Development of Lightweight Organic Aerogels for Thermal Insulation Applications

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Department of Mechanical and Industrial Engineering
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Abstract

Organic aerogels provide the solutions for many sectors, due to their extremely unique feature and their unique structure that are spread-out at different length scale. Organic aerogels are considered the next generation materials due to their high tunability and adaptability by the tailoring of their final properties. Tailoring of organic aerogels properties is the theme of many nanocellular and low-density materials research, however, such process experiences many challenges. The main two challenges of tailoring such materials are: (I) the synthesis of monolithic aerogels with strong mechanical properties while preserving their unique features, and (II) the deep understanding of the origin of such features and correlating each feature to a structural parameter. This work addressed both these challenges to have a deep understanding of organic aerogels and to integrate them into many sectors. The synthesis process focused mostly on pure organic aerogels without any composites, at first, to correlate the processing conditions to the micromorphological parameters. The micromorphological parameters were further studied to quantify each parameter that controlled the assembly of the aerogel three-dimensional network. Then, each parameter was correlated to the structural final property to better understand the uniqueness of the organic aerogels features. With the correlation build-up between the processing-structure-properties of organic aerogels, a heat transfer model was conducted on the structure. In such model, each heat
transfer mode was identified and linked to a structural parameter which controlled it. The organic aerogels were further modified to enhance their mechanical properties by the addition of nanofibers and nanosheets into the structure. The composites assembled homogeneously into the organic aerogel structure to create a uniform network of the aerogels particles along with the composites. With a such network, the mechanical properties of the aerogels increased dramatically while preserving their unique features. Finally, the operational limitations that are inherent to the organic aerogel were surmounted thru the modification of the aerogels chemical composition. The new aerogels could operate at high temperature and have a high fire retardancy ability. Furthermore, such aerogels could resist moisture, which makes these materials ideal to be used in high temperature and humid environments.
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Chapter 1 Introduction

1.1 Preamble

Substantial research is being conducted to improve energy utilization, maximize system efficiency, and reduce any environmental impact. According to Natural Resources Canada, in 2008, 31% and 30% of the total Canadian energy consumption was in residential/commercial and transportation sectors [1], generating over 65% of the total greenhouse gas emissions [2]. Space heating and air conditioning accounts for over 50% and 40% of worldwide total residential and commercial energy consumption [3]. Hence, significant research is being conducted to explore alternative green energy resources and improve efficiency of the energy systems. Little attention, however, had been paid on the preservation of energy and improvements of insulation materials. As any improvement on the thermal insulator sector would translate into an enormous energy savings and a reduction in the greenhouse gases. Thus, nanomaterials play a major role in this sector as they are considered superior materials because of their properties. Such materials possess unique features that could fill in the energy gap and exhibit a multifunctional characteristic that we need in our daily life. Organic aerogels are a class of nanomaterials that have unique features which could be tailored to produce the next generation of products with unique features and multifunctional characteristics. Aerogels have a high fragility and brittleness characteristics which hinders their infiltration in many sectors. In this work, the following aspects of organic aerogels are investigated. First, tuning the processing conditions to generate a morphology with the best features. Then, analyzing the relationship between the structure and the final properties of this aerogel. Finally, modifying the nanonetwork to generate an organic aerogel with unique features, strong mechanical properties, and multifunctional characteristics.

Chapter 1 starts by introducing the history of aerogels. A comprehensive review is then provided to cover both the synthesis along with potential limitations associated with aerogels. The chapter concludes by establishing the motivation and objectives of the research that target to
overcome some of the limitations for implementing aerogel in a wider range. Finally, the thesis layout and flow of chapters will be explained.

1.2 Definition

Organic aerogel was first introduced in 1989 by Pekala in his patent as an alternative and an improvement to Kistler’s inorganic aerogel by utilizing the sol-gel process [4, 5]. Aerogels came as an improvement to the conventional microcellular foams that were manufactured through the expansion of the polymer/gas mixtures [4, 6]. Existing microcellular foams are considered to have a high density, a discontinuous porosity, and a high atomic number. However, aerogels have a low density, a high porosity and a low atomic number generated from an organic precursor by using the sol-gel technology developed by Kistler. Pekala was the first to achieve a continuous nanoporous structure of organic aerogel with a density less than 100mg/cm$^3$ [4]. During the synthesis, the organic precursor went through a gel-solid like behavior to from its three-dimensional framework [4, 6, 7]. The framework of the structure consisted of molecules connected by various junction bonds. These bonds had covalent crosslinking, crystallization, ionic interaction, hydrogen bonding, and even chain entanglements to connect the gel network [4, 6, 7].

The most common organic based aerogel is made from the polymerization of resorcinol with formaldehyde. The resorcinol-formaldehyde (RF) chemical reaction occurred in an aqueous environment with a base or an acid activated site. The base catalyst is commonly used in RF formation by using sodium carbonate ($\text{Na}_2\text{CO}_3$) as the catalyst. The reaction starts by forming a hydroxymethyl derivative followed by the condensation of these derivatives to form a methylene or a methylene ether bridge linking two resorcinol molecules [7-9]. Each resorcinol can add up to three equivalent formaldehyde groups on 2, 4, and 6 ring positions. Sodium carbonate would activate the resorcinol sites thru the deprotonation of resorcinol through hydrogen abstraction to form a resorcinol anion, which would increase the electron density at 2, 4, or 6 ring positions of the resorcinol Fig 1-1 (1a) [8, 10]. This would cause an electrophilic aromatic substitution to partially positive charged carbonyl carbon of formaldehyde leading to hydroxymethylation; addition of –$\text{CH}_2\text{OH}$- group Fig 1-1 (1b) [8, 10]. The hydroxymethlation groups with formaldehyde presence would activate other sites on resorcinol leading to dihydroxymethlation Fig 1-1 (2) [8]. Another deprotonation would occur to hydroxymethlated resorcinol to generate a
reactive unstable o-quinone methide intermediate to react with the excess resorcinol to form a stable methyl bridge (cluster) Fig 1-1 (4) [8]. The bridge formed with the substituted resorcinol was faster than activating existing resorcinol rings, which would become a tetra-functional dimer with a higher probability to react than individual resorcinol molecule [10]. The final cluster would grow until it consumed all the formaldehyde and catalyst within the mixture. The overall reaction process for the RF is summarized in Fig 1-1.

Fig 1-1: Mechanism of base-catalyst RF aerogel synthesis [8]

The reaction of resorcinol and formaldehyde can also be formed in an acidic condition. In such condition the reaction proceeds by increasing the electrophilicity of formaldehyde Fig 1-2 (6) [8]. The reaction initiated with the protonation of formaldehyde by the nucleophilic attack, which results in forming a hydroxymethylation of resorcinol Fig 1-2 (7). The further protonation of hydroxymethyl groups results in OH$_2^+$ group formation Fig 1-2 (8) and this forms a o-quinone methide type Fig 1-2 (9). Then, the other resorcinol can attack the protonated hydroxymethylated
resorcinol to form methylene linkage Fig 1-2 (10) [8]. With further addition and condensation reactions, a crosslinked network is formed to generate the RF aerogels Fig 1-2 (11).

Fig 1-2: Mechanism of acid-catalyst RF aerogel synthesis [8]

Aerogel structure was produced under two procedures; sol-gel and polycondensation. The term sol-gel is the transition of the chemicals into the gel phase from the sol phase. At first the solution contained solid particles dispersed in a liquid solvent (sol) and then they aggregate throughout to form a three-dimensional network (gel). The solution was termed to be colloid with a continuous phase with different phase dispersed within [11]. At the sol-stage, the continues phase was presented by the liquid and the dispersed phase was presented by the solid particles which were dispersed throughout the liquid [8, 11]. However, at the gel stage the material behaved more
towards a solid like behavior where it had an interconnected network within. The gel stage had solid particles as the dominated phase with the liquid phase being dispersed throughout [8, 11]. When the liquid phase was extracted from the three-dimensional solid network and the structure was sustained, the gaps would be filled with air and the material was termed to be Aerogel [12].

**Sol-Gel chemical process**

The transition from sol to gel occurred at the point which the solid particles became connected together to form the network. The connection happened by the continuous motion of the solid particles within the liquid phase bouncing at random and colliding with each other [13]. The speed of the solid particles motion was highly dependent on the temperature of the colloid. As the reaction proceeded further with time for the transition from sol to gel, the viscosity approached infinity and the mixture became immobile and this was called the gelation process. Also, the point at which the network extended across the entire liquid causing it to be immobile was called the gel point and the time required to achieve it was termed the gel time. Pekala & Kong argued the requirements to achieve a successful gel via sol-gel route was by; I) multifunctional monomers, II) a high degree of crosslinking, III) a surface functional groups, and IV) a particle stabilization [10]. Pekala used the polycondensation of resorcinol (1,3 dihydroxybenzene) (C₆H₆O₂) with formaldehyde (CH₂O) under alkaline conditions to form organic based aerogels [10]. Organic aerogel also was synthesized with various organic precursor such as; polyimides, polyacrylamide, polyacrylonitriles, polyacrylates, polystyrene, and polyurethane [8]. RF aerogel were the most widely researched for its unique properties and conversion to carbon aerogel. RF aerogel structure could be tuned according to our goals and it was the easiest to manufacture compared to other organic based aerogels. For instance, in polyimide aerogel the gelation mechanism was more complicated due to the incorporation of a cross-linking agent. In such aerogels, they exhibit a shrinkage during fabrication when a cross-linker was not used [14]. Meador et.al fabricated a polyimide aerogel to be used as a flexible thermal insulator using 1,3,5-benzentricarbonyl trichloride (BTC) and they utilized subcritical and supercritical liquid extraction procedures in the synthesis [14]. The gel structure in this case appeared as somewhat fibrous as shown in **Fig 1-3**, in contrast to the pearl-necklace structure in organic aerogels such as RF and Polyurethane aerogels as shown in **Fig 1-4**. This structure was also found when using aromatic diamines such as 2,2-dimethylbenzidine (DMBZ), and 4,4-oxydianiline (ODA) with the synthesis of polyurea aerogels.
to form 3D cross-linked network [15]. Polyurea was normally formed by reacting isocyanates (-NCO) with amine (NH$_2$) in a polar, aprotic solvent, however, polyurea aerogels were formed by reacting 4,4-methylene diisocyanate (MDI) or polymeric MDI with a long chain aliphatic triamines in the presence of triethylamine catalyst [15]. Furthermore, the fiber-like network was observed in physically bonded aerogels derived from crystalline polymer i.e syndiotactic polystyrene (sPS) aerogels. For instance, Wang & Jana investigated the change in the surface morphology for sPS aerogels by dissolving polyethylene oxide (PEO) in the sol solvent [16]. All the above mentioned organic aerogels, besides RF, were complex in the synthesis. Therefore, we focused on the RF aerogel to test its structure for our objectives.

**Fig 1-3:** SEM for polyimide aerogels [16]
1.3 Synthesis of Resorcinol-Formaldehyde Aerogel

The procedure for making RF aerogel is explained as follows; First, mixing of the reactants together; resorcinol (C₆H₆O₂), formaldehyde (CH₂O), and sodium carbonate (Na₂CO₃) to start the gelation process as explained in the above sections. Formaldehyde normally contain deionized water and methanol within its structure to prevent formaldehyde from undergoing polymerization [9]. The concentration of resorcinol to formaldehyde was fixed according to the stoichiometric conditions of the reaction (R/F=0.5). However, the solid content, the dilution ratio, and the catalyst concentration could be varied at this stage of synthesis. The solid content was determined according to resorcinol mass in gram divided by the water used in volume (g/ml) in the mixture [17]. Also, the solid content could be presented as the resorcinol to the water content at a molar base ratio (R/W). For the dilution ratio it includes all the solid reactant to water content in molar bases (water/ (resorcinol+ formaldehyde+ sodium carbonate) [9, 18, 19]. Furthermore, catalyst concentration was modified at this stage and it had a big impact on the final aerogel structural properties and was always represented according to the resorcinol over the catalyst presence on a molar base ratio (resorcinol/catalyst) (R/C).

\[
C_6H_6O_2 + 2CH_2O \xrightarrow{Na_2CO_3} HOH_2C - C_6H_6O_2 - CH_2OH
\]  

(1.1)

Second, after the reactants were mixed together they were placed in an oven at an elevated temperature (80-90°C) for several days to ensure the gelation process within the structure and to
overcome any gravitational effect on the sample and restrict its deformation impact [4]. The sample would behave as a Hookean solid at the end of the curing stage [20]. The transition of the sol to the gel structure happened in a viscoelastic manner going through three phases; i) Newtonian liquid at the beginning of the reaction, ii) Viscoelastic transition network at the critical conversion, and iii) Hookean solid at the completion of reaction [20].

The third step was to prepare the sample for the drying stage, because with different drying conditions it would yield a different product. The evaporation techniques were dependent on the solvent used and its characteristics. Initial stage to prepare the sample was to replace the solvent within the sample with an organic solvent. This was to eliminate any polar group (water) with nonpolar solvent group within the sample. With the presence of a polar group, the sample would have a stickiness effect on the pore walls which may cause damage to the gel structure during the drying phase. Also, the solvent needs to be miscible with the final drying median.

1.4 Problem statement and Motivation

Extensive research in microcellular organic foam produced a new insight that would help in the development of the next generation of high performance nano-cellular organic foams i.e. Aerogels [21]. In recent years, nano-cellular foams have received a significant academic and industrial research attention for its unprecedented thermal insulation properties. These properties emerge from the small pore sizes (< 50 nm), eliminating the contribution of the gas phase in the thermal convection mode due to the Knudsen effect, which limits the vibration of gas molecules within pores [22]. Current foams made with PU, PS, or PIR often have a thermal conductivity of 30mW/m.K with room for improvement by an order of magnitude if a low-density nano-cellular foams were successfully developed (i.e Aerogel). However, aerogel still have not fully been utilized because of their high fragility.

Aerogel itself is an open-cell foam formed when an interstitial liquid inside the gel was replaced with gas under supercritical conditions. Aerogel structure handled under two formation techniques; Sol-gel and poly-condensation, each depending on; (I) Precursor, (II) Catalyst ratio (CR), (II) Hardeners, (III) Drying condition, and (IV) Curing temperature [23]. It emerges as a
super-insulator material with the highest heat barrier ever reported (12-18 mW/m. K at atmospheric pressure, 4-14 mW/m. K at vacuum pressure) [24]. Aerogel possess unique properties; low density, high porosity, high surface area, [15] and transparency [15]. Therefore, aerogel holds a high potential to be used in automotive, buildings, aerospace [10], environmental usage (oil-spill absorbent [12], CO2 capture [27]), and in medicine as well as a phantom material [28]. In phantom materials, aerogels mimic the porous structure found in human organs and are used to measure the amount of radiation needed when imaging such organs. Nonetheless, aerogel-based products remain expensive and exhibit poor mechanical properties (i.e. brittleness and fragility) [29]. Which limits their infiltration in a wide commercial applications. Organic aerogels were widely researched due to their diverse precursors used for fabrication [7, 10, 15, 16, 30-35]. With organic based precursor there is more room to tune the parameters to suit the intended needs of the final product. The motivation of this work is to expand the usage of aerogels in different fields by improve their mechanical properties while preserving their unique properties.

1.5 Objective and Scope of Work

The production of Aerogel for insulation is challenging and needs specially modified materials and understanding of their fundamental properties. Which includes two important parameters governing the quality of nano-cellular organic foam: I) The morphology of the nano-structured material, and II) The structural-to-properties relationships in nano-cellular foams. Organic aerogel was selected to research its material structure and further process. Starting with, Resorcinol-Formaldehyde (RF) as a precursor and Sodium carbonate as a catalyst would be used to produce RF aerogel for thermal insulation applications. Supercritical drying conditions would be used for exclusion of liquid in gel with CO₂ as the drying gas. In our research, based on organic aerogels, an innovative technology would be developed to produce organic aerogel foams.

The proposed research would cover advances in manufacturing processes and material design. The new product would be lightweight and cost-effective with unprecedented thermal insulation characteristics together with excellent mechanical properties. Such super-insulators
would significantly reduce the energy consumption and greenhouse gas emissions of heating and cooling systems in residential, commercial and transportation sectors.

The objective of this work is to produce a nanostructured material with a low thermal conductivity and strong mechanical properties. This main objective is divided into four sub-objectives. The first objective is to tune the RF synthesis process to achieve the desired thermal and mechanical properties (processing-to-structure). The second objective is to investigate the heat transfer mechanism in the RF nanostructure (structure-to-property). Third objective is to reinforce the RF matrix with composite materials. The fourth objective is to expand the operational range for the RF aerogels. The backbone of this work was advanced experimental approaches that enable testing and demonstrates innovation in design, integration, and implantation beyond existing technologies of foaming technology.

1.6 Organization of the Thesis

This research was divided into four main studies in four chapters, each study addressing a key concept in addressing the synthesis and analyzing the properties of RF aerogels. The final output of the combined analysis of these studies was a strong product that could replace existing organic based foams. The studies are divided as follows:

1. Synthesis of RF aerogel with different processing parameters to tune in the morphological features of the nanonetwork. In this study, the process-to-morphology parameters were identified to yield an RF aerogel with superior mechanical and thermal properties.

2. Study the different heat transfer modes and establish the morphology-to-structure relationship parameter for the RF structure. This sub-study involved the identification of each morphological parameter and correlating it to each heat transfer mode.

3. Develop a strong and hybrid RF aerogel to be used as standalone insulation material and as a replacement to current organic based foams. This hybrid RF aerogel was reinforced by the addition of strong nanofibers and nanosheets into the nanonetwork.


4. Expanding the operational range and the functionality of RF aerogel to be used in high temperature environments and humid environments.

Chapter 2

In this section, an RF aerogel with high structural porosity and superinsulation characteristics has been developed. The study involved synthesizing a pure RF aerogel without the addition of any composites or filler into the structure. The generated RF aerogel had a better elastic feature compared to the normal RF aerogel by utilizing the particle necking technique. This technique was developed by controlling the growth of the nanoparticles at the gelation stage. Which have yielded a new mixed configuration structure that has an elastic characteristic while maintaining their thermal properties. This study concluded into identifying the processing-to-structure relationship to optimize the synthesis process.

Chapter 3

In this chapter, the structural micromorphology of the RF aerogel was characterized and quantified using the fractal technique. In this technique, the morphological features along with the structural assembly for each pure RF samples were identified using Small Angel X-ray Diffraction (SAXS). Then a heat transfer analysis was conducted on the samples to calculate the contribution of each mode of heat transfer. Finally, each morphological feature was correlated to each heat transfer mode and quantified their influence on the thermal insulation characteristic. In this chapter, the structure-to-property correlation was identified to better understand the origin of the unique features the RF aerogel possess.

Chapter 4

To overcome the fragility and the brittleness of the RF aerogel, in this chapter a study was presented to add two types of strong nanofibers into the RF nanonetwork along with nanosheets. The mixture of the nanofibers and the nanosheets were highly combatable with the RF particles and provided a homogenous structure. The new reinforced RF consisted of RF particles co-assembled on the nanosheets and the nanofibers. The new samples had a substantial increase the sample mechanical properties while still maintaining a low thermal conductivity characteristic.
These samples could replace existing organic foams as thermal insulators and be used as a standalone material.

Chapter 5

RF aerogel still had some limitation from an operational point view, as they can only be operated at relatively low temperature and in a dry environment. In this chapter, the operational range for the RF aerogel has been expended by performing a carbonization process on the sample. With such process the RF aerogel was transformed into carbon aerogel with unique features and larger operational range. The new aerogel could be operated at high temperature and humid environments without any degradation or deformation.

Chapter 6

This chapter provides a summary of the overall work along with final remarks and the final conclusions. Recommendation for future work also presented in this chapter.

1.7 References


This Chapter starts the research by developing a new high porosity resorcinol-formaldehyde (RF) aerogel with improved particle necking. This RF aerogel was developed under CO_2 supercritical drying conditions without any structural shrinkage. The water content and the catalyst percentage were varied to modify the particles’ nucleation and growth mechanisms and to control particle-particle connections. The nucleation mechanism solely depended on the initial catalyst percentage; the number of nuclei increased with the catalyst percentage. However, the growth and connection of the particles depended on both the water content and the catalyst percentage through their effect on the pH value. As the water content increased to have a larger void fraction, the pH value decreased. Consequently, the spherical growth of the particles became dominant and, thereby, the connection of the particles became more difficult. But as the catalyst percentage increased, the pH value increased, and the connection of the particles became facilitated with the formation of necks around the particles. As a result, a mixed configuration structure was developed with a high void fraction. A 30% increase in the structural elasticity and a very low thermal conductivity of 0.0249W/mK were obtained.

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2.1 Introduction

Organic aerogels are highly porous nano-scale open-cell foams [1] that have exceptional features; a low density, a high porosity, a high surface area, and transparency [2-4]. These features exceed those of the currently available organic foams [5-7]. Thus, they have a strong potential for use in many critical areas including aerospace [8], oil-spill absorbency [9], and carbon dioxide capture [10]. They could also be used as a phantom material in medicine [11]. Nevertheless, aerogel-based products remain expensive with numerous technological challenges in their processing and exhibit such undesirable mechanical properties as brittleness and fragility [12]. These limitations hinder their wider commercial use. Thus, any improvements in their processing and mechanical properties that maintain their unique characteristics represent advances toward their marketability for use in low-level applications.

Aerogel is formed when the interstitial liquid inside a three-dimensional (3-D) network structure is replaced with gas under supercritical conditions. To overcome the structural capillary stresses that occur, two processes are active: sol-gel and polycondensation. During the synthesis process, the following parameters are influential: (i) the precursor kind, (ii) the catalyst ratio (CR), (iii) the drying condition, (iv) the water content, and (v) the curing temperature. These processing and materials parameters control the aerogel’s final morphological structures such as: (i) the pore size, (ii) the size distribution, and (iii) the connectivity of the particles [13]. In the initial stages of synthesis, the solution contains solid particles dissolved in a liquid (a sol). The particles then aggregate throughout the liquid to form a 3-D network (a gel). The solution becomes a colloid within the continuous phase with solid particles dispersed on a nanoscale within it [14]. During the viscoelastic transition from a liquid state (a sol) to a wet solid-like state (a gel), the solid particles become more dominant and start to interconnect to form a 3-D network while the liquid is co-continuous throughout the structure [14, 15].

Organic aerogels were first introduced by Pekala as an alternative and an improvement to Kistler’s inorganic silica aerogel. Pekala used the sol-gel process to achieve his goals [16, 17]. The aerogel structure consists of molecules connected by various junction bonds. These bonds contain, but are not limited to, covalent crosslinking, crystallization, ionic interaction, hydrogen bonding,
and/or chain entanglements [16, 18, 19]. These structural bonds are formed due to the random particles’ collisions during their Brownian motion within the liquid phase [14, 20]. The speed of their bouncing and random collisions is highly dependent on the colloid’s temperature. The reaction proceeds over time until the viscosity approaches infinity, and the mixture becomes immobile. This process is called the gelation process.

Resorcinol-formaldehyde (RF) aerogel has become synonymous with organic-based aerogels. The broad research and applications of RF are in accord with one’s target because of its inherently large number of parameters to be varied to tune the final gel structure according to one’s needs [2, 18, 21-28]. It is also the easiest to manufacture, compared to other organic based aerogels. In our chapter, the RF is formed under supercritical drying conditions to yield a monolithic aerogel with very low shrinkage [29]. The influence of the processing parameters, i.e., the drying conditions, the catalyst percentage, and the water content on the RF porous structure has been extensively studied in literature. Job et al. conducted several studies on the chemical kinetics of RF aerogel and the influence of each parameter on its porous structure [30-33]. Their studies show that any modification on the catalyst percentage and the water content has a direct correlation on the pH value during synthesis [30]. Their RF aerogels showed a reduction in the mechanical strength when the catalyst percentage and the water content were modified [31]. Their structure did not form a strong connection (necks) between the particles due to the high-water content used.

The catalyst concentration affects: (i) the reaction kinetics by changing the amount of formaldehyde consumed during polymerization that affects the number of particles, (ii) the solution’s basic pH value and, thereby, the degree of cross-linking between the particles occurring during gelation [22, 34, 35]. Pekala & Kong argued that the catalyst concentration affects the growth rate and the size of the polymer clusters when the crosslinking bonds form during gelation [22]. Schwan & Ratke studied the effect of the extreme water content in the RF structure [36]. The final product showed an interconnection between the particles (necks) with a heterogeneous structure. This provided a structure with high elasticity characteristics with high particle-size distribution [36].

Tuning all the processing parameters is essential to the final structural morphology. Hence, with enhanced structural morphology, the property will change accordingly. This chapter describes
the effects of the catalyst percentage and the water content on the structural morphology that determines the thermal conductivity and the structural integrity. First, a large number of particles were nucleated. Then, we promoted three-point directional growth of a particle, instead of its uniform growth, with pH control in order to enhance the particle-to-particle necking. A new mixed configuration structure was generated in this chapter compared to the conventional pearl necklace configuration. This change in the structural morphology was made to maintain the low thermal conductivity of the aerogel while enhancing its mechanical properties.

2.2 Methodology for the Formation of mixed configuration Structure

2.2.1 Background on RF aerogel processing

The RF aerogel synthesis process consists of mixing the reactants in an aqueous medium to initiate the gelation process as the first step. The sample would transition from a liquid to a gel at this stage, due to the crosslinking intensity between the bonds. Then the sample is placed in a high-temperature environment for ageing to strengthen the bonds during particle aggregation. Finally, the sample is prepared for drying by performing two solvent exchanges to extract the water from the 3D network. The overall synthesis process is illustrated in Fig 2-1.

![Fig 2-1: An illustration for the RF synthesis process](image-url)
The resorcinol’s reaction to formaldehyde proceeds in a two-phase poly-condensation mode at the mixing stage. The reaction is initiated by the deprotonation of the resorcinol at the 2, 4, and 6 positions of the benzene ring [15]. The electron density at these sites increases and creates a resorcinol anion to prepare for the formaldehyde polymerization into the ring [15, 37]. The formaldehyde acts as a di-functional monomer and forms covalent bridges at different resorcinol ring sites. These bridges are classified as methylene and methylene ether bridges and forms a hydroxymethyl which is the base of the colloid [15, 37].

The first phase of the gelation is particle nucleation, which is controlled by catalyst [38]. The second phase of gelation is the growth of the nucleated particles, which is controlled by two reactions: (i) the condensation reaction, and (ii) the addition reaction [39]. The condensation reaction causes uniform growth of each particle, whereas the addition reaction causes directional growth at the three potential sites. So, if the condensation reaction is dominant, the nucleated particles will grow their size more, but if the addition reaction is dominant, the nucleated particles will be connected with the neighboring particles more. Both reactions occur concurrently with different ratios, depending on the pH value of the solution [32]. For instance, if the solution is acidic, the condensation reaction develops more rapidly, and particle growth occurs at a faster rate. However, if the solution is basic, then the addition reaction develops more rapidly and generates a large number of sites to connect with other particles. These two competing reactions determine the size of the particles and their connections. An illustration of the growth mechanism is shown in Fig 2-2. Hence, the gel formation is the most critical processing step that determines all the structure characteristics that govern the properties eventually. In this context, this chapter focuses on the tuning of the gel formation step.
Organic aerogels are divided into two main structure configurations; pearl-necklace [31], and fibril configuration [26]. The pearl-necklace configuration exhibits a low thermal conductivity but its mechanical properties are weak due to the small contact area between the particles. However, for fibril configuration, the structure mechanical properties are strong but its thermal conductivity is high due to the good contact between the fibers. RF aerogels are well-known for its pearl-necklace configuration. But because of the weak mechanical properties, we proposed to yield a mixed configuration structure. This would be achieved by tuning the water content and the catalyst percentage at the mixing stage to modify particles connection during gelation.

2.2.2 Proposed methodology

The mixed configuration structure can be generated by controlling the nucleation and growth of particles at the gelation stage. The solution catalyst percentage and the initial pH value control the nucleation and the growth of particles as shown in Section 2.2.1. The first stage would be the generation of a large number of nucleation sites to produce numerous particles with an increased catalyst percentage. With the large number of particles, the next step is to control their growth and connections by tuning the condensation and addition reactions, respectively. Both reactions are accelerated according to the solution’s pH value. The pH value is influenced by the solution: (i) the catalyst percentage, and (ii) the water content (i.e., the void fraction). Because with the catalyst (Na$_2$CO$_3$), the solution shifts towards the basic condition due to the formation of a bicarbonate buffer (HCO$_3^-$) [37]. As the water content increases to have a larger void fraction, the

Fig 2-2: Particle growth mechanism in case of; (a) condensation reaction dominant at an acidic condition, and (b) addition reaction dominant at a basic condition
pH value decreases. Consequently, the spherical growth of the particles become dominant and, thereby, the connection of the particles become more difficult. But as the catalyst percentage increases, the pH value increases, and the connection of the particles become facilitated with the formation of necks around the particles. Hence, the combined effects of the catalyst percentage along with the water content are utilized to control the particles’ uniform growth while promoting a three-point directional growth between the particles. This combined effect generates a neck connection between the particles to yield a mixed configuration structure.

2.3 Experimental

2.3.1 Materials

Resorcinol (R) (99%) (Sigma-Aldrich), sodium carbonate (C) (Na₂CO₃, 99%), and formaldehyde (F) (Caledon labs) (10-15% methanol as stabilizer, 37% H₂O to prevent formaldehyde from undergoing polymerization were purchased [30]). Acetone (99%) and distilled water (W) were obtained from Caledon, Life Technologies, and Invitrogen, respectively. All the chemicals were used as received in the synthesis of resorcinol-formaldehyde (RF) aerogels. Carbon dioxide (CO₂) was used as a drying medium under supercritical conditions (99% purity from Linde Gas Canada).

2.3.2 Gel formation

The synthesis process is designed to yield a mixed configuration structure by modifying the catalyst weight percentage and the structural void fraction to achieve the best thermal and mechanical properties. The catalyst percentage is varied at different weight percentages; 0.01%, 0.02%, 0.03%, and 0.04%. Also, the structure’s void fraction is varied by modifying the amount of water at the mixing stage. Four different void fractions are used for each sample: 0.8, 0.9, 0.91, and 0.92. The samples are denoted as follows: “catalyst weight percentage-void fraction”, hence, for “0.04%-0.8” the catalyst percentage is 0.04 wt%, and the void fraction is 0.8.

The process starts with the mixing of resorcinol, (C₆H₆O₂) with sodium carbonate (Na₂CO₃) at different catalyst weight percentages within the solution until they had fully dissolved and homogenized. Then, formaldehyde (CH₂O) is added to initiate the reaction and to start
resorcinol’s polymerization with formaldehyde. The concentration of resorcinol to formaldehyde is fixed according to stoichiometric conditions (R/F = 0.5). Then the mixture is placed in the oven at an elevated temperature (60°C) (that is, below the water boiling point) for seven days to guarantee the gelation process within the structure, to sustain the monolithic structure, and to overcome any gravitational effect on the samples and to restrict their deformation [16].

2.3.3 Supercritical drying

During this stage, we prepared samples for drying. First, the aqueous solution (water) was replaced by an organic solvent exchange within the sample. This was done to eliminate any polar group (water) with a nonpolar solvent group to reduce the stickiness effect on the cell walls. The polar group would destroy the highly porous gel structure during the drying phase due to the high capillary stress generated by the extraction. This was affected by immersing the gel structure in an acetone bath for several days (3 days for 6 mm thickness) at 50°C until the acetone had fully infiltrated the structure. Then the acetone was exchanged with the liquid CO₂ for 3 days in a sealed chamber using a syringe pump to achieve the desired pressure. Finally, the pressure and temperature within the chamber were increased beyond the critical point of CO₂ (31°C, 1,072 psi). The liquid phase in this state transferred into a gas phase by going beyond the solvent’s critical point. The bonding amongst the CO₂ molecules will disappear while maintaining the density of the liquid. In other words, the fluid had the same density as the liquid but had the same intermolecular forces as in the gas phase. This caused the surface tension to decrease significantly. Thus, the capillary stress was reduced until it was eliminated. The final product sustained its gel structure without any shrinkage and was defined as an RF aerogel. Fig 2-3 shows the experimental setup used for supercritical CO₂ drying.
2.3.4 Characterization of the morphological structure

The gel’s morphological structure and its mechanical and insulation properties were analyzed to achieve the optimal synthesis conditions for insulation purposes. The gel morphology, highly dependent on the sample’s void fraction, was analyzed by calculating its bulk density, solid density, particle size, and pore volume. The bulk density ($\rho_b$) was measured by calculating the volume and the sample’s total mass after drying.

$$\rho_b (\text{bulk density}) = \frac{\text{mass}}{\frac{\pi}{4} (\text{sample diameter})^2 \times (\text{sample height})} \quad (2.1)$$

The solid density ($\rho_s$) represents the solid part within the structure and it was measured using a helium pycnometer (Quantachrom Instruments, Ultrapycnometer 1000). Finally, the total pore volume, porosity, and expansion ratio were also calculated from the bulk and the solid density data using:

$$V_p (\text{pore volume}) = \frac{1}{\rho_b} - \frac{1}{\rho_s} \quad (2.2)$$

$$\Pi (\text{porosity}) = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100\% \quad (2.3)$$

$$\phi (\text{expansion ratio}) = \frac{\rho_s}{\rho_b} \quad (4)$$
The particle size analysis was conducted using environmental scanning electron microscopy (ESEM) (Quanta FEG-250), and the images were analyzed using ImageJ software. The samples were coated with platinum before they were placed in the ESEM at a low vacuum with water vapor as the working environment acting to decrease the charging effect on the samples.

2.3.5 Characterization of the insulation and mechanical properties

The samples’ total thermal conductivity and thermal diffusivity were measured using a HotDisk TPS2500S thermal constant analyzer (Therm Test Inc). A C-5501 Kapton insulated sensor with a diameter of 6.4 mm along the transient plane was used as the source method. The sensor was placed between two solid aerogel samples with the same dimensions to measure the overall conductivity. The sensor measured both the heat generated and the temperature’s increase within the sample by measuring the transit change in the voltage over time [40].

The mechanical property of the samples was tested by conducting a compression test on the samples. The compression test was conducted using an Instron Microtester (5848) with 500N load cell. The test was conducted on a 25-mm x 6-mm cylindrical sample with a compression rate of 1.2 mm/min, according to the ISO 604-2002.

2.4 Results and Discussion

2.4.1 Optical appearance of RF aerogels

All the samples were gelled and fully dried except for the samples of (0.01 % - 0.90), (0.01 % - 0.91), (0.01 % - 0.92), (0.02 % - 0.91), and (0.02 % - 0.920 due to the low catalyst percentage and the high void fraction. The samples were partially gelled with a clear liquid solution on top of the gel portion. At different catalyst percentages, the samples’ colors changed as shown in Fig 2-4. They varied from dark red, to dark orange, when the catalyst percentage ranged from 0.04 wt% to 0.01 wt%, respectively. The color change was due to the structural coloring phenomena from the absorption and the reflection of the light spectrum, which resulted from the structural morphological difference that occurred when the catalyst percentage changed. With a smaller
particle size, the reflection of the visible light has changed which created the darker color appearance.

**Fig 2-4:** Final RF aerogel monolithic samples at different R/C; (a) 0.04%-0.8, (b) 0.03%-0.8, (c) 0.02%-0.8, (d) 0.01%-0.8, (e) 0.04%-0.9, (f) 0.03%-0.9, (g) 0.02%-0.9, (h) 0.04%-0.91, (i) 0.03%-0.91, (j) 0.04%-0.92, and (k) 0.03%-0.92

As the void fraction of the high catalyst percentage samples (i.e., 0.04 wt%) was increased, the samples’ appearance characteristics became the same and had a similar transparency effect. However, when the catalyst percentage decreased to 0.03 wt%, samples became opaque due to the change in the particle size. At 0.03 wt%, scattering increased with an increased particle size, which caused the radiation decay length to decrease below the sample thickness, resulting in an opaque appearance.

### 2.4.2 Morphological analysis

The aerogel samples’ porous structures are morphologically analyzed using Equations 2.1-2.4, and the data are shown in **Fig 2-5**.

When the catalyst percentage varied at a fixed void fraction, the overall sample bulk density, solid density, pore volume, expansion ratio, and porosity were fixed. However, when the
void fraction increased, the morphological parameters changed due to the increased gas content within the samples. This emerged from the increase in the pore size with the void fraction. As a result, the reactant (i.e., catalyst, resorcinol, and formaldehyde) dispersed more within the mixture at the gelation stage. This, in turn, resulted in an increased distance between the clusters with the void fraction [39]. Furthermore, during the drying stage, the water intrinsic to the structure was replaced with gas. Therefore, the increased void fraction was translated into a structural porosity and an increased pore volume, and expansion ratio at a fixed catalyst percentage. However, there were limits to the amount of the void fractions that can be used for gelation to occur. For example, at high void fractions and low catalyst percentages, the gelation of the samples failed. Because the amount of resorcinol and formaldehyde used was decreased, which leads to a weakly branched structure [39]. The pH value in this case was reduced towards the lower end of the acidic region, and this promoted the growth of particles to a higher degree than its connection, which resulted in a weak structural connection and only a partial gelation [39].

The morphological analysis showed a decreased particle size with the catalyst percentage. Because, during the gelation process, the particles’ size depends on the chemical compounds consumed at the nuclei sites. When the catalyst’s percentages increased, more nuclei sites occurred. Thus, a smaller amount of the reactant were consumed per site [41]. However, when the catalyst percentage was reduced, more reactant were consumed per site, and this triggered the particles to grow in size to fill the entire volume [41]. Also, with more catalyst, the pH values increased which result in an increased in the particles connections, which generated a high number of clusters. The clusters number controlled the sample pore size, as with more clusters the pores sizes were reduced. Hence, these concurrent changes in the particles and the pore sizes compensated each other in each sample at fixed void fraction.
**Fig 2-5:** Pore texture analysis, a) bulk density, b) solid density, c) pore volume, d) expansion ratio, e) porosity, and f) particle size

The structure in the SEM images shows how the particles are connected by pearl-necklace clusters with the gas enclosed inside the pores on a nano-scale. **Fig 2-6** shows the reduction in the particle size with the catalyst percentage. The particle-to-particle connections were limited to only their radius for samples with a low void fraction. As the void fraction increased, the particle connectivity grew larger and the pore size increased to fill the occupied volume, as **Fig 2-7** shows. With a high catalyst percentage and a high void fraction, the structure was oriented in a mixed configuration form, as the particle-to-particle connection exceeded its radius to form necks.
between the particles. These formations provided the elasticity needed with a high particle size distribution [42].

Fig 2-6: SEM images of RF aerogel monolithic samples at different catalyst wt% for $\nu_f = 0.8$; (a) 0.04 wt%, (b) 0.034 wt%, (c) 0.02 wt%, and (d) 0.01 wt%

At void fractions of 0.8, and 0.9 the particles’ sizes were fixed at a fixed catalyst percentage. The water at these void fractions did not influence the pH value due to the high basic pH conditions of the solution. However, when the void fractions increased to 0.91, and 0.92, the pH value of the system changed towards the acidic region. Hence, the particle growth was promoted as can be seen in Fig 2-7 (c & d) and formed a bimodal structure with a heterogeneous configuration in the mixed configuration structure.
2.4.3 Thermal insulation properties

The insulation properties of the RF samples were evaluated by measuring the thermal conductivity and the thermal diffusivity while varying the catalyst percentage and the void fraction. Two samples (25-mm x 6-mm) were placed in a hot disk thermal analyzer to measure the total thermal conductivity within the structure. The heat transfer through an aerogel medium is divided into three main categories: i) solid conductivity, ii) gas conductivity, and iii) radiation. Each is governed by an intrinsic morphological parameter. The solid conductivity of the structure was limited by the contact area between the particles, the solid conduction paths, and the scattering behavior of their heat carriers (phonons) [43, 44]. With the particle reduction, the contact area and the conduction path were reduced because of the reduction in the connection point between the particles. This was limited by the particle radius at a fixed void fraction. Thus, the insulation properties were enhanced when the catalyst percentage was increased as shown in Fig 2-8 (a). Also with the reduction of the particle size the structure was shifted closer to the mean free of path.
of the phonons, thus the Umklapp scattering for the phonons increased [45]. The Umklapp scattering diffuse the phonons and generates a thermal heat resistance at the interface [44-46].

**Fig 2-8:** Thermal analysis results for monolithic RF aerogels, a) thermal conductivity, and b) thermal diffusivity

With the particle size reduction, the amount of air filling the structure was increased which tends to slightly increase the gas conductivity. However, the solid conductivity was still more dominant at this stage, and this caused the overall thermal conductivity to decrease with the catalyst percentage. The gas conductivity in our structure was restricted due to the pore sizes, which were the same or smaller than the mean free path of the gas collisions [47]. Meanwhile, the radiation was minimized in the RF aerogel due to its absorption ability, which was generated from the high specific extinction coefficient (absorption and scattering). The RF aerogel’s carbon base provided a high extinction coefficient, which acts as an opacifier for the radiation part [48]. Further, the radiation was reduced more in a fine structure than in a coarse one due to the increased particle density [49].

When the void fraction was increased, the structure’s pores expanded. This expansion decreased the solid backbone and slightly increased the gas conductivity. This slight increase was insignificant in the overall structure at high catalyst percentage. Hence, in the case of a high catalyst percentage and a high void fraction, the solid conductivity was restricted due to the formation of a mixed configuration structure. As the void fractions increased even further, a high
scattering effect was generated due to the heterogeneous structure. However, when the catalyst percentage decreased at higher void fractions, the samples thermal conductivities increased due to the increased gas conductivity.

The thermal diffusivity in the structure is highly dependent on the material’s stored thermal energy over the conducted thermal energy. Since the thermal conductive energy was the same, the material’s thermal storage capabilities decreased. This reduction emerged from the increased void fraction at fixed catalyst percentage because the gas-specific heat was lower than the RF’s solid part, hence the increase in the thermal diffusivity. The lowest thermal conductivity achieved was below air thermal conductivity at room temperature (0.026 W/m-K) which provide our aerogel the superinsulation characteristics [40].

2.4.4 Mechanical properties

The RF aerogel monolithic samples were tested for compression with respect to their mechanical properties. Five cylindrical samples (25-mm x 6-mm) were used for testing, and the compression elastic modulus along with yield stress were measured as shown in Fig 2-9.

![Mechanical analysis for monolithic RF aerogels](image)

**Fig 2-9:** Mechanical analysis for monolithic RF aerogels, a) elastic modulus, and b) yield stress

The samples flattened during the compression test and their stiffness increased with the stress induced as shown in Fig 2-10. During compression, the pore walls crashed in on each other, which increased the gas molecules’ internal collisions [50]. Due to the intensity of these collisions,
an internal stress built up within the structure. As shown from Fig 2-10 (a) the samples became brittle with the catalyst percentage, due to the reduction in the particle-to-particle connections with the particle size reduction. However, when the void fraction increased, the sample ductility increased substantially at a fixed catalyst percentage, and its elastic region increased due to the large necks formed in the mixed configuration structure as shown in Fig 2-10 (b). These necks provide the samples with the elasticity characteristics as shown from the elastic modulus values in Fig 2-9 (a). As soon as the void fraction increased further, an increase in the particle size distribution emerged, which formed a heterogeneous connection (necks) between the particles. These necks enabled the elasticity effect and increased the stiffness during compression testing, as shown from Fig 2-10 (b).

Fig 2-10: Compression test results for monolithic RF aerogels, (a) $v_f=0.8$ with different catalyst wt%, and (b) 0.04 wt% with different $v_f$

These changes in the morphological and mechanical behaviors added another step by which to correlate each parameter with the final RF aerogel insulation characteristics. Fine tuning for RF aerogel structural parameters makes this product more commercially viable. Our study showed that RF’s mechanical properties were substantially enhanced while its insulation characteristics were fixed. Structural elasticity is essential for insulation purposes, and it provides greater durability during the operation by impeding RF aerogel as a sandwiched material in building insulation matrix.
2.5 Conclusion

We conducted a synthesis of resorcinol-formaldehyde (RF) aerogel with improved particle necking under supercritical conditions. A fine tuning of the catalyst percentage and the water content were conducted. A decoupling study of each parameter showed the effect they had on the morphological, thermal, and mechanical properties. The gelation process was highly sensitive to the initial catalyst percentage and the pH value. Both parameters controlled the nucleation and the growth mechanisms of the particles, which in return had a direct effect on the final morphological structure. The nucleation mechanism was solely depended on the catalyst percentage; as the number of nuclei sites increased with the catalyst weight percentage. However, the particles growth and neck connections were depended on the water content and catalyst percentage by modifying the solutions’ initial pH values. As the water content increased, to achieve low structural densities and have a larger void fractions, the pH value decreased and the spherical growth of the particles was promoted. Conversely, at high pH, a high number of connection sites on the particles were generated for the formation of necks. Both the catalyst percentage and water content were controlled to alter the connections between the particles during their growth. This combined effect generates a neck connection between the particles and yielded a mixed configuration structure. Finally, we found that RF aerogel’s mechanical properties were improved while its thermal insulation characteristics were maintained in the desired ranges when the void fraction was increased at a fixed catalyst percentage. This chapter contributes new insights into the fine tuning of the RF gelation process for both energy preservation and the commercialization of RF aerogel.

2.6 References


Chapter 3 Nanostructure to Thermal Property Relationship of Resorcinol Formaldehyde Aerogels Using Fractal Technique

After investigating the processing parameters which controlled the assembly and the structural parameters of our RF aerogel in Chapter 2. We investigated the relationship between the morphological features and the thermal properties of RF aerogel in this Chapter by using unique characterization technique to calculate the structure-to-property parameters. In this section, we characterized the morphological features of an organic resorcinol-formaldehyde (RF) aerogel and correlated each feature to the thermal insulation properties. Several RF aerogels were synthesized with different morphological features and structural assemblies. This was done by changing the catalyst percentages and the dilution ratios at the polymerization stage. Then, each morphological feature was assessed and categorized using two scales: the macro scale and the micro scale. We found that the macro-features were independent of the catalyst percentages and depended only on the dilution ratios. By contrast, the micro-features were highly sensitive to any changes during the polymerization process. These changes altered the samples’ three main micro-structural factors: (i) The structural assembly, (ii) The porous structure, and (iii) The fractal parameters. Thus, we characterized and quantified each component within these areas. Then, we assessed the structure’s heat transfer modes and classified them as follows: (i) Solid conductivity through the solid particles, (ii) Gas conductivity through the gas molecules, and (iii) Thermal radiation. We

1 The content of this chapter has been Published in Nanoscale Journal;
identified the morphological features in our RF samples and correlated them to each mode of the heat transfer. For example, the samples’ solid conductivity was highly dependent on the fractal parameters of our structure; that is, the particles’ roughness, the structural complexity, and the structural homogeneity. For those samples with extremely rough particles and a complex structure, the solid conductivity reached the lowest possible point. We also found that the total thermal conductivity was mainly controlled by the micro-morphological features, and that the solid conductivity was the most dominant heat transfer mode.

3.1 Introduction

The current research on the production of low-density materials focuses mainly on generating nanomaterials with a high porosity and a complex structure. The properties of these nanomaterials would be superior to their high-density counterparts. Foams and aerogels have been described as leaders in the production of low density nanomaterials due to their high porosity and complex structure [1-5]. Such materials are already being used in the aerospace, biomedical, and automotive industries [6-9]. Aerogels are considered to be a special class of open-cell foams, wherein highly ordered nanoparticles are connected to create a three-dimensional (3D) network. Our study focused on organic aerogels that have a unique structural assembly, and on how such an assembly can affect the products’ final properties.

Organic aerogels consist of the random nanoparticle growth that occurs during the gelation process, when the multifunctional organic monomers are polymerized [10-13]. This is the sol-gel process, wherein a monomer solution undergoes a viscoelastic transition from a liquid state (a sol) to a wet solid-like state (a gel) [2, 14, 15]. During this change, chemical and physical interactions occur between the particles to create colloidal clusters [12, 16]. The clusters grow to connect with each other until they fill all the available space. The growth of such clusters in the organic aerogels is categorized as a diffusion limited aggregation (DLA) of the particles via the Brownian motion. The nanonetwork generated by the DLA shows a dilation symmetry in which the structural roughness is invariant to scale changes. In this case, the structure is called as a fractal structure. This means that a magnified version of the particles’ surface roughness on a short-length scale
resembles its surface roughness on a large-length scale [17]. The parameter used to measure the surface roughness is called the fractal dimension [18]. The structural assembly and the random particle growth are both deduced from this parameter. This process gives the organic aerogels their porous complexity, and all their unique properties [19].

The polymerization of organic aerogels proceeds in two-stages: the addition reaction and the condensation reaction [14, 20]. Both reactions control the growth of the clusters. And they occur simultaneously during the gelation process, depending on whether or not the solution is in a basic or in an acidic condition [2]. For example, if the solution is basic, then the addition reaction and the cluster-cluster growth are encouraged. This creates more cluster branching [2, 17]. However, in an acidic condition, the condensation reaction and the monomer-cluster growth are more encouraged; that is, the clusters have large particles [2, 17]. Resorcinol-formaldehyde (RF) aerogel is one of the most common organic aerogels wherein the resorcinol is polymerized with the formaldehyde to create a nanonetwork [14, 20]. The consequent reaction is initiated by the resorcinol’s deprotonation at the 2nd, 4th, and 6th positions of the benzene ring, where it creates a hydroxyethyl derivative [12]. The hydroxyethyl groups grow larger by reacting with the excess formaldehyde within the solution. This happens until the first cluster is created, and it starts to crosslink with the other clusters [10, 14].

Many researchers have focused on the structure and the properties of RF aerogels. The identification of each RF structural parameter would help us to isolate each structural-to-property parameter. Thus, we could tune the morphology. Lu et al. studied the structural relationships with different modes of thermal conductivities within the RF aerogels [13, 21]. They found that each heat transfer mode was directly connected with a structural parameter. For example, when the density was increased, both the gas conductivity and thermal radiation were decreased. Meanwhile, the solid conductivity was increased with an increased density. Other researchers have investigated the relationships between the structural assembly and the mechanical properties. Pekala et al. synthesized an RF aerogel with a different particle size and particle connectivity by varying the solution’s catalyst percentage [22]. They found that the elastic modulus had increased whenever the particle connectivity was improved. In Chapter 2, we used the same technique to make an RF aerogel with a mixed configuration structure [2]. The connectivity between this structure’s particles was comparable to the particles’ diameters. The connections between the particles
increased the samples’ elasticity by 30% while their thermal characteristics remained unchanged. Other researchers have investigated how the porous structure (empty space) affects the RF’s mechanical properties. Rapp et al. modified the RF clusters’ porosity and branching, and found that a weak branching between the clusters resulted in a low RF mechanical strength in the RF aerogels [23].

In this chapter, we synthesized the RF aerogels with different morphological features by varying the dilution ratios and the catalyst percentages. We then divided these features into macro and micro scales, based on the scale of their measured parameters. The samples’ micro-morphologies, which controlled the random assembly of our network, were characterized and classified into two main parts: a solid part and a gas part. In the solid part, we analyzed the structural fractal parameters, the particles’ sizes, their surface area, and their connectivity. We quantified each of those parameters. In the gas part, we computed the pore sizes, the pore shapes, and the pore classification. Afterwards, the samples’ assemblies were evaluated and correlated to the quantified values of our fractal parameters. Following this, we correlated each structural feature and structural assembly with the samples’ total thermal conductivity and diffusivity. We calculated the heat transfer mode and linked it to the structural morphology and assembly within the samples. This unique detailed characterization of our RF aerogels provided a tangible and numerical proof on the correlation between the samples’ structural features and the thermal properties of RF aerogels.

3.2 Fractal structures and assembly

During the sol-gel process, the resorcinol formaldehyde aerogel particles exhibited a statistical growth, which caused them to assemble randomly, and to create a porous structure with pores of different sizes [24]. While these pores accumulate in a disorderly manner, they often display a “dilation symmetry” [10]. This dilation symmetry is one of the fractal structure’s characteristics wherein the structure has a pattern that repeats across a given range of scales [25, 26]. The concept of fractal structure was originally introduced by Mandelbort in his famous Mandelbort set [27, 28]. And he also applied the fractal theory to complex rough structures such as mountains, clouds, and other objects that appear in nature [28]. The roughness of those
structures is described by one parameter: the fractal dimension D [19, 28]. This dimension provides a quantitative measure of the roughness and the disorder of fractal structures [17].

The fractal dimension of any fractal structure can be evaluated by using small angle x-ray spectroscopy (SAXS). The SAXS measures the periodicity of a certain periodic structure in the nanometer size range [28]. This is done by measuring the differential cross section of an irradiated sample (the intensity) I(q) versus the scattering vector magnitude (q) [29] as follows in Equation (1):

\[ q = \frac{4\pi}{\lambda} \sin\theta \]  

(3.1)

where θ is half the scattering angle, and λ is the wavelength of the incident radiation. When plotting the log-log scale of I(q) versus q, it was observed that the fractal structure’s scattering behavior obeyed the power law that originated mainly from the roughness of the samples’ surfaces [28, 30]. The power law is presented as follows [28]:

\[ I(q) \propto q^{-\alpha} \]  

(3.2)

where α is the power law exponent and the slope of the scattering curve. This exponent controls whether or not the classification of the structure is fractal. For example, a structure is a fractal if it is \( \alpha \neq 1, 2, 4 \) or anything besides these numbers. The structure would have either a self-repeating pattern or a naturally “rough” structure [28, 31]. If the structure was branded to be fractal, then α would be classified as follows:

\[ \alpha = \begin{cases} 
\alpha < 3, \text{Mass fractal}, & \alpha = D_m, \text{ where } D_m < 3 \\
3 < \alpha < 4, \text{Surface fractal}, & \alpha = 6 - D_s, \text{ where } 2 < D_s < 3 
\end{cases} \]  

(3.3)

where \( D_m \) is the fractal dimension for a structure which has a roughness that penetrates throughout the bulk volume, and \( D_s \) is the fractal dimension for a structure that only has a surface roughness [28]. The mass fractal represents the structure’s overall roughness; however, the surface fractal represents the roughness of the individual nanoparticles within the structure. We focused on evaluating the roughness of the aerogel particles through the surface fractal values; that is, the particles were rough when the \( D_s \) was 3, but they became smoother when it was at 2.
The scattering curve generated from the SAXS is divided into sub-regions, each of which provided data about the structure’s assembly. Specifically, we focused on the Guinier and the Porod regions. When the Guinier region is present at an early stage of the curve, that region is used to derive the nanoparticles’ radius of gyration through the following approximation:

\[ I(q) = I(0) \cdot \exp \left( -\frac{q^2 R_g^2}{3} \right) \]  

(3.4)

where \( R_g \) is the radius of gyration, which is defined as follows:

\[ R_g^2 = \frac{\int_V \rho_e(r) |r|^2 dV}{\int_V \rho_e(r) dV} \]  

(3.5)

where \( \rho_e(r) \) is the scattering length density at a distance \( r \) from the center of the particle. The radius of gyration can be found experimentally by applying the above equations on the plotted data of \([q^2, \ln(I)]\) and fitting in a straight line [28]. For homogeneous spherically-shaped particles, the radius of those particles \( R \) can be approximated as follows by:

\[ R_g = \left(\frac{3}{5}\right)^{1/2} R \]  

(3.6)

The Porod region is present at the tail of the SAXS curve, as this region is directly related to the structure’s complexity. The curve in this region obeys the Porod law as follows:

\[ I(q) = K_g q^{-4} + C \]  

(3.7)

where \( K_g \) is the Porod constant, which is obtained by fitting the line of \([q^4, I(q^4)]\). This constant is defined as follows:

\[ K_g = \lim_{q \to \infty} q^4 I(q) \]  

(8)

The Porod constant in our work was correlated to the structure’s complexity by its correlation to the surface-to-volume ratio as follows [28]:
\[
\frac{S}{V} = \frac{K_g}{2\pi(\Delta \rho_e)^2}
\]  

(3.9)

where $\Delta \rho_e$ is the difference in the scattering length densities of the materials’ two phases. In the above equation, the value of the surface-to-volume ratio translates the structure’s complexity. And this is proportional to the Porod constant. With a high Porod constant value, the structure is highly complex.

3.3 Experimental Section

3.3.1 Materials

Resorcinol (R, 1,3-Benzenediol, ≥ 99%), and sodium carbonate (C) (Na$_2$CO$_3$, 99%), were purchased from Sigma-Aldrich. A formaldehyde solution (F, 10-15% methanol as a stabilizer, 37% H$_2$O to prevent the formaldehyde from undergoing polymerization) was purchased from Caledon labs [32]. Acetone (HPLC, ≥99%) and distilled water (W) were obtained from Caledon, Life Technologies, and Invitrogen, respectively. All the chemicals were used as received in the synthesis of the resorcinol-formaldehyde (RF) aerogels. Carbon dioxide (CO$_2$) was used as a drying agent under supercritical conditions (99% purity from Linde Gas Canada).

3.3.2 RF aerogel synthesis process

Multiple samples of the RF aerogel were prepared by modifying their catalyst weight percentages and their dilution ratios. Three different catalyst weight percentages were used: 0.02%, 0.03%, and 0.04% which corresponds to R/C molar ratios of 700, 500, and 300, respectively. These percentages were also varied using three different dilution ratios (DR): 10, 18, and 22. The dilution ratio represents the ratio between the solid reactants to the liquid contents in molar base at the mixing stage, and it was calculated as follows:

\[
DR(\text{dilution ratio}) = \frac{\text{Water+methanol}}{\text{Resorcinol+Formaldehyde+Sodium carbonate}}
\]  

(3.10)

We began the synthesis process by mixing the resorcinol with sodium carbonate at different percentages in water. Then, the formaldehyde was added to the mixture to start the polymerization
reaction. The concentration of resorcinol to formaldehyde was fixed at stoichiometric conditions (R/F=0.5). The mixture of these ingredients initiated the gelation process, wherein the particles began to grow and to form clusters. During this process, the nuclei sites were activated and started to form nanoclusters. This is shown in the RF solution visualization during the gelation stage in Fig 3-1. Then, the samples were heated in an oven at 60°C to accelerate the gelation process [33]. The solvent within the samples was extracted by applying the CO₂ supercritical drying process. This was done to eliminate any shrinkage in the samples. We have provided a detailed, stepwise guide to the synthesis process and have explained the chemical reactions involved in chapter 2 [2].

![Image](image.png)

**Fig 3-1:** RF solution visualization during the gelation

### 3.3.3 Characterization

We analyzed the gel’s morphological structure and its insulation properties. The bulk density ($\rho_b$) was measured by calculating the volume and the samples’ total mass after drying. The solid density ($\rho_s$) represents the solid part of the structure, and it was measured using a helium pycnometer (Quantachrom Instruments, Ultrapycnometer 1000) [34]. In the pycnometer, the gas penetrates the porous structure, and its volume is recorded. The porosity and expansion ratio were calculated from the bulk and the solid densities as follows:
\[ \Pi(\text{porosity}) = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100\% \] (3.11)

\[ \phi(\text{expansion ratio}) = \frac{\rho_s}{\rho_b} \] (3.12)

The samples’ porous texture was characterized by nitrogen adsorption-desorption isotherm analysis, performed at 77 K using Autosorb iQ (Quantachrome Instruments). The samples were outgassed for 15 hr at room temperature and at a pressure of 10^{-3} \text{ Pa prior to the nitrogen adsorption analysis. From the nitrogen analysis, the samples’ pore size distributions were measured using the Barrett-Joyner-Halenda (BJH) theory. The samples’ surface areas were evaluated using the Brunauer-Emmett-Teller theory. The measured surface areas values are only used as a comparison between the samples, because of the machine limitation of accurately measuring such values. This limitation originated from the limitation of gas movements in the structure, due to the Knudsen effect.}

The samples’ micromorphology and their particle sizes were investigated using environmental scanning electron microscopy (ESEM) (Quanta FEG-250), and the images were analyzed using ImageJ software. The samples were coated with platinum before they were placed in the ESEM at a low vacuum setting and water vapor was used to decrease the charging effect on them.

Our structure’s fractal characteristics and their structural assemblies were measured using automated small angle x-ray scattering (SAXS) from Anton Paar (SAXspace). The RF samples were packed into a 1-mm thick sample holder. The scattered intensity of the CuKα-radiation (\(\lambda = 0.154 \text{ nm}\)) was recorded for each scattering angle, \(\theta\), at 298K.

The samples’ total thermal conductivity was measured using a HotDisk TPS2500S thermal constants analyzer (Therm Test Inc.). A C-5501 Kapton insulated sensor with a diameter of 6.4 mm along the transient plane was used as the source method. The hot disk thermal analyzer sensor was sandwiched between two cylindrical aerogel samples (25-mm x 6-mm). The sensor measured both the heat generated and the temperature’s increase within the sample by measuring the transit change in the voltage over time.
3.4 Results and Discussion

3.4.1 RF morphology assembly

We identified and measured the morphological changes in our samples. These were divided into two main sections: macro-morphology and micro-morphology. In the macro-morphology section, the sample parameters, which identified the structure’s macro-assembly, were measured. These parameters were as follows: the bulk density, the skeletal/solid density, the expansion ratio, and the porosity. They are summarized in Fig 3-2.

![Fig 3-2: Macro-morphology parameters: (a) bulk density, (b) solid density, (c) expansion ratio, and (d) porosity](image)

Given the above parameters, the samples’ overall macro-morphologies were independent of the catalyst percentage and were highly dependent on the dilution ratio. For example, when the dilution ratio increased, the samples’ porosities (empty space) and the expansion ratios increased, while their bulk densities decreased. This was because their gas volume had increased after the
drying stage. And when the dilution ratios increased, the amount of solvent (water) intrinsic to the structure also increased. During the drying stage, the deep-seated water in the structure was replaced with gas. Thus, the gas volume increased after the drying stage [2]. However, the dilution ratio that could be used for gelation to occur had limits. For example, at a high dilution ratio of 22 and with a low catalyst percentage of 0.02%, the sample’s gelation failed. This was because the amount of resorcinol and formaldehyde used had been decreased, and this created a weakly branched structure [35]. Furthermore, at this same dilution ratio of 22, the samples showed some dependency on the catalyst percentages. This was mainly due to, the increased in the structural local heterogeneity, and to the pycnometer measurement limitations. The gas movement in the structure was restricted during the measurements, due to the small pores in those samples. In such pores, the gas molecules were affected by the Knudsen effect, which increased their collisions with the pore walls and decreased their diffusion within the structure [13].

The samples’ micro-morphologies were identified as having two main sections: the solid part and the gas (empty) part. The solid part included the samples’ particle sizes, necks, fractal parameters, and surface areas. The gas part included the pore sizes and shapes and the pores classifications. Our samples were assembled at a micro-level, as shown by the high magnification SEM images in Fig 3-3.

![Image of SEM images](image_url)

**Fig 3-3:** Micro-assembly of the RF structure at different catalyst percentages for DR=10: (a) 0.04wt%, (b) 0.03wt%, and (c) 0.02wt%

Our macro-morphology parameters were independent of the catalyst percentages. But the sample structural assembly changed with the catalyst percentages, as observed in our earlier work [2, 12]. The particle sizes, their necks, and their number all changed with the catalyst percentage.
Their size was inversely proportional to the catalyst percentage, as it decreased when the catalyst percentages increased. This occurred because during the gelation stage a particle’s size depends on the chemical compounds consumed at the nuclei sites [36]. Chapter 2 showed that, with an increased catalyst percentage, the number of nuclei sites increased [2]. Thus, with lower catalyst percentages, the chemical compounds per nuclei site were increased, and this caused the particles to grow spherically, and to form clusters with big particles that filled the structure’s volume [12]. Also, with a high number of nuclei sites, the number of particles in the final structure was increased. We deduced from the SEM images that the final parameter was the particle connectivity; that is, their necks. In this form, the particles had connected through a point or a surface contact [2].

When the dilution ratio increased, the structural configuration changed and formed a mixed configuration at the higher dilution ratios, as Fig 3-4 shows. With an increased dilution ratio, the particle connectivity grew larger and filled the occupied volume. Thus, the particle-to-particle connection exceeded its radius and formed necks between the particles. When the dilution ratio increased even further, as is shown in Fig 3-4 (c), a heterogeneous configuration with a bimodal conformation of the particle sizes emerged. This was due to the influence of the dilution ratio on the pH values. Then, the pH values influenced the particles’ spherical growth during the gelation process [2]. Thus, the particles experienced heterogeneous growth due to the inconsistent amount of reactant on each nuclei site. The samples’ particle sizes are summarized in Table 3-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR = 10</td>
<td></td>
</tr>
<tr>
<td>0.04wt%</td>
<td>16.2±5.2</td>
</tr>
<tr>
<td>0.03wt%</td>
<td>34.6±11.2</td>
</tr>
<tr>
<td>0.02wt%</td>
<td>43.1±14.5</td>
</tr>
</tbody>
</table>
$DR = 18$

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<tbody>
<tr>
<td>0.04wt%</td>
<td>20.5±12.7</td>
</tr>
<tr>
<td>0.03wt%</td>
<td>32.6±7.6</td>
</tr>
<tr>
<td>0.02wt%</td>
<td>58.8±15.5</td>
</tr>
</tbody>
</table>

$DR = 22$

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<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04wt%</td>
<td>59.8±13.9</td>
</tr>
<tr>
<td>0.03wt%</td>
<td>66.8±14.6</td>
</tr>
</tbody>
</table>

**Fig 3-4: Micro-assem**

3.4.2 Small angle x-ray spectroscopy (SAXS) structural analysis

We evaluated the structure’s fractal parameters using a SAXS machine. This analysis identified the particles’ roughness, the structural complexity, and the homogeneity. The particles’ surface roughness was linked to the surface’s fractal dimension values by using a power-law model in our SAXS analysis. The surface fractal values in **Fig 3-5 (a)** showed a slight dependency on the
catalyst percentages. When the catalyst percentage decreased, the surface fractal values decreased, which indicated the formation of smoother surfaces. This happened because, with the high catalyst percentages, the number of nuclei were dramatically increased during the gelation stage. A large number of particles were produced by this process, which increased the three-point connection between each particle. Each of those connections had alerted the topography of each particle to generate rougher particle surfaces at their mutual contact points.

**Fig 3-5:** SAXS structural analysis for the RF samples at DR=10 and the different catalyst percentages: (a) Porod constant and surface fractal, and (b) Actual particle size and size of the homogeneous sphere
**Fig 3-6:** SAXS structural analysis of the RF samples at 0.04wt% with different dilution ratios: (a) Porod constant and surface fractal, and (b) Actual particle size and size of the homogeneous sphere

When the dilution ratio increased, the RF particles’ surface roughness was almost independent of the dilution ratio, as is shown in Fig 3-6 (a). The surface fractal values changed slightly, especially at a high dilution ratio of DR = 22. This was because the increased dilution ratio increased the pore volume and, thereby, contributed to the particle connections, i.e., the formation of necks. These connections at the dilution ratio of 22 elongated, but did not form any new branches, as is shown in Fig 3-4’s SEM images. At high dilution ratios, the cluster branching was suppressed during the gelation process. Therefore, the surface fractal value declined.

The second parameter was the structural complexity, which was linked to the Porod constant values. In this situation, a highly complex structure possesses high values. Fig 3-5 (a) shows that at high catalyst percentages, the samples had high Porod constant values. This was mainly due to the high volume-to-surface ratio; that is, the structure’s complexity. The structural complexity resulted from the high cluster branching and the high number of particle connections, which were caused by the large number of nuclei present under these conditions. When the dilution ratio increased to 18, the complexity of the structure increased, as is shown by the increased Porod constant values in Fig 3-6 (a). This increase was generated by the high branching activity between the clusters. And, when the dilution ratio was increased to 18, the space between the clusters increased, which forced the clusters to form new branches to connect with each other. Despite these new branches, the particle sizes were homogenous, as is shown from the inset SEM images.
in Fig 3-6 (a). However, when the dilution ratio increased further to \( DR = 22 \), the structural complexity diminished, as is shown by the reduced Porod constant values. This happened because at this dilution ratio (22), the clusters’ branching had been suppressed during the gelation stage and a heterogeneous configuration, with a bimodal conformation of the particle sizes, had emerged, as is also shown by the inset SEM images in Fig 3-6 (a). This means that at this stage, the particles had grown spherically instead of forming connections between each other. Thus, the structure’s complexity was diminished, despite the increased space between the clusters.

The final parameter was the structure’s homogeneity, which was derived by comparing actual particle sizes with their theoretical sizes if they had a homogeneous spherical shape. The homogeneous sphere size was calculated from the radius of gyration using Equation (3.6). show how the samples’ homogeneity decreased when the catalyst percentage decreased and when the dilution ratio increased. This was indicated by the large deviation between the actual particle size and the size of a homogeneous sphere. The homogeneity of the particles was directly correlated to the particle growth during the gelation stage; that is, by the amount of reactant consumed on each nuclei site [36]. Thus, when this was inconsistent, the particle growth was classified as heterogeneous [2]. When the catalyst percentage was high, the nuclei sites consumed a consistent number of reactants, which produced uniform particle growth at a constant growth rate [12]. This created a homogeneous particle with a semi-spherical shape. When the dilution ratio was increased to 18, the particle sizes were the same size as the homogeneous spheres. This was because the structure still had a high number of nuclei sites, which could generate the homogeneous growth of each particle. However, at a dilution ratio of 22, the structure experienced a heterogeneous particle conformation. These conditions had produced nuclei sites that were non-uniformly dispersed within the solution at the gelation stage, which was due to the high volume of water (solvent) used. With this non-uniform dispersion, the particles’ growth rate was inconsistent, and this explained the heterogeneity of their sizes.

3.4.3 RF porous morphology

The samples’ porous morphologies were evaluated by the nitrogen adsorption analysis. Fig 3-7 and Fig 3-8 show the adsorption and desorption isotherms, along with the BJH pore size distributions for the samples. All of the isotherms in those conditions were classified as type VI,
with hysteresis in the desorption loops. The hysteresis loops occurred because the pore cavities were larger in diameter than their openings; that is, ink-bottle shape pores. The samples had the same hysteresis loops shape, which means that the pore shapes were independent of the catalyst percentages and the dilution ratios, and that their sizes were in the mesoporous region [36]. However, the average pore size was changed with the catalyst percentages, as shown by the peak shifts in Fig 3-7 (b). When the catalyst percentage increased, the average pore size decreased in size. This was due to the increased number of nuclei that resulted from the increased catalyst percentages during the gelation stage. The higher number of nuclei increased the number of clusters which formed and became more entangled and/or branched [12].

When the dilution ratio increased, at first the pore sizes decreased, but when the dilution ratio was increased further, they did not change. This was because when the dilution ratio increased, the spacing between the clusters had increased while the number of nuclei sites remained the same. Thus, while the clusters were connecting, the pores within the structure had increased in size to fill the volume, as Fig 3-4 shows.

![Fig 3-7](image)

**Fig 3-7:** Nitrogen adsorption/desorption analysis for the RF samples at DR=10 and at different catalyst percentages: (a) Isotherms of N$_2$ at 77K, and (b) BJH pore size distribution
Fig 3-8: Nitrogen adsorption/desorption analysis for the RF samples at 0.04wt% and at different dilution ratios: (a) Isotherms of N\textsubscript{2} at 77K, and (b) BJH pore size distribution

The samples’ total surface areas were calculated using the BET analysis of the nitrogen adsorption, in Table 3-1, the surface areas are summarized. When the catalyst percentage decreased, the BET surface area also decreased. This was because the particle numbers and their sizes controlled the surface area. Therefore, at a high catalyst percentage, the number of particles was high while their sizes were small. Furthermore, when the dilution ratio increased, it diminished the total surface area. This was because the number of particles had decreased in the same volume.

Table 3-2: BET surface area of the RF aerogel samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DR = 10)</td>
<td></td>
</tr>
<tr>
<td>0.04wt%</td>
<td>378</td>
</tr>
<tr>
<td>0.03wt%</td>
<td>295</td>
</tr>
<tr>
<td>0.02wt%</td>
<td>228</td>
</tr>
</tbody>
</table>

\(DR = 18\)
3.4.4 Thermal properties

We assessed the samples’ thermal properties by measuring their thermal diffusivity and their thermal conductivity at room temperature (23°C). These were both determined by using the hot disk thermal analyzer. We also evaluated the different modes of heat transfer within the samples and correlated this to their morphological features.

The following three main types of heat transfer forms were used in our samples: (i) Solid conductivity through the nanoparticles, (ii) Gas conductivity through the gas molecules situated within the pores, and (iii) Thermal radiation through both the solid and empty spaces [26]. Fig 3-9 shows each form of the heat transfer, each of the heat transfer modes was directly correlated with, and highly dependent upon, a morphological parameter. We relied on our macro and micro morphological analysis to explain the samples’ thermal conductivity results. In our analysis, we assumed that no coupling effect had occurred within the solid-gas phase.
Fig 3-9: Different forms of heat transfer through the aerogels; (a) solid conductivity through the solid part, (b) gas conductivity through the pores, (c) thermal radiation, (d) solid conductivity values for the RF aerogels, (e) gas conductivity values according to the Knudsen model, and (f) thermal radiation values of the RF aerogels.

3.4.4.1 Solid conductivity

Fig 3-9 (d) shows that the solid conductivity was highly sensitive to both micro and macro solid features of the samples. The sample’s solid conductivity was controlled by the movements of the energy carriers’ (i.e., phonons, atoms, and molecules) through the solid part [37]. Therefore, in this heat transfer mode any disturbance in the energy carriers became either an improvement or a deterioration. It is well-known that the energy carrier in the solid conductivity transfer depends on the contact area between the particles and the solid conduction path as well as the scattering of the energy carrier at the interface (interface thermal resistance) [26, 38, 39]. The contact area between the particles depended on the particle sizes, their neck formations, and their surface roughness. When these areas were improved, the energy carrier’s movement between them also improved [40]. The solid conduction path depended on the particle connections (that is, the necks), the structural complexity, and the number of particles [41]. Improved neck connections between the particles enhanced the paths between them, which increased the energy carrier’s solid path. However, when the structural complexity and the number of particles were increased, the solid
conduction path within the structure was also increased. Thus, in the above cases, when the conduction path (i.e., the length) was increased and the contact area between the particles was decreased, the samples’ solid thermal conductivity was decreased. This analysis matched the structural features found in each of the measured samples. **Fig 3-9 (d)** shows their corresponding solid conductivity. The final feature that influenced the solid thermal conductivity was the scattering behavior, which occurred at the interfaces between the linked particles. On a nanoscale the energy carrier here had a particle duality feature [42]. This meant that the energy carrier (that is, the phonons) would act like a particle and/or an electromagnet wave, depending on the scale and the interface condition [42]. Thus, the phonons in the structure exhibited a scattering behavior during the crossover between the particles. Consequently, a thermal interface resistance to those carriers was generated. In this feature, the conductivity depended on the number of particles, their surface roughness, and their overall structural homogeneity. A greater number of particles increased the number of interfaces, which became an interface thermal resistance. At the interface, the phonons displayed a discontinuous heat transfer and a slight temperature jump or temperature slip condition. Thus, the solid thermal conductivity was drastically decreased by a greater number of particles in the nanostructure [39, 43]. The second parameter was the particles’ surface roughness, which governed the scattering effect of the energy carrier. In samples with a high surface roughness, the phonon scattering was increased, which meant, the phonons’ lifetimes were diminished [44]. With this reduction in the phonons’ lifetimes, the solid thermal conductivity was dramatically decreased. Also, with more rough surfaces, the particles’ overall surface areas were increased, and thus, the thermal energy dissipation was also increased. In the case of highly homogeneous structures, wherein the particle sizes were close to each other, the phonon scattering behavior was decreased. And this was because in such structures the mismatch between the particles was reduced, which reduced the phonons’ scattering behavior [42]. The solid conductivity of each sample was calculated by evaluating the gas conductivity and the thermal radiation separately, and by then subtracting their values from the total thermal conductivity.

**3.4.4.2 Gas conductivity**
The gas conductivity in our porous structure was transferred through the collision of gas molecules situated within the pores. Heat was first transferred through the solid nanoparticles to the gas layer situated next to the particles. The molecular temperature in this gas layer had increased, which caused the molecules to vibrate. With these vibrations, they started to oscillate and collide with other molecules that were situated at a distance, defined as the mean free path distance. This is the average distance a gas molecule travels between successive collisions, and it is 69 nm for air. Thus, with pore sizes smaller than the mean free path, the molecular collisions were restricted, which, in turn, diminished the gas conductivity in these pores. Meanwhile, the surface area played a major role in the heat dissipation. With a higher surface area, the samples heat dissipation capabilities were increased. This also increased the gas-solid interface between the solid particles and the pores, which increased the thermal interfacial resistance between the two interfaces. Thus, the gas conductivity values were decreased. Fig 3-9 (e) shows that the gas conductivity in our structure was governed by the nanostructure’s porous morphology. The porous morphologies were identified according to the pores’ sizes, their shapes, and their surface areas. We managed the pore sizes by controlling both the formation and size of the interconnected solid particles and branching clusters in the samples. The gas conductivity values were evaluated by first calculating the Knudsen number as follows:

\[ \text{Kn} = \frac{l_{\text{mean}}}{d} \]  

(3.13)

where \( d \) is the pore size, and \( l_{\text{mean}} \) is the mean free path of the gas molecules. From the Knudsen number, the samples’ gas conductivity was evaluated using the following model [21]:

\[ \lambda_{\text{gas}} = \frac{\lambda_g^0 \Pi}{1+2\beta K_n} \]  

(3.14)

where \( \lambda_g^0 \) is the bulk gas conductivity, 26 mW/m. \( K, \beta \) is the efficiency of the energy transfer between gas molecules, 1.94, and \( \Pi \) is the porosity. The gas conductivity values were evaluated from Equation (14) and are shown in Fig 3-9 (e).

3.4.4.3 Thermal radiation
The last mode of heat transfer in the structure is thermal radiation, which is generated by the electromagnetic wave propagation (that is, the photons) moving through the structure. In this mode, the electromagnetic waves can be attenuated by scattering, absorption, or transmission in the structure. Hence, the size of the solid structure and its chemical composition play a major role in enhancing or suppressing the thermal radiation. For example, the photons would be scattered if their wavelengths were smaller than the particle sizes. The wavelengths in the infrared (IR) range, were between 0.7 – 350 µm [37]. Our solid morphological structure showed that our particle sizes were an order of magnitude smaller than the IR range; thus, the photons in our structure could only be transmitted through or absorbed [37].

Due to the high atomic number of the organic-based aerogel, compared with that of the inorganic aerogel, the structure had a high absorption capacity for thermal radiation. And therefore the RF aerogel was classified as an optically thick and opaque material [38]. In such materials, the electromagnetic waves were absorbed at each interface then transmitted to the next one and, thus, the energy of those transmitted waves was reduced at the interfaces [45]. The modeling of the thermal radiation at those interfaces is still to be investigated, due to the complex chemical and structural factors involved in nanocellular foams. The latest mathematical model to interpret the photons movement through those interfaces was presented by Wang et.al, in which the interfaces were assumed to be thin films [46]. However, in aerogels, the particles have a pearl-necklace shape for which this model cannot be applied. The current method to estimate the thermal radiation in highly porous organic aerogel is by evaluating the absorption capability within the structure through experimental techniques such as FTIR [47]. The quantitative measure of the absorption capabilities of such materials were presented in one parameter, which was defined as the extinction coefficient. This depends on the photon’s mean free path in the solid materials as well as on the temperature [37]. In our material, the thermal radiation is measured according to the Rossland diffusion approximation as follows:

\[ \lambda_{\text{radiation}} = \frac{16 n^2 \sigma T_r^3}{3 K_e \rho_b} \]  

(3.13)

where \( n \) is the refraction index, 1.05 for RF aerogel, \( \sigma \) is the Stefan-Boltzmann constant \((5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4)\), \( T_r \) is the environmental temperature (298K), and \( K_e \) is the Rossland specific
extinction coefficient (50.1 m$^2$/kg) for RF [38]. Based on the above equation, the thermal radiation within our samples is evaluated and plotted in Fig 3-9 (f).

3.4.4.4 Total conductivity

Fig 3-10 shows the measured values of the overall thermal diffusivity and conductivity of the RF aerogels. At first glance, the thermal conductivities were almost independent of the samples’ densities when the catalyst percentage was 0.04wt%. Under those conditions, the samples had a high number of particle sizes, high surface areas, small pore sizes, small particle sizes, and a highly complex and homogeneous structure, compared with other samples of the same dilution ratio. In this condition, despite the increase in the gas conductivity and thermal radiation values, when the dilution ratio was increased the solid conductivity contribution controlled the overall thermal conductivity. This was because the solid conductivity was only dependent on the micro-morphological changes. Thus, the total thermal conductivity existed independent of the density; that is, it was a macro-morphological feature. Meanwhile, at constant dilution ratios, the samples’ thermal conductivities increased when the catalyst percentages increased from 0.02% to 0.04wt%. When the catalyst percentages decreased, the samples’ micro-morphological features changed dramatically, as follows: (i) The number of particles decreased, (ii) The particle and pore sizes increased, (iii) The overall surface area decreased, and (iv) The samples’ branching and their random clustering decreased. These parameters showed before that the catalyst percentage increased the solid conductivity within our samples along with gas conductivity. Therefore, the total thermal conductivity was increased when the catalyst percentage was decreased.
3.5 Conclusion

We synthesized a RF aerogel with different morphological features and a structural assembly by altering the catalyst percentages and the dilution ratios during the polymerization stage. The RF structure’s assembly were also generated by the statistical growth of the nanoparticles during this stage. The samples that formed possessed a variety of unique morphological features. These were characterized and classified into two main forms according to their scale: (i) Macro, and (ii) Micro. Then, the structural parameters within each form was quantified and correlated to the samples’ thermal insulative properties to evaluate each structural-to-thermal parameter. The heat transfer within our sample was assessed and divided into three main forms: (i) Solid conductivity, (ii) Gas conductivity, and (iii) Thermal radiation. The value for each heat transfer form was calculated and linked to the governing morphological features. We found that the samples’ overall thermal conductivity was highly sensitive to any change in the micro-morphological features. In addition, it was independent of the macro features when the catalyst percentage was high. We also found that the solid conductivity was the most dominant form of heat transfer in the structure, and that it was highly dependent on the micro-features. These included any changes in the structure’s fractal parameters; that is, particle surface roughness, complexity, and homogeneity. Any of these could change the solid conductivity. Extremely rough particles and complex structures placed the solid conductivity at lowest possible level. In this
chapter, we identified each RF structural parameter and how it affected the samples’ thermal characteristics. Our research enabled us to single out each structural-to-property parameter and to tune our morphology accordingly to generate RF samples with the optimal thermal insulation properties.

3.6 References


Chapter 4 Reinforced Resorcinol Formaldehyde Aerogel with Co-Assembled Polyacrylonitrile Nanofibers and Graphene Oxide Nanosheets

In previous chapters, the RF aerogels still considered weak to be used as a standalone material for thermal insulation. Thus, in this chapter we fabricated a hybrid RF aerogel with high structural stability and strength by the addition of polyacrylonitrile (PAN) nanofibers into RF nanonetwork. The PAN solution was electrospun to produce PAN nanofibers. These were then oxidized to produce oxidized polyacrylonitrile (O-PAN) nanofibers. The two fibers were added to the RF nano-network to generate a hybrid RF aerogel, and so that the oxidization effect on the fibers could be observed. During the gelation process, the RF particles assembled themselves onto the surfaces of the electrospun PAN and O-PAN fibers. This increased the RF’s structural stiffness, strength, and resilience. Then, the graphene oxide (GO) nanosheets were added to the mixtures to provide a cross-linkage between the fibers. This increased the number of RF particles on the fiber surface by an order of magnitude, as the interconnection between the fibers had been increased. This doubled both the strength and resilience of the final RF aerogels and tripled their stiffness. Meanwhile, their lightweight characteristics were maintained, and their thermal conductivities were below 30 mW/m.K.

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4.1 Introduction

Organic aerogels consist of nanoparticles that are in contact to form a three-dimensional (3-D) nano-network of highly porous open-cell foams. Their unique properties include a high surface area and a low density. They also offer super thermal insulating characteristics [1, 2]. When they first emerged as super insulating materials, they had the highest heat barrier ever reported (12-18 mW/m.K at atmospheric pressure, 4-14 mW/m.K at vacuum pressure) [3]. They surpassed other organic based foams by an order of magnitude as thermal insulators [4-7]. Despite their unique properties, aerogels have still not fully replaced conventional foams on an industrial scale. This is mainly because their fragility and brittleness are much greater than that of organic-based foams [8, 9]. Thus, many researchers have been investigating reinforcing aerogel 3-D network foams with the aim of preserving their unique features while making them competitive with commercial foams [10-14]. The first organic aerogels were introduced by Pekala. He used resorcinol-formaldehyde (RF) as the organic backbone of the 3-D network [3]. RF was introduced as a substitute to Kistler’s inorganic silica aerogel as a super insulator due to its high extinction coefficient [15]. Our previous work showed a 30% increase in the RF’s aerogel structural elasticity. At the same time, its super insulation features were preserved without adding any fillers to the network [16]. In this chapter, a hybrid RF aerogel was introduced with an electrospun nanofiber added inside the nanonetwork to enhance the structural mechanical properties.

Reinforcing an aerogel structure has been extensively investigated by the research community. To date, only two approaches have been implemented for reinforcing the aerogel structures. The first approach was the introduction of fibers into the aerogel network [12, 17, 18]. Many researchers adopted this approach. Li et al. used polyurethane nanofibers in silica-based aerogels to reinforce the connection between the silica particles by introducing a thin film and, thereby, to produce a bendable silica aerogel [19]. Other researchers, such as Xu et al., used bacterial cellulose to decrease the brittleness of lignin RF aerogel by improving the compatibility of the aerogel particles and the fibers [17]. A nanostructure with similar mechanical behavior as
CNT-based carbon foams was produced. In one study by Shi et al., polyacrylonitrile fibers were introduced into the silica aerogel network as reinforcements. The structure gained strength with the fibers’ presence. Also, the fibers modified the silica aerogel’s oil-absorption ability, making their surfaces superhydrophobic [20].

A second approach is to use one-dimensional (1-D) nanofibers and two-dimensional (2-D) nanosheets as the building blocks for the aerogel’s 3-D network [21-23]. Huang et al., for instance, synthesized an elastic carbon aerogel by freeze-drying electrospun oxidized polyacrylonitrile (O-PAN) fibers connected through the graphene oxide (GO) nanosheets [21]. The backbone of this approach was the construction of a homogenous structure using electrospun fibers. In another study by Liu et al., a similar approach was taken to generate a graphene aerogel with carbon fibers [24]. The graphene acted as a bridge to connect the networks, which resulted in an aerogel with a high interfacial shear strength. Other researchers investigated the addition of organic and inorganic nanofibers to formulate a 3-D nanofibrous aerogel [22]. The mixture of these organic and inorganic fibers provided the structure with the elasticity and the stiffness needed to produce a superelastic and ultralight aerogel. However, to formulate a 3-D network, a crosslinking agent needs to be incorporated into the organic fibers.

In this chapter, a hybrid RF aerogel was synthesized by bonding the RF nanoparticles with an electrospun nanofiber. The synthesis process began by electrospinning the polyacrylonitrile (PAN) into submicron-scale fibers, and then dispersing them in the RF solution prior to the gelation stage. During gelation, the RF particles started to nucleate on the surface of the fibers, forming a blueberry-like configuration, due to their low surface energy [17]. In another synthesis, O-PAN electrospun fibers, which have a better water wettability, were used to increase the number of RF particles on the surface of the fibers. Further, GO nanosheets were added to both O-PAN and PAN mixtures, separately. The number of RF particles on the fibers was dramatically increased by an order of magnitude with the GO’s presence, due to the increased surface area on the fibers. As a result, the resilience and the strength of the hybrid RF aerogels became doubled, and the stiffness became tripled compared to the conventional RF aerogels. All these were achieved while their thermal conductivities were maintained below 30 mW/m.K.
4.2 Methodology

The hybrid RF aerogel in this work was produced by combining the two approaches described above. In this approach, both organic nanofibers and organic nanosheets were added simultaneously to the RF network to reinforce its structure. The fibers need to have a high aspect ratio, a high mechanical strength, and a good compatibility with the RF particles. Meanwhile, the nanosheets need to have a high surface area and a good compatibility with both the RF particles and the fibers. With these features, the nanofibers and the nanosheets acted as the building blocks for the RF particles to assemble on.

The first step was to produce a specific type of nanofibers for a successful addition into the structure. Such fibers need to have an extremely high aspect ratio and a mechanical strength as mentioned above, and these qualities can be achieved by electrospinning [25]. In this technique, an external electrical field was applied to a capillary spinneret containing a polymer solution [26]. This created continuous submicron fibers. Once these fibers have been generated, the second step was to change the existing linear molecular configuration into an aromatic ladder configuration. This was done by placing the nanofibers into an oxygen-rich environment to accelerate the oxidization process. Then, the nanofibers were dispersed in a solvent using a homogenization process to ensure that they were scattered evenly when the RF particles were present. At this stage, the nanosheets were added to the nanofiber mixture, where they formed chemical bonds with the fibers and acted collectively as a crosslinker. These mixtures were the building blocks for the RF structure. And the gelation process began as soon as the reactants were added to the mixture. The RF particles started to nucleate on the surface of the fibers, where they formed physical bonds. Finally, the solvent within the structure was extracted by supercritical drying of the samples. This also maintained their monolithic appearance. Fig 4-1 summarizes how the nanofibers and nanosheets were added to the RF structure.
4.3 Experimental section

4.3.1 Materials

Polyacrylonitrile (PAN, Mw=150,000 g/mol), resorcinol (R, 1,3-Benzene-diol, ≥ 99%), sodium carbonate (C) (Na2CO3, 99%), N, N-Dimethylformamide (DMF, ≥ 99.8%), and graphene oxide (GO, 2 mg/mL, mixture in H2O) were purchased from Sigma-Aldrich. The GO was used due to its high compatibility with the RF aerogel. A formaldehyde solution (F, 10-15% methanol as a stabilizer, 37% H2O to prevent formaldehyde from undergoing polymerization) was purchased from Caledon labs. Acetone (HPLC, ≥99%) and distilled water (W) was obtained from Caledon, Life Technologies, and Invitrogen, respectively. Ethanol (Anhydrous Ethyl Alcohol) was purchased from Commercial Alcohols. All the chemicals were used as received in the synthesis of the RF aerogels. Carbon dioxide (CO2) was used as a drying medium under supercritical conditions (99% purity from Linde Gas Canada).

4.3.2 Characterization

The gel’s morphological structure and its mechanical and insulation properties were analyzed. The bulk density ($\rho_b$) was measured by calculating the volume and the sample’s total mass after drying. The solid density ($\rho_s$) represented the solid part of the structure, and it was measured using a helium pycnometer (Quantachrom Instruments, Ultrapycnometer 1000). In the
pynometer, the gas penetrates the porous structure, and its volume is recorded. The porosity and the expansion ratio were calculated from the bulk and solid density using:

\[ \Pi(\text{porosity}) = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100\% \]  

(4.1)

\[ \phi(\text{expansion ratio}) = \frac{\rho_s}{\rho_b} \]  

(4.2)

The porous texture of the samples was characterized by nitrogen adsorption-desorption isotherm analysis, performed at 77 K using Autosorb iQ (Quantachrome Instruments). The samples were outgassed for 15 hr at room temperature and at a pressure of \(10^{-3}\) Pa prior to the nitrogen adsorption analysis. Using the nitrogen analysis, the pore-size distribution of the samples was determined with the Barrett-Joyner-Halenda (BJH) theory [27].

The micromorphology and the particle size of the samples were investigated using environmental scanning electron microscopy (ESEM) (Quanta FEG-250) with an energy-dispersive X-ray spectrocope (EDX) detector, and the images were analyzed using ImageJ software. The samples were coated with platinum before they were placed in the ESEM at a low vacuum setting with water vapor acting as the working environment to decrease the charging effect on them.

Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer Spectrum one) was conducted on the fibers and the fiber-reinforced RF samples to measure the spectral transmittance and evaluate the chemical bonds. The spectral transmittance was collected by averaging 4 scans in the spectral range of 4,000-550 cm\(^{-1}\) (wave length from 2.5 to 18 µm) with a spectral resolution of 4 cm\(^{-1}\). Before running the FTIR test, the airborne H2O and CO2 background noise was registered.

X-ray photoelectron spectroscopy (XPS) was conducted on the GO nanosheets to evaluate their surface composition and their functional groups using a Thermo Scientific Theta Probe (ThermoFisher Scientific) with monochromatic Al K\(\alpha\) X-ray source.

The total thermal conductivity of the samples was measured using a HotDisk TPS2500S thermal constants analyzer (Therm Test Inc). A C-5501 Kapton insulated sensor with a diameter of 6.4 mm along the transient plane was used as the source method. The sensor was placed between
two solid aerogel samples with the same dimensions to measure the overall conductivity. The sensor measured both the heat generated and the temperature’s increase within the sample by measuring the stepwise change in the voltage over time.

A compression test of the samples was conducted using an Instron Microtester (5848) with a 500 N load cell. A 25 mm x 6 mm cylindrical sample was used with a compression rate of 1.2 mm/min, according to the ISO 604-2002.

### 4.3.3 Electrospinning of the PAN fibers

In the last decade, electrospun fibers were used extensively in building nanomaterial structures [25]. The fibers were generated when the applied electrostatic forces at the spinneret tip overcame the polymer solution capillary forces. The hemispherical droplet at the spinneret tip deformed into a cone (Taylor cone) [26, 28]. The process of synthesizing continuous defect-free nanofibers highly depends on the polymer solution viscosity and the surface tension, which were both controlled by the polymer concentration in the solution [29, 30]. In our study, the electrospinning of the PAN fibers was optimized to produce fibers with an average diameter of 90 nm. The PAN fibers produced by tuning the processing window are shown in Fig 4-2.

![Electrospun PAN fibers](image)

**Fig 4-2:** Electrospun PAN fibers

The polymer solution used for the electrospinning was prepared by dissolving the PAN in the DMF solution at 5wt%. The polymer solution was spun from a 20-ml syringe clamped onto a
syringe pump (NE-1000, New Era Pump) with a 1 ml/hr pumping rate. The syringe was connected to a stainless-steel needle (spinneret) with a gauge number of 17 (having an inner diameter of 1.06 mm). The spinneret was connected to 20 kV through a high voltage power supply (Gamma High Voltage Research). The distance from the spinneret to the collector was set to 10 cm.

4.3.4 Preparation of nanofiber mixtures

After the PAN fibers were obtained, they were oxidized to modify their molecular structure by placing them into an oven for 2 hr at 250°C to produce oxidized-PAN (O-PAN). The linear molecular structure of PAN was converted into an aromatic ladder structure, as shown in Fig 4-3 (a), and their surface became more hydrophilic and this would facilitate their interaction with the RF particles during the gelation process [21]. Both fibers (PAN/O-PAN) were then dispersed separately, at 0.5 wt% in a water/ethanol mixture using a high-speed homogenizer (WSB 50) for 1 hr at 18,000 rpm. The water/ethanol mixture consisted of 25 wt% ethanol to eliminate any sedimentation or settling of the fibers and the nanosheets during gelation. This produced a uniform nanofiber/nanosheet mixture, as shown in the SEM images of Fig 4-3 (c).

Fig 4-3: Schematic diagram showing the preparation of nanofiber mixture; (a) oxidization of the PAN fibers, (b) change in color of the PAN fibers’ mat, and (c) the fibers’ homogenization process
4.3.5 Preparation of fiber-reinforced RF aerogel

The dispersed mixtures of the PAN and O-PAN were used separately to investigate the oxidization effect on the final samples. Then, the GO nanosheets were added to both mixtures to investigate their effect as a crosslink between the nanofibers. The functional groups on the GO nanosheets would increase the interconnection between the fibers [21].

The process was begun by mixing the resorcinol (R, C6H6O2) and the sodium carbonate (C, Na2CO3) in the PAN and O-PAN fiber mixtures, separately at a fixed catalyst percentage (0.04 wt%) and a void fraction (Vf) of 0.8 (that was set by using 25 ml of the fiber mixture, contains 0.5wt% fibers, and 99.5wt% ethanol plus water). Then, the formaldehyde (F, CH2O) was added to initiate the reaction, and to start the resorcinol’s polymerization with it [31]. The concentration of resorcinol to formaldehyde was fixed to their stoichiometric conditions (R/F = 0.5). Next, the 0.25 wt% of GO solution was added to the fiber mixtures using sonicating process (Q700 Sonicator). The mixture was then placed in an oven at an elevated temperature of 60°C for seven days to guarantee the gelation process within the structure and to sustain a monolithic structure, as well as to restrict any structural deformations.

4.3.6 Supercritical drying

Due to the nanoporous structure of our samples, the best approach to extract the solvent from the structure while maintaining the structural integrity was to dry the samples at supercritical conditions. This reduced the capillary force exerted on the pores during extraction [1]. The samples were prepared for the drying process by exchanging the solvents within the structure multiple times. The exchanges started by replacing the water in the structure with acetone then with CO2. Each exchange took 3 days due to the slow diffusion of the solvents into the porous structure [32]. When the CO2 fully infiltrated into the structure, the samples were placed in a sealed chamber and the temperature and the pressure increased to 40°C and 1,500 psi, beyond the critical point of CO2 (31°C and 1,072 psi). This caused the capillary force to be reduced until it was eliminated. The final product sustained its gel structure with negligible shrinkage.
4.4 Results and Discussion

There were three major parameters involved in the formation of fiber-reinforced RF aerogels: (i) The void fraction of the samples, which controlled their macro-morphological properties [16]; (ii) The oxidization process for the fibers before they were added into the RF structure; and (iii) The presence of GO as a crosslink for the fibers. These three parameters gave us the opportunity to control the RF microstructure and, thereby, the thermal and mechanical properties of the final product.

4.4.1 Fiber oxidization

The oxidization process can be traced from the FTIR spectra of the PAN and O-PAN fibers in Fig 4-4. The intensity of the transmittance peaks at 2,935 cm$^{-1}$, 1,453 cm$^{-1}$, and 1,360 cm$^{-1}$ in the O-PAN fibers decreased compared to the PAN spectra. Those peaks were attributed to the vibration of the CH group in different modes such as: CH, CH2, and CH3, which suggest the initiation of the cyclization reaction [33, 34]. The nitrile group (C≡N) in O-PAN decreased compared to PAN as shown by the decrease in the 2,243 cm$^{-1}$ peak intensity. The oxygen’s presence at this stage transforms the C≡N into C=N with the formation of the aromatic ladder structure in the O-PAN fibers as shown in Fig 4-3 (a) [21]. By further oxidizing the PAN fibers, new bonds were formed in the O-PAN fibers due to the oxidation and the dehydrogenation reactions. The bonds formed were: C=O, C=C (N-H), and C=C-H. These bonds were traced by their three characteristics peaks at 1,716 cm$^{-1}$, 1,620 cm$^{-1}$, and 809 cm$^{-1}$, respectively [35]. With the formation of these bonds in the O-PAN, the C-CN bond in the PAN started to decrease as shown by the reduction in the 1,075 cm$^{-1}$ peak intensity [33, 35].
4.4.2 Fiber interaction with the GO

The surface composition of the GO nanosheets and their functional groups were evaluated by the XPS test as shown in Fig 4-5. The XPS survey spectra recorded the C, N, O, Si, and S elements in the GO. The GO consisted mostly of carbon (61% by mass) and oxygen (32% by mass), as shown in the inset table in Fig 4-5 (a). Fig 4-5 (b) shows the deconvolution of the C1s spectra, where the peaks of 286.9, 288, and 289 eV were attributed to C-O, C=O, and C(O)O bonds, respectively [36]. This means our GO nanosheets were highly oxidized and their functional groups contained a wide variety of oxygen groups attached to carbon such as: epoxy (C-O-C), carbonyl (C=O), carboxyl (C-OOH), and hydroxyl (C-OH) groups [37, 38].

When the GO was added to the fiber mixtures, a chemical interaction between the fibers and the functional groups on the GO nanosheets occurred. This was shown by the FTIR spectra in Fig 4-5 (c). For example, the peak at 1,620 cm\(^{-1}\) in the O-PAN fibers belonged to the transmittance of the N-H group [33]. These peaks changed slightly to 1,630 cm\(^{-1}\), when the GO was added to the mixture, which suggested a chemical interaction between the O-PAN fibers and the GO nanosheets [39].
Fig 4-5: The analysis on the GO nanosheets; (a) XPS spectra of GO survey, (b) XPS deconvoluted C1s region in the survey, and (c) FTIR spectra of O-PAN and GO

4.4.3 Processing and the microstructure of the fiber-reinforced RF aerogels

A successful introduction of the electrospun fibers in the RF aerogel was achieved. As demonstrated in Fig 4-6 (a), the EDX analysis shows that the nitrogen concentration appears along the fiber line, as the nitrogen only appears in the chemical structure of the fibers. At an early stage of the gelation process, some of the RF particles started to nucleate on the surface of the fibers. This was due to the low surface energy of the fibers. This can be seen in the SEM images of the samples with the PAN fibers in Fig 4-6 (b, c). With the nucleation of the RF particles on the PAN fibers, a blueberry-like configuration was formed. When the GO was added to the mixtures, a multiform physical interconnection between the fibers and the RF particles increased. This is shown in Fig 4-6 (c) by the increased number of the RF particles on the fibers. Mainly this was due to the hydrogen bonding occurred between the PAN fibers and the GO nanosheets. The hydrogen bonds formed between the nitrogen atom on the PAN fibers and the hydroxyl on the GO nanosheets. They also formed between the carboxyl groups on the edge of the GO nanosheets, as
shown in Fig 4-7 (a) [21]. With these chemical bonds, the surface area of the PAN fibers increased. This increased the number of RF particles on the fiber surfaces.

Further, when the fibers were oxidized to produce the O-PAN, they were covered by the RF particles, and were more incorporated into the structure than the PAN fibers had been, as shown in Fig 4-6 (d). This was due to the formation of tertiary amino groups in the O-PAN fibers during the oxidization process, which changed the surface of the nanofibers more hydrophilically, as shown in Fig 4-7 (b) [21]. With the amino groups present, strong hydrogen bonds formed between the GO and the amino functional groups on the O-PAN fibers as suggested by the FTIR results in Fig 4-5 (c). Fig 4-7 (c) & (d) shows the SEM images of the mixture of both the O-PAN and the O-PAN+GO nanosheets used in the RF synthesis. In Fig 4-7 (c), the surface of the O-PAN fibers was clear without any defects or impurities. When the GO nanosheets were added, they assembled themselves on the surface of the O-PAN fibers and intertwined as shown in Fig 4-7 (d). Thus, the surface area increased on the O-PAN fibers and, consequently, a high number of RF particles assembled on the O-PAN fibers, as shown in Fig 4-6 (e).

Fig 4-6: (a) EDX analysis of the SEM of (0.5wt%O-PAN, 0.25wt%GO) sample, SEM images of fiber- reinforced RF aerogel; (b) 0.5wt%PAN, (c) 0.5wt%PAN, 0.25wt%GO, (d) 0.5wt%O-PAN, and (e) 0.5wt%O-PAN, 0.25wt%GO
Fig 4-7: The interaction between the nanofibers and the nanosheets; (a) illustration on the PAN and the GO chemical bonds (b) illustration on the O-PAN and the GO chemical bonds, (c) SEM images of O-PAN fibers, and (d) O-PAN fibers + GO nanosheets.

The adsorption and desorption isotherms of the samples are shown in Fig 4-8 (a). These isotherms were classified as type IV according to IUPAC, with hysteresis in the desorption loops [1]. This means the pore textures were in the mesoporous region for all the samples [40]. Hence, the addition of the fibers and the GO nanosheets to the RF network did not alter the overall pore texture. This was seen by the constant average pore size in the samples as shown in the BJH pore...
size distribution in Fig 4-8 (b). This was mainly due to the fixed void fraction for all the samples at the gelation stage [41].

![Fig 4-8: (a) Adsorption and desorption isotherms of N₂ on the fiber-reinforced RF aerogels at 77K, (b) BJH pore size distributions of fiber-reinforced RF aerogels.](image)

As shown in Table 4-1, the RF particle size was increased by the added fibers. It is known that the particle size depends on the nuclei’s movement in the solution during the RF’s gelation process [16, 42, 43]. With the PAN fibers present, the nuclei’s movement around them was restricted. Therefore, the particles that had been nucleated earlier were forced to grow larger to connect with each other rather than to nucleate additional nuclei [16, 42]. When O-PAN fibers were used, the particle size increased even further, because the movement of the RF nuclei was more restricted due to the O-PAN fibers’ high hydrophilicity with water [21]. Despite the RF’s microstructural changes, the macro-morphological properties of the samples remained the same when the void fraction was fixed, as Table 1 shows. This was attributed to the constant gas content within the structure at a fixed void fraction. The pore size distribution values were also fixed with a constant gas content, as Fig 4-8 (b) [16, 44]. However, it must be noted that when the macro-morphological properties are being measured, their values could be distorted by the pycnometer’s measurement limitations. The Knudsen effect, which negatively affects the permeation of the gas molecules into the porous structure [45], could result in measurement discrepancies.
Table 4-1: Macro-morphological properties of the fiber-reinforced RF aerogels

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk density (g/cm³)</th>
<th>Skeletal density (g/cm³)</th>
<th>Expansion ratio</th>
<th>Porosity (%)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure RF</td>
<td>0.221±0.012</td>
<td>1.56±0.04</td>
<td>7.1±0.5</td>
<td>85.8±1.1</td>
<td>16.2±5.5</td>
</tr>
<tr>
<td>0.5%PAN</td>
<td>0.238±0.008</td>
<td>1.56±0.08</td>
<td>6.5±0.4</td>
<td>84.6±1.0</td>
<td>19.7±2.7</td>
</tr>
<tr>
<td>0.5%PAN, 0.25%GO</td>
<td>0.239±0.006</td>
<td>1.61±0.08</td>
<td>6.7±0.4</td>
<td>85.1±1.0</td>
<td>19.8±2.8</td>
</tr>
<tr>
<td>0.5%O-PAN</td>
<td>0.232±0.002</td>
<td>1.59±0.01</td>
<td>6.8±0.4</td>
<td>85.3±1.1</td>
<td>26.4±3.1</td>
</tr>
<tr>
<td>0.5%O-PAN,0.25%GO</td>
<td>0.255±0.005</td>
<td>1.53±0.01</td>
<td>6.0±0.1</td>
<td>83.4±0.2</td>
<td>28.3±4.1</td>
</tr>
</tbody>
</table>

4.4.4 Thermal insulation of the fiber-reinforced RF aerogels

The thermal insulation feature was found by measuring the thermal conductivity of the samples. For each measurement, two samples (25 mm x 6 mm) were placed in a hot-disk thermal analyzer to measure the total thermal conductivity within the structure. The heat transfer through an aerogel medium is divided into three main categories: i) Solid conductivity (i.e., conduction through the solid), ii) Gas conductivity, and iii) Radiation [46]. These categories were governed by the morphological changes in each sample.

The solid conductivity was highly dependent on the contact area between the particles, the solid conduction paths, and on the scattering behavior of their heat carriers (phonons) [46, 47]. When the fibers were added to the samples, the thermal conductivity was increased by 5 mW/m.K (20% increase), with a confidence level of 99% (P=0.627%) when compared with the pure RF samples at a fixed void fraction, as shown in Fig 4-9 (a). This was mainly due to the high thermal conductivity through the solid parts of the PAN/O-PAN fibers [48].

On the other hand, the gas conductivity in our structure was dependent on the void fraction and the pore size [41]. The movements of the gas molecules were governed by the pore size, and this could be quantified by the Knudsen number (Kn) as follows:
\[
\text{Kn} = \frac{\langle l_{\text{mean}} \rangle}{d}
\]  

(4.3)

where \((d)\) is the pore size, and \(\langle l_{\text{mean}} \rangle\) is the mean free of gas molecules, 68 nm at ambient conditions [4]. From the Knudsen number, the gas conductivity in our samples was evaluated using the following model:

\[
\lambda_{gas} = \frac{\lambda^0_g \Pi}{1 + 2\beta K_n}
\]

(4.4)

where \(\lambda^0_g\) is the bulk gas conductivity, 26 mW/m. K, \(\beta\) is the efficiency of the energy transfer between gas molecules, 1.94, and \(\Pi\) is the porosity. The gas conductivities of our samples are shown in Fig 4-9 (b). Since, the pore sizes and the void fraction were fixed in all our samples, the gas conductivities of the samples were constant [41].

Meanwhile, the radiation was dependent on the aerogel nanonetwork as well as the material absorption ability, which was governed by its specific extinction coefficient (absorption and scattering). Now, with the addition of the GO, it was observed that the total thermal conductivity of the samples was slightly reduced due to the great suppression of the radiation heat transfer by the infrared shadowing effect from the GO despite an increased solid conductivity [4, 49, 50]. With the presence of GO, the extinction coefficient value in those samples increased, and the thermal radiation was suppressed more.

**Fig 4-9**: Thermal conductivity results for the fiber-reinforced RF aerogels: (a) total conductivity, and (b) gas conductivity
4.4.5 Mechanical properties of the fiber-reinforced RF aerogels

The mechanical properties of the samples were evaluated by measuring their elastic modulus (slope at 0.2\% strain), yield stress, and resilience during the compression test, as Fig 4-10 shows. The samples were cylindrical with 25 mm x 6 mm dimensions.

The addition of the fibers into the RF increased the stiffness of the samples. This was evident in the sudden increase of the elastic modulus values, as shown in Fig 4-10 (a). The fibers also oriented themselves in the same direction as the load during the compression process, as shown in Fig 4-10 (d). These orientations increased the area where the load had been applied. Thus, the samples stiffness and strength were increased. Fig 4-11 shows the actual fiber orientation after a compression load had been applied on the samples. Even after the compression loading, the RF particles were strongly attached to the surface of the fibers, as shown in Fig 4-11 (b). The direction of the fiber orientation was deduced from the SEM images of the samples before and after the compression test.
The sample that had the O-PAN fibers and the GO nanosheets had three times (300%) the stiffness and twice (200%) the strength and the resilience of the pure RF aerogel, as shown in Fig 4-10. This was indicated by the increased number of the RF particles on the surface of the fibers. The SEM images show that the number of RF particles was increased by an order of magnitude.
when both the O-PAN and the GO were used together. Thus, the energy that had dissipated during the compression loading, which had travelled through the RF particles to the fibers, had been improved. This, in turn, increased the strength and the resilience of the samples. The GO sheets had also been responsible for the sudden increase in strength. This effect was attributed in part to the anchoring that occurred between the GO sheets and the RF particles. It was further due to the effects of the cyclic epoxide groups on the GO sheets [36, 49]. With these two phenomena present, the fracture energy was depleted when the samples experienced external loads.

All the samples flattened during the compression test without any breakage, with a rise in their stiffness when the stress was applied, as shown in Fig 4-12. During this stage, the samples went through densification stage because the pore walls crashed on each other, which increased the internal collisions of the gas molecules [51]. The intensity of these collisions increased with the stress and, thus, a stress was built up within the structure.

![Graph showing compressive stress vs. compressive strain for different compositions](image)

**Fig 4-12:** Overall behavior of the samples under compression

### 4.5 Conclusion

A hybrid resorcinol-formaldehyde (RF) aerogel was synthesized with nanofibers under supercritical drying conditions. Polyacrylonitrile (PAN) was electrospun to obtain submicron and
homogenous fibers to reinforce the RF structure. The PAN fibers were oxidized to produce oxidized polyacrylonitrile (O-PAN) nanofibers with tertiary amino groups. This was done to increase their surface wettability. The PAN/O-PAN electrospun fibers, along with the graphene oxide (GO) nanosheets, were used as the building blocks for the RF particles during the gelation process. The RF particles nucleated on the surface of the added fibers and formed into a blueberry-like configuration. The stiffness, the resilience, and the strength of the samples depended highly on the number of RF particles on the nanofiber surface. Thus, when the GO nanosheets and the O-PAN fibers were added, the number of RF particles on the fiber surface increased by an order of magnitude. This was due to the increased surface area and the increased hydrophilicity of the O-PAN fibers. This process produced a hybrid RF aerogel with three times the stiffness and double the strength and resilience of conventional RF aerogels. The hybrid RF aerogel’s thermal conductivity was increased by 5 mW/m.K (20% increase) due to the increased solid conductivity of the samples when the fibers were present in the structure. This hybrid aerogel could successfully replace the existing organic-based foams and could be used as a stand-alone material in thermal insulation applications.

4.6 References


Chapter 5 Carbon Aerogels as Thermal Insulators in High-Temperature and Humid Environments

In previous chapters, the RF aerogels still had operational limitations because of their highly porous and open cell nature. In this chapter, the operational limitations of RF aerogels were addressed. We generated a highly porous carbon aerogel with a high thermal stability and a wider operational range by carbonizing organically-based aerogels. The carbonization process was conducted on resorcinol-formaldehyde (RF) aerogels using a tube furnace with hydrogen as the working environment at a temperature of 800°C. The hydrogen modified the RF aerogels’ chemical composition by transforming them into their basic chemical elements of carbon and hydrogen. When the oxygen was removed from the RF structure, a highly functionalized carbon aerogel with unique new features resulted. These new carbon aerogels had a high surface area of 779.22 m²/g. This was due to the expansion in the micropore volume region during the carbonization process. Furthermore, they had a higher thermal stability, with an operational range that exceeded 450°C, while their unique features were maintained without degradation. The samples also had fire retardancy capabilities, as the time for the carbon aerogel to burn became twice that of their RF counterpart. The samples could also resist water and moisture without any compromise to their structural integrity, or to their thermal insulation characteristics. This was mainly due to the reduction of the samples’ hydrophilic groups (C=O and C-O) after the oxygen

1 The content of this chapter has been submitted for publications in the Carbon Journal;
had been removed during the carbonization process. After this process, the carbon aerogels strength had substantially increased, and their behavior was more brittle than the RF samples’. Finally, the carbon aerogels had a thermal conductivity of 53mW/m.k, which made them ideal for use in high temperature and humid environments.

5.1 Introduction

Organic aerogels have been considered superior nanomaterials ever since their introduction by Pekala in 1989 [1, 2]. Their unique features which include their low thermal conductivity, light weight, transparency, high surface area, and high porosity [3-10] make them immensely superior to current nanomaterials. Thus, they have a high potential for use in many applications, which include the aerospace industry, oil-spill absorbency operations, carbon dioxide capture, and in construction projects [11-15]. However, until now, organic aerogels have not been commercially viable due to their fragility and limited operational conditions. They are also considered weak, when compared with other nanofoams and they can only be used in dry, low-temperature environments. Therefore, many researchers have endeavored to overcome these limitations by addressing each of them individually. First, in an effort to solve the aerogels’ structural fragility, fillers and composites were added to the structure [16]. However, the second obstacle, the limited operational ranges, is more challenging given the organic and porous nature of these aerogels. Such aerogels burn in high temperature environments and collapse when their surfaces connect with water. This could be resolved by conducting a surface modification or by altering the structure’s chemical composition, so that an organic aerogel with moisture resistance and high thermal stability could be produced. In our study, we made organic aerogels for high-temperature and extremely humid environments to be used in thermal insulation applications.

Resorcinol-formaldehyde (RF) aerogels are the most common organically-based aerogels. In these, the resorcinol is polymerized with the formaldehyde to create a highly porous structure [17-19]. Much research has been devoted to altering the chemical compositions of RF aerogels to synthesize carbon aerogels. Carbon aerogels represent the pyrolyzed version of the RF aerogels. This means they transform their most basic elements of carbon and hydrogen to extract the oxygen from them. This is the carbonization process, wherein the samples are placed in a high temperature environment under an inert gas flow. Horikawa et al. studied the carbonization of RF aerogels
under nitrogen using different catalytic percentages and catalytic types [20]. Their results showed that the carbon aerogels’ porous texture was almost independent of the RF aerogel’s catalytic percentages before the carbonization took place. Job et al. conducted a similar analysis on the same kind of carbon aerogels, and they varied the water content, along with the catalyst’s percentage. All of their samples shrank during carbonization, and they were dependent on the catalytic percentage [21]. For example, the samples with a higher catalytic percentage were more sensitive to shrinkage during the carbonization process. Feng et al. introduced oxidized-polyacrylonitrile (PAN) fiber felt into the carbon aerogel structure to limit the shrinkage effect [22]. Their fiber-reinforced carbon aerogel had a lower shrinkage percentage because the PAN felt limited the shrinkage at the carbonization stage. There was a common theme for the carbon aerogel in all the above studies. Their surface areas each substantially increased during the carbonization phase. This was due to their ultrafine microstructures. Thus, researchers began working extensively to develop this feature in many applications. With such a structure and feature, the carbon aerogels were highly able to hold electrical charges in batteries. They could also be used as electrodes in supercapacitors, and could even act as catalytic supporters in chemistry applications [23-26]. Fischer et al. used a carbon aerogel as an electrode in a supercapacitor. They found that such an aerogel had a high electrical capacity that could be tuned to the samples’ microstructure [23].

In this study our aim was to compare the operational range of carbon aerogels and their final properties with the RF aerogel’s. The carbonization process transformed this working structure into a whole new material with wide range of capabilities. Previous data published on such a process has been limited to the carbonization process itself. We have expanded the scope of our work to highlight the advantages of carbon aerogels, and to identify their operational ranges. The carbon aerogels used in this work had a high thermal stability and could be operated at temperatures of higher than 450°C without degrading. The sample also resisted moisture, without inducing any cracks or collapsing the structure while maintaining its thermal insulation characteristics.
5.2 Carbonization of the RF aerogel

Carbonization is the transformation of an organically-based material into a pure carbon, or a carbon residue, through the pyrolysis process. In this complex process there are several simultaneously occurring reactions. These include dehydration, condensation, hydrogen transfer, and isomerization [27]. The main component of this process is the use of an inert gas that flows through the structure at high temperatures for prolonged periods. Past studies have all used nitrogen as the working gas for this purpose at different temperatures. In our study, we used pure hydrogen gas with the RF aerogel. Hydrogen was more effective than nitrogen in removing the oxygen within our samples. This was because the hydrogen reacted with the oxygen within the samples and created water vapor as a byproduct.

The first step in creating the carbon aerogels was to synthesize the RF aerogels. This process consisted of mixing the reactants in an aqueous medium to start the gelation process. The gelation process had two-phases: the nucleation phase and the growth phase [28]. In the nucleation phase, nuclei formed around the active catalyst sites and the reactants then attached to them to form nanoparticles. Then, the nanoparticles entered the second phase and the particle grew larger. The particles continued to grow until they formed a connection and created the first cluster. Then, each cluster grew and connected with the other clusters, which created the RF aerogel’s complex and porous structure. The sample then experienced an ageing process to strengthen its structure, and to increase its crosslinking density [2]. Finally, the aqueous medium trapped in the structure was replaced with air through a supercritical drying process. After we synthesized the RF aerogels, they were placed in a high temperature environment under inert gas to conduct the carbonization process. Since hydrogen is highly instable in nature, the samples were purged with nitrogen to stabilize the environment before the hydrogen gas was added. After this, the hydrogen flow going through the samples at a high temperature activated the carbonization process. Fig 5-1 summarizes the overall synthesis of the carbon aerogel.
5.3 Experimental Section

5.3.1 Materials

Resorcinol (R, 1,3-Benzenediol, ≥ 99%) and sodium carbonate (C) (Na₂CO₃, 99%) were purchased from Sigma-Aldrich. A formaldehyde solution (F, consisting of 10-15% methanol as a stabilizer and 37% H₂O to prevent the formaldehyde from polymerizing) was purchased from Caledon Labs [29]. Acetone (HPLC, ≥99%) and distilled water (W) were obtained from Caledon Labs, Life Technologies, and Invitrogen, respectively. All the chemicals were used in an as received condition to synthesize the resorcinol-formaldehyde (RF) aerogels. Carbon dioxide (CO₂) was used as a drying agent under supercritical conditions (99% purity from Linde Gas Canada).

5.3.2 RF aerogel synthesis process

Carbon aerogels were prepared at a catalyst weight percentage of 0.04%, which corresponded to R/C molar ratio of 300. This percentage was used at a dilution ratio (DR) of 10. The DR represented the ratio between the solid reactants to the liquid content in the molar base during the mixing stage. It was calculated as follows:

\[
DR\text{(dilution ratio)} = \frac{\text{Water+ methanol}}{\text{Resorcinol + Formaldehyde + Sodium carbonate}}
\] (5.1)

We began the synthesis by mixing the resorcinol (C₆H₆O₂) with the sodium carbonate (Na₂CO₃) in water. Then, the formaldehyde (CH₂O) was added to the mixture to start the polymerization reaction. The concentration of the resorcinol to the formaldehyde was fixed under...
stoichiometric conditions (R/F=0.5). Mixing these ingredients initiated the gelation process, wherein the particles began to grow and to form clusters. During this process, the nuclei sites were activated and started to form nanoclusters. Then, the samples were heated in an oven at 60°C to accelerate the gelation process [2]. The solvent within the samples was extracted by means of a CO₂ supercritical drying process. This was done to eliminate any shrinkage in the samples [30]. Then the samples were placed in a tube furnace in a hydrogen-rich environment to start the carbonation process. This was conducted using a Thermolyne tube furnace (Thermo Scientific). The samples were first purged with nitrogen for 30 minutes at a flow rate of 500 cm³/min. Then, a hydrogen flow rate of 250 cm³/min. was used to start the carbonization process. The samples were heated to 800°C for 2 hours at a heating rate of 5°C/min., and then they were cooled to room temperature at the same rate.

5.3.3 Characterization

We analyzed the gel’s morphological structure and its insulation properties. The bulk density (\( \rho_b \)) was measured by calculating the volume and the samples’ total mass after drying. The solid density (\( \rho_s \)) represented the structure’s solid part, and it was measured using a helium pycnometer (Quantachrom Instruments, Ultrapycnometer 1000). In the pycnometer, the gas penetrated the porous structure, and its volume was recorded. The porosity and expansion ratios were calculated based on both the bulk and solid densities as follows:

\[
\Pi(\text{porosity}) = (1 - \frac{\rho_b}{\rho_s}) \times 100\%	ag{5.2}
\]

\[
\phi(\text{expansion ratio}) = \frac{\rho_s}{\rho_b}	ag{5.3}
\]

The samples’ porous texture was characterized by a nitrogen adsorption-desorption isotherm analysis, which was performed at 77 K using an Autosorb iQ (Quantachrome Instruments). The samples were outgassed for 15 hr at room temperature at a pressure of 10⁻³ Pa, prior to the nitrogen adsorption analysis. From the nitrogen analysis, the samples’ pore size
distributions were measured using the Barrett-Joyner-Halenda (BJH) theory. The samples’ surface areas were evaluated using the Brunauer-Emmett-Teller theory.

The samples’ micromorphologies and their particle sizes were investigated using environmental scanning electron microscopy (ESEM) (Quanta FEG-250), and the images were analyzed using ImageJ software. The samples were coated with platinum before they were placed in the ESEM at a low vacuum setting, and water vapor was used to decrease the effects of charging on them.

X-ray photoelectron spectroscopy (XPS) was conducted on the aerogel samples to evaluate their surface composition and their functional groups by using a Thermo Scientific Theta Probe (ThermoFisher Scientific) with a monochromatic Al Kα X-ray source.

The thermogravimetric analysis (TGA) was performed in an air atmosphere under isothermal and non-isothermal conditions. The isothermal analysis was tested at different temperatures: 450°C, 400°C, and 300°C using a TGA Q50 (TA Instruments).

The samples’ total thermal conductivity was measured using a Hot Disk TPS2500S thermal constants analyzer (Therm Test Inc.). A C-5501 Kapton insulated sensor, with a diameter of 6.4 mm along the transient plane, was used as the source method. The hot disk thermal analyzer sensor was sandwiched between two cylindrical aerogel samples. The sensor measured both the heat generated and the temperature’s increase within the sample by measuring the transit change in the voltage over time.

5.4 Results and Discussion

5.4.1 Structural morphology and assembly

After the carbonization process was conducted, the samples shrank in size due to loss of the chemical elements in the structure. However, the samples’ internal structure did not change as both of them were highly porous and had the pearl-necklace configuration, which is shown in the SEM images in Fig 5-2. The only difference between the two structures was in their particle sizes,
as these increased with the carbonization. This was mainly due to the shrinkage that the sample experienced, and which triggered the particles to diffuse into each other.

![Image of aerogel samples before and after carbonization with SEM images of their surfaces](Image)

**Fig 5-2:** The samples’ appearance before and after carbonization and the SEM images of their surfaces

The samples’ morphological features were determined both before and after the carbonization. **Table 5-1** summarizes the values of those features. All of the data has shown that the shrinkage affected both the density and the particle size. However, at the same time, the solid density also increased because of the samples’ changed chemical composition. Therefore, the occurrence of these two concurrent changes in both the bulk and solid densities, meant that the samples’ overall porosity was not affected by the carbonization process.

**Table 5-1:** Morphological parameters of aerogel samples before and after carbonization

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk density (g/cm³)</th>
<th>Solid density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Expansion ratio</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF aerogel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon aerogel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

103
The samples’ surface chemistry was also studied using an XPS test. The test showed a large increase in the carbon percentage and a big drop in the oxygen content. Fig 5-3 (a) shows these changes in the elemental intensities values for the carbon and oxygen and their percentages Fig 5-3 (b) shows the deconvolution of the C1’s spectrum. Clearly, the oxygen bonds were reduced after the carbonization took place. For example, the C=O was eliminated during the carbonization process, and it was mostly substituted with C-C/C=O bonds. Also, the intensity of the C-O bond peak was substantially reduced after the carbonization process. The reduction of these bonds, and the increase in the C-C/C=O bonds, strongly indicated that the carbonization process had been highly effective.

<table>
<thead>
<tr>
<th></th>
<th>RF aerogel</th>
<th>Carbon aerogel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.22</td>
<td>0.31</td>
</tr>
<tr>
<td>1.56</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>85.8</td>
<td>84.3</td>
<td></td>
</tr>
<tr>
<td>7.07</td>
<td>6.38</td>
<td></td>
</tr>
<tr>
<td>16.2</td>
<td>46.4</td>
<td></td>
</tr>
</tbody>
</table>

Fig 5-3: XPS spectra of the samples; (a) Surface compositions’ survey of the different chemicals, and (b) Deconvoluted C1’s region in the survey

5.4.2 Porous morphology

We analyzed the porous morphologies of the RF aerogel and the carbon aerogel using the nitrogen adsorption analysis method. Fig 5-4 (a) shows the adsorption and desorption isotherms.
These had a type IV isotherm with a hysteresis behavior in the desorption loops, which meant that the pore sizes were mostly in the mesoporous region [31]. Also, the adsorbed volume amounts were higher in the carbon aerogel than in the RF aerogel, which indicated an increased total pore volume after the carbonization process. Fig 5-4(b) shows the BJH pore size distribution for both samples before and after carbonization. The carbonization had not affected the average pore size.

![Graph showing nitrogen adsorption/desorption analysis for the RF and carbon aerogels.](image)

**Fig 5-4:** Nitrogen adsorption/desorption analysis for the RF and carbon aerogels: (a) Isotherms of N2 at 77K, and (b) BJH pore size distribution

The samples’ total surface areas, along with their total pore volumes, for both the micro and mesoporous ranges are summarized in Table 5-2. After the carbonization process, the surface area value for the carbon aerogel doubled, and this large increase is clearly shown. In addition, the micropore volume also increased, and this resulted in the formation of micro size pores (2 < nm).

**Table 5-2:** Porous parameters of aerogel samples before and after carbonization

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>Mesoporous volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF aerogel</td>
<td>377</td>
<td>2.31</td>
<td>0.008</td>
<td>2.29</td>
</tr>
<tr>
<td>Carbon aerogel</td>
<td>779</td>
<td>2.86</td>
<td>0.128</td>
<td>2.73</td>
</tr>
</tbody>
</table>
5.4.3 Operational behavior

To simulate the samples’ real-life operation, we conducted multiple tests to identify their operational ranges. First, we measured the maximum operational temperature at which the samples would burn. This was accomplished using non-isothermal thermogravimetric analysis, with air as the working environment. Fig 5-5 shows the non-isothermal temperature sweep, as well as the samples’ maximum operational temperatures before and after carbonization.

Before the carbonization process, the RF aerogel started to burn at a temperature of 247°C, as shown by the first dip in the weight percentage in Fig 5-5. This was mainly due to the thermal instability of the RF polymer which contained (C, H and O) [32]. When the temperature continued to increase, the sample kept on burned until it reached a temperature of 450°C. After the
carbonization, the samples had a high thermal stability, even when the temperature exceeded 485°C. At 549°C, they were fully burned out.

The carbon aerogels had a higher operational temperature than the RF aerogels. Their thermal stability was tested at different temperatures by doing an isothermal thermogravimetric analysis. Fig 5-6 shows the carbon aerogel thermal behavior at different temperatures. The samples were highly stable at different temperatures over time. But the total time needed for the sample to fully burn out varied with the temperature. For example, they needed 11 mins to burn out when the temperature was 450°C. However, at a temperature of 400°C, they could hold their structure for 2 hours, and they could do the same for more than 5 hours at 300°C. This confirms that carbon aerogels can be used under high temperature conditions and still maintain their unique features.

We also tested the samples’ fire retardancy capacity by observing their behavior in a vertical burning test under a flame, as Fig 5-7 shows. The samples went through three phases before they degraded. At first, cracks formed due to the exposure to high temperatures. These cracks then propagated throughout the structure until the degradation stage began, wherein the samples started to lose some of their parts. The carbonization process had enhanced the samples’ fire retardancy, as the time for the samples to degrade had almost doubled. It had increased from 26 seconds to 44 seconds. The carbon samples’ fire retardancy was excellent, when the flame did not self-propagate.
Fig 5-6: Isothermal thermogravimetric analysis of carbon aerogel at different temperatures

Fig 5-7: Samples’ behavior under a torch flame (a) RF aerogel, and (b) Carbon aerogel

Next, we simulated a condition to show how the samples’ behaved in a humid environment. Aerogels are inherently highly porous and open-cell materials. This structure creates a good path
for the water to be absorbed at the surface. Thus, the samples’ behavior was tested when their surfaces encountered water, as Fig 5-8 shows.

![Figure 5-8: Samples’ behavior when in contact with water: (a) RF aerogel, and (b) Carbon aerogel](image)

As Fig 5-8 shows, the RF samples cracked when they encountered water. This was mainly due to the buildup of residual stresses in the sample. These stresses were generated by the different water evaporation rates throughout the sample. The primary reason for the RF aerogel’s high absorption ability was the presence of such hydrophilic groups as C-O and C=O, as shown in Fig 5-3’s XPS results. These groups will act as a bridge between the samples’ structure and any polar solvent which, in this case, was water. However, the carbon aerogel’s surface was water resistant and demonstrated hydrophobic behavior. For the most part, this occurred due to the removal of oxygen from the structure’s chemical composition and the loss of the hydrophilic groups.

### 5.4.4 Mechanical Properties

We evaluated the samples’ mechanical behavior before and after carbonization by conducting a compression test on them. The samples flattened during the compression test, and their stiffness increased with the induced stress, as Fig 5-9 shows.
The carbonization process changed the samples’ overall behavior: the carbon aerogels became stiffer and more brittle than the RF aerogels. The RF aerogels lost their ductility after the carbonization process. This was because the samples’ had lost their oxygen. However, in the carbon aerogel, the samples’ strength was substantially increased with the carbon aerogel. This was due to the high percentage of carbon that was left after the carbonization process.

5.4.5 Thermal conductivity

The samples’ thermal conductivity was assessed by using the hot disk thermal analyzer for both samples before and after carbonization. The samples were also tested under a vacuum condition and in a highly humid environment, with a relative humidity ($\phi$) of 80%. Table 5-3 summarizes the samples’ thermal conductivity values.

**Table 5-3: Thermal conductivity values under different conditions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal conductivity</th>
<th>Thermal conductivity under vacuum</th>
<th>Thermal conductivity ($\phi=80%$)</th>
</tr>
</thead>
</table>

Fig 5-9: Compression test results for monolithic samples before and after carbonization
The heat transfer within an aerogel medium is divided into three main forms: (i) Solid conductivity, (ii) Gas conductivity, and (iii) Thermal radiation [33]. In our study, each of these heat transfer forms was governed by a morphological parameter. And the solid conductivity transfer was dependent on the contact area between the particles and the solid conduction path as well as on the energy carrier’s scattering at the interface (interface thermal resistance) [34, 35]. The gas conductivity was controlled by the porous structure and, for the most part, by the pore size. The thermal radiation was mainly dependent on the material’s ability to absorb the thermal electromagnetic waves. Thus, due to the RF aerogel’s unique structure, the sample had already possessed a high thermal insulation characteristic before the carbonization took place. However, after the carbonization, this samples’ thermal conductivity was increased by the shrinkage that occurred during the process. With the samples’ shrinkage, the solid conductivity and the thermal radiation were substantially increased. While the gas conductivity in the RF and the carbon aerogel were both similar (~ 4mW/. K). Also, it was so because both samples had a similar pore size. The gas conductivity values were deduced by subtracting the total thermal conductivity values from the thermal conductivity values under vacuum conditions.

<table>
<thead>
<tr>
<th></th>
<th>(mW/m.K)</th>
<th>(mW/m.K)</th>
<th>(mW/m.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF aerogel</td>
<td>23.19</td>
<td>19.05</td>
<td>---*</td>
</tr>
<tr>
<td>Carbon aerogel</td>
<td>53.88</td>
<td>48.96</td>
<td>58.7</td>
</tr>
</tbody>
</table>

*Sample cracked during testing

5.5 Conclusion

In this work, a carbon aerogel with high thermal stability and an expanded operational range was generated through the carbonization of a resorcinol-formaldehyde (RF) aerogel. The RF samples were carbonized in a tube furnace at 800°C using hydrogen as the working environment. The hydrogen reduced the oxygen presence in the chemical composition of the RF samples, and transformed the structure to their basic chemical elements of carbon and hydrogen. The RF
samples were transformed into carbon aerogels with a unique new feature. The resultant carbon aerogels had high surface area values, which were due to the expansion in the micropore volume during the carbonization process. The carbon aerogels exceeded the RF samples’ temperature operational range, as they operated at temperatures exceeding 450°C, without compromising their structure. In addition, the samples could resist moisture without compromising their structural integrity. This was mostly due to a substantial reduction in the hydrophilic groups in the RF sample during the carbonation process. Also, the samples fire retardancy capabilities were tested, and it took the carbon aerogels twice as much time to burn than their RF counterparts. This was mainly due to the reduced oxygen percentage in the carbon aerogels after the carbonization of the RF samples. Finally, the carbon aerogels had low thermal conductivity characteristics of 53mW/m. K, which makes them suitable for use as thermal insulators in both high temperature and humid environments.

5.6 References


Chapter 6 Summary and Future Work

6.1 Summary & conclusions

The focus of this research was on the synthesis of Resorcinol-Formaldehyde (RF) aerogels for thermal insulation applications and identifying their unique features. A brief introduction about the topic was given in Chapter 1 along with the motivation and the flow of the chapters to address both, the synthesis process and the definitions. The thesis work was divided into four main studies spread onto four main chapters. The first study was the synthesis of the RF aerogel without the addition of any composites, this study was shown in Chapter 2. In this chapter, the correlation between the processing conditions and the structural assembly of the RF aerogel was identified and controlled. The size and the connection of the RF aerogel particles were controlled by tuning in the processing conditions. In this chapter, the samples elasticity increased by 30% from the integration of a mixed configuration in the structure, while their thermal conductivity was kept at 24 mW/m. K. Building on Chapter 2 with the identification of the processing-to-structural parameters, the structure-to-properties parameters were identified in Chapter 3. In Chapter 3, the structural morphological features were identified and quantified. Also, each mode of the heat transfer within the RF sample was modeled and quantified. Afterwards, each structural feature was correlated to the thermal heat transfer mode of the RF sample. However, after understanding the assembly of the RF samples and studying their thermal insulation properties, the RF still fragile and weak. Thus, in Chapter 4, a reinforced RF aerogel was developed to be able to compete with existing thermal insulation material and could be used as a standalone thermal insulator. The aerogel in this chapter was made by the addition of nanofibers and nanosheets into the RF structure. The reinforced RF aerogel had high elastic, strength, and resilience values of 4.4MPa, 458KPa and 28.1J/m³, respectively. These values superseded the current organic foams used in building insulation. Finally, the RF samples still had some limitations, as they could be only operated at
low temperatures and dry environments. In Chapter 5, a study was conducted on expanding the operational ranges of the RF thru carbonization process to generate carbon aerogels. The new aerogels had high operational temperatures with a fire retardancy characteristics and could also resist moisture. The samples were able to operate at temperatures of 450C without effecting the structural integrity.

In Chapter 2, the RF structure was modified by controlling two main processing parameters at the synthesis process: (i) The catalyst percentage, and (ii) The water content. A fine tuning of the catalyst percentage and the water content were conducted. A decoupling study of each parameter showed the effect they had on the morphological, thermal, and mechanical properties. The catalyst percentage controlled the nucleation stage of the nanoparticles, which in return controlled the number of the particles. The water content modified the pH value of the solution, when in return controlled the growth of the particles. The growth mechanism for the RF particles has been shown to be in two forms: (i) spherical growth, and (ii) three-point connection (i.e. necking). The RF mixture at the synthesis was controlled by first, controlling the catalyst percentage and second the water content. As the water content increased, to achieve low structural densities and have a larger void fractions, the pH value decreased, and the spherical growth of the particles was promoted. Conversely, at high pH value, a high number of connection sites on the particles were generated for the formation of necks. Both the catalyst percentage and water content were controlled to alter the connections between the particles during their growth. This combined effect generated a neck connection between the particles and yielded a mixed configuration structure. With the new structure formation, the RF’s aerogels elasticity increased 30% while their thermal insulation characteristics were maintained.

After identifying the processing conditions which controlled the structural morphology of the samples, a study on the structural-to-properties behavior was conducted. This study is shown in Chapter 3. In this chapter, RF aerogels with different morphological features were synthesized by altering the catalyst percentages and the dilution ratios at the polymerization stage. The RF’s structure and the Nano assembly were generated from the statistical growth of the nanoparticles at the gelation stage. In this study, the growth mechanism and their assembly throughout the structural was studied by characterizing the morphological features. The morphological features of the RF aerogel were identified and divided into two main categories: (i) The micro-
morphological features, and (ii) The macro-morphological features. The microfeatures were identified and quantified using the fractal technique. In such technique, the structural assembly and the nanoparticles topography were identified. Then, the heat transfer within our sample was assessed and divided into three main forms: (i) Solid conductivity, (ii) Gas conductivity, and (iii) Thermal radiation. The value for each heat transfer form was calculated and linked to the governing morphological features. It was observed that the samples’ overall thermal conductivities were highly sensitive to any change in the micro-morphological features. In addition, it was independent of the macro features when the catalyst percentage was high. The solid conductivity was the most dominant form of heat transfer in the structure, and that it was highly dependent on the micro-features. These included any changes in the structure’s fractal parameters; that is, the particle surface roughness, the complexity, and the homogeneity. Any of these could change the solid conductivity. Extremely rough particles and complex structures placed the solid conductivity at the lowest possible level.

In the previous studies, the RF samples still experienced weak mechanical properties compared to existing thermal insulation materials. Thus, in Chapter 4 a reinforced RF was fabricated to be able to compete with existing thermal insulation material and used as a standalone insulation material. In this study, a three-dimensional reinforced RF aerogel was developed with a high structural stability and strength. The new RF samples was generated by the addition of polyacrylonitrile (PAN) nanofibers into the structural nanonetwork. The PAN nanofibers were produced thru the electrospinning process of PAN solution. Then the PAN fibers were oxidized to produce oxidized PAN (O-PAN). Then both the two fibers were added into the network along with the addition of graphene oxide (GO) sheets. The graphene oxide (GO) sheets were added to the mixtures to provide a cross-linkage between the fibers. The RF particles nucleated on the surface of the added fibers and formed into a blueberry-like configuration. The samples stiffness, resilience, and strength depended highly on the number of the RF particles on the nanofibers surfaces. Thus, when the GO sheets and the O-PAN fibers were added, the number of the RF particles increased on the fibers surfaces by an order of magnitude. This was due to the O-PAN fibers increased surface area and their increased hydrophilicity. Thus, a hybrid RF aerogel with three times the stiffness and double the strength and the resilience of conventional RF aerogels was generated. The hybrid RF aerogel’s thermal conductivity was increased by 5 mW/m.K (20%
increase) due to the samples increased solid conductivity when the fibers were present in their structure.

Despite the development of the RF aerogels in the previous studies, they still hold some limitation. The samples could only be operated in low temperature and dry environments. To overcome such limitations, the chemical composition of the RF structure was modified thru the carbonization process. In Chapter 5, the carbonization process was conducted on the RF structure using hydrogen as the carbonizing gas in a tube furnace at 800°C. The hydrogen modified the chemical composition of the RF aerogels and transformed them into their basic chemical elements, carbon and hydrogen. The oxygen was removed from the RF structure, which created a highly functionalized carbon aerogel with new unique features. The new carbon aerogels had a high surface area of 779.2 m²/g, due to the expansion in the micropore volume region with the carbonization process. The carbon aerogels exceeded the temperature operational range of the RF samples, as they operated at temperatures exceeding 450°C without compromising their structure. Furthermore, the samples could resist moisture without compromising their structural integrity. This was mainly due to the substantial reduction in the hydrophilic groups from the RF sample during the carbonation process. Also, the samples fire retardancy capabilities were tested, and the time that took for the carbon aerogels to burn doubled compared to their RF counterpart. This was mainly due to the reduction in the oxygen percentage in the carbon aerogels after carbonizing the RF samples. Finally, the carbon aerogels had low thermal conductivity characteristics of 53mW/m. k, which makes them suitable to be used as a thermal insulator for both high temperature and humid environments.

6.2 Recommendations for Future Work

The synthesis of organic aerogels along with the analysis on their unique thermal properties was addressed in this work. This work was initiated to better understand the assembly of the complex network the organic aerogels generates during their synthesis. However, despite the millstones achieved in this work, there is still the need to conduct intensive research in this area. The research would address other concepts that are still not fully understood. The nanonetwork in these materials is generated from the a random and the statistical growth of the basic elements of the network (i.e. nanoparticles). Therefore, one of elements for future researchers to focus on is on
simulating the assembly of such network. One method to study this aspect is by conducting a numerical simulation using molecular dynamics technique. In such technique, researchers would be able to understand how the particles connect and assemble. Then, the network could be modified to target only the particles which enhance the final features. In Chapter 3, an experimental study on the assembly of the nanoparticles along with a unique way to characterize was introduced. In this study, an initial analysis on the nanoparticles assembly during the gelation was shown. By building on these results and use them as inputs for the numerical simulation, future researchers could be able to better understand the assembly of such particles.

The modeling of the heat transfer in organic aerogels was also addressed in this work, however, there is still many theories on this topic that need to be challenged or proved. At the scale of the nanoparticles within the aerogels, the heat transfer is more complicated, because the laws of classical physics and quantum physics comes into clash. In the nanoscale heat transfer, the energy carriers experienced a particle duality phenomenon, as explained in Chapters 2, 3, and 4. In this phenomenon, the energy carriers experience the characteristics of particles (i.e. mass and energy), also they have the waves characteristics (i.e. wave length and frequency). They can change their form according to the scale and the materials properties. Thus, the heat transfer need to be studied further to better understand the mechanism which makes the aerogel thermally super insulating materials.

Finally, the aspect of reinforcing the RF aerogel structure can be further expanded by using other types of nanofibers with high elasticity features. Thermoplastic polyurethane (TPU) are an ideal candidate to be used as elastic nanofibers into the RF structure. Such fibers have hard segments and soft segments, where the hard segments provide the stiffness to overcome the shrinkage during the drying. While the soft segments provide the aerogel with elasticity characteristic that could integrate such material into existing structures. Furthermore, the loading of the fibers could be altered to modify the mechanical properties. In case of high fiber loading, the nanofibers will assemble to create a fibers network with the aerogels as their backbone. With such fiber network, an optimization on the fibers loading need to be conducted. At high fiber loading the mechanical properties would increase substantially on the expense of the thermal insulation features. Furthermore, in this research the work was mostly focused on resorcinol
formaldehyde aerogel. Thus, expanding the results of the RF to other polymeric aerogels would increase the infiltration of organic aerogels into many sectors.