclically loaded for a high number of cycles, however this is an auxiliary goal in the context of this proposal.

Design Components
Volume fraction of carbon fibers
Porosity: pore size, pore density
Monolith shape and thickness

Desired Performance
1. Act as a thermal insulator
2. Joule heating capability
3. Flexible, durable mechanical properties

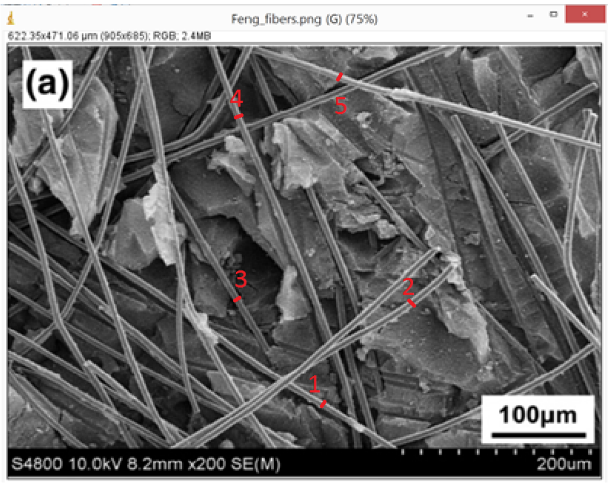
Volume fraction of the carbon fibers within the composite will have a very heavy effect on thermal and electrical conduction. Varying this fraction will strongly affect the CFCA properties. Porosity and density also strongly affects the heat transfer mechanisms and thermal conductivity of carbon aerogels.(Handbook) This, combined with the volume fraction, will be the design components of interest in this project. Monolith shape is important to consider with regards to testing the composite, it must be large enough to exhibit bulk properties as well has a suitable shape to undergo a bending test. We will also specify desired thicknesses for our fabric component product for desired performance. The overall goal of the project is to design an aerogel that thermally performs as well as industrial synthetic down, with marginal heat generation from Joule heating.

3.2 Modeling

3.2.1 Microstructure

We modeled the carbon fiber-reinforced carbon aerogel microstructure using MATLAB to generate a simplified model of the material. The microstructure model is made up of a carbon aerogel matrix with randomly distributed carbon fibers of a specific length and specific diameter. In this model we have assumed that the fibers will distribute randomly in our prototype, the fiber length and diameter are uniform, and tunneling within the aerogel matrix (through the carbon pores) is negligible. The tunneling probability through pores has been considered to be negligible because the voltage being applied to our sample, 5eV, is greater than the barrier to tunneling (4.81eV), given by the work function of carbon. This means there is full transmission of current. Tunneling is likely to be seen at less than 10 nm pore size.[23] Our material is based off of Feng et al.'s studies which yielded pore sizes[3] of 20 to 150 nm which would mean tunneling is unlikely in our sample. As seen in equation **(1)**, the energy of an electron under a 5V applied voltage is approximately equal to the barrier energy, indicating there is a negligible amount of tunneling.

$$T = \frac{1}{1 + ma^2 V_0 / 2h_{bar}^2} \qquad \textbf{(1)}^{24}$$



#	Position in Image	Diameter (nm)
1	Bottom	6.275
2	Mid-right	8.13
3	Mid-left	8.075
4	Top-left	7.589
5	Top-right	8.593

Figure 3.2. Shown is a measurement of the diameter of carbon fibers using an SEM image from a paper by Feng et al.[3] We have measured the distribution of fibers to be 7.7324 +/- 0.795 nanometers using ImageJ.

The other two assumptions of uniform length and diameter are justifiably based on the ImageJ measurement made in **Figure 3.2** above, which show the uniform width and the uniformity of lengths from PAN-based carbon fiber manufacturers. The MATLAB code used to create the microstructural model is provided in **Appendix A**.

In order to generate this random distribution we first generate the first endpoint randomly. The second point is placed by adding the length at a random angle chosen from a given range which we defined. These correspond to the endpoints. After the coordinates of the lines have been stored, an algorithm was used to determine whether a point (assuming a certain mesh size) in the coordinate system was inside of a fiber or inside of the aerogel matrix. If the point was within the fiber then it was made red, and if the point was within the aerogel then the point was made blue. A sample of the generated microstructure is shown in **Figure 3.3**.

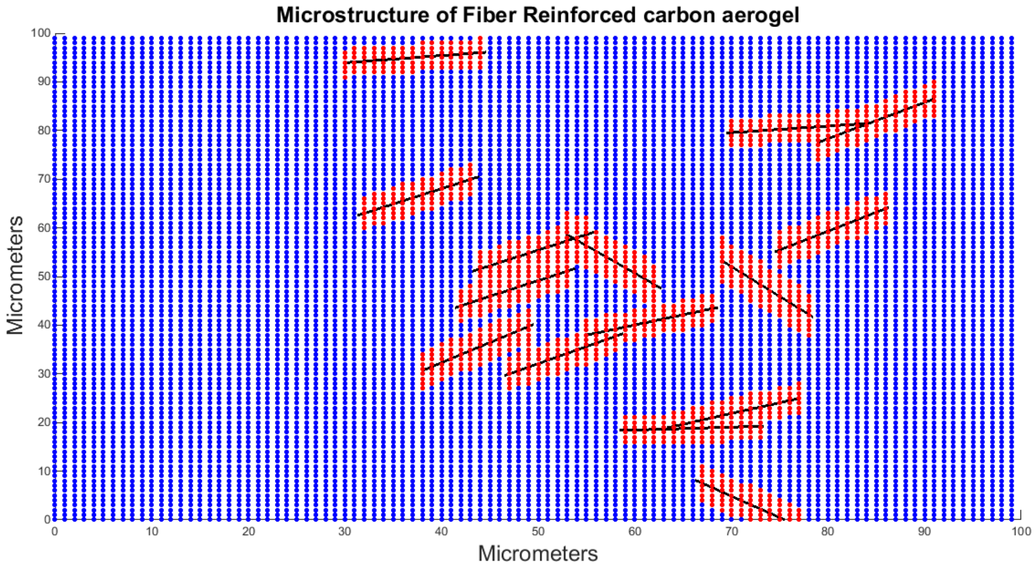


Figure 3.3. Shown is the microstructure of a CFCA composite generated in MATLAB. The red dots represent points within the carbon fiber, the blue dots are within the carbon aerogel, and the lines are the carbon fibers.

The code that was used to check if the point was within a fiber or aerogel was also used to generate four separate counters. Two of the counters determine the amount of points belonging to the carbon aerogel and the carbon fibers along each one-dot-wide column; while the other two counters determine the amount of times that the color of the points change from red to blue and blue to red within each one-dot-wide column. The use of these counts in determining sheet resistance is outlined in the electrical modeling section found later in Chapter 3. This code can be found in **Appendix A.**

3.2.2 Electrical Properties

In order to model the electrical resistance of our composite material, we relied on a generated model microstructure in MATLAB as discussed in 3.2.1 Microstructure. The algorithm that generates the microstructure includes counters, as described above, which determine the amount of carbon fiber, carbon aerogel, cross-overs between fiber and aerogel, and cross-overs between aerogel and fiber. These counts are then inputted into the following equation **(2)**:

$$\begin{aligned} R_{column} &= (\#\,blue) * (R_a) + (\#\,red) * (R_f) + \\ &(\#\,red - blue) * (R_{t_{rb}}) + (\#\,blue - red) * (R_{t_{br}}) \end{aligned} \qquad \textbf{(2)}$$

where "# blue" and "# red" are the counts of blue and red dots, respectively; R_a and R_f are the resistances of one aerogel and one fiber point, respectively; "# red – blue" and "# blue – red" are the counts of the cross-overs from fiber to aerogel and aerogel to fiber, respectively; and R_{t_rb} and R_{t_br} are the tunneling resistances of fiber to aerogel and aerogel to fiber, respectively.

The equation above for R_{column} finds the resistance of a wire that has a width of one point. The number of R_{column}'s found will be determined by the width of our 2D figure/sheet of the CFCA composite. The R_{column} is modeled as a circuit in series; however when combining the R_{column}'s to find the sheet resistance, we consider each R_{column} as a resistance in a parallel circuit. The equation **(3)** below acts to combine the R_{column}'s in a parallel circuit to find the total sheet resistance of our generated microstructure:

$$R_{sheet} = \left(\sum_{i=1}^{\frac{width}{diameter}} \frac{1}{R_{column}(i)} \right)^{-1} \qquad \textbf{(3)}$$

where R_{sheet} is the sheet resistance, width is the defined width of our sheet, and the diameter is the diameter of each point as defined in our code. **Figure 3.4** below illustrates our equivalent circuit model, illustrating a sample sheet with a width of two-points/columns. Each column is represented in series, and the columns are in parallel with each other. Included in the model, as mentioned above, are the tunneling resistances, and the resistances of the carbon aerogel and fiber. Initially, we assumed a 12V battery just for simplicity in our calculations, however we have had to reconsider this because the power dissipated from the fabric is too large. Therefore, we have considered a 5V battery, and in the final design would include a voltage regulator and a resistor to regulate current output if necessary.

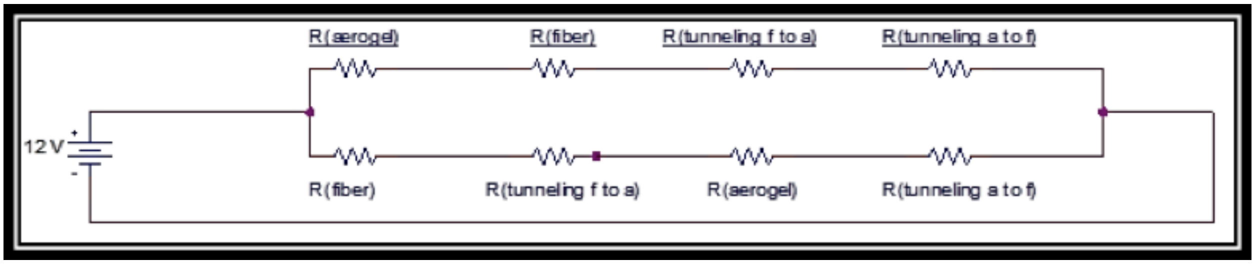


Figure 3.4. Shown is the equivalent circuit model for the CFCA composite with a width of two columns. R(tunneling f to a) is the tunneling resistance from fiber to aerogel and R(tunneling a to f) is the tunneling resistance from aerogel to fiber.

The analytical solutions/geometrical extremes for resistivity to our equivalent circuit model: lower limit should correspond to the resistivity of carbon fiber and an upper limit of carbon aerogel. If we take a random sheet to create our microstructure model, and none of the fibers are contained within the sheet, then we are at the lower limit of the resistivity. If the volume fraction of the fibers within the aerogel matrix is 100%, then we are at the upper limit of the resistivity, which corresponds to the resistivity of carbon aerogel.

These analytical solutions will guide us when evaluating our current model, as upper and lower bounds for the electrical resistivity and therefore if our numerical model falls between these limits we will consider it valid at least as a first approximation.

3.2.3 Thermal Properties

Our thermal model depends on thermal conductivity (*k*) values reported in literature as 0.073W/m-K. We have created a non-steady state model to determine ‘time to thermal failure’, which we tested through a range of reported thermal conductivities. Our current model was written in MATLAB to calculate heat loss via conduction of an approximated human body. Our model relies on a discrete 1-D approach to Fick’s First Law of Diffusion as it applies to heat transfer, as shown in equation **(4)**, which we have solved for a 2-D discrete system as equation

(5). In this case T_{hot} is the body temperature associated with the wearer of the fabric, while T_{cold} is the hostile outside temperature.

$$J = -k\frac{dT}{dx} \tag{4}$$

$$J = -k * l * \frac{T_{hot} - T_{cold}}{dx} \tag{5}$$

For this model we have geometrically simplified the body in question to a cylinder length *l* to be 1.83m, radius *r* of 13cm, and mass *m* of 90.72kg (or 200lbs). We chose these values to approximate an average male soldier 6ft tall and 200lbs in weight. The cylinder is also wrapped in an intermediate insulating layer of varying thickness *x*, and coefficient of thermal conductivity *k*, intended to represent our insulating aerogel fabric. We assume this cylinder to start as a finite heat source *Q* described in equation **(6).**

$$Q = m * c * T \tag{6}$$

Here we have assumed an average thermal heat capacity c of the human body to be 3.46 kJ/kg-k, and the initial temperature *T* to be 310K or 98.6F. Currently we are using a time step of 1s, and allowing the simulation to run for 10,000s. At each time step we account for heat lost to the body via the hostile thermal gradient, and then reassess the body temperature as a function of the remaining heat.

In order to model metabolic heat generation by the wearer's body, we have assumed heat generation by the body to be constant, and independent of temperature. For a sedentary male wearer weighing 200lbs, we assumed a maintenance calorie intake of 2400kcal/day (1cal = 4.184J). Assuming this energy is burned at a consistent rate throughout the day, this predicts a maximum of 115.7W of power generation. This level of heat generation is not always necessary though, especially when the body temperature is very close to or above the desired healthy temperature. To account for this thermoregulation, we have instituted a simple controls algorithm into our calculations that will modulate the heat generated at the end of each time step. If *i)* The current body temperature is above the critical temperature for a fever (we have assumed this to be 99.8°F) then the heat generated by the body is reduced by 0.5W, if *ii)* the body temperature is below the onset of hypothermia temperature (we have assumed this to be 95°F), then the heat generation by the body is increased by 0.5W, *unless* it has reached the maximum value of 115.7W **iii)** and otherwise if the body temperature is inside this critical range, then the heat generated by the body remains the same between time steps. This algorithm relies on the assumption that the maximum rate the heat generation can change is 0.5W/s. This value is currently being used as a placeholder, and further investigation would be necessary to determine the best value for each individual type of wearer, as the value is dependent on the individual metabolism and activity in question. **Figure 3.5**

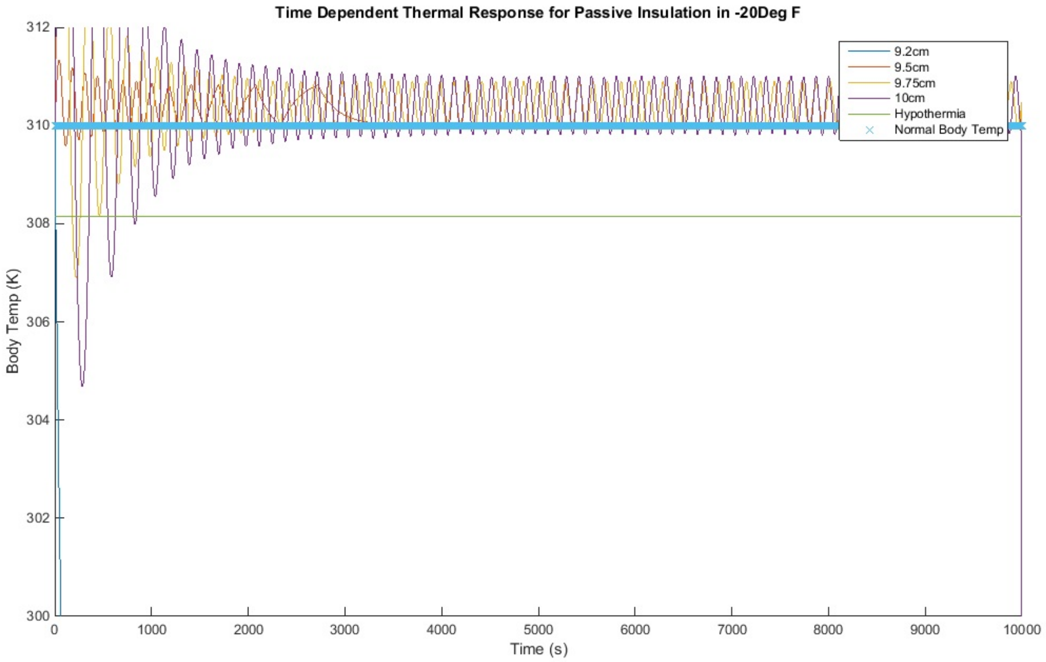


Figure 3.5. Model of thermal response of the wearer with the actively heated insulation layer in a cold weather environment.

Finally, to account for joule heating across the fabric, we've calculated the resistance of the fabric using equation **(7)** and the power generated by a fixed current drop across the fabric via equation **(8).**

$$R = \rho * (I / A) \tag{7}$$

$$P = I * R \tag{8}$$

In this case ρ is the resistivity, as calculated by our electrical modeling, l is the length of the fabric, or in this case 1.83m, and A is the cross sectional area of the fabric, calculated as a function of insulating thickness. We've assumed that any power generated by thermoelectrical losses goes directly into the body, and have not accounted for any thermal interactions with the fabric. Since we are essentially modeling a cylinder of varying thickness, we can account for the cross sectional area with equation **(8)**

$$A = 2\pi r * x \tag{8}$$

Where r is the radius of the body in question, previously defined as 13cm, and x is the insulating thickness, a controlled variable.

3.3 Prototype Synthesis

3.3.1 Design Considerations

There are 2 main stages of synthesis of the RF aerogel: the first stage involves preparation of the sol mixture and gelation and curing of the gel, and the second stage is the drying of the wet gel. The most important factors in the first stage are: catalyst concentration, initial gel pH, and the concentration of the solids in the sol. The important factors in the second stage are: the difference between the surface tensions of the solvent before and after drying. The carbon aerogels are made in the third stage through carbonization.[18] The following **Table 1** shows the different processing parameters and their effects.

Table 1: Adapted from Al Muhtaseb et. Al- processing parameters and their effects.[18]

Factor	Effect
Decreasing Reactant Concentrations (equivalent to reducing R/F, R/W, or R/C ratios)	smaller particles and pore sizes, less compaction of gel structure, increase surface area of xerogels
Acid Catalyst Concentration	at low RF concentrations: small, smooth, fractal aggregates of particles with wide PSDs at high RF conc: no fractal aggregates, very narrow PSDs, may reduce gelation time

Increasing gel pH	Increase surface area and pore volumes of carbon aerogels, insignificant effect on surface area of carbon xerogels, increase in pore volume of carbon xerogels at high density of reactants
Gelation and Curing	Required for improving the crosslinking of polymer particles
Solvent Exchange	Necessary for supercritical drying with CO_2, facilitates replacement with drying media, reduction of surface tensions upon subcritical evaporation
Subcritical Drying	Production of dried dense polymers called xerogels, causes significant shrinkage of especially wide pores, effects can be insignificant if gels were synthesized with high mechanical strength
Supercritical Drying with CO_2	Production of dried light polymers called aerogels, insignificant shrinkage of pore structure, high surface area and pore volumes, requires high pressures and solvent exchange of CO_2
Supercritical Drying with acetone	Uses lower pressures than CO_2, eliminates the need for exchanging solvent with CO_2, requires higher temperatures though, may cause partial thermal decomposition of dried gels
Freeze Drying	Produces dry polymers known as cryogels which are mostly mesoporous. Usually results in brittle gels. Based on sublimation of liquid solvent
Increasing Pyrolysis temperature	Reduces oxygen content, surface area and pore volume of xero and carbon aerogels, increases macropore size distributions, increases micropore distributions when very low R/C ratios are used

Drying occurs after one has made a cross-linked gel and is necessary to transform the cross-linked gel to a xerogel (via subcritical drying) or an organic aerogel (via supercritical drying).[18] Supercritical drying occurs at elevated temperatures and pressures and requires a supercritical dryer while subcritical drying is done at ambient pressure and room temperatures but requires additional solvents and chemicals.[2] Below in **Table 2** we have summarized findings on the two drying techniques from across our literature review. Supercritical drying is advantageous because of the avoidance of crossing the direct liquid-gas phase boundary. Freeze drying can be used, but it more likely to cause cracking and collapse due to the solid-gas boundary crossing.

Table 2: Supercritical vs. Subcritical Drying vs. Freeze Drying

Supercritical Drying		Subcritical Drying		Freeze Drying	
Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages
No surface tension is exerted across the pores and the dry aerogel is able to retain its original morphology[25]	Requires High pressures, is complicated, expensive, dangerous when not using CO2, and not able to be mass produced[5]	Cheap, simple, not energy extensive[6]	May induce differential shrinkage and thus cracking due to the huge difference of the coexisting vapor and liquid phases[5]	Quicker due to lack of solvent exchange	Expansion of water can damage micro-crystallites[26]
Can Achieve low densities ~0.1 g/cm^3 (Feng 2012)	Energy Consuming[6]	Can be use to scale up production of Aerogels[6]	Produces higher density[5]		Expansion can disrupt electrical conductivity[26]
Able to withstand large capillary actions[6]	RF gels are prepared in water, which is poorly soluble into liquid CO_2 [27]	Higher compressive strength and stiffness and enhanced water resistance[18]	Less optical transparency, higher thermal conductivity, and smaller maximum dimensions, usually a few cm[27]		Aerogels formed can be more brittle than those formed by supercritical drying[11]
Can use alcohols Acetone is a very efficient drying agent, leading to low bulk densities and to low shrinkages, close to those already observed when using carbon dioxide instead and using acetone takes away the need to do solvent exchange[27]	If you use acetone then you need high temperatures due to the high critical temperature of acetone (235.1°C) which is more dangerous[18]				

If you use CO2 then only need to get to a temperature of 31.1°C to supercritically dry it[2]	If you use CO2 then you need to do solvent exchange which can range anywhere from 3-5 days[18]				

When synthesizing the aerogel we seek to control the density, porosity, surface area, shrinkage and tendency to crack, and the flexibility of the aerogel. The density of the aerogel has considerable impact on the thermal and electrical performance of the material. Thermal conductivity in polycrystalline carbon materials, including carbon aerogels, is mainly governed by phonon transport.[28] Phonons preferentially travel along the carbon particle matrix, while electronic heat transport is disrupted by the large number of crystallite boundaries, which serve as scattering sites. Therefore, the density of the carbon network determines how well carbon aerogel conducts heat. Several groups have reported significant density dependence of the thermal conductivity of carbon aerogels. Bock, et. al. report thermal conductivities **(8)** with an exponential dependence on density

$$\lambda \propto \rho^{\alpha} \tag{8}$$

where λ is thermal conductivity, ρ is density, and a=2.2.[29] Lu, et. al. report a similar exponential dependence with a =1.5 ± 0.1.[28] The density of the material is easily controlled by controlling the R/W and R/C ratios during sample preparation. Electrical conductivity **(9)** of the material can similarly be tuned by controlling density. Lu, et. al. reports an identical density dependence on electrical conductivity:

$$\sigma \propto \rho^{a} \tag{9}$$

where σ is electrical conductivity, ρ is density, and a =1.5 ± 0.1.[28]

Another important aspect of the aerogel design is the selection of the solvent used during drying. The conversion from conventional gel to aerogel relies on the removal of liquid from the cross-linked matrix without collapsing the porous network. Ambient drying with water as the interstitial liquid would create sufficient capillary pressure to collapse the majority of pores as the sample dries. Thus, it is important to dry the sample when it contains a solvent that does not create significant capillary pressures as it evaporates. Although the initial interstitial liquid in our design will be water, multiple solvent exchanges can wholly replace all water within the gel with less destructive liquids. Ideally, we would like to supercritically dry our sample with acetone, as it does not exhibit any damaging capillary effects when drying and requires lower pressures than CO_2.[18]

The final aspect of our design that we need to consider is the amount of carbon fibers that will be interspersed throughout the aerogel matrix. Adding carbon fibers to a carbon aerogel creates a composite material that is more mechanically robust and flexible than pure carbon aerogels.[3] The filling fraction of these fibers within our sample must also be considered. There will exist an upper limit of fibers added at which the composite material will no longer function as a thermal insulator. Seeing as how carbon fibers conduct heat over twice as well as carbon aerogels of similar density[3], it is important to include in the material design an amount carbon fibers in the aerogel matrix so that the system functions as both a flexible material and thermal insulator, at the interface of the trade-off. As a side note, it is important to initially impregnate the RF gel with pre-oxidized polyacrylonitrile (PAN) fibers so that, when the sample is pyrolyzed, the PAN fibers will pyrolyze at the same rate as the RF aerogel. By doing so, the sample will be free of cracks and defects that would originate from differential shrinkage.[3]

3.3.2 Product Design

We plan to use polyacrylonitrile (PAN) fiber felt and an RF aerogoel to create our composite since research has shown this combination results in low shrinkage and no cracks.[3] We plan to impregnate the felt with the RF solution, set the gel through heat aging and solvent exchange, supercritical drying, and carbonizing the sample. This process is diagrammed in **Figure 3.6** and the resulting composite is shown in **Figure 3.7**.[3]

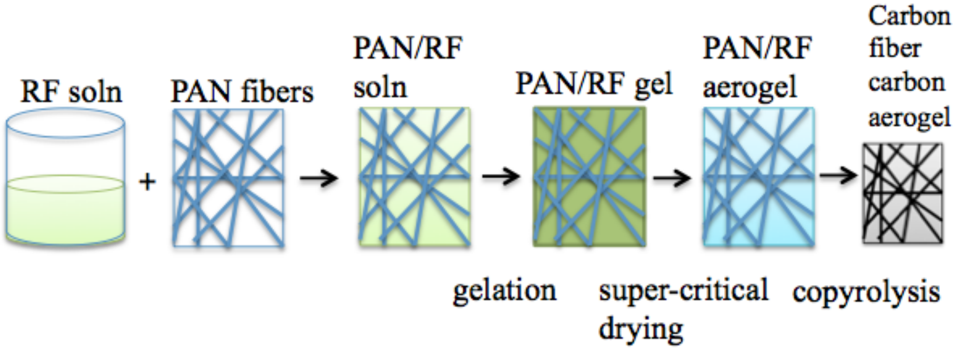


Figure 3.6. Carbon fiber RF aerogel composite synthesis diagram adapted from Feng 2012.[3]

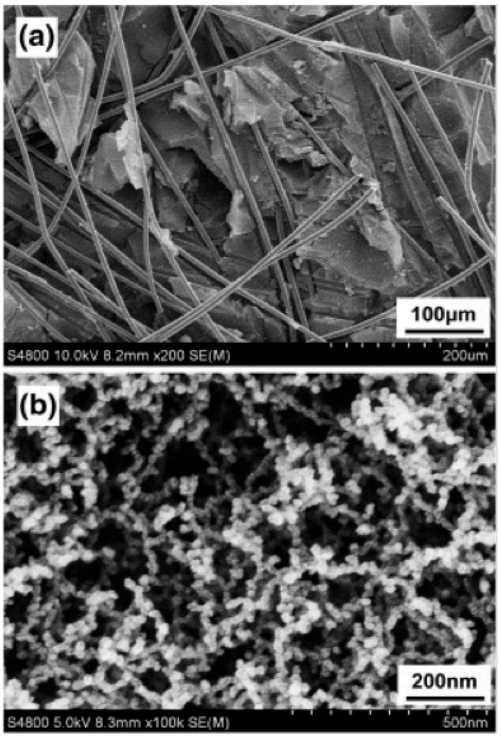


Figure 3.7.[3] (a) Carbon fiber-reinforced carbon aerogel and (b) Carbon aerogel

The ratio of resorcinol to water in the solution. the ratio of catalyst to resorcinol solution, heating times and temperatures, and fiber characteristics all affect the structural characteristics of the composite, and thus the thermal and electrical properties as a result. We plan to use varying process parameters determined from our design of experiments in order to yield a composite with maximum electrical conductivity with respect to minimum thermal conductivity.

Based on preliminary data found on this trade-off in our literature review for carbon aerogels, we will begin our design with a goal density of 100-300 mg/cm.[25] Because these types of composites vary greatly with synthesis specifics, we will not be able to rely on the study by

Feng et al. for specific thermal and electrical property predictions. We will have to find a density most likely within that range that will yield our most optimal property trade-off while remaining flexible and mechanically durable.

In addition, we will also be making composite samples without reinforcement of the carbon fibers to give us a reference of the carbon aerogel properties. This way, we can test both the fibers alone and the aerogel alone for thermal, electrical, and mechanical properties, which should help us develop our models as well as predict an optimal density. Our main challenge at this point is obtaining PAN fiber felt. All other materials are easy to find.

Our attempts and variations of our Standard Operating Procedure for the synthesis of CFCA are detailed in Appendix C: Standard Operating Procedures for Synthesis of Aerogels and Chapter 4 Section 4.2: Prototype Outcome and Characterization.

3.3.3 Design of Experiment

Experimental design is an important contribution to the overall design in our project. If we were developing this composite for industry, we would need to do an extensive set of experiments in order to obtain information about the various parameter effects in order to find the most optimal composition and processing of the composite. This information would also be helpful for future development and experiments done in the field of electrically conductive, thermally insulating carbon fiber-reinforced carbon aerogels. We have designed an experiment that would achieve these goals if we had more time and resources to complete it.

Independent Variables:

- R/W ratio- which heavily affects the density of the aerogel, and thus the resulting electrical and thermal conductivity
- Fiber fraction- increases both electrical conductivity and flexibility, but also has an upper limit where the composite would no longer function as a thermal insulator and/or it would no longer resistively heat

Constants: Although it could be beneficial to vary some of these components in future testing, they do not affect the aerogel or composite properties as greatly as those listed in the independent variables. To limit and simplify the experiment to obtain more information about the above listed, we would hold the following aspects constant:

- R/C, R/F ratios- these ratios have been shown to not heavily affect aerogel properties
- Pyrolysis parameters
- Solvent used in drying
- Drying procedure

Experimental Design: The following experimental design will vary the two independent variables chosen across 5 levels each. Each combination would be made in triplicate. Each sample would then be tested to determine: electrical conductivity, thermal conductivity, and flexibility. Each of these measured properties will be evaluated by Taguchi loss functions across the various parameter combinations. Taguchi loss functions are widely used to evaluate product performance for changes in variable in order to determine the significance and effect of each involved factor.[30] Each measured property will be evaluated to determine the best combination of R/W ratio and fiber fraction to maximize each respective loss function.

Independent Variables: 2 variables with 5 levels each (the R/W ratio and fiber fraction are in weight fractions of the solution step)

Condition Key	**1**	**2**	**3**	**4**	**5**
R/W ratio (a)	0.01	0.05	0.10	0.15	0.20
Fiber fraction (b)	0.10	0.15	0.20	0.25	0.30

Samples: Each sample number would be synthesized in triplicate.

Sample Number	**R/W Ratio (a)**	**Fiber Fraction (b)**	**Duplicate Check**
1	1	1	11
2	1	2	12
3	1	3	13

4	1	4	14
5	1	5	15
6	2	1	21
7	2	2	22
8	2	3	23
9	2	4	24
10	2	5	25
11	3	1	31
12	3	2	32
13	3	3	33
14	3	4	34
15	3	5	35
16	4	1	41
17	4	2	42
18	4	3	43
19	4	4	44
20	4	5	45
21	5	1	51
22	5	2	52
23	5	3	53
24	5	4	54
25	5	5	55

Measured Properties: Every sample would be tested for each property. The Taguchi loss functions are used to evaluate measurements in terms of desired properties. For example, we want to minimize thermal conductivity in order to retain as much heat as possible in the composite to serves its purpose as an insulator. In that case, we would use the "less is better" loss function, because we want low thermal conductivity.

Property	**Test**	**Desired Loss Function**	**Loss Function**
electrical conductivity	four-point probe (S/m)	more is better	-10log((1/n)summation(1/y^2))
thermal conductivity	hot wire test (W/mK)	less is better	-10log((1/n)summation(y^2))
Flexural Strength	bending (bending stress vs. displacement) (MPa/mm)	less is better	-10log((1/n)summation(y^2))
y= mean response of run			
n=sample size(number of experimental runs)			

Electrical conductivity can be easily measured using a four-point probe test. Due to the varying composition of this composite, it would be important to fully characterize the sample across several orientations and probe placements.

Thermal conductivity can be easily measured via the hot wire method. This a standard transient dynamic technique in which the temperature rise in a defined distance from a hot wire that is embedded in the test material. In order to calculate thermal conductivity, you assume that the heat source has a constant and uniform output along the length of test sample. The thermal conductivity can be derived directly from the resulting change in the temperature over a known time interval. However, it is easier to just use a thermal conductivity tester which gives you the thermal conductivity of your sample instead of having to derive it.

The bending strength can be measured via the three point bend test. In the three point bend test you are able to measure the bending strength also known as the flexural strength.

Flexural strength is the measurement of the sample's ability to resist deformation under load. In the three point bend test the two ends of the sample are fixed and the load is applied in the middle of the sample. The flexural strength is the strength represented when the material fails and ruptures which is seen in a graph of bending stress vs. displacement.

Measured Property Analysis: Each triplicate sample of each parameter combination would be tested and the properties would be analyzed in terms of the variance and in terms of the desired loss function. A table like the one below would be constructed for each of the three measured properties.

Experimental Run Responses: Test 1- i.e. Electrical Conductivity							
Sample number	**(a)(b)**	**Run 1**	**Run 2**	**Run 3**	**Mean**	**Variance**	**Loss Function**
1	11	11R1	11R2	11R3	avg(11R1+11R2+11R3)	var(11R1, 11R2, 11R3)	-10log((1/3)summation(1/mean^2))
2	12	12R1	12R2	12R3	avg(12R1+12R2+12R3)	var(12R1, 12R2, 12R3)	-10log((1/3)summation(1/mean^2))
3	13	...	...	...	...	...	...
...	...	...	...	...	...	...	...
24	54	...	...	...	...	...	...
25	55	55R1	55R2	55R3	avg(55R1+55R2+55R3)	var(55R1, 55R2, 55R3)	-10log((1/3)summation(1/mean^2))

Parameter Effect Analysis: Each level of both independent variables would be analyzed in terms of the mean, variance, and loss function. For example, the mean value of the specified property of every sample made with parameter a1 would be averaged and listed in the table below. Then each loss function value for the specified property of every sample made with parameter a1 would be averaged and listed as such in the "loss function" section in the table below. The same would be done for variance. We would seek to *minimize* variance and *maximize* the desired loss function. For example, we would determine which combination a_nb_n for n=1-5 yields the smallest variance for each property and which combination a_nb_n yields the maximum loss function for each property.

Parameter Effect		
	R/W Ratio (a)	**Fiber Fraction (b)**
Mean	a1	b1
	a2	b2
	a3	b3
	a4	b4
	a5	b5
Loss Function	a1	b1
	a2	b2
	a3	b3
	a4	b4
	a5	b5
Variance	a1	b1
	a2	b2
	a3	b3
	a4	b4
	a5	b5

Ideally, there would be overlap between the ideal parameter combinations for variance and loss function across all three measured properties. However, it is likely that it would take some expertise judgments to evaluate the weighting of the two parameters on the resultant properties and select a few combinations to continue testing.

Auxiliary measurements that we might also consider are:

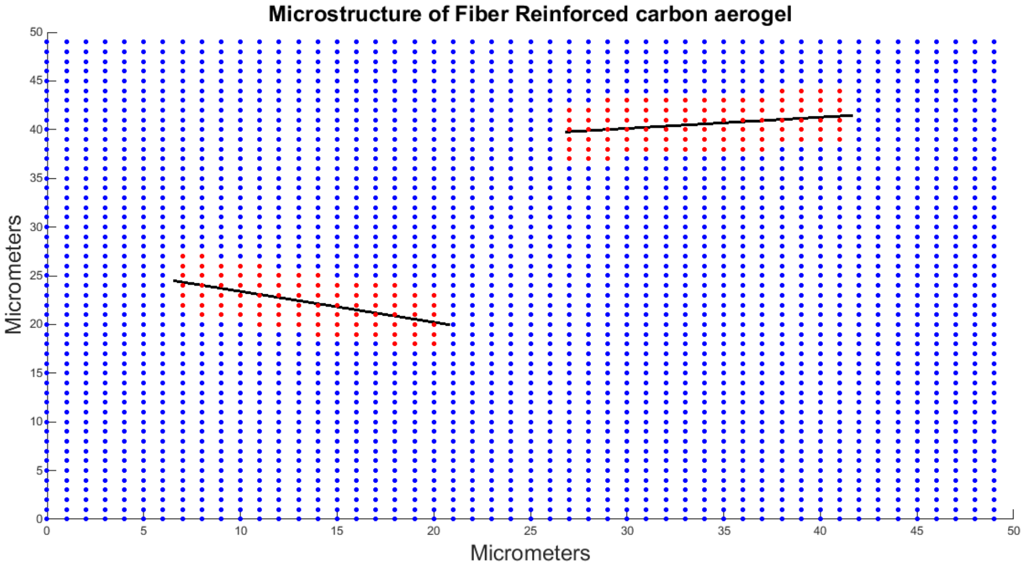
- Density (by neutron scattering)- density is the main affector of thermal and electrical conductivity
- Sound velocity/ mean freepath- indicative of electrical conductivity
- shrinkage after drying- related to density, flexibility, and crackage
- microcrystallite (nodule) size- related to conductivity

Chapter 4: Results and Discussion

4.1 Modeling

We were able to model the microstructure in MATLAB while including a carbon fiber count input parameter within the code so that we could vary the volume fraction of the fibers while calculating the sheet resistance. Two plots of the microstructure are shown below in **Figure 4.1**, one with a low fiber volume fraction of 0.0756 **(a)**, and one with a high volume fraction of 0.3848 **(b)**. There are significant differences between the two microstructures, and they arise from the fact that we have measured the 2D sheet resistance, and not the resistance in 3D. The 2D sheet resistance is a simplification and it was used because a 3D model was not plausible within the time constraint of a semester. Also, it is much more computationally intensive to do 3D, and it already takes ~ 10 minutes to form a 2D microstructure in MATLAB.

(a)



(b)

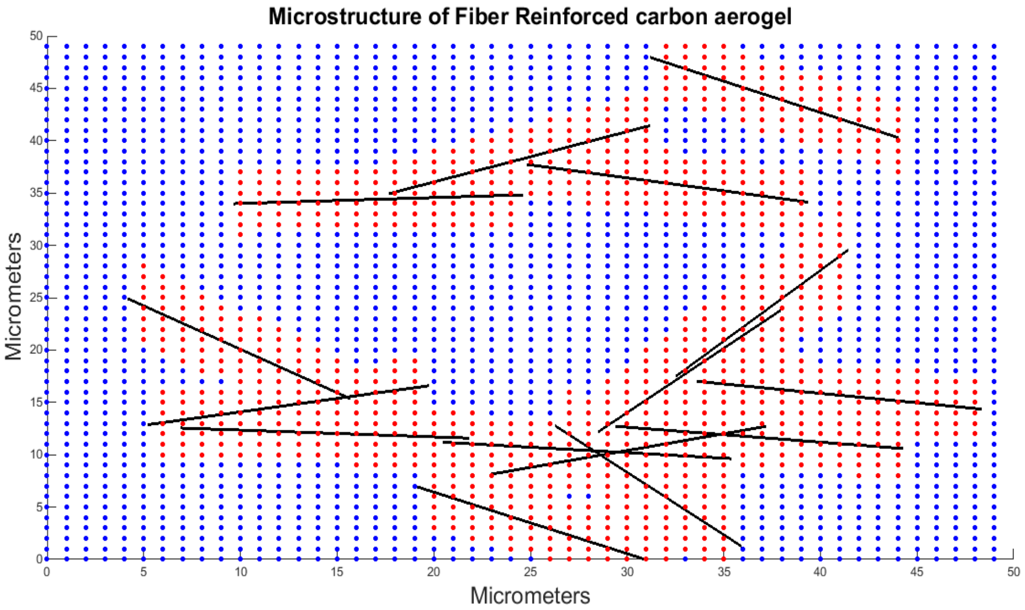
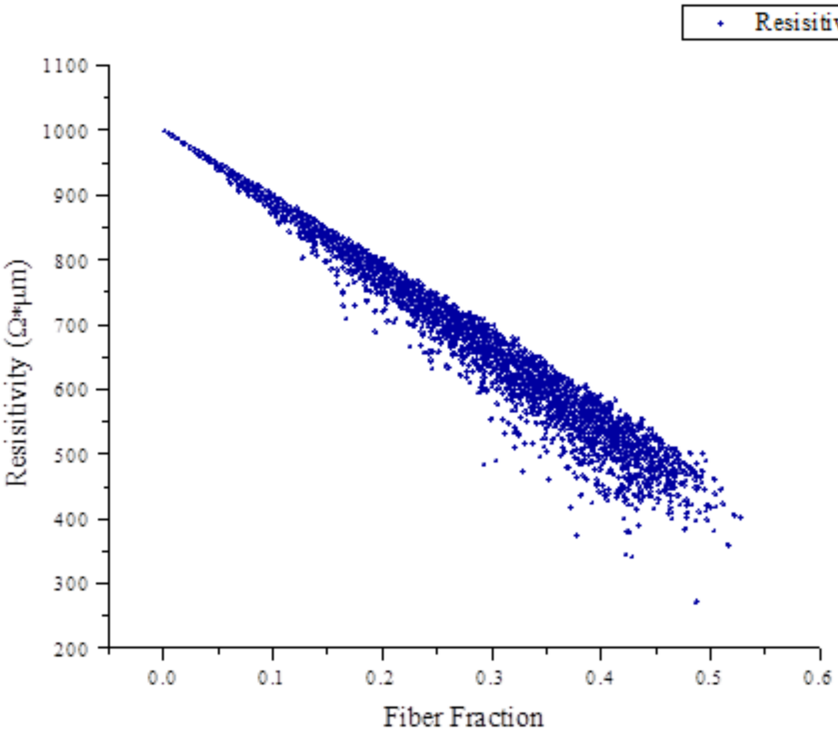


Figure 4.1. Microstructures generated from MATLAB with carbon fiber volume fractions of 0..0716 (a) and of 0.3788 (b). The red dots represent the parts of the microstructure within the diameter of the fibers (represented as black lines). The blue dots are representative of the carbon aerogel matrix.

The sheet resistance was calculated from the generated microstructures by the method outlined in Section 3.2.2 "Electrical Properties." A sample of how the line scans were done is shown in **Figure 4.2** below. The sheet resistance, calculated by considering each of the line scans as part of a parallel circuit, is tabulated with the respective volume fractions. The distribution of the fiber volume fraction within the sheet is included. There is a distribution of volume fraction because the algorithm inputs a certain number of fibers, but they are given a random orientation and position. Therefore, the fibers may overlap with each other in a 2D sheet and the entire fiber may not be represented within the sheet resistance calculation. Also, the fiber placement within the coordinate system may preclude the entire fiber from being included in the microstructure. Due to these factors the volume fraction varies from calculation to calculation, leading to variations in the sheet resistance, and the entire distribution of 4000 points (volume fraction vs. sheet resistance) are shown below in **Figure 4.2.** All the microstructures generated were a 50 by 50 µm.



.

Figure 4.2: A distribution of the sheet resistances corresponding to a given fiber volume percentage. For each point a new random microstructure was generated and sheet resistance calculated.

The sheet resistance is related to the resistivity by a factor of 1 μm, since this is the thickness of the sheet, to obtain units of Ω-µm. Therefore, any resistance shown on these graphs can be converted to a resistivity value by using this factor. With this factor we have tested this numerical model via comparison to the geometrical extremes. The geometrical extremes are described as a sheet without any fibers within it and a sheet completely filled by fibers. Using the resistivities of 1000 Ω-µm for the carbon aerogel and 32.99 Ω-µm for the carbon fibers.[31]

We wanted to create a sample close the sample that Feng et al. made. We calculated the fiber fraction of the Feng sample to be about 36% (calculation can be found in Appendix IV). However the spread for resistance of 36% seemed fairly wide with about 540-640 ohms discounting outliers. Considering this we decide to use 20% which had a smaller range of 760-800 ohms. The distributions of the sheet resistances are shown in **Figure 4.3** for the 36% (+/- 1%) volume fraction of fibers **(a)** and 20% (+/- 1%) volume fraction of fibers **(b)**.

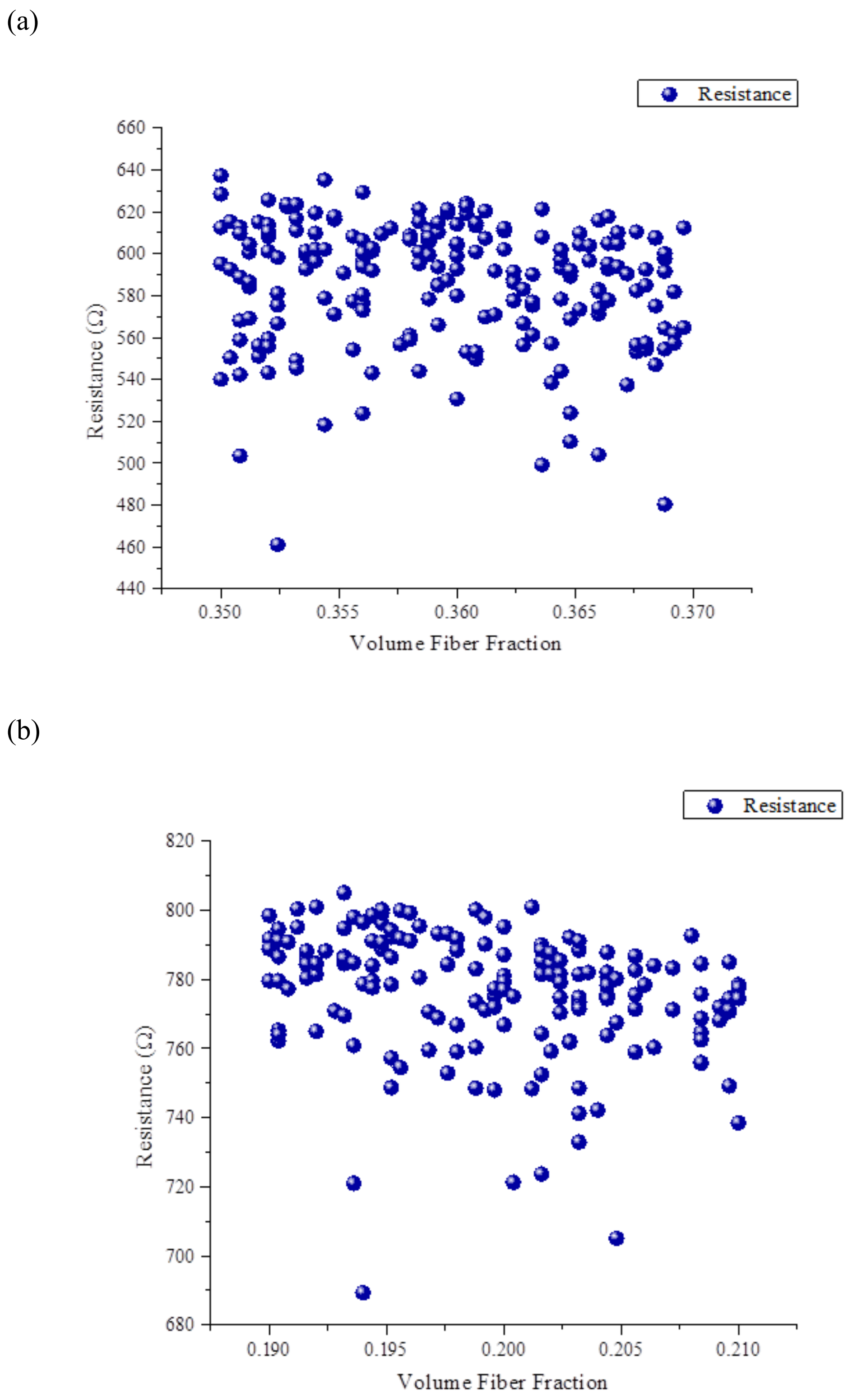
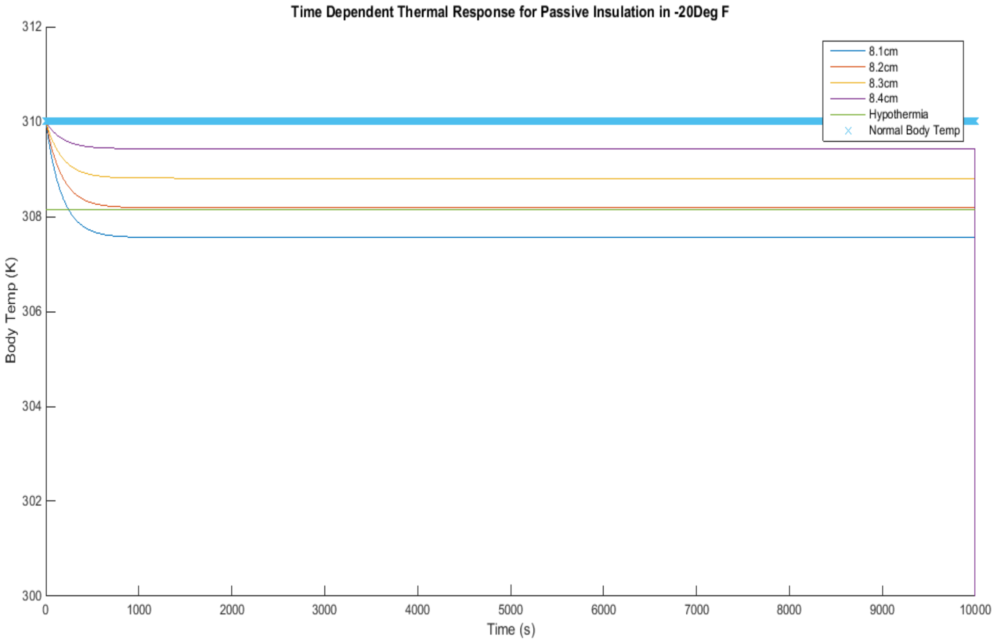


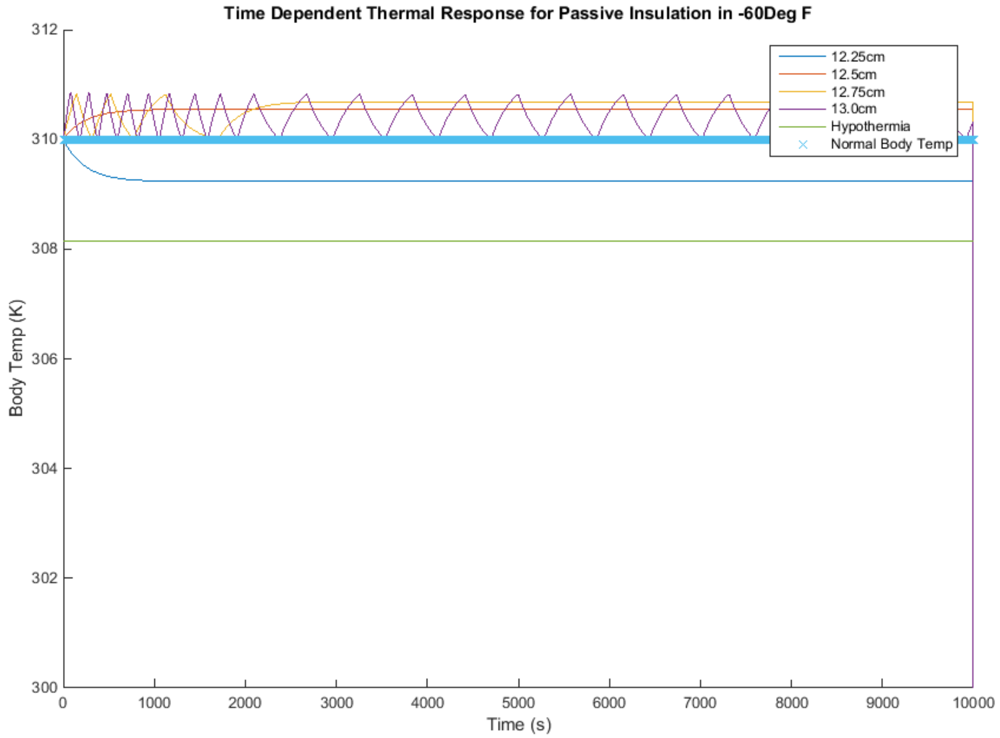
Figure 4.3. Shown are the sheet resistance distributions for 36% (+/- 1%) **(a)** and the 20% (+/- 1%) **(b)** fiber volume fractions.

To test our thermal model we applied two hostile temperatures, -20F, and -60F. -20F was originally applied as a test stress level, simply as a predictor to establish what types of performance may be achievable. In such an environment we predicted the wearer could survive at a steady state temperature above a hypothermic level with an insulating thickness of approximately 8.1cm. **Figure 4.4(a).** Next we tested a stress level of -60F, mentioned earlier in Ch. 1 as the Army's maximum possible gradient, and found a wearer could survive with an insulating thickness of approximately 12.25cm. **Figure 4.4(b)**. These models suggest that as a standalone insulation layer, our fabric could feasibly perform in the harshest considerable design environments.

(a)



(b)



.

Figure 4.4 Critical insulating thicknesses for -20°F(a) and -60°F(b).

Table 3. Joule heating inadequacy (assumes cylindrical shell of length *l*=1.83m.

Resisitivity (Ω-m)	Thickness (m)	Resistance (ohms)	Current Applied (A)	Power Generated (W)
6.40E-04	0.05	0.00373	0.1	0.000373
6.40E-04	0.05	0.00373	0.5	0.001865
6.40E-04	0.05	0.00373	1	0.003729
6.40E-04	0.05	0.00373	10	0.037299
6.40E-04	0.05	0.00373	100	0.372994

Additionally, we considered the feasibility of generating heat via joule heating. Originally we had considered dropping a 12V potential across the fabric along the length of the cylinder, however given the low resistance of the fabric, this would be nearly analogous to shorting out our power source, and obvious electrical fire hazard. Instead, we considered a system in which the current applied to the fabric would be regulated by an outside source. The results, shown in **Table 3** suggest that in the current cylindrical shell geometry, insubstantial power is being generated via joule heating, even at extremely high applied currents. Given that upwards of 1kW of thermal power can be transferred in our most hostile thermal environment, the benefits from joule heating seem insignificant in this fabric configuration. Alternatively, we considered how much heat could be generated if the fabric was instead applied to a larger system in the form of thin strips. By applying a current across a much smaller surface area, it becomes possible to increase the resistance, and therefore the power generated **Table 4**.

Table 4. Power generation could be increased if current is applied across thin strips instead of bulk fabric.

Resisitivity (Ω-m)	**Cross Sectional Area (m^2)**	**Resistance (ohms)**	**Current Applied (A)**	**Power Generated Per Strip (W)**
6.40E-04	0.0001	1.17E+01	0.1	1.17E+00
6.40E-04	0.0001	1.17E+01	0.5	5.86E+00
6.40E-04	0.0001	1.17E+01	1	1.17E+01
6.40E-04	0.0001	1.17E+01	10	1.17E+02
6.40E-04	0.0001	1.17E+01	100	1.17E+03

So for example, it seems possible that if 10 strips were evenly distributed around the body with this given geometry, a 5A source could generate nearly an additional 60W of power. While this is still fairly energy intensive, it seems possible that if smaller geometries could be processed, these strips could find value as a single aspect of a larger composite fabric, given their low density and thermal conductivity.

4.2 Prototype Outcome

4.2.1 First Experiment

We did a preliminary prototype based on the procedure presented by Schwan et al. in which they made a flexible RF aerogel.(Schwan 2013). The goal of this prototype was to see if we could replicate their results achieved and carbonize the RF aerogel and make a carbon aerogel. We used the materials from **Appendix B** and the procedure from **Appendix C.I**.

Ratios:

The R/W molar ratio was systematically varied from 0.005 to 0.013

The R/F molar ratio was fixed at 0.5

The molar ratio of R/C was fixed at a value of 50 (gelation did not occur in ratios above 50)

Discussion/Results:

This procedure did not yield a flexible RF aerogel that we had hoped for. In this experiment, we were not able to store our samples in the oven for 7 days. This was due to a conflict with another class needing to use the furnace we had access to in the MEMIL lab. We had 5 days available so we increased the temperature to 100 degrees Celsius in attempt to ensure full gelation. The oven-cured sample was black instead of brown in color and was quite brittle. We expect this to be due to a few factors. First were the sample volumes. The study by which we designed our protocol never indicated how much of each chemical or material they used, just the ratios of their samples. We poured 10 mL of solution into our sample holders. In retrospect, we should have known from our literature review that there would be significant volume shrinkage and should have used a greater volume of solution to obtain a bulk sample, not a thin slab. We also expect our small sample size to have contributed to the difficulty in getting exact ratios that the paper called for which in turn affects the ability to get the flexible RF aerogel. We also faced difficulty in adjusting the pH to 5.0-5.6. When using nitric acid to lower the pH of the RF solution we would add a small drop and the pH would jump from 6.0 to 2.5-3. Out of the 10 samples made only 3 were able to be adjusted to 5-5.6 pH. We could have diluted the acid or used a buffer in the solution to address this. Furthermore, our sample likely evaporated due to the seal. At this time we did not have proper seals on the beakers and they were covered with foil and sealed with rubber bands. This likely contributed to the gels drying out. Our sample did not complete a proper gelation step, most likely because we had to increase the temperature due to lack of time in the oven. Instead, gelation occurred too quickly which resulted in a gel that was dried out and brittle at the end. However, we still believe it would be beneficial to explore if this process to make flexible carbon aerogels using ambient drying due to its potential scalability. Ambient drying would eliminate some need for expensive equipment and materials such as a supercritical dryer.

4.2.2 Second Experiment

We did a secondary prototype based on the procedure presented by Feng et al. in which they made a carbon fiber reinforced aerogel using pre-oxidized PAN fibers.[3,32] We used the ratios for the materials that were presented in Feng 2012 as opposed to Feng 2011, because they were able to get lower densities for the aerogel. However, we did not have access to a supercritical drier so we attempted the two other common drying techniques: ambient drying derived from Feng 2011 and freeze drying derived from Tamon 2001.[33] The goal of this prototype was to see if we could get similar results achieved in Feng 2012 using different drying methods. Due to equipment limitations, we used freeze-drying. We used the materials from Appendix B and the procedure from **Appendix C.II** and **C.IV**.

Ratios:

W/R ratio of 90
R/C ratio of 490
F/R ratio of 2

The actual values we were able to achieve were: a W/R ratio 90.002, R/C ratio of 481.37, and a F/R ratio of 2.008. The calculations for the ratios are presented in **Appendix D.I.**

Initial Beaker:

314 grams of Deionized Water (W)
24.004 grams of Resorcinol (R)
13.144 grams of Formaldehyde (F)
0.048 grams of Sodium Carbonate (C)

Table 5: Amount of Solution in Each Beaker After Splitting Up the Solution

Sample 1	Sample 2	Sample 3	Sample 4
86.654g solution	87.025g solution	89.201g solution	86.026g solution

Our apparent solution density was 1.00659 g/cm^3 and the calculation is presented in **Appendix D.II.**

We attempted to produce an aerogel of 20% by volume fraction filling of carbon fibers, for sample 1 and sample 3, which was calculated from the modeling team from section 4.1. Our actual volume fraction filling of fibers that we were able to achieve were 18.85% and 20.02% for sample 1 and 2 respectively and the calculations are shown in **Appendix D.III**.

Discussion/Results:

We attempted to transform the gelated solutions through three different drying techniques: supercritical drying, ambient drying, and freeze drying. In Experiment 1 we attempted to produce a flexible RF aerogel via ambient drying. In Experiment 2 we attempted to produce a carbon aerogel and carbon fiber reinforced aerogel via ambient drying and freeze drying. While struggling to obtain access to a supercritical drier, we originally used ambient drying in attempt to obtain a proof of concept based on Feng 2011, using Feng 2012 synthesis parameters in hopes of creating a low density carbon fiber-reinforced aerogel. After that failure, we were able to secure a freeze dryer which prevented the need to do extensive solvent exchange which would give us enough time to do characterization. Ideally, we would use a supercritical drier as they did in Feng 2012 in order to create a low density high porosity aerogel.

We had originally designed our material to be immersed in liquid CO_2 over the course of several hours and then supercritically dried by controlling around CO_2's critical point (304.25 K at 7.39 MPa). We pursued two potential supercritical dryers in the University's Nanocenter and in Dr. Reza Ghodssi's MSAL facility. The supercritical dryer in the Nanocenter was unfortunately shut down for maintenance when we attempted to use it, and is still non-operational at the time of writing this report. After we had secured an appointment with Dr. Ghodssi's group, we discovered that his machine had a chamber size of only 10 mL as it is primarily used for combatting stiction in MEMS devices. However, this chamber size is much too small to fabricate our aerogel samples. Additionally, the dryer only allowed for a 15 minute CO_2 purge duration, which was not a sufficient amount of time to ensure that our ultra-porous material could completely undergo solvent exchange with the liquid CO_2. These are the only two driers to which we were given access.

Because of our inability to secure an operational supercritical dryer with a sufficiently large chamber, we decided to pursue an ambient drying process. Although this process is less than ideal, it is possible to transform a gelated sample to an aerogel if the water within the gel was exchanged with a liquid that exhibits low capillary pressures when drying. Aerogel pores are least damaged when immersed in acetone and left to dry under ambient conditions.[27] Therefore, we performed an acetone solvent exchange with the water-based gels over the course of 5 days and then placed them in an oven at 50 C until the samples were dry. Both a pure RF gel and an RF/PAN fiber composite gel were fabricated.

Additionally, we freeze-dried both a pure RF gel and an RF/PAN fiber composite gel with a Labconco FreeZone 2.5L Benchtop Freeze Dry System provided by Dr. Liangbing Hu. The water within the samples were frozen at -55 °C for 4 hours and then sublimated from the gel overnight via vacuum (<0.04 mbar). Freeze-drying the samples was relatively successful. Upon visual inspection, both samples seemed mechanically robust and capable of being elastically deformed (although the RF/PAN composite was much more adept at resisting plastic deformation. Both samples also seemed adequately porous and were able retain their initial shape.

It is important to note that there were other equipment limitations preventing the group from properly synthesizing our carbon aerogel. We were unable to obtain a low vacuum pump and chamber to degas our fiber-impregnated samples, which would rid the samples of any air pockets and voids. We also struggled to gain access to a furnace with function of 1000 °C and input N_2 into the chamber to pyrolyze our RF aerogels. Were we able to obtain this furnace (and, to a lesser degree, the vacuum system), we would have been able to proceed with the planned material characterization.

Chapter 5: Conclusions

In conclusion, we were able to design a microstructure model that is a function of the length, diameter, and orientation of the fibers within a carbon aerogel matrix, all of which control the fiber volume fraction. We successfully calculated a reasonable sheet resistance from carbon fiber reinforced carbon aerogel model using a line scan method, that took into account each conduction pathway and considering them as parallel circuit pathways. The sheet resistance multiplied by the thickness (resistivity) showed good agreement with our geometrical extremes as it always fell between the input parameters of 1000 $\Omega - \mu m$(aerogel resistivity) and 32.99 $\Omega - \mu m$(fiber resistivity). The model can be varied by changing the fiber content and sizing, if other groups were interested in modeling different composite compositions. Also, if other groups were interested in understanding the resistivity of other composite materials with various fibers and matrices, this may be a useful numerical model.

Our applied thermal model was used to measure passive insulating performance, which is based on the figure of merit shown in equation **7**, which accounts for the gradient, and the coefficient of thermal conductivity of the material in question. This model has simplified heat loss across the body to conduction, and does not account for radiation or convection losses.

$$FOM = k * \frac{dT}{dx} \tag{7}$$

The thermal model has shown that our material will be able to insulate as well as synthetic down (PrimaLoft), given our fabric and Primaloft have nearly identical *k* values. Using this model, we also determined a critical thickness for the temperatures of -20^{o}F and -60^{o}F, where the fabric will indefinitely insulate the body. Also, we have discovered that the Joule heating will not dissipate enough power to provide significant heating as compared to the body generation. Therefore, in future designs and uses of this material we will need to create geometries that make better use of the level of current density in this material. One way to do this would be to divide the fabric into thin, small strips of the material placed at susceptible points on the body.

5.1 Future Design Work and Prototyping

The modeling that we have completed can act as a first approximation to the thermal insulation and electrical resistivity that our carbon fiber reinforced carbon aerogel will possess. However, as part of our design we want to consider possible improvements to our design and future work that could implement said improvements. The first and most obvious improvement would be to model the microstructure in 3 dimensions, as this is a simplification solely based on computational difficulty and time. In order to speed up the creation of a 3D microstructure model, we would most likely need to use a supercomputer like the University of Maryland's Deepthought2 computer. The microstructure could still be made in MATLAB, however changes would need to be made within the algorithm. Instead of creating a 2D vector for the carbon fibers, it would be 3D, and the line scans would turn into plane/sheet scans, which may no longer act as a good approximation.

One way to improve the microstructure model would be to generate the carbon aerogel matrix around a carbon fiber felt using a Kinetic Monte Carlo simulation. The generation of the carbon aerogel from random movements of the carbon particles around the fibers would lead to a better representation of experimental properties.

A further goal in future work would be to figure out a method to determine whether the Joule heating and the thermal insulation work symbiotically or if one effect deters the other. In our current thermal model, we assume heat syncs within the body, and not within the material. One macroscopic virtual test would be to model the two components separately and then together, perhaps in a multiphysics program like COMSOL, which can simulate heat transfer in porous media. If the two components together lead to a smaller amount of time to complete heat transfer from the body to the environment (surrounding air) than the added time to complete heat transfer from the individual Joule heating and thermally insulating components.

One of the main challenges in prototyping our project was securing a supercritical drier. A supercritical drier was essential to making the aerogel with high porosity and low densities, ~0.1 g/cm^3.[3] Ambient dried aerogels are only able to achieve densities of ~0.3 g/cm^3. Besides missing a supercritical drier, we also were not able to impregnate the PAN fibers under vacuum. This allowed for a lot of air bubbles to form and thus lowering the porosity of the aerogel. Using a vacuum would allow for a proper RF/PAN sol gel to be made. Another issue with lack of equipment we ran into was the limitations with the freeze dryer. Our freeze dryer could only freeze dry water and not other solvents. This prevented us from doing any solvent exchange with other solvents. Freeze drying without doing solvent exchange at times results in the destruction of the gel structure and can lead to macropore growth.[18] The last equipment issue we ran into was lack of a furnace to carbonize our samples. Without this, we could only make RF aerogels and not carbon or carbon fiber reinforced aerogels.

In the future we would ideally test more parameters and characterize our aerogel. We would adjust the R/W ratios, because it greatly affects the density which in turn affects the electrical and thermal conductivity of the aerogel. As shown in Szczurek 2011, the higher the R/W ratio, the higher the density.[27] We would ideally want to find the lowest possible R/W ratio we could use to form the carbon fiber reinforced aerogel in order to get the lightest possible aerogel. We would do SEM in order to see how our microstructure model agrees with our prototype. We would use a hot wire test and four point probe test to test our thermal conductivity and electrical conductivity. Lastly, we would do mechanical testing using a 3 point bend test.

5.2 Ethical and Environmental Impact

This advanced wearable material offers a variety of drawbacks to traditional advanced textiles. Pyrolyzation of the RF aerogel releases water vapor, carbon monoxide, and carbon monoxide into the atmosphere. Pyrolysis must be done in an inert environment or else the RF aerogel will just burn, producing harmful greenhouse gases. Carbon aerogels have many appealing properties to be used as a fabric component for low temperature applications. If we are able to successfully design a carbon fiber reinforced aerogel sheet, it could change the advanced fabric components industry used for various outdoor applications. Currently, the outdoor industry has not seen a material with the capabilities that carbon aerogel fabric components can provide, pending a successful design and prototype. It could create a new standard for other jacket materials to be measured up against in terms of being lightweight, yet still an effective thermal insulator. The carbon fiber reinforced aerogel fabric component could be used in conjunction with flexible components, in order to take advantage of the desirable properties of the composite and still make the equipment flexible. Furthermore, CFCA fabric component sheets could not only be used for cold temperatures but moderate temperature clothing as well, if the properties are tuned via process parameters.

Besides its impact on everyday outdoor clothing it could also have an impact in the military industry as well. If we can tune the properties to make it more durable and still lightweight, a good waterproof insulator could help improve our current military equipment. As previously stated, the ECWCS contains 7 different layers of varying fabric components in order to insulate a soldier from a variety of hostile environments. Our conductive carbon aerogel fabrics have thermal conductivities on par with synthetic down, specifically when compared with top of the line commercial PrimaLoft. It is evident this project has the possibility of impacting the everyday life of a wide range of people, from the normal commuter to the adventurous outdoorsmen to the soldier in the military protecting our nation, and thus is a worthy project to pursue.

Additionally, such a material could eventually help to improve the current commercial market of insulating fabric components, allowing for new fields of tactical application in previously inaccessible harsh environments. More importantly, higher performing insulating materials could help save lives in scenarios where existing insulating technology currently can not perform.

5.3 Broader Impact

Because our design is for a carbon fiber reinforced aerogel instead of just the carbon aerogel, it increases the range of applications that our product could be used for. Our goal is still to design an aerogel that can be used as a fabric component, but since adding the carbon fiber makes it mechanically durable and flexible it is possible that it could be used as the main fabric component and not just a single part. It could create a new standard for other jacket materials to be measured up against in terms of being lightweight, mechanically durable, flexible, and yet still an effective thermal insulator.

We still would like to pursue its impact in the military industry. As previously stated, the Army's Extended Climate Warfighter Clothing System (ECWCS)[1] contains 7 different layers of varying fabric components in order to insulate a soldier from temperatures as low as -60°F. So if we could successfully create a carbon fiber reinforced aerogel fabric component sheet to be incorporated to outerwear, it has the possibility of being lighter while still as effective in protecting our military from the various elements. And now the component will be able to last longer which is a benefit from adding the carbon fiber.

Outside the scope of our design project, another application of our work could be in space and aircraft technology. Carbon aerogel could be utilized either on the surface of or as a part of the outer craft material. Aircrafts are regularly exposed to cold air and moisture in the atmosphere, therefore ice formation can occur on the outside material of a plane. The formation of ice on an aircraft material can degrade its performance by increasing weight and drag of the plane. There have been many studies addressing this issue, and there are two main approaches to the problem: electro-thermal ice protection systems, where the ice is melted as it contacts the surface of the material due to resistive heating; and anti-icing materials systems which make use of hydrophobic and immiscibility effects to keep water from wetting the material's surface. Our aerogel, in theory, could provide the effects of both systems as carbon aerogels can both electrically conduct and are hydrophobic.[34] This is one example of the wide variety of applications that could make use of an actively heated aerogel.

References

1. Use and Care of the Extended Cold Weather Clothing System (ECWCS). Natick, MA

2. Steiner S. AEROGEL.ORG. 2012.

3. Feng J, Zhang C, Feng J. Carbon fiber reinforced carbon aerogel composites for thermal insulation prepared by soft reinforcement. Materials Letters. 2012;67(1):266–268.

4. Schwan M, Ratke L. Flexibilisation of resorcinol–formaldehyde aerogels. Journal of Materials Chemistry A. 2013;1(43):13462.

5. Hwang S-W, Hyun S-H. Capacitance control of carbon aerogel electrodes. Journal of Non-Crystalline Solids. 2004;347(1-3):238–245.

6. Wu D, Fu R, Zhang S, Dresselhaus MS, Dresselhaus G. Preparation of low-density carbon aerogels by ambient pressure drying. Carbon. 2004;42(10):2033–2039.

7. Structures and Properties of the Goose Down as a Material for Thermal Insulation. Textile Research Journal. 2007;77(8):617–626.

8. Donovan JG. Synthetic down. 1986 May 13.

9. Kistler SS. Coherent Expanded-Aerogels. The Journal of Physical Chemistry. 1931;36(1):52–64.

10. Aegerter MA, Leventis N, Koebel MM eds. Aerogels Handbook. New York, NY: Springer New York; 2011.

11. Brinker J, Scherer G. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing. 1st ed. San Diego: Academic Press; 1990.

12. Sehaqui H, Zhou Q, Berglund LA. High-porosity aerogels of high specific surface area prepared from nanofibrillated cellulose (NFC). Composites Science and Technology. 2011;71(13):1593–1599.

13. Thapliyal PC, Singh K. Aerogels as Promising Thermal Insulating Materials: An Overview. Journal of Materials. 2014;2014:1–10.

14. Hrubesh LW. Aerogel applications. Journal of Non-Crystalline Solids. 1998;225:335–342.

15. Von Meier A. Electric Power Systems: A Conceptual Introduction. Wiley; 2006.

16. Ramakrishnan B, Zhu L, Pitchumani R. Curing of Composites Using Internal Resistive Heating. Journal of Manufacturing Science and Engineering. 2000;122(1):124.

17. Pääkkö M, Vapaavuori J, Silvennoinen R, Kosonen H, Ankerfors M, Lindström T, Berglund LA, Ikkala O. Long and entangled native cellulose I nanofibers allow flexible aerogels and hierarchically porous templates for functionalities. Soft Matter. 2008;4(12):2492.

18. Al-Muhtaseb S a., Ritter J a. Preparation and Properties of Resorcinol-Formaldehyde Organic and Carbon Gels. Advanced Materials. 2003;15(2):101–114.

19. Livernore L. Organic aerogels from the polycondensation of resorcinol with formaldehyde. 1989;24:3221–3227.

20. Pekala RW, Farmer JC, Alviso CT, Tran TD, Mayer ST, Miller JM, Dunn B. Carbon aerogels for electrochemical applications. Journal of Non-Crystalline Solids. 1998;225:74–80.

21. Drach V, Wiener M, Reichenauer G, Ebert H-P, Fricke J. Determination of the Anisotropic Thermal Conductivity of a Carbon Aerogel–Fiber Composite by a Non-contact Thermographic Technique. International Journal of Thermophysics. 2007;28(5):1542–1562.

22. Fan Z, Tng DZY, Lim CXT, Liu P, Nguyen ST, Xiao P, Marconnet A, Lim CYH, Duong HM. Thermal and electrical properties of graphene/carbon nanotube aerogels. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2014;445:48–53.

23. Serway RA. Physics for Scientists and Engineers with Modern Physics. Saunders College Pub.; 1996.

24. Griffiths DJ. Introduction to Quantum Mechanics. Pearson Prentice Hall; 2004.

25. Pekala RW. Low density, resorcinol-formaldehyde aerogels. 1991.

26. Bryning MB, Milkie DE, Islam MF, Hough LA, Kikkawa JM, Yodh AG. Carbon Nanotube Aerogels. Advanced Materials. 2007;19(5):661–664.

27. Szczurek a., Amaral-Labat G, Fierro V, Pizzi a., Masson E, Celzard a. Porosity of resorcinol-formaldehyde organic and carbon aerogels exchanged and dried with supercritical organic solvents. Materials Chemistry and Physics. 2011;129(3):1221–1232.

28. Lu X, Nilsson O, Fricke J, Pekala RW. Thermal and electrical conductivity of monolithic carbon aerogels. Journal of Applied Physics. 1993;73(2):581.

29. Bock V, Nilsson O, Blumm J, Fricke J. Thermal properties of carbon aerogels. Journal of Non-Crystalline Solids. 1995;185(3):233–239.

30. Taguchi G, Chowdhury S, Wu Y. Taguchi's Quality Engineering Handbook. NJ: John Wiley & Sons; 2005.

31. Taipalus R, Harmia T, Zhang MQ, Friedrich K. The electrical conductivity of carbon- ® bre-reinforced polypropylene / polyaniline complex-blends : experimental characterisation and modelling. 2001;61:801–814.

32. Feng J, Feng J, Jiang Y, Zhang C. Ultralow density carbon aerogels with low thermal conductivity up to 2000°C. Materials Letters. 2011;65(23-24):3454–3456.

33. Yamamoto T, Nishimura T, Suzuki T, Tamon H. EFFECT OF DRYING METHOD ON MESOPOROSITY OF RESORCINOL–FORMALDEHYDE DRYGEL AND CARBON GEL. Drying Technology. 2001;19(7):1319–1333.

34. Wan C, Lu Y, Jiao Y, Jin C, Sun Q, Li J. Fabrication of hydrophobic, electrically conductive and flame-resistant carbon aerogels by pyrolysis of regenerated cellulose aerogels. Carbohydrate polymers. 2015;118:115–8.

Appendices

A. MATLAB code
B. Materials
C. Standard Operating Procedures for Synthesis of Aerogels
D. Calculations

Appendix A: MATLAB Code

MicroStructure Code

```
data=[];
x1=[];
y1=[];
x2=[];
y1=[];
a=mod(g,20);
n=50;
d=6;
length=15;
angleRange=60;
angleRange=angleRange*(pi()/180);
%creates random starting X and Y points
for i=1:a
   x1(i)=rand()*(n-length);
   y1(i)=rand()*(n);
end
%creates an endpoint based on angle range and length
for j=1:a
   angle=(rand()*angleRange*2);
   y2(j)=y1(j)+length*sin(angleRange-angle);
   x2(j)=x1(j)+length*cos(angleRange-angle);
end
hold all
i=1;
j=1;
%sets up temporarry vectors to plot to allows us to plot the fibers
while i<=a*2
tempx(i)=x1(j);
tempx(i+1)=x2(j);
tempy(i)=y1(j);
tempy(i+1)=y2(j);
lengths(j)=sqrt((x2(j)-x1(j))^2 + (y2(j)-y1(j))^2);
line(tempx(i:i+1),tempy(i:i+1),'Color','k','LineWidth',2);
i=i+2;
j=j+1;
end
%creates vector of points in the 2d space
%creates vectors of points inside and outside fibers to be plotted
INx=[];
INy=[];
OUTx=[];
OUTy=[];
```

```
p(1)=0;
p(2)=0;
k=1;
l=1;
check=[];
fiberPoints=[];
carbonPoints=[];
interfaceFC=[];
interfaceCF=[];
v=1;
totFib=0;
totCarb=0;
Flaps=[];
%loops throught all points line scan
for j=1:n
p(2)=0;
fiberPoints(j)=0;
carbonPoints(j)=0;
interfaceFC(j)=0;
interfaceCF(j)=0;
Flaps(j)=0;
   for i= 1:n
  check(v)=inFiber(p,x1,y1,x2,y2,d,a);
   if check(v)==1
      if v>1
         if check(v-1)==0
            interfaceFC(j)=interfaceFC(j)+1;
         end
      end
  fiberPoints(j)=fiberPoints(j)+1;
  totFib=totFib+1;

 % INx(k)=p(1);
  %INy(k)=p(2);
  Flaps(j)=Flaps(j)+overlaps(p(1),p(2),x1,y1,x2,y2,d,a);
  %k=k+1;
   else
      if v>1
         if check(v-1)==1
            interfaceCF(j)=interfaceCF(j)+1;
         end
      end
   carbonPoints(j)=carbonPoints(j)+1;
   totCarb=totCarb+1;
   %OUTx(l)=p(1);
   %OUTy(l)=p(2);
```

```
    %l=l+1;
        end
p(2)=p(2)+1;
v=v+1;
    end
p(1)=p(1)+1;
end
%plots points based if inside or outside fiber
hold all
scatter(INx,INy,15,'filled','red')
scatter(OUTx,OUTy,15,'filled','blue')
title('Microstructure of Fiber Reinforced carbon aerogel')
xlabel('x-axis') % x-axis label
ylabel('y-axis') % y-axis label
axis([0,n 0,n])
hold off
data(2,g)=SheetResistance(n,fiberPoints,carbonPoints,interfaceFC,interfaceCF,Flaps);
%calculates area of fibers in the 2d space using fiber points andc carbon
%points
data(1,g)= totFib/(n*n);
```

Code for in fiber Function

```
function [inside]=inFiber(q,x1,y1,x2,y2,d,A)
j=1;
a=0;
b=0;
c=0;
distance=0;
isInside=0;
while j<=A
    if q(1)>x1(j) && q(1)<x2(j)
          %find equation for a line in form ax+by+c=0
                 a=y1(j)-y2(j);
                 b=x2(j)-x1(j);
                 c=x1(j)*y2(j)-x2(j)*y1(j);
                 %find distance from p to line
                 distance=abs((a)*q(1)+(b)*q(2)+c)/sqrt(a^2+b^2);
                    if distance<=(d/2)
                        isInside=1;
                        break;
                    end
             end
     j=j+1;
end
inside=isInside;
end
```

Sheet Resistance Code

```
function SheetR=SheetResistance(n,fiberPoints,carbonPoints,interfaceFC,interfaceCF,flaps)
% It has been determined how many blue dots there are, signifying how many
% carbon aerogel segments there are; same with red dots, and how many times
% they cross over.
L = 1; % 1 um defined as the length of each dot
A = (L)^2;
p_r = 31.99;%resistivity of carbon fiber
p_b = 1000;%resistivity of carbon aerogel
r_r = ((p_r)*L)/A; %resistance of carbon fiber (red)
r_b = ((p_b)*L)/A; %resistance of carbon aerogel (blue)
r_trb =28.69;%tunneling resistance red-blue
r_tbr =28.69;%tunneling resistance blue-red
 % width of sheet is 10 um; width of sheet, depends on microstructure code?????
R=[];
for i = 1:n
    R(i) =
(carbonPoints(i))*(r_b)+(fiberPoints(i))*(r_r)+(interfaceCF(i))*(r_tbr)+(interfaceFC(i))*(r_trb)+
(flaps(i)*r_tbr);
    R(i)=1/R(i);
end
SheetR = sum(R)^(-1);
%Store resistance as R(1), R(2), R(3), R(4),... etc.
%Each individual R is parallel circuit, therefore:
%sheetresistance = (to n of 1/(R(i)))^(-1)
```

Thermal Code

```
clear all
clear global
dt=1;%s
t_f=10000;%s
%Fixed Model Properties
Q = zeros(4, (t_f/dt));
th = zeros(4, (t_f/dt)+1);
% use mcT=q to determine initial body energy
m = 90.72; %kg, or a 200lb person
c = 3.47; %kj/kg-K
th(1, 1) = 310; %K or 98.6F
t_crit = 310.82;%K or 99.8F
tc = 244.3;%k, or -20F
t_hypo =308.15;%K or
Q_bh = m * c * th(1, 1);
Q(1, 1) = Q_bh; %kj

L=1.83;%m
r1 = 0.13;%m
```

```
%Experimental Variables
k=0.073; %W/m-k, material property of fabric

%Body Generated Heat
%Low end or Sendentary ~2400KCal/day
%1 Kcal=4184J
%~10000kJ/day --> 115.7J/s=115.7W
%Highly Active
%Estimated to be ~5000cal/day
% 20920kJ/day --> 242.1J/s=242.1W
%Which makes the mean ~178.9W
q_gen_sed = []
q_gen_sed(1) = 115.7;

j=1;
for r_f = .05: .05: .20
   i=1;
   Q(j, 1) = Q_bh; %kj
      for i= 1:1:t_f/dt
      th(j, i) = Q(j, i)/(m*c);

      q_side(j,i) = (L*2*3.14*k)*(tc-th(j,i))/(log((r1+r_f)/r1));%W--> Body heat lost through side
of 'cylinders'

      q_flat(j,i) = (-k*(th(j,i)-tc)/r_f)*(3.14*r1^2);%W -->Body Heat lost through top and bottom
of 'cylinders'

      Q(j, i+1)= Q(j,i)+(q_side(j,i)+2*q_flat(j,i)+q_gen_sed(i))*dt; % Total Body heat as a
function of current time step

      if  th(j,i) >= t_crit
         q_gen_sed(i+1)=q_gen_sed(i)-.5;
      elseif th(j,i) <= 310 && q_gen_sed(i)<q_gen_sed(1)
         q_gen_sed(i+1)=q_gen_sed(i)+.5;
      elseif th(j,i) < t_crit
         q_gen_sed(i+1)=q_gen_sed(i);
      end
      i=i+1;
   end
   j=j+1;
end
Time = [0:dt:t_f];


x = Time;
y1 = th(1,:);
```

```
y2 = th(2,:);
y3 = th(3,:);
y4 = th(4,:);
Death = repmat(308.15,1,(t_f/dt+1));
Normal = repmat(310.0, 1, (t_f/dt+1));

hold on
plot (x,y1,x,y2,x,y3,x,y4,x,Death,x, Normal, 'x')
title ('Time Dependent Thermal Response for Passive Insulation')
xlabel ('Time (s)')
ylabel ('Body Temp (K)')
axis ([0 inf 300 312])
legend('2cm','4cm','6cm','8cm','Hypothermia')
hold off
```

Appendix B: Materials

- Resorcinol (98% from Sigma Aldrich)
- Formaldehyde (37% in water, stabilized with 10% methanol, Merck)
- Sodium carbonate anhydrous (Aldrich)
- 2.0 N nitric acid (standardized solution, Alfa Aesar) (used for first experiment not second)
- Carbon Fibers (Ashbury carbon fibers) (used for first experiment not second)
- Deionized Water, for synthesis
- Acetone, washing the gels prior to ambient drying (pure, technical grade, Th. Geyer)
- Pre-oxidized Pryon PAN staple fibers (Zoltek) (used for second experiment not first)

Appendix C

I. Synthesis of RF flexible aerogel derived from Schwan 2013

Do 1-7, 10 at room T, takes ~12 days

1. For synthesizing a gel with R/W = 0.008, dissolve 5.0 g of resorcinol in 97.5g of deionized water
2. Add 7.4 g of formaldehyde to the solution
3. Stir solution for 5 minutes
4. Then add 0.096 g of sodium carbonate
5. Stir solution for another 5 minutes
6. Next, adjust to pH to the range of 5.4–5.6 with 0.5–0.6 mL nitric acid
7. Weigh sample holder (or zero it). pour in the solution to the sample holder. weigh out the fibers before putting them into the sample holder with the solution (for with the fiber).
8. Stir solution for a few minutes
9. Now seal it and place it in an oven for 1 week at 80 degrees Celsius. After 1 week gelation should occur and the color should change from transparent to orange/orange brown
10. After taking it out the oven, cool it down to room temperature
11. After it cools down to room temperature wash it with acetone for next 3 days
12. Dry in an oven at 80 degrees Celsius for 24 hours
13. The aerogel should be flexible

II. Ambient Drying of carbon fiber reinforced aerogel (derived from Feng 2011 and 2012)

1. Dissolve 24g of Resorcinol in 314g of water using stir plate and stir bar
2. Add 13.12g of Formaldehyde to the solution
3. Stir solution for several minutes
4. Add .048g of sodium carbonate
5. Stir solution for several minutes
6. Split the solution evenly into one sealed container for the carbon aerogel and one sealed container for the carbon fiber aerogel composite
7. Keep both RF solutions sealed at room temperature for 1 day
8. For the Composite impregnate it with Preoxidized PAN fibers under vacuum
    a. Note: was not able to impregnate under vacuum so attempted to force the bubbles out by pushing down on them as impregnating them into the solution
9. Place the solutions in an oven at 50 degrees C for 1 day and 95 degrees C 2 days
10. Do solvent exchange with acetone for 7 days, changing the acetone once every day
11. Place in the oven and dry for 50 degrees for 3 days and 100 degrees for 1 day
12. The obtained PAN/RF aerogel composite and RF aerogel was carbonized at 1000 °C for 1 h in a flowing nitrogen atmosphere (200 mL/min)

III. Supercritical drying of carbon fiber reinforced aerogel (derived from Feng 2012)

1. Dissolve 24g of Resorcinol in 314g of water using stir plate and stir bar
2. Add 13.12g of Formaldehyde to the solution
3. Stir solution for several minutes
4. Add .048g of sodium carbonate

5. Stir solution for several minutes
6. Split the solution evenly into one sealed container for the carbon aerogel and one sealed container for the carbon fiber aerogel composite
7. Keep both RF solutions sealed at room temperature for 1 day
8. For the Composite impregnate it with Preoxidized PAN fibers under vacuum
9. Place the solutions in an oven at 50 degrees C for 1 day and 95 degrees C 2 days
10. Do solvent exchange with acetone for 7 days and petroleum ether for 3 days, changing the solvents once every day
11. Supercritically dry the aerogel with petroleum ether
12. The obtained PAN/RF aerogel composite and RF aerogel was carbonized at 1000 °C for 1 h in a flowing nitrogen atmosphere (200 mL/min)

IV. Freeze drying of carbon fiber reinforced aerogel (derived from Feng 2012 and Tamon 2001)

1. Dissolve 24g of Resorcinol in 314g of water using stir plate and stir bar
2. Add 13.12g of Formaldehyde to the solution
3. Stir solution for several minutes
4. Add .048g of sodium carbonate
5. Stir solution for several minutes
6. Split the solution evenly into one sealed container for the carbon aerogel and one sealed container for the carbon fiber aerogel composite
7. Keep both RF solutions sealed at room temperature for 1 day
8. For the Composite impregnate it with Preoxidized PAN fibers under vacuum
9. Place the solutions in an oven at 50 degrees C for 1 day and 95 degrees C 2 days
10. Gel was frozen at -55 C (218 K) for 4 hours and then placed under vacuum for 1 day
11. The obtained PAN/RF aerogel composite and RF aerogel was carbonized at 1000 °C for 1 h in a flowing nitrogen atmosphere (200 mL/min)

Appendix D

I. Calculations of Ratios

Grams of R	**Grams of W**	**Grams of C**	**Grams of F**
24.004	314	0.048	13.144
Mol of R	**Mol of W**	**Mol of C**	**Mol of C**
4.587	0.0510	2208.2	2.285
W/R ratio	**R/C ratio**	**F/R ratio**	
90.022	481.37	2.008	

II. Calculating Apparent Solution Density

DI water = 314g and has a density of 1 g/cm^3 so 314 cm^3 of W in solution
Resorcinol = 24.004g and has a density of 1.28 g/cm^3 so 18.753 cm^3 of R in solution
Formaldehyde = 13.144g and has a density of 0.8153 g/cm^3 so 16.122 cm^3 of F in solution
Sodium Carbonate = 0.048g and has a density of 2.54 g/cm^3 so 0.0189 cm^3 of C in solution
Total Mass = 351.196 g
Total Volume = 348.894 cm^3
Therefore Apparent solution density = Total Mass/Total Volume = 1.00659 g/cm^3

III. Calculation of Amount of PAN fibers to Add to solution

Sample 1

$$86.654g\ solution\ x\ \frac{24.004g\ R\ +\ 13.1g\ F+\ 0.048g\ C}{351.196g\ total\ solution}$$
$$= 9.167g\ of\ R, F, and\ C\ in\ sample\ 1 = mass\ of\ RF\ aerogel$$

Assuming a 52.1% Loss by mass from going from RF aerogel to carbon aerogel

$$Mass\ of\ CA = 0.479\ g\ mass\ RF$$
$$Mass\ of\ CA\ =\ 4.3957g\ CA/0.097\ g/cm^3\ =\ 45.32\ cm^3$$

0.097 g/cm^3 is the density of the carbon aerogel reported in Feng 2012
45.32 cm^3 CA = 0.8 V_{total} we want 20% volume fraction of fibers
V_{total} = 56.65 cm^3 = 56.65 ml
Therefore in order to get 20% volume fraction of fibers we need to have:
56.65 ml - 45.32 ml = 11.33 ml or 11.33 cm^3 of PAN fibers
11.33 cm^3 x 1.37 g/cm^3 (density of the PAN fibers) = 15.52g of PAN fibers that must be added to achieve 20% volume fraction of fibers
Actual amount added: 14.633g = 10.681 ml of PAN fibers
10.681 ml/56.65 ml x 100% = 18.85% for the actual volume fraction filling

Sample 3

$$89.201g\ solution\ x\ \frac{24.004g\ R\ +\ 13.1g\ F+\ 0.048g\ C}{351.196g\ total\ solution}$$
$$= 9.425g\ of\ R, F, and\ C\ in\ sample\ 3 = mass\ of\ RF\ aerogel$$

Assuming a 52.1% Loss by mass from going from RF aerogel to carbon aerogel

$$Mass\ of\ CA = 0.479\ mass\ RF$$

$$Mass\ of\ CA\ =\ 4.515g\ CA/0.097\ g/cm^3\ =46.54\ cm^3$$

$0.097\ g/cm^3$ is the density of the carbon aerogel reported in Feng 2012

$46.54\ cm^3$ CA = 0.8 V_{total} we want 20% volume fraction of fibers

$V_{total} = 58.18\ cm^3 = 58.18$ ml

Therefore in order to get 20% volume fraction of fibers we need to have:

58.18 ml - 46.54 ml = 11.64 ml or $11.64\ cm^3$ of PAN fibers

$11.64\ cm^3$ x $1.37\ g/cm^3$ (density of the PAN fibers) = 15.94g of PAN fibers that must be added to achieve 20% volume fraction of fibers

Actual amount of PAN fibers added: 15.96g = 11.64 ml of PAN fibers

11.64 ml/58.18 ml x 100% = 20.02% for the actual volume fraction filling

IV. Calculation of Volume Fraction from Feng Paper

Density (fibers) = $0.112\ g/cm^3$

Density (aerogel) = $0.097\ g/cm^3$

Density (fiber/aerogel composite) = $0.174\ g/cm^3$

Volume fraction of fibers = x

$0.174\ g/cm^3 = (x)*(0.112\ g/cm^3) + (1-x)*(0.097\ g/cm^3)$

x = 0.3608 = <u>36.08%</u>