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Fabrication and Analysis of TEOS- and MTES-based Aerogels Prepared via Rapid Supercritical Extraction

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FABRICATION AND ANALYSIS OF TEOS- AND MTES-BASED AEROGELS
PREPARED VIA RAPID SUPERCRITICAL EXTRACTION

By

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* * * * *

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ABSTRACT

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Silica aerogels were prepared using the precursor tetraethylorthosilicate (TEOS) and an organically modified TEOS derivative (methyltriethoxysilane, MTES) via a rapid supercritical extraction (RSCE) method. Multiple consistent batches of monolithic TEOS-based aerogels were fabricated via an eight-hour RSCE process. Fabricating TEOS-based aerogels with an RSCE method offers some distinct advantages. The main advantage is the relative simplicity of the RSCE approach: liquid precursors are mixed and poured into a mold in a hydraulic hot-press, where gelation, aging and extraction of liquid from the pores occur. The precursor recipe employs TEOS, ethanol, water, oxalic acid to catalyze hydrolysis, and ammonia to catalyze the subsequent polycondensation reactions. Earlier work on silica aerogels by our group focused on the use of tetramethylorthosilicate (TMOS)-based precursor mixtures. Reaction of TEOS to form sol gels yields ethanol as a byproduct. A process that releases ethanol, rather than methanol (as in the TMOS-based aerogels) may be more appealing for commercial applications, involving scale-up of the process. The TEOS-based aerogels have good optical transparency, bulk densities of $0.099(\pm 0.003) \text{ g/cm}^3$, surface areas of $460(\pm 10) \text{ m}^2/\text{g}$, and contain internal and external Si-O framework bonds as observed in FTIR spectra. Using SEM, the surface morphology of the aerogel samples was studied. MTES-based aerogels were also successfully fabricated using Union's RSCE process, but with less consistent results than for the TEOS-based aerogels. About half the MTES aerogels remained monolithic. FTIR spectra indicate that the aerogels are organically modified; Si-CH₃ groups are present in the aerogel framework. The MTES aerogels are hydrophobic.

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Chapter 1: Introduction

1.1 Motivation and Goals of the Project

Union's Aerogel Lab has created its own patented method for fabricating aerogels using a supercritical technique. The lab has done extensive work on tetramethylorthosilicate (TMOS) aerogels. Tetraethylorthosilicate (TEOS) aerogels were chosen for this project because TEOS is less expensive than TMOS and because ethanol can be used as the solvent in the preparation of TEOS-based aerogels. Methanol is used as the solvent when fabricating TMOS aerogels. Ethanol is a more attractive solvent for scale-up of the rapid supercritical extraction (RSCE) process because it is more environmentally friendly than methanol. Preliminary work was performed by high school student Thomas Hughes on TEOS aerogels. His results indicated that TEOS xerogels and aerogels could be fabricated, but could not be reproduced consistently. Thomas's TEOS aerogels were white opaque and powdery. Goals for this project include reproducibly fabricating high quality TEOS-based translucent aerogel monoliths with high surface areas using the RSCE process, optimizing the fabrication procedure and fully characterizing these silica materials. Two applications for TEOS aerogels are for window and thermal insulation applications. For the window applications, the TEOS aerogels need to be optically transparent and monolithic, and for the thermal insulation applications the TEOS aerogels need to have low thermal conductivity.

Methyltriethoxysilane (MTES) aerogels were chosen for the second part of the project. MTES is a TEOS derivative; modified silica aerogels would be a logical extension of my work with TEOS aerogels. MTES aerogels had never been fabricated by the RSCE method before. They are of particular interest because researchers had prepared flexible MTES aerogels by other aerogel fabrication methods. A unique potential application of flexible aerogels, soft robots, was of interest to Prof. Rieffel of Union's Computer Science Department. The goal for the fabrication

of MTES aerogels is to create high quality monolithic aerogels that are flexible. Applications for MTES aerogels in building soft robots include laser or optically controlled soft robots. The requirements for the MTES aerogels for any of the soft robot applications are that the aerogels be monolithic, flexible, robust and durable. These aerogels also need to be able to be fabricated in a variety of shapes for different types of robots. MTES aerogels could also be made into humidity sensors because of their hydrophobic properties. A requirement for the MTES aerogel applications in humidity sensing and optical (laser) soft robots is that the aerogels need to be optically transparent, as well.

1.2 Xerogels, Sol-Gels, Cryogels and Aerogels

What is a Sol-Gel? A sol is a suspension of colloidal particles with diameters in the range of 1-1000 nm that are dispersed in a liquid.¹ A gel consists of a sponge-like, three-dimensional solid network whose pores are filled with another substance, which is usually a liquid. These “wet” gels are also called aquagels, hydrogels or alcogels.¹

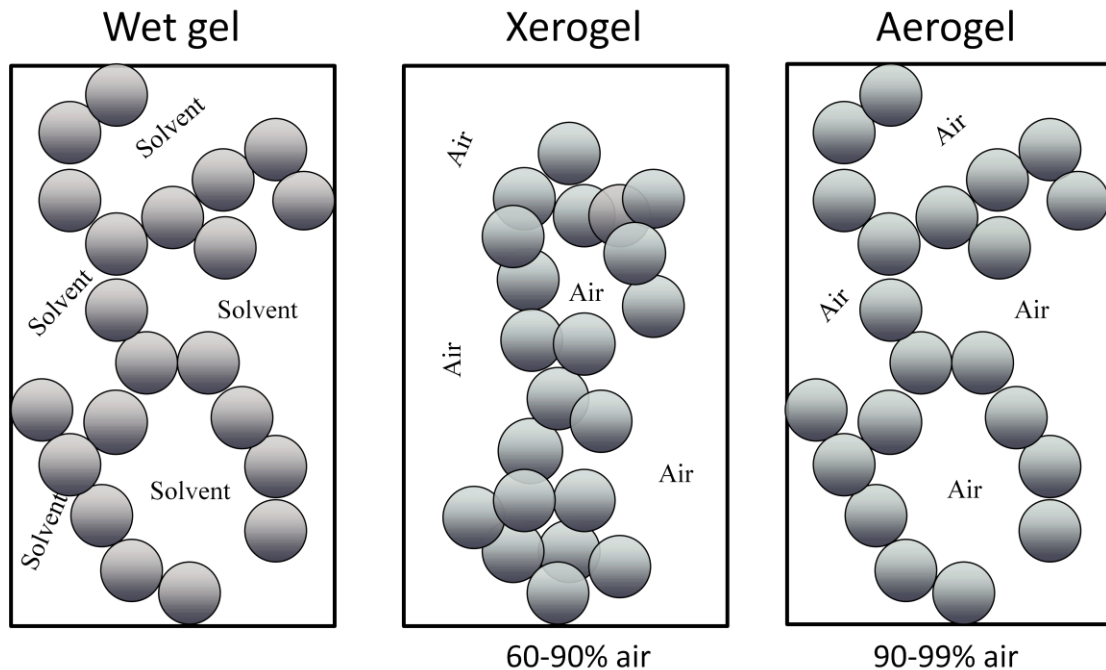
What is a Xerogel? A xerogel is a sol-gel material that is formed upon conventional drying of a wet gel under ambient conditions with simultaneous large shrinkage of the uniform gel body.¹

What is a Cryogel? A cryogel is a sol-gel material that is fabricated when the pore liquid of a wet gel is removed by freeze-drying.¹

What is an Aerogel? An aerogel is a sol-gel material that is fabricated when the pore liquid of a wet gel is replaced by air without decisively altering the network structure or the

volume of the gel body.¹ When a sol gel is dried under ambient conditions, the porous nanostructure collapses due to surface tension caused by the evaporating solvents and a xerogel is formed. If, however, the solvent is extracted supercritically, the surface tension is reduced, preserving the porous nanostructure, resulting in an aerogel monolith. A schematic showing the difference between the sol-gel mixture and a supercritically dried aerogel as well as an ambiently dried xerogel is shown below in Figure 1-1.

Figure 1-1: Schematic Representation of a wet gel, a xerogel and an aerogel



Aerogels can be prepared as powders, granulates, or monoliths, any of which can have either amorphous or crystalline portions.¹ Aerogels are 90-99% air by volume² and silica aerogels are generally made up of less than 10% silicon dioxide.³ Silica aerogels are generally very porous^{4,5} with low to ultralow densities (0.003-0.500 g/cm³).^{1,4,6} Silica aerogels also can have high optical

transmission in the visible region (~85-90%),^{4,6} low sound velocity (~100-300 m/s, compared to quartz glass which is 5000 m/s),^{1,4} and large specific surface area (~500-1600 m²/g).^{5,6}

Furthermore, silica aerogels have low thermal conductivity (0.01-0.015 W/mK),⁴ low dielectric constant (<2.0),⁵ low refractive index¹ and low rigidity.¹

Silica aerogels also have form stability and are non-flammable; they are brittle, have a compressive strength of 0.15-0.30 N/mm,² and have an elastic compression of 2-4%.¹ Silica aerogels have tensile strengths of 0.020 N/mm,² low acoustic impedance ($Z=10^4$ - 10^5 kg/m²s), excellent temperature stability and can be sintered at low temperatures to be processed to extremely pure and totally homogeneous glasses.¹ Aerogels have high selectivities in catalytic processes and nearly all oxides relevant for catalytic applications can be prepared as aerogels. In addition, for compositions with two or three substances, aerogel mixtures of metal oxides, or metal particles on oxide carriers can be formed.¹

Types of Aerogels: Aerogels can be fabricated from a wide variety of starting materials, some of which include silica (TEOS, tetramethylorthosilicate (TMOS)), titania, alumina, chromia, iron, nickel, copper, lead, and carbon.¹ Other starting materials include organic starting materials, such as resorcinol/formaldehyde (RF), melamine/formaldehyde (MF), and phenolic Novolak resin (phenol/formaldehyde: PF) to fabricate carbon aerogels.¹

Aerogel Applications: Some aerogel applications include thermal super-insulators in solar energy systems, refrigerators and thermos flasks, very efficient catalysts and catalytic supports, and radio luminescent devices.⁶ Other aerogel applications include transparent thermal insulation for windows (bathroom, staircase, ceiling or super-insulating filler in double-walled window systems³), cooling/heating systems and high temperature batteries, solar energy

(paneling house walls or for coating solar energy collectors), and film coatings (optical coatings for solar cells and coating on IR detectors to obtain a kind of shield against the heat radiating from a substrate).¹

Further applications of aerogels include gas filters with pores in the 20-100 nm range, thickening of liquids (rocket fuels), cosmic dust collection and fixation on the outside of spacecrafts, which enables a soft landing of extraterrestrial particles and later investigation by optical methods.¹ Finally, aerogels can be used as heat-storage devices for automobiles, active catalysts or catalytic substrates, fillers, gellifying agents.³ For TEOS aerogels, the most relevant applications are thermal insulation and window applications because they can be tailored to be translucent.

Aerogel Synthesis: There are many ways to fabricate aerogels. One of these methods is a supercritical drying method using a methanol solvent extraction.⁷ Another method is a two-step (acid-base) sol-gel process, which uses strong acidic catalysts, such as HCl, low temperatures and an autoclave system.³ The supercritical drying method brings the solvent to supercritical temperature and pressure, whereas an autoclave system exchanges the solvent with CO₂ under high pressure. In Figure 1-2, the sol-gel reaction mechanism that is used to make the wet gels that become aerogels can be seen. Other methods include ambient pressure techniques, conventional supercritical extraction (CSCE), and rapid supercritical extraction (RSCE).²

In ambient-pressure techniques one attempts to dry the wet gel at ambient pressure. These techniques are good for synthesizing aerogel films and powders, but not for synthesizing aerogel monoliths.² Ambient pressure drying can also be accomplished by treating the surface with a surfactant or surface-tension-reducing chemical, or aging the gel in alkoxide/alcohol

solutions to stiffen the microstructure and avoid collapse due to capillary forces. Furthermore, ambient pressure drying can be achieved by manipulating the surface of the gel to aid in solvent evacuation, which uses a solvent exchange with hexane, followed by a surface modification with a silylation process to promote a reversible shrinkage.²

Figure 1-2: Sol-Gel Reaction Mechanism

Formation of the wet sol-gel:

First, a hydrolysis reaction (catalyzed by acid)



For TEOS R = C₂H₅, For TMOS R = CH₃

Followed by polycondensation reactions (catalyzed by the base, ammonia)

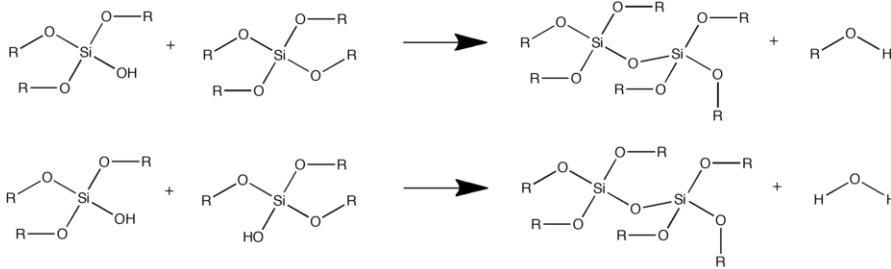


Figure 1-2 shows the reaction mechanism for the sol-gel process of alkoxysilanes.

Conventional supercritical extraction (CSCE) is a multi-step technique designed to eliminate surface tension by bringing the sol-gel to the critical point of the solvent in its pores. Above the critical point there is no surface tension, so the solvent can be evacuated without damage to the gel structure. Generally for this technique pressure vessels are used.² This technique can also be done after one or more solvent exchanges with CO₂ inside a pressure vessel.² CSCE using a solvent exchange with CO₂ is the most commonly used method of fabricating aerogels. It is also a “cold” method, meaning that the process does not take place under high temperature conditions.

Other fabrication methods include drying in organic solvents (a “hot” method, which takes place under high temperature conditions), and freeze-drying.¹ The freeze-drying technique produces cryogels, which are generally non-transparent powders. The microstructure of a cryogel is governed by the size of ice microcrystals that are formed during the freeze-drying process. Cryogels tend to be more macroporous than aerogels made using supercritical extraction methods.⁷

Rapid supercritical extraction (RSCE) is a technique designed to perform the solvent extraction under supercritical conditions and is a one-step reactant-to-aerogel process.² This is described in more detail in the next section of this chapter.

1.3 Rapid Supercritical Extraction (RSCE)

Rapid Supercritical Extraction (RSCE): Rapid supercritical extraction techniques use a confined mold in either a pressure vessel or a hydraulic hot-press. The precursor material is confined in a mold to inhibit gel deformation so that higher heating rates can be used.⁷

Union’s Rapid Supercritical Extraction (RSCE) Method: Union’s RSCE method is an alcohol supercritical extraction technique, which uses a hydraulic hot-press to both heat and seal a mold. The liquid precursor mixture is poured into a metal mold and the mold is then sandwiched between pieces of Kapton film or stainless steel sheets and high-temperature gasket material and placed in the hot-press.⁷ For a typical run, the hot-press is closed to seal the liquid mixture inside the mold and the hot-press provides the compressive restraining force. The aerogel precursors react to form a wet gel with porous nanostructure during the heating process.⁷ The mold and mixture are then brought above the supercritical temperature of the solvent (for example, methanol or ethanol). The pressure in the mold is not controlled; it is a

function of the temperature of the system. Once a supercritical state is reached the pressure is decreased and the supercritical fluids are released, leaving behind an aerogel. For Union's RSCE process, the temperature level, temperature increase and decrease rate and hot-press restraining force can be controlled. The mold size and precursor volume is also selected.⁷ Two significant advantages of this method over conventional methods are that (1) there is less solvent waste due to the lack of solvent-exchange steps, and (2) aerogel monoliths can be prepared in hours, rather than days.

1.4 TEOS Aerogels

TEOS Aerogel Synthesis and Characteristics: TEOS aerogels have been produced using a variety of methods by a variety of groups. Rao et al. note that monolithic and transparent silica aerogels can be produced.⁸ Rao et al. noted that low strength acid catalysts (0.01 N) yielded monolithic and transparent silica aerogels when using a two-step method, in which the first step prepares the silica sol-gel by hydrolysis and condensation of silicon alkoxides and the second step supercritically dries the sol-gel in an autoclave using a solvent exchange with N_2 .⁸ They also noted that a short chain length solvent (ethanol) produced the best silica aerogels. The ratio of the precursor:solvent:water was kept constant at 1:4:4 with a catalyst concentration of 0.01 N.⁸ The acid catalysts that produced the best TEOS aerogels were HCl, HNO_3 and H_2SO_4 , which resulted in aerogels that had 80% transmission at 900 nm. The path length for these aerogels was not mentioned. It was also found that greater catalyst concentration decreases the gelation time.⁸

Pajonk et al. prepared aerogels by a two-step method similar to the method by Rao,³ in which the first step prepares the silica sol-gel by hydrolysis and condensation of silicon alkoxides and the second step supercritically dries the sol-gel in an autoclave.³ The acid catalysts that

produced the best TEOS aerogels were HCl, HNO₃ and H₂SO₄, which resulted in transparent (70%) and shrunken aerogels. The path length for these aerogels was not mentioned. When using organic acid catalysts (tartaric acid and citric acid), however, the silica aerogels had densities of 0.23 g/cm³, were monolithic, had good transparency (65%), and little volume shrinkage ($\leq 15\%$).³ The path length for these aerogels was not mentioned.

In a review of aerogels by Pierre and Pajonk, they mention that supercritical drying can either be hot or cold, meaning that the method goes to high temperature or does not go to high temperature, respectively.⁹ They also mentioned that the hot method has a poorly controlled aging process, while the temperature and pressure are being increased, and the resulting aerogels are hydrophobic.⁹ The cold method, which has better controlled aging processes, resulted in more hydrophilic aerogels. They note that aerogels dried with a solvent exchange with CO₂ typically have a pore volume above 90% of the sample volume and a surface area that can exceed 1000 m²/g.⁹

Hedge and Rao also used a two-step sol-gel process, but methanol was used for the solvent exchange.⁴ Another difference is that the temperature and pressure in the autoclave was higher than previously reported. These TEOS aerogels had a gelation time of only 18 hours at 50°C and had porosity of 99%, a bulk density of 0.018 g/cm³ and optical transmission of 75% for a molar ratio of TEOS:MeOH:acidic (H₂O):basic (H₂O) of 1:99:10.42:14.58.⁴ The path length for these aerogels was not mentioned.

Rao and Parvathy obtained the best quality aerogels (in terms of monolithicity and transparency) using a molar ratio of TEOS:EtOH:H₂O of 1:5:8.¹⁰ These TEOS aerogels were also prepared via a two-step method using an autoclave with N₂.¹⁰ In other work by Rao and Parvathy,¹¹ they found that the density of the aerogels increases with an increase in the concentration of the catalyst; their aerogels had densities of 0.08-0.6 g/cm³.

Other researchers who have used similar two-step TEOS aerogel fabrication methods include Tamon et al. who used liquid CO₂ for the solvent exchange in the autoclave,¹² Mulder et al.,¹³ Meador et al. who used (3-aminopropyl)triethoxysilane (APTES) and 1, 6-bis(trimethoxysilyl)hexane (BTMSH) as their base catalysts¹⁴ and Li et al. who incorporated electrospun polyurethane nanofibers into their TEOS sol-gels.¹⁵ In one of Pajonk's works, he notes that it can take three weeks to make TEOS sol-gels with base catalysts, but with citric acid as the catalyst sol-gels could be obtained within three days.¹⁶ These citric acid catalyzed TEOS aerogels had surface areas of 800 m²/g, transparency of 65% and bulk densities of 0.23 g/cm³. The path length for these aerogels was not mentioned.

Rao and Bhagat produced TEOS aerogels by a two-step (acid-base) sol-gel process, in which oxalic acid was used as the acid catalyst and ammonia was used as the base catalyst.⁶ They found that adding the base catalyst after 24 hours produced the highest optical transmission, the best monolithicity and the lowest volume shrinkage. The TEOS aerogels fabricated from a molar ratio of 1:6.9:3.5:2.2 of TEOS:EtOH:acidic (H₂O):basic(H₂O) had high transparency (~90%) and low volume shrinkage (<10%).⁶ The path length for these aerogels was not mentioned. The researchers chose this two-step process because it offered better control over the rates of hydrolysis and condensation reactions. For their supercritical drying process, they used a solvent exchange with N₂ in their autoclave.⁶ This work was the basis for the initial work done by Thomas Hughes on RSCE TEOS aerogels in our lab using the recipe seen in Table 1-1, which was modified from Rao and Bhagat.⁶

Table 1-1: Initial TEOS Aerogel Recipe

Part I: Ingredient Name	Amount (mL)
TEOS (tetraethylorthosilicate)	7.75
EtOH (ethanol)	10.00
H ₂ O (water)	0.25
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	3.00
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 1.5 M	0.67

Our TEOS RSCE aerogels are made from a mixture of TEOS, water, ethanol, and an acid catalyst (oxalic acid), which catalyzes the hydrolysis reaction. Afterwards, a base catalyst (ammonia) is added to afford a polymerization reaction that leads to a silicon-oxygen matrix surrounded by solvent. Our TEOS aerogels are fabricated in about eight hours using Union's RSCE method. Conventionally, silica aerogels are made in an autoclave with a CO₂ drying process that takes days to a week or more to complete. Some characteristics of our RSCE TEOS aerogels include low density, relatively high optical transmission, monolithicity, and low surface areas compared to the literature on silica aerogels for fabricating TEOS aerogels using techniques other than Union's RSCE method.

1.5 MTES Aerogels

MTES Aerogel Synthesis and Characteristics: In Rao et al., a two-step acid-base catalyzed sol-gel process, which undergoes supercritical drying, is used.¹⁷ They employed methanol as the solvent, and oxalic acid and ammonia as the catalysts. Their sol-gels were aged in a methanol bath and then supercritically dried in an autoclave above the critical temperature and pressure of methanol under inert atmosphere.¹⁷ They found that their aerogels were elastic, flexible and superhydrophobic. They also found that the rates of the hydrolysis and condensation reactions were optimized when 0.001-M oxalic acid and 10-M ammonia were

used.¹⁷ Furthermore, Rao et al. found that the optimal aging period of the sol gels was two days for highly flexible aerogels.

Our MTES RSCE aerogels are made from a mixture of MTES, water, ethanol, and an acid catalyst (oxalic acid), which catalyzes the hydrolysis reaction. Afterwards, a base catalyst (ammonia) is added to afford a polymerization reaction that leads to a silicon-oxygen matrix surrounded by solvent. Conventionally, silica aerogels are made in an autoclave with a CO₂ drying process that takes days to a week or more to complete, whereas, in this work MTES aerogels are fabricated using Union's RSCE method. The recipe for our MTES aerogels was modified from the paper by Rao et al. on TEOS aerogels.⁶ Characteristics of our MTES RSCE aerogels include some optical transmission in the near-IR (generally MTES aerogels have been reported to be opaque) and monolithicity.

1.6 Characterization Methods for Aerogels

Characterization methods for aerogels include measurements of bulk density⁴ and skeletal density,⁷ porosity⁴ and surface area,² optical transmission in the UV-Visible⁴ and the near-infrared regions,² thermal conductivity, pore diameter (BJH desorption),⁷ and volume shrinkage measurements.⁶ Other characterization methods include Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), mechanical strength, contact angle, acoustic measurements and differential thermal analysis (DTA).⁵ Also the surface morphologies of the aerogels can be studied using scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM).⁶

Bulk density is a measurement of the mass of a sample divided by the volume of a sample. For monolithic cylindrical aerogels the bulk density of a sample can be found using the following equation:

$$\text{Bulk density} = \frac{\text{mass of sample (g)}}{\text{volume of the sample (cm}^3\text{)}} = \frac{\text{mass of sample (g)}}{\pi r^2 h \text{ (cm}^3\text{)}}$$

The skeletal density of a sample is a measurement of the ratio of the mass of the sample to the sum of the volumes of the sample excluding the pores within the sample.

Porosity is a measure of the void spaces in a sample (air space in the case of aerogels) and is calculated by taking the volume of the voids over the total volume to find a percentage between 0 and 100%.

Surface area is a measurement of how much exposed area a sample has, and is expressed in m^2/g . For an aerogel the surface area includes the exposed area of the outer surface of the material as well as the surface of the material exposed inside the pores.

Optical transmission is a measurement of the amount of light that is able to pass through a material expressed as a percent. A perfectly translucent material would have an optical transmission of 100%.

Thermal conductivity is a measure of a material's ability to conduct heat.

Raman spectroscopy and Infrared (IR) spectroscopy provide information about the vibrational states of molecules. Different vibrational motions are usually observed with each method due to the selection rules for differentiating between the vibrational motions. IR spectroscopy requires a change in the dipole moment of a molecule to occur resulting from vibrational motion, whereas Raman spectroscopy requires a change in the polarizability of a molecule to occur resulting from vibrational motion.

The mechanical strength of a material is the ability of a material to withstand applied stress (compressive, tensile or shear) without failure, as seen in Figure 1-3. In this project, the mechanical strength of the aerogels is determined in regards to compressive stress along the y-axis of a cylinder (see Figure 1-3a).

Figure 1-3: Stress as Applied to Cylindrical Aerogel Samples

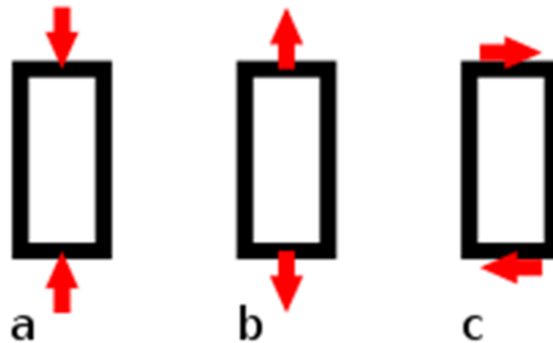


Figure 1-3 shows schematically (a) the compressive stress (b) the tensile stress and (c) the shear stress applied to cylindrical aerogel samples.

The contact angle of an aerogel is the measurement of the angle at which a liquid, in this case, deionized water interfaces with the aerogel surface. The shape of the droplet is determined using Young's equation, where a contact angle less than 90° indicates a hydrophilic surface and a contact angle greater than 90° indicates a hydrophobic surface. Superhydrophobic surfaces have contact angles greater than 150° .

A scanning electron microscope images a sample by rastering it with a high-energy beam of electrons. The electrons interact with the atoms in a sample, producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. When the electrons interact with the atoms of the sample the types of signals produced include secondary electrons (the electrons displace the sample atom's electrons), back-scattered electrons (BSE, the electrons from the beam bounce back out of the sample), characteristic X-rays, Auger and chemiluminescence. Generally, the secondary electrons are studied to produce a high-resolution image of the sample surface. The

characteristic x-rays can be used to study the composition of a sample when an SEM is employed with energy-dispersive x-ray (EDX) measurements.

A TEM images a sample using a beam of electrons that is transmitted through an ultra thin specimen. The electrons interact with the sample as they pass through. The image is formed from the interaction of the electrons transmitted through the sample; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEM's are capable of imaging at a significantly higher resolution than light microscope. Thus, TEM's are capable of imaging at the atomic scale, but we do not have a TEM at Union.

An AFM produces a topographical map (in the range of 5 μm to 200 nm) of a sample's surface based on the interaction between a sample surface and a cantilever driven by a piezoelectric material. A change in the amplitude for tapping mode or a change in deflection for contact mode of the cantilever is measured as it interacts with the sample surface.

In this thesis project, I describe the synthesis and characterization of TEOS-based and MTES-based aerogels prepared via Union's RSCE method.

Chapter 2: Experimental

2.1 Experimental Methods for TEOS Xerogels and Aerogels

This experimental work was performed during the spring, summer and fall of 2010, and in the winter and spring of 2011.

Materials: Tetraethylorthosilicate (TEOS) and oxalic acid dihydrate were procured from Sigma-Aldrich Chemical Co., and were used without further purification. Reagent grade ethanol and ammonia were procured from Fisher Scientific, and were used without further purification. Other materials used include silicone spray, stainless steel foil, Kapton, cold-rolled steel molds, graphite sheets, Maxipetters, digital pipets, varied glassware (beakers, volumetric flasks, stirring rods), mortars and pestles, and spatulas.

Preparation of Oxalic Acid (0.01 M): To prepare a 100-mL batch of 0.01 M oxalic acid, 0.09003 g of oxalic acid dihydrate is added to a 100-mL volumetric flask that is subsequently filled to the mark with deionized water and mixed thoroughly.

Preparation of Ammonia (1.5 M, 0.75 M and 0.375 M): To prepare a 500-mL batch of 1.5 M ammonia solution, 50.7 mL of 14.8-M (concentrated) ammonia is added to water in a 500-mL volumetric flask that is then filled to the mark with deionized water. To prepare a 100-mL batch of 0.75 M ammonia solution, a 1:2 dilution of the 1.5-M stock solution is employed, in which 50 mL of 1.5-M ammonia is added to a 100-mL volumetric flask that is then filled to the mark with deionized water. To prepare a 100-mL batch of 0.375 M ammonia solution, a 1:2

dilution of the 0.75-M solution is employed: 50 mL of 0.75-M ammonia is added to a 100-mL volumetric flask that is then filled to the mark with deionized water.

Preparation of Xerogel Batches: A TEOS-based precursor recipe was adapted from Rao.⁶

Batches # 1-4 were prepared on 4/30/10 using the following recipe (Table 2-1):

Table 2-1: TEOS Xerogel Recipe (4/30/10)

Part I: Ingredient Name	Amount (mL)
TEOS (tetraethylorthosilicate)	3.88
EtOH (ethanol)	5.00
H ₂ O (water)	0.125
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	1.50
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 1.5 M	0.085

Each of the four batches was prepared in the same manner, with the exception of the wait time (the time between the mixing of Part I of the recipe and the addition of the ammonia in Part II of the recipe). For each of the four batches the ingredients in Part I were added to a test tube, left to sit for five minutes and the ingredients were then mixed together with the sonicator for fifteen minutes, except for Batch #1 which did not have the five minute wait before mixing Part I. The wait times for each batch can be seen in the table below (Table 2-2). The wait time is started immediately after the fifteen minutes of sonication.

Table 2-2: TEOS Xerogel Preparation Conditions (4/30/10)

Batch #	Wait Time (minutes)
1	0 (immediate addition of Part II of the recipe)
2	15
3	30
4	45

After the addition of Part II of the recipe, Batches #1 and 2 were sonicated for an additional five minutes, and Batches #3 and 4 were stirred using a mechanical stirrer and stir bar for five minutes to mix in the ammonia. Afterwards each batch was covered with parafilm and left to gel under ambient conditions.

Batches #A, B and C were prepared on 5/14/10 using the following recipe (Table 2-3):

Table 2-3: TEOS Xerogel Recipe (40 mL total) (5/14/10)

Part I: Ingredient Name	Amount (mL)
TEOS (tetraethylorthosilicate)	15.50
EtOH (ethanol)	20.00
H ₂ O (water)	0.500
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	6.00
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 1.5 M	0.500 (per 15 test tubes)

All of the batches (A, B and C) were prepared from one large batch, where the ingredients in Part I of the recipe were added to a beaker and were then mixed together with the sonicator for fifteen minutes. Then 2.5-mL of the total batch was pipeted into every test tube; each test tube corresponded to a particular batch (A1-A5, B1-B5, and C1-C5). The wait times for each batch can be seen in the table below (Table 2-4). The wait time is started immediately after the fifteen minutes of sonication.

Table 2-4: TEOS Xerogel Preparation Conditions (5/14/10)

Batch #	Amount of Liquid Used from the 40 mL Total (mL)	Wait Time (minutes)
A1, B1, C1	2.5 (for each)	0 (immediate addition of Part II of the recipe)
A2, B2, C2	2.5 (for each)	15
A3, B3, C3	2.5 (for each)	30
A4, B4, C4	2.5 (for each)	45
A5, B5, C5	2.5 (for each)	105

For all of the test tubes in Batch A, sonication was used for five minutes after the addition of the ammonia. For all of the test tubes in Batch B, the addition of the ammonia was mixed with a stir bar and mechanical stirrer; the solution in each test tube was stirred for five minutes. For all the test tubes in Batch C, a stirring rod was used for mixing after the addition of the ammonia.

Batches #A and B were prepared on 5/21/10 using the following recipe (Table 2-5):

Table 2-5: TEOS Xerogel Recipe (40 mL total) (5/21/10)

Part I: Ingredient Name	Amount (mL)
TEOS (tetraethylorthosilicate)	15.50
EtOH (ethanol)	20.00
H ₂ O (water)	0.500
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	6.00
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 1.5 M	0.134 (per 10 test tubes)

Each of the batches (A and B) was prepared from one large batch. The ingredients in Part I of the recipe were added to a beaker and were then mixed together with the sonicator for fifteen minutes. Then 4 mL of the total batch was pipeted into every test tube; each test tube corresponded to a particular batch (A1-A5 and B1-B5). The wait times for each batch can be seen in the table below (Table 2-6). The wait time is started immediately after the fifteen minutes of sonication.

Table 2-6: TEOS Xerogel Preparation Conditions (5/21/10)

Batch #	Amount of Liquid Used from the 40 mL Total (mL)	Wait Time (minutes)
A1, B1	4 (for each)	0 (immediate addition of Part II of the recipe)
A2, B2	4 (for each)	15
A3, B3	4 (for each)	30
A4, B4	4 (for each)	45
A5, B5	4 (for each)	105

For each of the test tubes in Batch A, sonication was used for five minutes after the addition of the ammonia. For each the test tubes in Batch B, a stirring rod was used after the addition of the ammonia. A modified batch (M) was made from the recipe detailed in Table 2-5, except the amounts of H₂O and EtOH were switched. Part I of the recipe was sonicated for fifteen minutes and then Part II of the recipe was added seven days later.

Batches #A and B were prepared on 5/28/10 using the following recipe (Table 2-7):

Table 2-7: TEOS Xerogel Recipe (40 mL total) (5/28/10)

Part I: Ingredient Name	Amount (mL)
TEOS (tetraethylorthosilicate)	15.50
EtOH (ethanol)	20.00
H ₂ O (water)	0.500
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	6.00
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 1.5 M or 0.75 M	0.192 (per 14 test tubes)

Each of the batches was prepared from one large batch; the ingredients in Part I of the recipe were added to a beaker and were then mixed together with the sonicator for fifteen minutes. Then 3 mL of the total batch was pipeted into each test tube corresponding to each tube number in each batch (A1-A7, and B1-B7). The wait times for each batch can be seen in the table below (Table 2-8). The wait time is started immediately after the fifteen minutes of sonication. For all of the test tubes in Batch A and B, a stirring rod was used to mix in the ammonia. After the various xerogel preparations, the “best” xerogel recipe was chosen based on optical transparency and gelation time. The “best” recipe was translucent and gelled quickly, but not immediately, so that the mixture could be poured into a mold to make aerogels. After the best recipe was chosen, the TEOS aerogels could be fabricated.

Table 2-8: TEOS Xerogel Preparation Conditions (5/28/10)

Batch #	Amount of Liquid Used from the 40 mL Total (mL)	Wait Time (minutes)
A1, B1	3 (for each)	45
A2, B2	3 (for each)	1hr 45 min
A3, B3	3 (for each)	2hr 45 min
A4, B4	3 (for each)	5hr 45 min
A5, B5	3 (for each)	17hr 45 min
A6, B6	3 (for each)	23hr 45 min
A7, B7	3 (for each)	47hr 45 min

Another modified batch (M1-M6) was fabricated on 5/30/11 using the recipe in Table 2-1, except the amount of 1.5 M ammonia was 0.335 mL. Part I of the recipe was sonicated for fifteen minutes. The wait times for the addition of Part II of this batch can be seen in Table 2-9 below.

Table 2-9: Modified Batch Preparation Conditions (5/30/10)

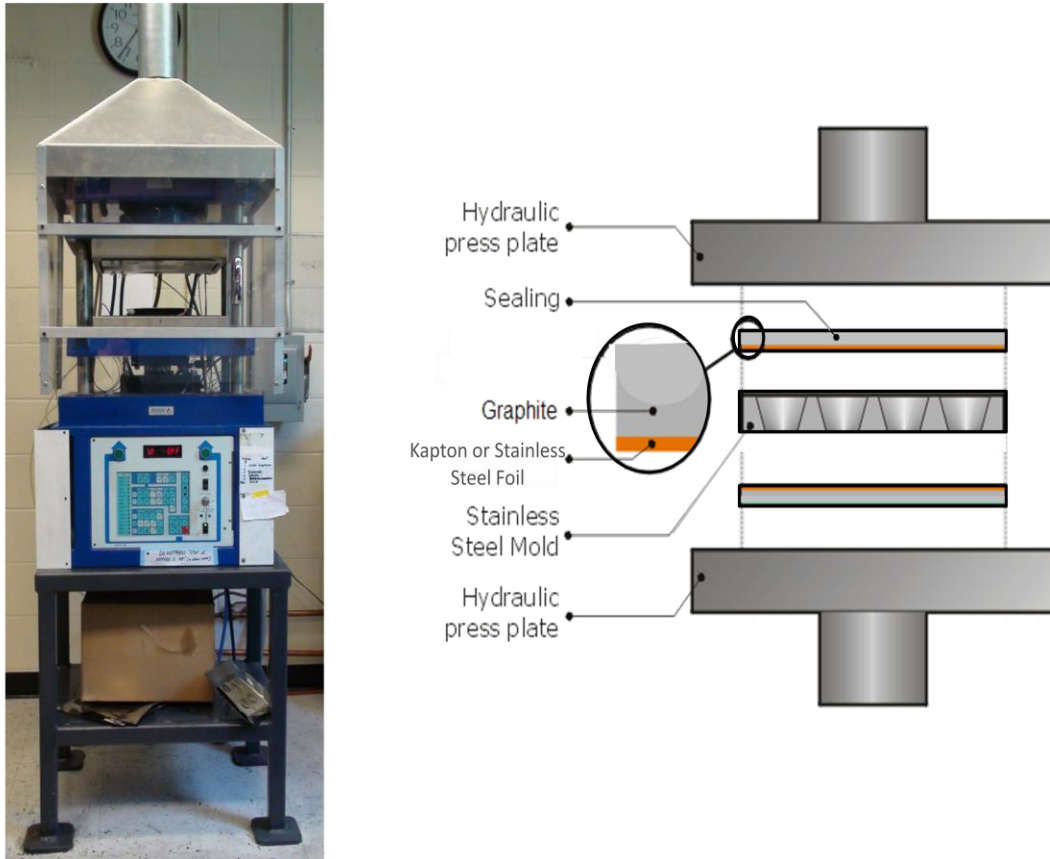
Batch #	Amount of Liquid Used from the 10 mL Total (mL)	Wait Time (minutes)
M1	2	1 day
M2	2	2 days
M3	2	3 days
M4	2	4 days
M5	2	5 days
M6	10 (made a full batch)	5 days

For Batch M6 a full 10-mL batch was made, whereas for Batches M1-M5 2 mL of the 10-mL batch were used for each.

Process: Mold Design, Sealing the Mold and Hot-Press Parameters: To seal the mold correctly a graphite sheet must be placed on top of the bottom hot-press plate followed by a layer of either Kapton or stainless steel foil, then the mold, followed by another layer of Kapton

or stainless steel foil and finally, another layer of graphite (as seen in Figure 2-1). Kapton was used for aerogels Batches #1-8 and stainless steel foil was used for Batches #9-21.

Figure 2-1: Hot Press and Schematic of the Sealed Mold



The mold schematic seen in Figure 2-1 was modified from the schematic created by Smitesh Bakrania. The mold is then sealed using Program 1 on the hot-press, which can be seen in Tables 2-10 and 2-11 below. The program detailed in Table 2-10 was used for Batches #1-9 and the program in Table 2-11 was used for Batches #10-21.

Table 2-10: Hot Press Parameters for Setting the Mold: Batches #1-9

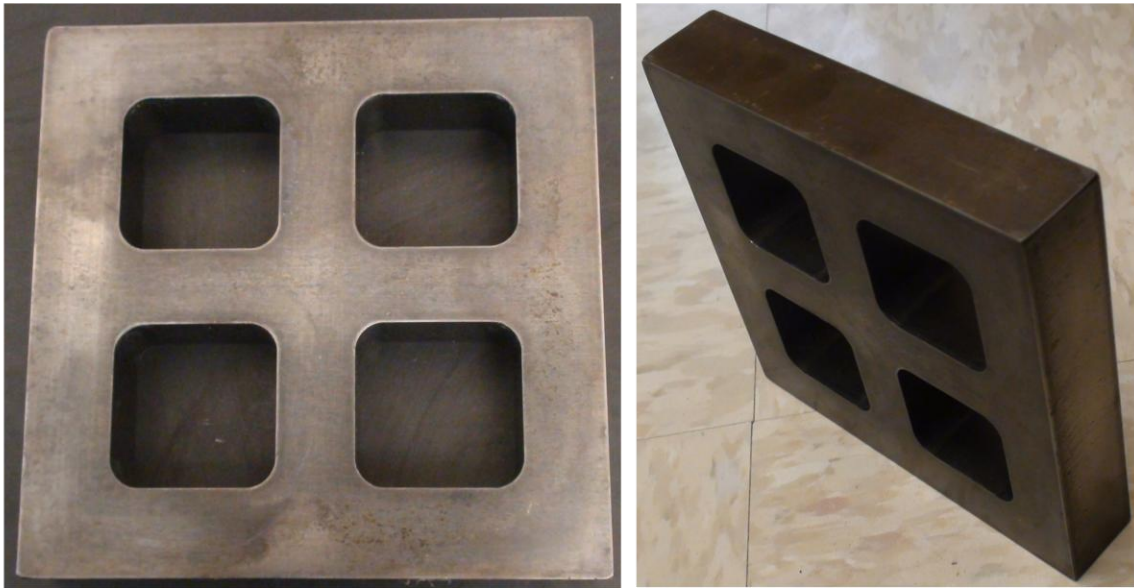
Step #	Temperature (°F) or (°C)	Rate	Force	Rate	Dwell: Time (minutes)	Duration Of Each Step (minutes)
1	off	200 °F/min or 111 °C/min	10k lbs. or 44 N	600k lbs./min or 2.7 N/min	10	10
2-5	END STEP					
Duration of Entire Program: 10 minutes						

Table 2-11: Hot Press Parameters for Setting the Mold: Batches #10-21

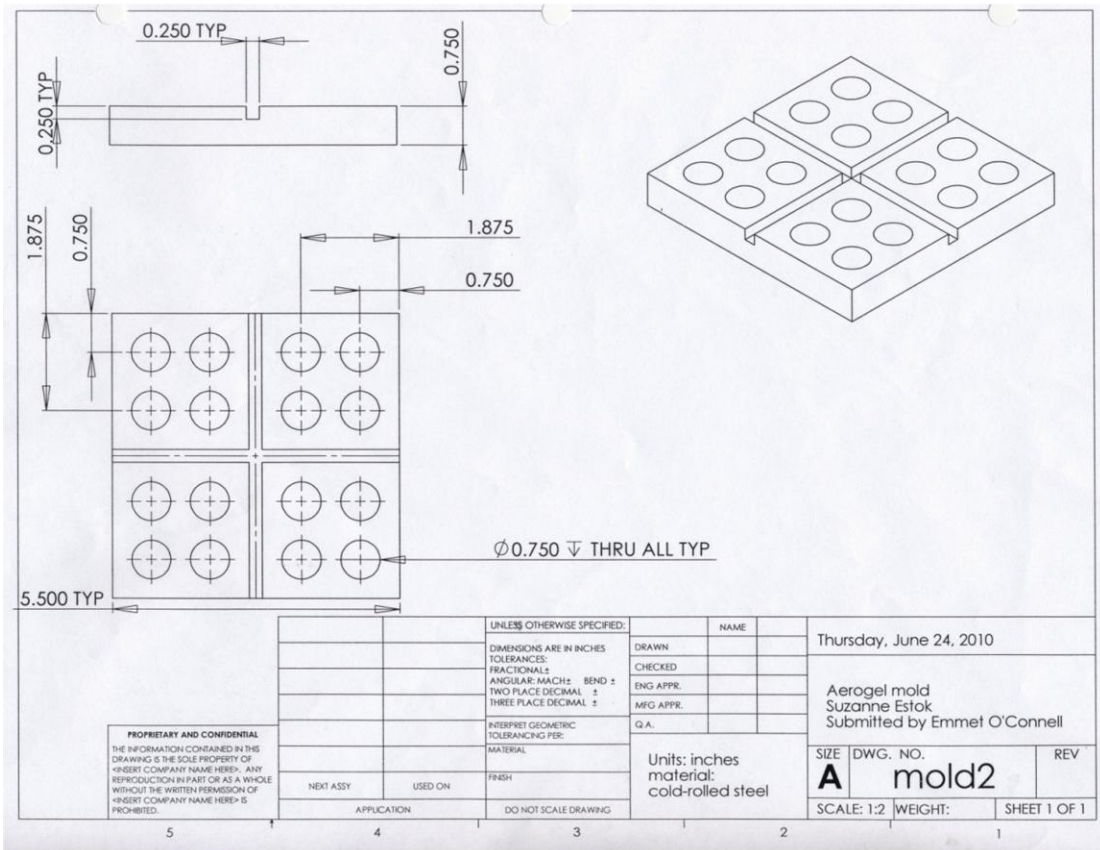
Step #	Temperature (°F) or (°C)	Rate	Force	Rate	Dwell: Time (minutes)	Duration Of Each Step (minutes)
1	off	200 °F/min or 111 °C/min	20k lbs. or 89 N	600k lbs./min or 2.7 N/min	10	10
2-5	END STEP					
Duration of Entire Program: 10 minutes						

For Batches #1-4, the mold was uncoated, whereas for Batches #5 and 6, the mold was completely sprayed (both top and bottom) with a non-stick silicone spray (CRC Industrial Dry PTFE Lube: Dry Film Lubricant). For Batches #7-13, half the wells in the mold were sprayed with the silicone spray and half were left unsprayed. For Batches #14-21, the whole mold was sprayed with the silicone spray. For Batches #1-7, a 4-well square mold (as seen below in Schematic 2-1 well size: 1.5" by 1.5" by 1") was used with a 120-mL aerogel recipe, whereas for Batches #8-21 a custom mold (as seen below in Schematic 2-2 well size for each of the 16 wells: 3/4" diameter by 3/4" height) was used with a 100-mL aerogel recipe:

Schematic 2-1: Original Square Mold



Schematic 2-2: Custom Mold



Preparing the Aerogel Mix and Hot-Press Parameters: A TEOS-based precursor recipe was adapted from Rao.⁶ To prepare the 100- or 120-mL sol-gel mixture that is poured into the sealed mold, the reagents listed under Part I of the 20-mL recipe (given below in Table 2-12) are scaled up appropriately and mixed together, then sonicated for 15 min after which the recipe is left to rest for another 45 min. Hydrolysis of the TEOS occurs in this step. Subsequently, in Part II of the recipe, base catalyst is added to the mixture and the mixture is stirred with a glass stirring rod. The polycondensation reactions occur in this step.

Table 2-12: TEOS Aerogel Recipe

Part I: Ingredient Name	Amount (mL)
TEOS (tetraethylorthosilicate)	7.75
EtOH (ethanol)	10.00
H ₂ O (water)	0.25
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	3.00
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 0.375 M or 0.75 M	0.67

For Batch #2, the base catalyst was added immediately after sonication of Part I of the recipe. For Batches #1-6, 0.75-M ammonia was used, whereas for Batches #7-21, 0.375-M ammonia was used. Once both parts of the mixture were added, the mixture was poured into the sealed mold to undergo rapid supercritical extraction.² Processing parameters are detailed in Tables 2-13, 2-14, and 2-15. The hot-press program detailed in Table 2-13 was used for Batches #1-9, the hot-press program detailed in Table 2-14 was used for Batch #10 and the hot-press program detailed in Table 2-15 was used for Batches #11-21.

Table 2-13: Hot Press Parameters for Making TEOS Aerogels: Batches #1-9

Step #	Temperature	Rate	Force	Rate	Dwell: Time (minutes)	Duration Of Each Step
1	90 °F or 32 °C	200 °F/min or 111 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	602	10 hrs 6 min
2	550 °F or 288 °C	3 °F/min or 2 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	30	3 hrs 4 min
3	550 °F or 288 °C	200 °F/min or 111 °C/min	1k lbs. or 4.4 N	1k lbs./min or 0.004 N/min	30	1 hr 10 min
4	100 °F or 38 °C	3 °F/min or 2 °C/min	1k lbs. or 4.4 N	600k lbs./min or 2.7 N/min	1	2 hrs 31 min
5	END STEP					
Duration of Entire Program: 16 hours 51 minutes						

Table 2-14: Hot Press Parameters for Making TEOS Aerogels: Batch #10

Step #	Temperature	Rate	Force	Rate	Dwell: Time (minutes)	Duration Of Each Step
1	90 °F or 32 °C	200 °F/min or 111 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	602	10 hrs 6 min
2	480 °F or 249 °C	3 °F/min or 2 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	30	2 hrs 10 min
3	480 °F or 249 °C	200 °F/min or 111 °C/min	1k lbs. or 4.4 N	1k lbs./min or 0.004 N/min	30	1 hr 10 min
4	100 °F or 38 °C	3 °F/min or 2 °C/min	1k lbs. or 4.4 N	600k lbs./min or 2.7 N/min	1	2 hrs 31 min
5	END STEP					
Duration of Entire Program: 15 hours 57 minutes						

Table 2-15: Hot Press Parameters for Making TEOS Aerogels: Batches #11-21

Step #	Temperature	Rate	Force	Rate	Dwell: Time (minutes)	Duration Of Each Step
1	90 °F or 32 °C	200 °F/min or 111 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	2	6 min
2	550 °F or 288 °C	2 °F/min or 1 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	30	4 hrs 20 min
3	550 °F or 288 °C	200 °F/min or 111 °C/min	1k lbs. or 4.4 N	1k lbs./min or 0.004 N/min	30	1 hr 10 min
4	100 °F or 38 °C	3 °F/min or 2 °C/min	1k lbs. or 4.4 N	600k lbs./min or 2.7 N/min	1	2 hrs 31 min
5	END STEP					
Duration of Entire Program: 8 hours 7 minutes						

2.2 Experimental Method for MTES Xerogels and Aerogels

This experimental work was performed during the fall of 2010, and the winter and spring of 2011.

Materials: Methyltriethoxysilane (MTES) and oxalic acid dihydrate were procured from Sigma-Aldrich Chemical Co., and were used without further purification. Reagent grade ethanol, reagent grade methanol and ammonia were procured from Fisher Scientific, and were used without further purification.

Preparation of Oxalic Acid (0.01 M and 0.1 M): For the preparation of 0.01 M oxalic acid see section 2.1. To prepare a 100-mL batch of 0.1 M oxalic acid, 0.9003 g of oxalic acid dihydrate is added to a 100-mL volumetric flask that is subsequently filled to the mark with deionized water and mixed thoroughly.

Preparation of Ammonia (10 M, 1.5 M, 0.75 M and 0.375 M): For the preparation of 1.5 M, 0.75 M and 0.375 M ammonia see section 2.1. To prepare a 100-mL batch of 10 M ammonia solution, 60.76 mL of 14.8-M (concentrated) ammonia is added to a 100-mL volumetric flask that is then filled to the mark with de-ionized water.

Preparation of Xerogel Batches: A MTES-based precursor recipe was adapted from the TEOS-based recipe (Table 2-12) previously adapted from Rao.⁶ Batch #1 samples (1A1, 1A2, 1B1, 1B2, 1C1, and 1C2) were prepared using the following recipe (Table 2-16):

Table 2-16: MTES Xerogel Recipe: Batch #1

Part I: Ingredient Name	Amount (mL)
MTES (methyltriethoxysilane)	3.88
EtOH (ethanol) or MeOH (methanol)	5.00
H ₂ O (water)	0.125
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	1.50
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 1.5 M or 0.75 M or 0.375 M	0.335

Batches #1A1, 1B1 and 1C1 all used ethanol as the solvent, whereas Batches #1A2, 1B2 and 1C2 all used methanol as the solvent. Batches #1A1 and 1A2 both used 0.375-M ammonia, whereas Batches #1B1 and 1B2 used 0.75-M ammonia. Batches #1C1 and 1C2 used 1.5-M ammonia. For each of the six batches the ingredients in Part I were added to six test tubes and the mixtures were then sonicated for fifteen minutes. After forty-five minutes the ammonia was added to each batch. After the addition of Part II of the recipe, all six batches were stirred for a few seconds with a glass stirring rod. Afterwards each batch was covered with parafilm and left to gel under ambient conditions.

Batch #2 samples (2A1, 2A2, 2B1, 2B2, 2C1, and 2C2) were prepared using the following recipe (Table 2-17):

Table 2-17: MTES Xerogel Recipe: Batch #2

Part I: Ingredient Name	Amount (mL)
MTES (methyltriethoxysilane)	3.88
EtOH (ethanol)	5.00
H ₂ O (water)	0.125
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M or 0.1 M	1.50
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 14.8 M (concentrated) or 1.5 M or 0.75 M	0.335

Batches #2A1, 2B1 and 2C1 all used 0.01 M oxalic acid, whereas Batches #2A2, 2B2 and 2C2 all used 0.1 M oxalic acid. Batches #2A1 and 2A2 both used 14.8-M (concentrated) ammonia, whereas Batches #2B1 and 2B2 used 0.75-M ammonia. Batches #2C1 and 2C2 used 1.5-M ammonia. For each of the six batches the ingredients in Part I were added to six test tubes and the mixtures were then sonicated for fifteen minutes. After forty-five minutes the ammonia was added to each batch. After the addition of Part II of the recipe, all six batches were stirred for a few seconds with a glass stirring rod. Afterwards each batch was covered with parafilm and left to gel under ambient conditions.

Batch #3 samples (3A1 and 3A2) were prepared using the following recipe (Table 2-18):

Table 2-18: MTES Xerogel Recipe: Batch #3A

Part I: Ingredient Name	Amount (mL)
MTES (methyltriethoxysilane)	1.058
EtOH (ethanol)	10.30
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	0.536
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 1.5 M	0.536

Batch #3 samples (3B1 and 3B2) were prepared using the following recipe (Table 2-19):

Table 2-19: MTES Xerogel Recipe: Batch #3B

Part I: Ingredient Name	Amount (mL)
MTES (methyltriethoxysilane)	1.058
EtOH (ethanol)	5.15
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	0.536
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 1.5 M	0.536

The only difference in the recipes for Batches #3A and 3B is the amount of ethanol added to each batch. Batches #3A1-2 and 3B1-2 all used 1.5-M ammonia and 0.01-M oxalic acid. For each of these four batches, the ingredients in Part I were added to four test tubes and the ingredients were then mixed together with the sonicator for fifteen minutes. For Batches #3A1 and 3B1, Part II of the recipe was added at the same time as Part I of the recipe, whereas for Batches #3A2 and 3B2 Part II of the recipe was added after forty-five minutes. After the addition of Part II of the recipe, Batches #3A2 and 3B2 were stirred for a few seconds with a glass stirring rod. Afterwards each batch was covered with parafilm and left to gel under ambient conditions.

Batch #4 samples (4A1-4A9 and 4B1-4B9) were prepared using the following recipe (Table 2-20):

Table 2-20: MTES Xerogel Recipe: Batch #4

Part I: Ingredient Name	Amount (mL)
MTES (methyltriethoxysilane)	3.88
EtOH (ethanol)	3.42
H ₂ O (water)	0.112
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M or 0.1 M	1.35
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 14.8 M (concentrated) or 10 M or 1.5 M	0.301

Batches #4A1 through 4A9 used 0.1-M oxalic acid, whereas Batches #4B1 through 4B9 used 0.01-M oxalic acid. Batches #4A1-4A3 and 4B1-4B3 used 1.5-M ammonia. Batches #4A4-4A6

and 4B4-4B6 used 10-M ammonia, whereas Batches #4A7-4A9 and 4B7-4B9 used 14.8-M (concentrated) ammonia. For each of the eighteen batches, the ingredients in Part I were added to six test tubes and the ingredients were then mixed together with the sonicator for fifteen minutes. The wait times for each batch can be seen in the table below (Table 2-21), where the wait time is started immediately after the fifteen minutes of sonication.

Table 2-21: MTES Xerogel Preparation Conditions

Batch #	Wait Time (minutes)	Batch #	Wait Time (minutes)
4A1	0 (immediate addition of Part II of the recipe)	4B1	0 (immediate addition of Part II of the recipe)
4A2	45	4B2	45
4A3	1 hr 45 min	4B3	1 hr 45 min
4A4	0 (immediate addition of Part II of the recipe)	4B4	0 (immediate addition of Part II of the recipe)
4A5	45	4B5	45
4A6	1 hr 45 min	4B6	1 hr 45 min
4A7	0 (immediate addition of Part II of the recipe)	4B7	0 (immediate addition of Part II of the recipe)
4A8	45	4B8	45
4A9	1 hr 45 min	4B9	1 hr 45 min

After the addition of Part II of the recipe, Batches #4A2-4A3, 4A5-4A6, 4A8-4A9, 4B2-4B3, 4B5-4B6 and 4B8-4B9 were stirred for a few seconds with a glass stirring rod. Afterwards each batch was covered with parafilm and left to gel under ambient conditions.

Process: Mold Design, Sealing the Mold and Hot-Press Parameters: The hot-press and the layers necessary for surrounding the mold when being placed in the hot-press is shown in Figure 2-1. The mold is then sealed using Program 1 on the hot-press, which is given in Table 2-10. For all batches, the mold was completely sprayed (both top and bottom) with a non-stick silicone spray (CRC Industrial Dry PTFE Lube: Dry Film Lubricant). For all batches a custom mold was used (as seen in Schematic 2-2).

Preparing the Aerogel Mix and Hot-Press Parameters: A MTES-based precursor recipe was adapted from Rao.^{6,17} To prepare the 50-mL sol-gel mixture that is poured into the sealed mold, the reagents listed under Part I of the various recipes (given below in Tables 2-22, 2-23, 2-24) are mixed together and then sonicated for 15 min after which the recipe is left to rest for another 45 min or 1 hour and 45 minutes. Batches #1-4 and 6 were left to rest for 45 minutes, whereas Batch #5 was left to rest for 1 hour and 45 minutes. Hydrolysis of the MTES occurs in this step. Subsequently, in Part II of the recipe, base catalyst is added to the mixture and the mixture is stirred with a glass stirring rod. The polycondensation reactions occur in this step. Once both parts of the mixture were added, the mixture was poured into the sealed mold to undergo rapid supercritical extraction.² For MTES Batches #1-6, two different recipes were used in each batch: half the mold was filled with the mixture from the first recipe and half the mold was filled with the mixture from the second recipe.

Table 2-22: Ingredients in Recipes 1 and 2 for MTES Aerogel Batches #1, 2, 3 and 4

Part I: Ingredient Name	Amount (mL)
MTES (methyltriethoxysilane)	19.38
EtOH (ethanol)	25
H ₂ O (water)	0.625
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M	7.50
Part II: Ingredient Name	Amount (mL)
NH ₃ (ammonia): 1.5 M or 0.75 M	1.676

For Batches #1-4 Recipe 1, the base catalyst (0.75 M) was added 45 minutes after sonication of Part I of the recipe, as was the base catalyst (1.5 M) for Batch #1-4 Recipe 2.

Table 2-23: Ingredients in Recipes 1 and 2 for MTES Aerogel Batch #5

Part I: Ingredient Name	Amount (mL)	Recipe 2 was made by changing the concentration of oxalic acid from 0.1 M in Recipe 1 to 0.01 M.
MTES (methyltriethoxysilane)	42.70	
EtOH (ethanol)	37.64	
H ₂ O (water)	1.232	
H ₂ C ₂ O ₄ (oxalic acid): 0.01 M or 0.1 M	14.86	
Part II: Ingredient Name	Amount (mL)	
NH ₃ (ammonia): Concentrated = 14.8 M	3.311	

For Batch #5 Recipes 1 and 2, the base catalyst was added 1 hour and 45 minutes after sonication of Part I of the recipe.

Table 2-24: Ingredients in Recipes 1 and 2 for MTES Aerogel Batch #6

Part I: Ingredient Name	Recipe 1	Recipe 2
	Amount (mL)	Amount (mL)
MTES (methyltriethoxysilane)	27.18	19.38
EtOH (ethanol)	23.67	25
H ₂ O (water)	0.784	0.625
H ₂ C ₂ O ₄ (oxalic acid)	9.45 of 0.1 M	7.50 of 0.01 M
Part II: Ingredient Name	Amount (mL)	Amount (mL)
NH ₃ (ammonia)	2.11 of 14.8 M	1.676 of 1.5 M

For Batch #6 Recipes 1 and 2, the base catalyst was added 45 minutes after sonication of Part I of the recipe.

Processing parameters are detailed in Tables 2-25, 2-26, 2-27 and 2-28. The hot-press program detailed in Table 2-25 was used for Batch #1; the hot-press program detailed in Table 2-26 was used for Batches #2 and 3, the hot-press program detailed in Table 2-27 was used for Batch #4 and the hot-press program detailed in Table 2-28 was used for Batches #5 and 6.

Table 2-25: Hot Press Parameters for Making MTES Aerogels: Batch #1

Step #	Temperature	Rate	Force	Rate	Dwell: Time (minutes)	Duration Of Each Step
1	90 °F or 32 °C	200 °F/min or 111 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	2	6 min
2	550 °F or 288°C	2 °F/min or 1 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	30	4 hrs 20 min
3	550 °F or 288 °C	200 °F/min or 111 °C/min	1k lbs. or 4.4 N	1k lbs./min or 0.004 N/min	30	1 hr 10 min
4	100 °F or 38 °C	3 °F/min or 2 °C/min	1k lbs. or 4.4 N	600k lbs./min or 2.7 N/min	1	2 hrs 31 min
5	END STEP					
Duration of Entire Program: 8 hours 7 minutes						

Table 2-26: Hot Press Parameters for Making MTES Aerogels: Batches #2-3

Step #	Temperature	Rate	Force	Rate	Dwell: Time (minutes)	Duration Of Each Step
1	90 °F or 32 °C	200 °F/min or 111 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	602	10 hrs 6 min
2	550 °F or 288 °C	2 °F/min or 1 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	30	4 hrs 20 min
3	550 °F or 288 °C	200 °F/min or 111 °C/min	1k lbs. or 4.4 N	1k lbs./min or 0.004 N/min	30	1 hr 10 min
4	100 °F or 38 °C	3 °F/min or 2 °C/min	1k lbs. or 4.4 N	600k lbs./min or 2.7 N/min	1	2 hrs 31 min
5	END STEP					
Duration of Entire Program: 18 hours 7 minutes						

Table 2-27: Hot Press Parameters for Making MTES Aerogels: Batch #4

Step #	Temperature	Rate	Force	Rate	Dwell: Time (minutes)	Duration Of Each Step
1	90 °F or 32 °C	200 °F/min or 111 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	302	5 hrs 6 min
2	550 °F or 288 °C	2 °F/min or 1 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	30	4 hrs 20 min
3	550 °F or 288 °C	200 °F/min or 111 °C/min	1k lbs. or 4.4 N	1k lbs./min or 0.004 N/min	30	1 hr 10 min
4	100 °F or 38 °C	3 °F/min or 2 °C/min	1k lbs. or 4.4 N	600k lbs./min or 2.7 N/min	1	2 hrs 31 min
5	END STEP					
Duration of Entire Program: 13 hours 7 minutes						

Table 2-28: Hot Press Parameters for Making MTES Aerogels: Batches #5-6

Step #	Temperature	Rate	Force	Rate	Dwell: Time (minutes)	Duration Of Each Step
1	90 °F or 32 °C	200 °F/min or 111 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	2	6 min
2	550 °F or 288 °C	1 °F/min or 0.6 °C/min	40k lbs. or 178 N	600k lbs./min or 2.7 N/min	30	8 hrs 10 min
3	550 °F or 288 °C	200 °F/min or 111 °C/min	1k lbs. or 4.4 N	1k lbs./min or 0.004 N/min	30	1 hr 10 min
4	100 °F or 38 °C	3 °F/min or 2 °C/min	1k lbs. or 4.4 N	600k lbs./min or 2.7 N/min	1	2 hrs 31 min
5	END STEP					
Duration of Entire Program: 11 hours 57 minutes						

2.3 Experimental Methods of Characterization

IR spectra were taken for samples from all TEOS aerogel batches and of MTES aerogel Batch #5, with a Nicolet Avatar 330 FT-IR with a Smart Orbit Diamond ATR 30,000-200 cm⁻¹ plate using a resolution of 4 cm⁻¹ and 32 scans.

Surface areas for all TEOS aerogel batches were acquired with a Micromeritics Tristar 3000 and a Micromeritics Smartprep degasser using the standard parameters for our lab. The samples were degassed for 2 hours at 90°C and then for 10 hours at 200°C.

Surface morphology of TEOS aerogels was observed and pore sizes were estimated with a Zeiss Evo 50 Scanning Electron Microscope in conjunction with a Denton Vacuum Desk IV Sputter Coater, under parameters noted in later figures.

Bulk densities for TEOS aerogels were obtained using an Ohaus Explorer Pro (Model EP64C) balance and the equation:

$$\text{Bulk density} = \frac{\text{mass of sample (g)}}{\text{volume of the sample (cm}^3\text{)}} = \frac{\text{mass of sample (g)}}{\pi r^2 h \text{ (cm}^3\text{)}}$$

where $r = \frac{3}{8}$ inches = 0.375 inches = 0.148 cm and $h = \frac{3}{4}$ inches = 0.75 inches = 0.30 cm.

Optical transmission was taken with a HP/Agilent 8453 Diode Array Spectrophotometer over the range of 400-1100 nm for the TEOS aerogels and over the range of 600-1100 nm for the MTES aerogels. Spectra were measured of thirteen monolithic aerogels from TEOS aerogel Batches #17-19 with path length = height of cylindrical monolith = 1.91 cm. Spectra were measured of eight monolithic aerogels from MTES aerogel Batch #5 with path length = height of cylindrical monolith = 1.5 cm.

Raman spectroscopy was taken with a DeltaNu Advantage 200A Raman Spectrometer averaging 64 scans at low resolution with baseline correction for samples from TEOS aerogel Batches #16-19.

Mechanical strength was studied with a MTS Insight (Electromechanical: 5kN Standard Length) Mechanical Tester for two samples from TEOS aerogel Batch #20.

Contact angles were acquired using a Kruss Drop Shape Analyzer DSA 100 for seven samples from six different recipes (the recipes from MTES aerogel Batches #2, 3, 5 and 6).

Chapter 3: Results and Discussion

3.1 Results and Discussion for TEOS Aerogels

The goals of the project were to fabricate high quality TEOS-based translucent aerogel monoliths with high surface areas using the RSCE process, and to fully characterize these silica materials. The goals of this project were met. Monolithic and optically transparent TEOS-based aerogels were fabricated using Union's RSCE process. These aerogels were successfully characterized using FTIR, Raman, optical transmission, bulk density, SEM and surface area measurements. Aerogels were produced with various surface areas, pore sizes, optical transparencies (according to UV/Vis/NIR absorbance), and acoustic properties.

During this project, time was spent fabricating the xerogel batches to get an idea of what recipes led to good sol gels and would, therefore, be reasonable starting points for aerogel synthesis. Thus, the xerogel recipes were used as the starting point for the systematic fine tuning of the aerogel recipes. Furthermore, time was spent during this project on the assorted methods used to characterize the aerogels because the group has not previously published work with TEOS aerogels and a full characterization of their properties was necessary. For the preliminary work done by Thomas Hughes, a precursor mixture of TEOS, ethanol, and water (molar ratio of 1.0:4.9:6.3), with oxalic acid to catalyze hydrolysis, followed by aqueous ammonia to catalyze the polycondensation reactions was used. The resulting monolithic RSCE aerogels have average bulk density of $\sim 0.088 \text{ g/cm}^3$, average pore diameter ca. 40 nm, average BET surface areas up to $320 \text{ m}^2/\text{g}$, and skeletal density of 2.04 g/cm^3 .

TEOS Xerogels

The xerogel samples in the various batches ranged from translucent to somewhat opaque, where some of the samples had translucent and cloudy sections. The gelation time for

each of the xerogel batches can be seen in Table 3-1 and the gelation time of the two modified batches can be seen in Table 3-2.

Table 3-1: Gelation Time of TEOS Xerogel Batches

Batch #	Batch Date	Gelation Time	Batch #	Batch Date	Gelation Time
1	4/30/2010	< 26 hrs 35 min	B2	5/21/2010	Just over 1 hr 30 min
2	4/30/2010	< 26 hrs 25 min	A3	5/21/2010	< 1 hr 15 min
3	4/30/2010	< 26 hrs 5 min	B3	5/21/2010	< 1 hr 15 min
4	4/30/2010	< 25 hrs 50 min	A4	5/21/2010	> 1 hr
A1	5/14/2010	< 1 hr 25 min	B4	5/21/2010	< 1 hr
B1	5/14/2010	Just over 1 hr 25 min	A5	5/21/2010	immediately
C1	5/14/2010	Just over 1 hr 25 min	B5	5/21/2010	immediately
A2	5/14/2010	< 1 hr 10 min	A1	5/28/2010	1 hr
B2	5/14/2010	< 1 hr 10 min	B1	5/28/2010	1 hr
C2	5/14/2010	< 1 hr 10 min	A2	5/28/2010	5 min
A3	5/14/2010	< 1 hr 10 min	B2	5/28/2010	> 20 min and < 5 hrs
B3	5/14/2010	< 1 hr 10 min	A3	5/28/2010	10 min
C3	5/14/2010	< 1 hr 10 min	B3	5/28/2010	> 21 hrs and < 45 hrs
A4	5/14/2010	< 1 hr 10 min	A4	5/28/2010	immediately
B4	5/14/2010	< 1 hr 10 min	B4	5/28/2010	69 hrs 25 min
C4	5/14/2010	< 1 hr 10 min	A5	5/28/2010	1 min
A5	5/14/2010	immediately	B5	5/28/2010	81 hrs 46 min
B5	5/14/2010	immediately	A6	5/28/2010	immediately
C5	5/14/2010	immediately	B6	5/28/2010	51 hrs 27 min
A1	5/21/2010	< 1 hr 45 min	A7	5/28/2010	immediately
B1	5/21/2010	Just over 1 hr 45 min	B7	5/28/2010	27 hrs 27 min
A2	5/21/2010	< 1 hr 30 min			

Table 3-1: Each xerogel batch was prepared on the indicated date and the sol-gel formation time is given by the gelation time. The < and > arrows indicate batches that gelled between observation times.

Table 3-2: Gelation Time of Modified TEOS Xerogel Batches

Batch #	Batch Date	Gelation Time
M	5/21/2010	< 1 hr 30 min
M1	5/30/2010	> 5 days
M2	5/30/2010	> 4 days
M3	5/30/2010	> 3 days
M4	5/30/2010	5 min
M5	5/30/2010	immediately
M6	5/30/2010	immediately

Table 3-2: Each xerogel batch was prepared on the indicated date and the sol-gel formation time is given by the gelation time. The < and > arrows indicate batches that gelled between observation times. The modified batches are batches in which more H₂O was added than ethanol, instead of adding more ethanol than H₂O (non-modified batches).

From the gelation times of the various batches (seen in Table 3-1), the most attractive aerogel recipe candidates are the recipes that have short gelation times (< 1 hour), but do not gel immediately so that the liquid mixture can be poured into the mold before it gels under ambient conditions. Some of the possible candidates include Batches #B4 (5/21/10), A1-3, A5 and B1 (5/28/10). Then, from the potential candidates based on gelation time, the xerogels that were the most translucent were chosen as the best possible candidates for making TEOS aerogels that were high quality translucent aerogel monoliths. Some of the possible candidates include Batches #A3 and B1 from 5/28/10, which were visually uniform, translucent gels and gelled in reasonable amounts of time (10 minutes and 1 hour, respectively).

For the modified batches (as seen in Table 3-2), none of these recipes could be potential aerogel recipes because of the volume of water in the recipe, which would not be a good solvent for the RSCE process. Water is not a good solvent for the RSCE process because our hot-press cannot take water to its supercritical temperature (374°C) and pressure (22.1 MPa), which is how the solvent is eliminated from the aerogel matrix in Union's RSCE process. Our hot-press can achieve the supercritical temperature (243°C) and pressure (6.3 MPa) of ethanol.

TEOS Aerogels

The recipe initially used for fabricating TEOS-based aerogels resulted in opaque monolithic aerogels. For that preliminary work, we used a precursor mixture of TEOS, ethanol, and water, with oxalic acid to catalyze hydrolysis, followed by aqueous ammonia to catalyze the polycondensation reactions. The recipe for the preliminary work can be seen in Table 1-1. The recipe was refined during fabrication of several batches (#1-6), and this resulted in aerogel materials with varying opacity. The final recipe (Table 2-11) was used for Batches #7-21. The aerogels fabricated in Batches #7-21 are optically translucent.

Physical Description and Photographs of TEOS Aerogels

Monolithic, translucent TEOS-based aerogels were fabricated using Union's RSCE process. All of the TEOS aerogel batches were monolithic and Batches #1-6 were opaque. Batches #7-21 were translucent. Seen in Figure 3-1 are digital photographs taken of some of the aerogel batches fabricated during summer and fall 2010, including some photos of aerogels with the optical transmission holder. Some of the samples have a pinkish tint, but many of the samples have a bluish tint. One of the samples from Batch #8 has a clear burn pattern. Batches #17-21 were the most optically transparent TEOS aerogels produced.

Fourier Transform-Infrared Spectroscopy (FT-IR)

Ideally for a high surface area silica material, such as silica aerogels, the external Si-O framework should produce a bigger signal in the IR spectrum than the internal Si-O framework. These signals should be distinguishable if there are ligands on the framework to create a shift in the peaks. The internal and external (surface) O-Si-O frameworks can be distinguished because

A typical IR spectrum for RSCE TEOS-based silica aerogels can be seen in Figure 3-2, where three silica peaks are noted. Every IR spectrum obtained for all the aerogel batches contained silica peaks at about 1073 cm^{-1} , 796 cm^{-1} and 451 cm^{-1} . Here, the silica peak (1073 cm^{-1}) has a major signal from the external Si-O framework with the minor signal of the internal Si-O framework appearing as a shoulder on the side.⁹ There were no –OH stretching peaks or –CH stretching signals observed in the spectra; therefore, only the expected silica peaks appear in the IR spectra indicating that no significant amount of water has been adsorbed by the aerogel. This observation is consistent with RSCE TMOS aerogels, but is not expected because there should be left-over Si-O-H and Si-O-CH₂CH₃ groups from incomplete polycondensation reactions in the aerogel framework.

Surface Area Analysis

A bar graph depicting the surface areas of all the batches of RSCE TEOS-based aerogels through Batch #19 can be seen in Figure 3-3, where the lowest surface area is $211\text{ m}^2/\text{g}$ (Batch #2) and highest surface area is $475\text{ m}^2/\text{g}$ (Batch #16). Most of the samples have surface areas $>325\text{ m}^2/\text{g}$. The uncertainty in the BET surface area measurements ranges from $10\text{--}20\text{ m}^2/\text{g}$. Each sample was measured under standard BET surface area conditions and was degassed for 12 hours prior to analysis. As was described in the experimental chapter Batches #1-6 were fabricated with slightly varying recipes due to fine-tuning of the recipe. As noted by the purple arrow, Batches #7-19 were fabricated with the same recipe. As noted by the red arrow, the surface areas of the various aerogel batches became more consistent for the higher numbered batches (Batches #16-19). Also the higher numbered batches had consistently high surface areas. The average surface area of Batches #16-19 was $460\text{ m}^2/\text{g}$ and the standard deviation was $10\text{ m}^2/\text{g}$.

Figure 3-2: Representative TEOS-based Aerogel IR Spectrum

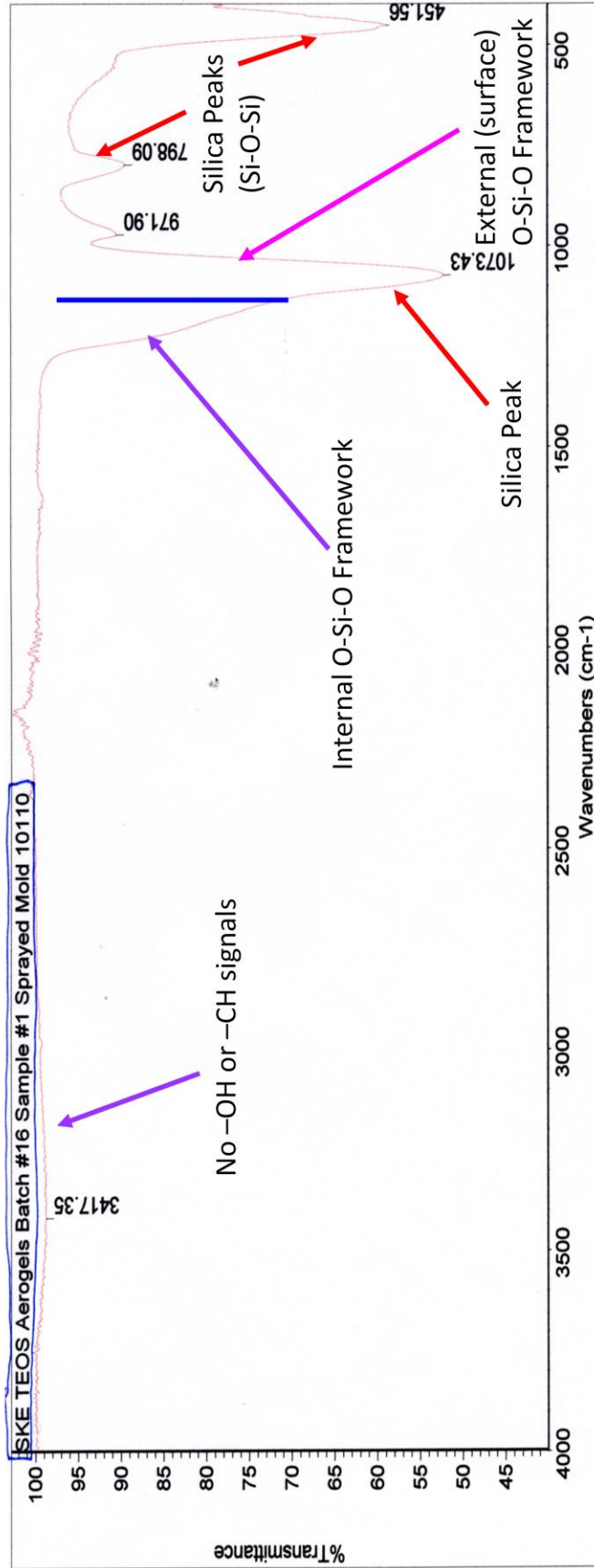


Figure 3-2: A representative TEOS aerogel IR spectrum is shown, where the specific silica peaks are noted at 1073, 798 and 451 cm⁻¹. The internal O-Si-O framework (silica bonds inside the aerogel) is distinguishable from the external O-Si-O framework (silica bonds on the surface (pore surface or outer surface) of the aerogel) because the amount of external framework bonds should be greater than the amount of internal framework bonds due to the highly porous nature of aerogels. The spectrum was taken with a resolution of 4 cm⁻¹ and 32 scans.

We can consistently produce TEOS aerogels with high surface area (0.5 g of our TEOS aerogels has as much surface area as a tennis court). Our TEOS RSCE aerogels have surface areas lower than TEOS aerogels prepared via other methods, where the literature states that the surface areas can be routinely as high as 700 to >1100 m²/g,¹⁸ or even as high as 1600 m²/g for very high quality silica aerogels.¹ These high quality silica aerogels are generally prepared via a two-step sol-gel CSCE method. Our TEOS RSCE aerogel surface areas are below the literature values for TMOS RSCE aerogels, and our group has also noted that the RSCE TMOS aerogels have surface areas significantly below the literature values for TMOS aerogels prepared via other methods. TMOS-based RSCE aerogels prepared at Union had surface areas around 500 to 600 m²/g and up to as high as 1000 m²/g,⁷ while their counterparts in the literature had surface areas at least as high.¹⁹

Optical Transmission

Optical transmission spectra of thirteen monolithic TEOS-based RSCE aerogels can be seen in Figure 3-4 and representative % optical transmission data are listed in Table 3-3. Using optical transmission it was found that the aerogel samples had up to 74% transmission in the Near-IR and up to 45% transmission in the visible region. For the 900-1100 nm range the optical transmission of most aerogels was greater than 60%. Therefore, the RSCE TEOS aerogels were translucent in the Near-IR and are somewhat cloudy in the visible region. These aerogels would be useful as the insulation for cloudy windows, such as some skylights or frosted bathroom windows. Typical silica aerogels prepared from TEOS-based recipes using a two-step acid-base sol-gel process have optical transmission of 75% transmission in the visible region and the path length of the aerogels was not given.⁴ In my results, there is considerable sample-to-sample variation even within batches. The path lengths may have slight variations due to cracking of the

samples. For our RSCE TEOS aerogels it could be possible to optimize the recipe to yield more translucent materials in the visible region, which would be desirable if the RSCE TEOS aerogels were used as the insulation for windows because the windows would then be translucent instead of cloudy. Therefore, the windows could be used as the windows in the rooms of homes instead of as skylights or in the other windows that are desirable as being cloudy.

Raman Spectroscopy

A typical Raman spectrum can be seen in Figure 3-5. This spectrum was taken of a crushed sample from Batch #16, averaging 64 scans at low resolution with baseline correction. All of the aerogel samples studied had the two expected silica peaks at about 496 and 1260 cm^{-1} . The peak at 496 cm^{-1} corresponds to small 6 or 8-membered rings (3-SiO or 4-SiO respectively), and the peak at 1260 cm^{-1} corresponds to fused silica (Si-O stretching).²⁰ Since there is no peak at about 600 cm^{-1} , which also corresponds to the presence of 6-membered rings, this could mean that only the 8-membered rings are present.²⁰

Bulk Density

Bulk densities were measured of 48 monolithic TEOS-based RSCE aerogels. The mean density was 0.099 g/cm^3 , with a standard deviation of 0.003 g/cm^3 . All the bulk densities measured fell within the range of 0.094 to 0.104 g/cm^3 , which is in the range expected for silica aerogels (generally¹ in the range of 0.003-0.300 g/cm^3). We did not attempt to alter the recipe and processing conditions to make lower-density aerogels. Our RSCE TEOS aerogels are a low density form of silica compared to glass, which is a high density form of silica (bulk density of 2-2.5 g/cm^3).

Figure 3-3: Surface Areas of TEOS-based Aerogel Batches

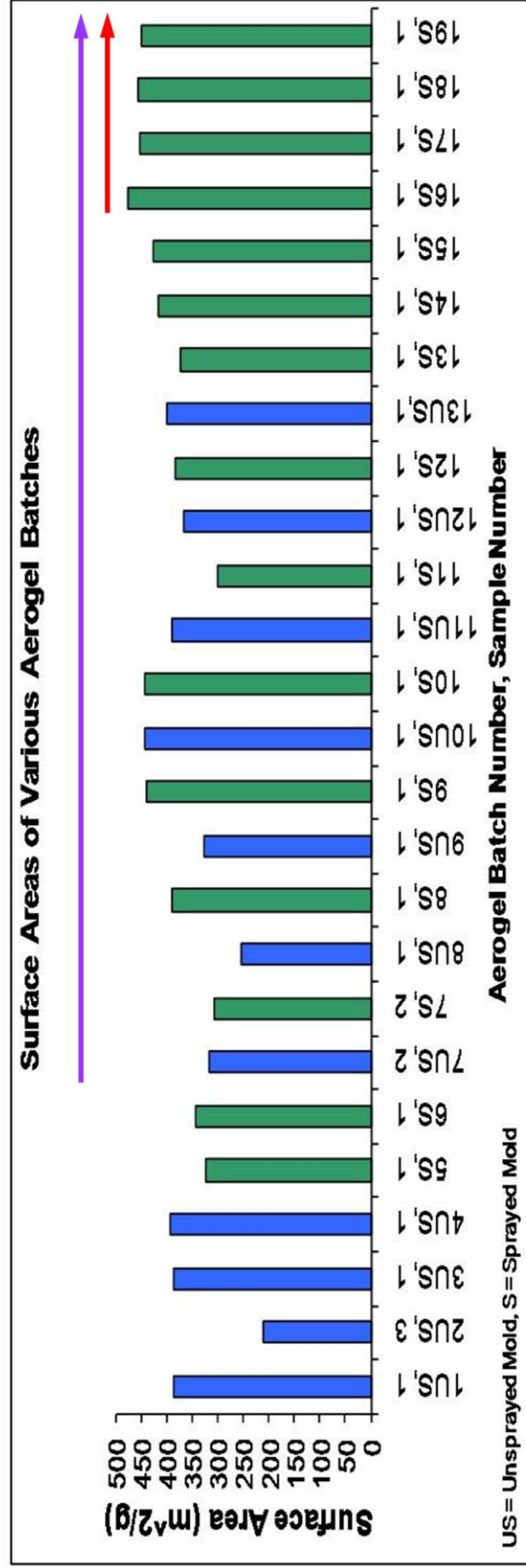


Figure 3-3: All of the surface areas for the TEOS-based aerogel batches are shown in the bar graph above, where the batch labels on the x-axis mean, for example: 1US, 1 = batch #1 unsprayed side of the mold, 1st sample analyzed. Batches where the surface area given is for a sample other than the first sample analyzed is due to a malfunction of the system while analyzing the first or in one case the first and second samples. The blue bars indicate batches where the mold was not sprayed with a non-stick spray and the green bars indicate batches where the mold was sprayed with a non-stick spray. The purple arrow indicates all the batches made from the same aerogel recipe. The red arrow indicates the consistency of the surface areas between the higher numbered batches (#16-19), where the average of the four batches is 460 m²/g and the standard deviation of the four batches is 10 m²/g.

Figure 3-4: Optical Transmission Spectra

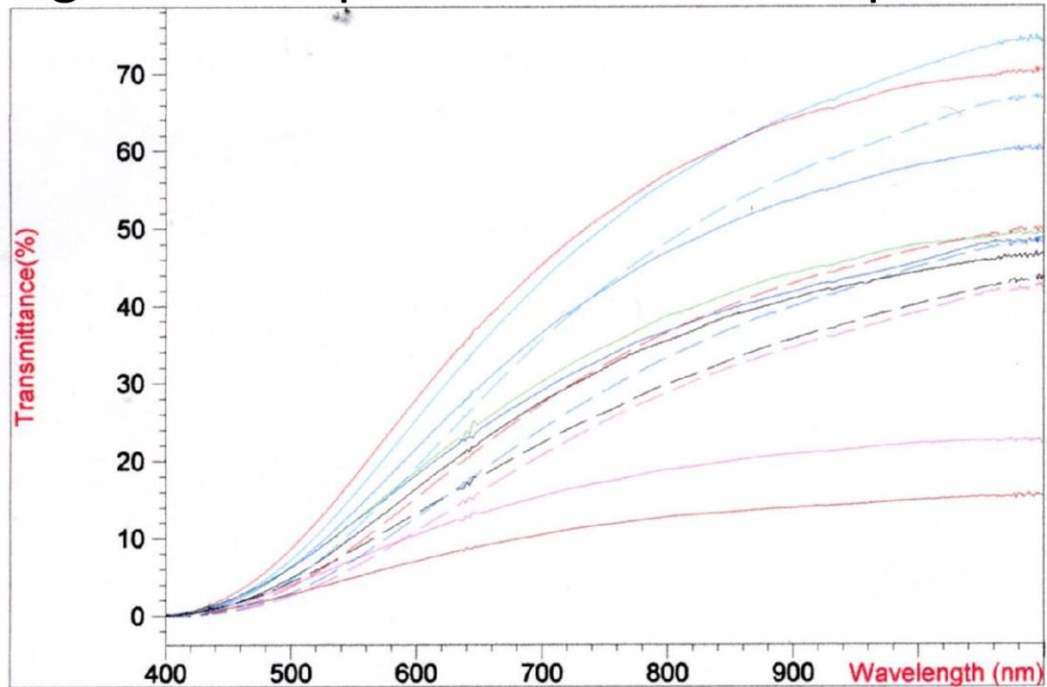


Figure 3-4: Thirteen optical transmission spectra were taken of aerogels from Batches #17-19. The spectra were acquired over the range of 400-1100 nm with path length = height of cylindrical monolith = 0.750 in = 1.91 cm.

Table 3-3: Representative % Optical Transmission (TEOS)

Sample Name	Wavelength (nm)					
	600	700	800	900	1000	1100
Batch #17 Sample #1	16.5	27.6	35.5	40.9	44.4	46.5
Batch #17 Sample #3	28.0	45.4	57.1	64.1	68.4	70.1
Batch #17 Sample #6	21.7	36.5	47.0	53.6	58.0	59.9
Batch #17 Sample #8	25.4	43.3	56.1	64.7	70.7	74.2

Table 3-3: Representative optical transmission data are shown for four of the thirteen samples.

Figure 3-5: Raman Spectrum of a Representative Aerogel Sample

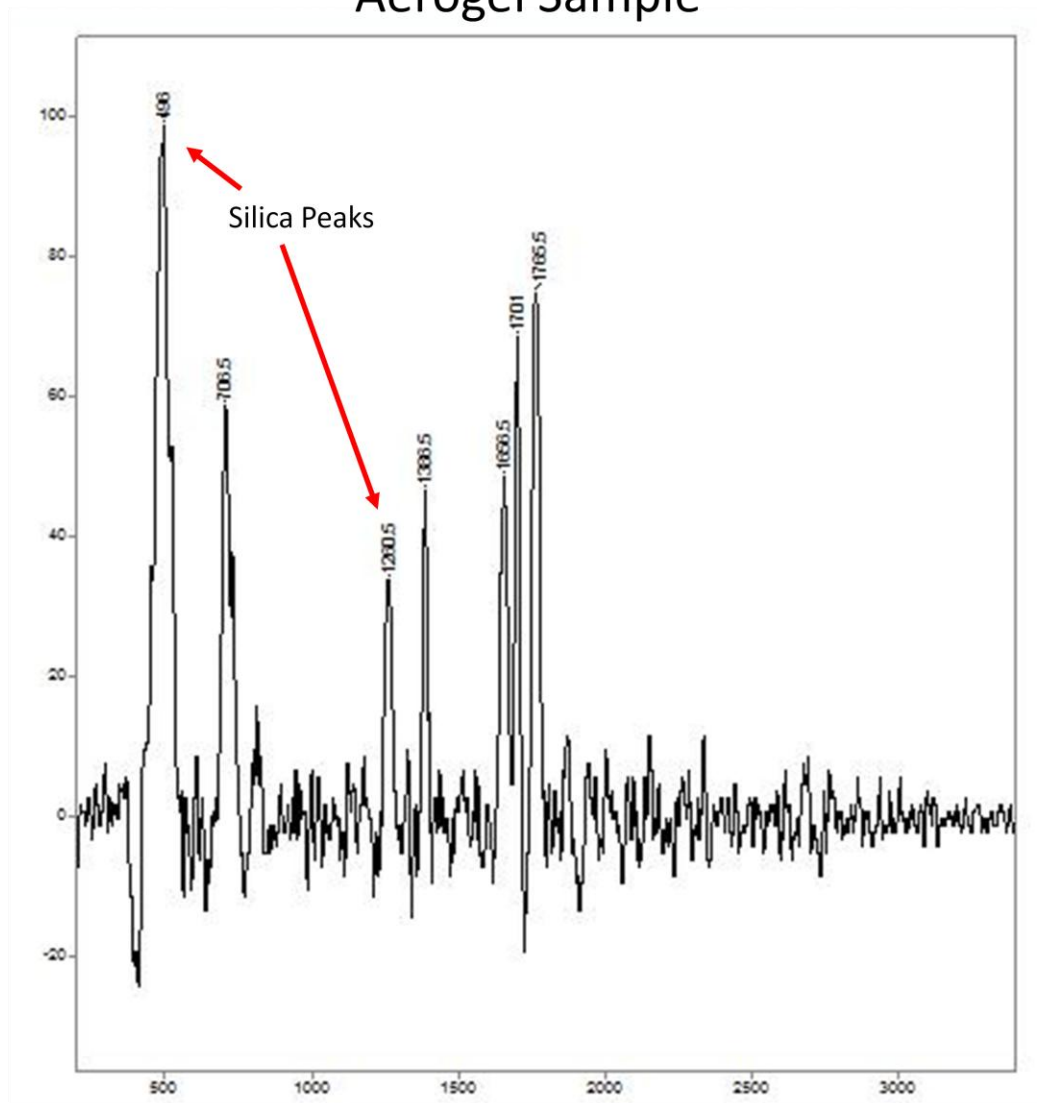


Figure 3-5: The representative Raman spectrum of an aerogel sample was taken by averaging 64 scans at low resolution with baseline correction.

Scanning Electron Microscopy (SEM)

Using SEM, the surface morphology of the aerogel samples was studied at magnifications that allowed for imaging at scales in the 1 mm to 200 nm range. The SEM images can be seen in Figures 3-6 to 3-12, along with the parameters used to obtain each image.

In Figure 3-6, the layered morphology of TEOS aerogels can be seen in the image from Batch #1 and the 200 μm image from Batch #3. The 20 μm image from Batch #3 shows the fracture lines where the sample split when it was crushed. All of the images in Figure 3-6 were of non-sputter-coated samples.

Figure 3-6: SEM Images of TEOS Aerogels from Batches #1 and 3

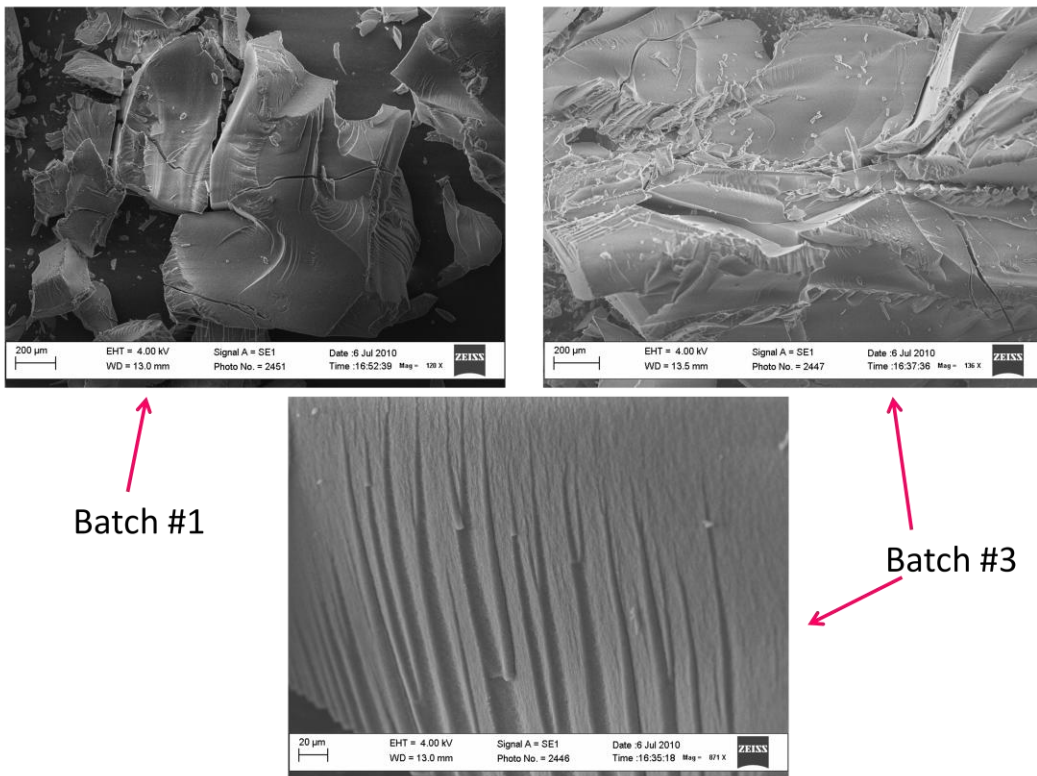


Figure 3-6: SEM image of a non-sputter-coated sample from Batch #1 was taken at 120X and displayed with a scale of 200 μm . SEM images of non-sputter-coated samples from Batch #3 were taken at 136X and 871X, respectively and displayed with a scale of 200 μm and 20 μm , respectively.

In Figures 3-7 and 3-8, the aerogels imaged are from Batch #4 and are displayed in descending scale bar size. In Figure 3-7, the overall structure of crushed TEOS aerogel samples

can be seen. In Figure 3-8, the texture of the TEOS aerogels can be seen, especially in the image on the left, along with the unique structure of the TEOS aerogels in the image on the right.

Figure 3-7: SEM Images of TEOS Aerogels from Batch #4 at 200 μm

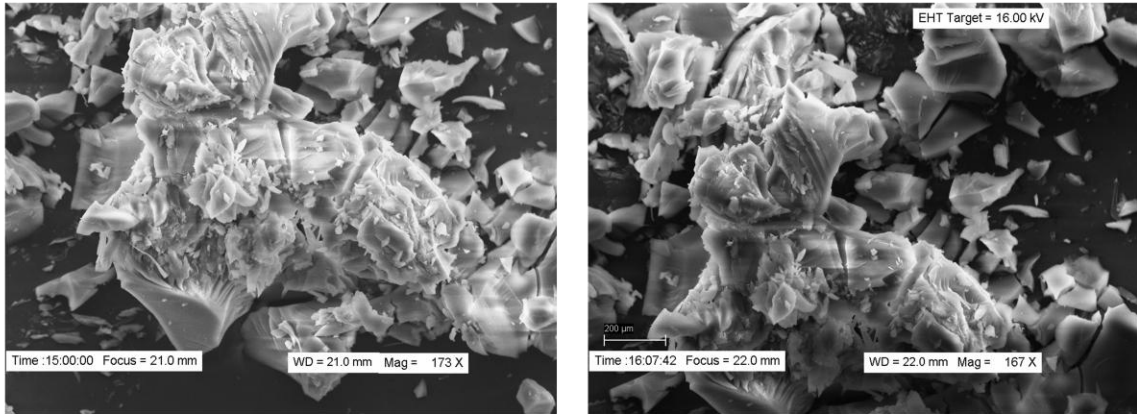


Figure 3-7: SEM images of samples from Batch #4 were taken at 173X and 167X magnification, respectively, and are displayed with a scale of 200 μm .

Figure 3-8: SEM Images of TEOS Aerogels from Batch #4 at 200 and 20 μm

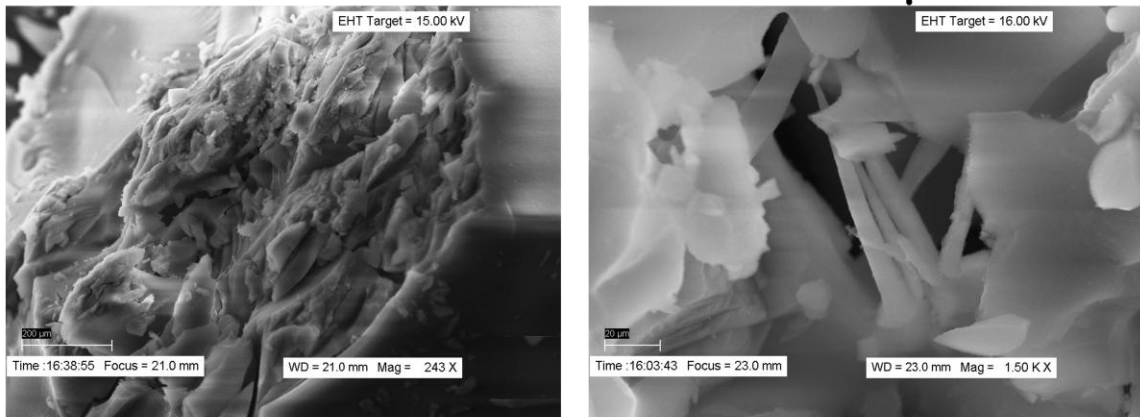


Figure 3-8: SEM images of samples from Batch #4 were taken at 243X and 1.50KX magnification and are displayed with a scale of 200 μm and 20 μm , respectively.

The samples in Figures 3-9 and 3-10 are all sputter-coated samples. The images in Figure 3-9 show the unique surface texture of the aerogels. The aerogels seem to have a soft, fuzzy texture in these images. The image on the left in Figure 3-10 also seems to have a soft, fuzzy texture and displays more of the lines where the aerogel cracked when the monolith was crushed. In this image, the surface texture looks soft, where the texture is due to the visibility of the pores in the aerogel. The dark region of the image notes the depth of the structure, as compared to the 1 μm scale bar.

Figure 3-9: SEM Images of TEOS Aerogels from Batch #4 at 200 and 100 μm

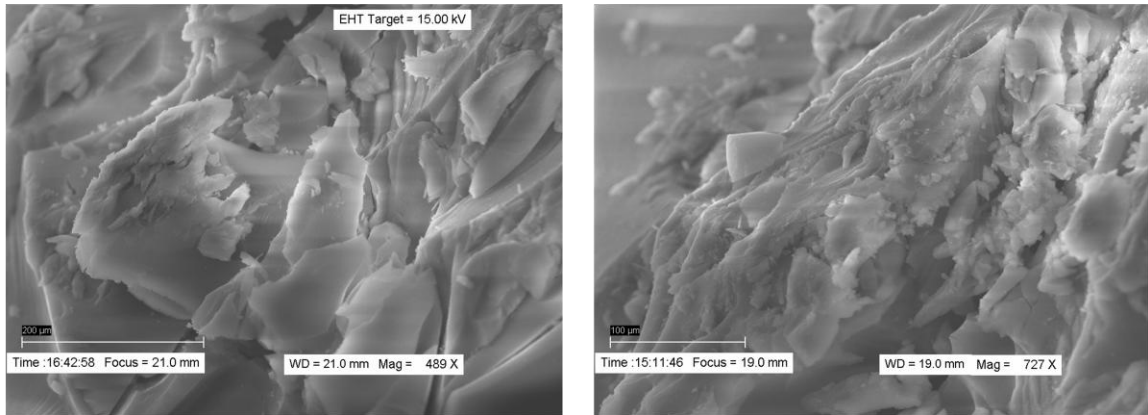


Figure 3-9: SEM images of sputter-coated samples from Batch #4 were taken at 489X and 727X magnification, respectively, and are displayed with a scale of 200 μm and 100 μm , respectively.

Figure 3-10: SEM Images of TEOS Aerogels from Batch #4 at 20 and 1 μm

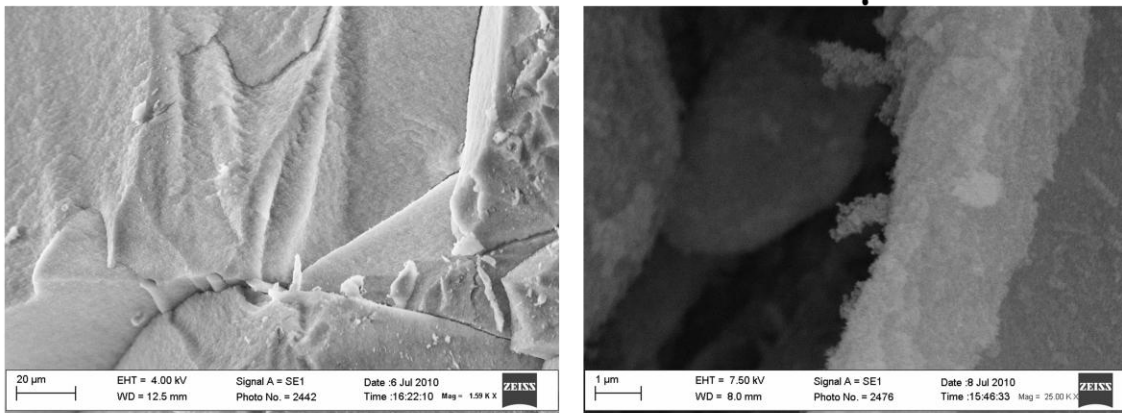


Figure 3-10: SEM images of sputter-coated samples from Batch #4 were taken at 1.59KX and 25.00KX magnification and are displayed with a scale of 20 μm and 1 μm , respectively.

In Figures 3-11 and 3-12, images of more sputter-coated samples are seen. In Figure 3-11, pore sizes are estimated on the two unique features sticking out of the side of the aerogel seen in the image on the right of Figure 3-10. The pore sizes in the two images were estimated to be 39 and 47 nm. In these two images the pores are clearly visible and the scale bar represents 200 nm. In Figure 3-12, samples from Batch #16, one of the most optically transparent batches, again shows the layered structure of the aerogels, as well as the fracture patterns of the sample.

Figure 3-11: SEM Images of TEOS Aerogels from Batch #4 at 200 nm

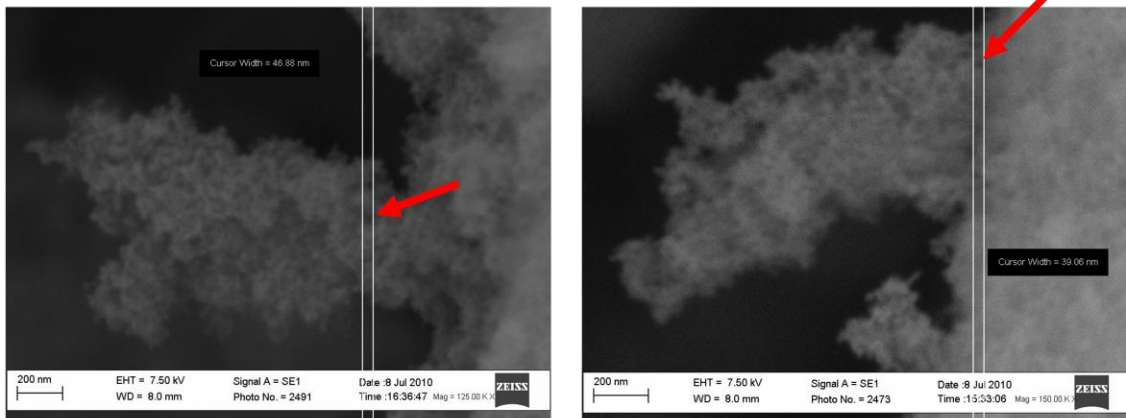


Figure 3-11: SEM images of sputter-coated samples from Batch #4 were taken at 125KX and 150KX magnification, respectively, and are displayed with a scale of 200 nm. The pore diameter measured using the white bars in the figure on the left is marked by the red arrow, where the pore diameter is about 47 nm. The pore diameter measured using the white bars in the figure on the right is marked by the red arrow, where the pore diameter is about 39 nm.

Figure 3-12: SEM Images of TEOS Aerogels from Batch #16

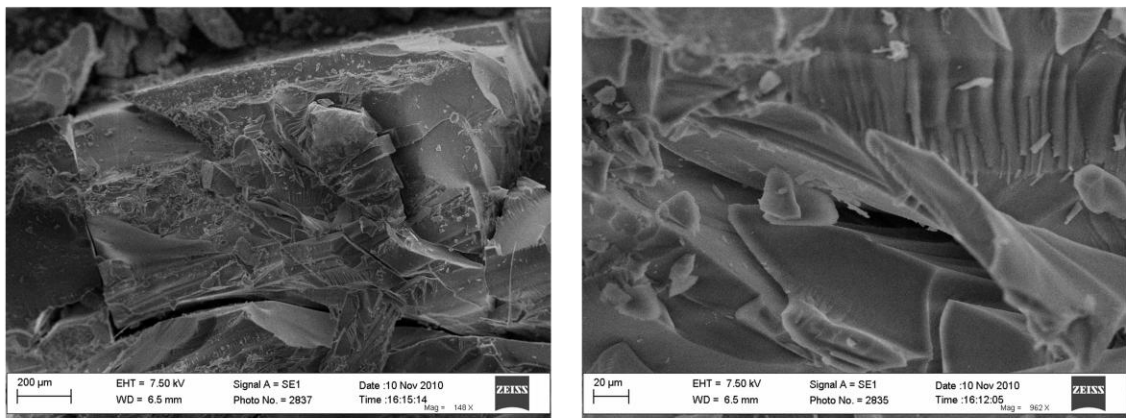


Figure 3-12: SEM images of sputter-coated samples from Batch #16 were taken at 148X and 962X magnification, respectively, and are displayed with a scale of 200 μm and 20 μm, respectively.

The reason that a multitude of images from Batch #4 are presented here is due to the fact that the samples from this particular batch imaged well in the SEM compared to some of the other samples tried. The difficulties in imaging the aerogel samples arose from their non-conductive nature, which caused the samples to build up a charge during imaging, producing low-quality images. Some batches did not need to be sputter-coated and imaged reasonably well, whereas other batches needed to be sputter-coated to obtain high quality images.

Porosity

In the SEM images taken under high magnification (see, for example, Figure 3-11), the pore sizes of the aerogels were estimated, using a measuring function of the SEM, to be 25 to 105 nm in diameter. These pore sizes are greater than some of the smallest pore sizes measured in the literature on TEOS aerogels, where 12 to 17 nm pore sizes were measured.¹⁸ The literature also notes the general range of pore sizes for TEOS aerogels to be 20-150 nm,¹ which is consistent with our range of measurements. It should be noted, however, that using the SEM to measure pore sizes is not the standard method of measuring the porosity of aerogels. The standard method of measuring the porosity of the aerogels is with BJH porosimetry on the Micromeritics Tristar 3000.

Acoustic Properties

I unexpectedly discovered that some of the aerogel samples make a bell-like sound when rattled; most of the aerogel samples have a hard rubber-like sound. The bell-quality of the samples was noticed to various degrees. The unexpected acoustic properties of some of the aerogels necessitate further study into the resonance frequencies of these aerogels as well as

stress testing to see if they have a higher strength than their non-bell-like sounding counterparts.

Mechanical Strength

Preliminary data for the TEOS aerogels was taken of samples from Batch #20, but the acquired stress-strain curves were not very high quality, probably due to the cracks in the samples tested thus far. A crack in the sample would lead to failure of the aerogel material at a stress/strain below the limit which an aerogel of that type can normally endure.

3.2 Results and Discussion for MTES Aerogels

The goals of the project were to fabricate high quality MTES-based flexible aerogel monoliths using the RSCE process, and to fully characterize these silica derivative materials. Some of the goals have been met because monolithic MTES-based aerogels were fabricated using Union's RSCE process and partially characterized.

During this project, time was spent fabricating the various xerogel batches to get an idea of what recipes led to good sol gels and would, therefore, be reasonable starting points for aerogel synthesis. Thus, the various xerogel recipes were used as the starting point for the optimization of the aerogel recipes. Furthermore, time was spent during this project on the various methods used to characterize the aerogels because MTES aerogels had never been made in this lab before and a full characterization of their properties was necessary before publication.

MTES Xerogels

The gelation time of the various xerogel batches can be seen in Table 3-4, where the time it took for each batch to gel is given. The arrows (< and >) indicate that a batch gelled between times that it was checked, so the precise gelation time is not known. The batches that are listed as gelling in multiple days gelled sometime after 7 days.

Table 3-4: Gelation Time of MTES Xerogel Batches

Batch #	Batch Date	Gelation Time	Batch #	Batch Date	Gelation Time
1A1	10/22/10	<48 hrs	4A1	1/21/11	immediately
1A2	10/22/10	<6 days	4A2	1/21/11	multiple days
1B1	10/22/10	< 24 hrs	4A4	1/21/11	multiple days
1B2	10/22/10	< 24 hrs	4A7	1/21/11	>7 days
1C1	10/22/10	< 24 hrs	4A8	1/21/11	<7 hrs
1C2	10/22/10	< 24 hrs	4A9	1/21/11	<8 hrs
2A1	10/28/10	<19 hrs	4B1	1/21/11	multiple days
2A2	10/28/10	<19 hrs	4B2	1/21/11	multiple days
2B1	10/28/10	multiple days	4B3	1/21/11	<7 days
2B2	10/28/10	multiple days	4B4	1/21/11	>7 days
2C1	10/28/10	multiple days	4B5	1/21/11	>7 days
2C2	10/28/10	multiple days	4B6	1/21/11	<8 days
3A1	1/20/11	multiple days	4B7	1/21/11	>7 days
3A2	1/20/11	multiple days	4B8	1/21/11	>7 days
3B1	1/20/11	immediately	4B9	1/21/11	<24 hours
3B2	1/20/11	<48 hrs			

Table 3-4: Each xerogel batch was prepared on its corresponding date and the sol-gel formation time is given by the gelation time. The < and > arrows indicated batches that gelled in between observation times.

The various batches were generally monolithic and were white, translucent or were part white and part translucent. For example, a few batches were white on the bottom layer and translucent on the top layer when the batch finally gelled. From the gelation times of the various batches (seen in Table 3-4), the most likely aerogel recipe candidates are the recipes that have short gelation times (< 1 hour), but do not gel immediately so that the liquid mixture

can be poured into the mold before it gels under ambient conditions. Some of the possible candidates include Batches #2A1-2 and 4A8-9 because these batches did not gel immediately, but gelled significantly more quickly than the other batches. Then, from the potential candidates based on gelation time, the xerogels that were the most translucent and most flexible were chosen as the best possible candidates for making MTES aerogels that were high quality flexible aerogel monoliths with, hopefully, some translucency. To determine the flexibility of the xerogel batches, each xerogel was prodded with a glass stirring rod to see how much it could be compressed. Some of the possible candidates include Batches #2A1 and 4A1, where both batches were translucent, but neither batch was flexible as a wet sol gel.

MTES Aerogels

Recipes for making MTES aerogels were adapted from the recipes published by Rao and Bhagat,⁶ and Nadargi.¹⁷ For the preliminary work, we used a precursor mixture of MTES, ethanol, and water with oxalic acid to catalyze hydrolysis, followed by aqueous ammonia to catalyze the polycondensation reactions.

After establishing which xerogel recipes were the best MTES aerogel candidates some of the recipes were used to make aerogels. These recipes include Batches #1B1, 1C1, 4A8-9 and 4B9. It was found however, that even though the gelation times were not very fast and the batches were somewhat translucent the resulting aerogels were mostly opaque and did not always gel before the first step of the hot-press program completed. The status of the gelation was known because un-gelled batches that underwent the hot-press program would have the aerogel's ingredients remain in the supercritical solvent that was released during the program, resulting in a nearly empty mold. Some of these recipes also shrunk excessively or looked to be more crystalline than aerogel-like when removed from the hot-press. Furthermore, no flexible

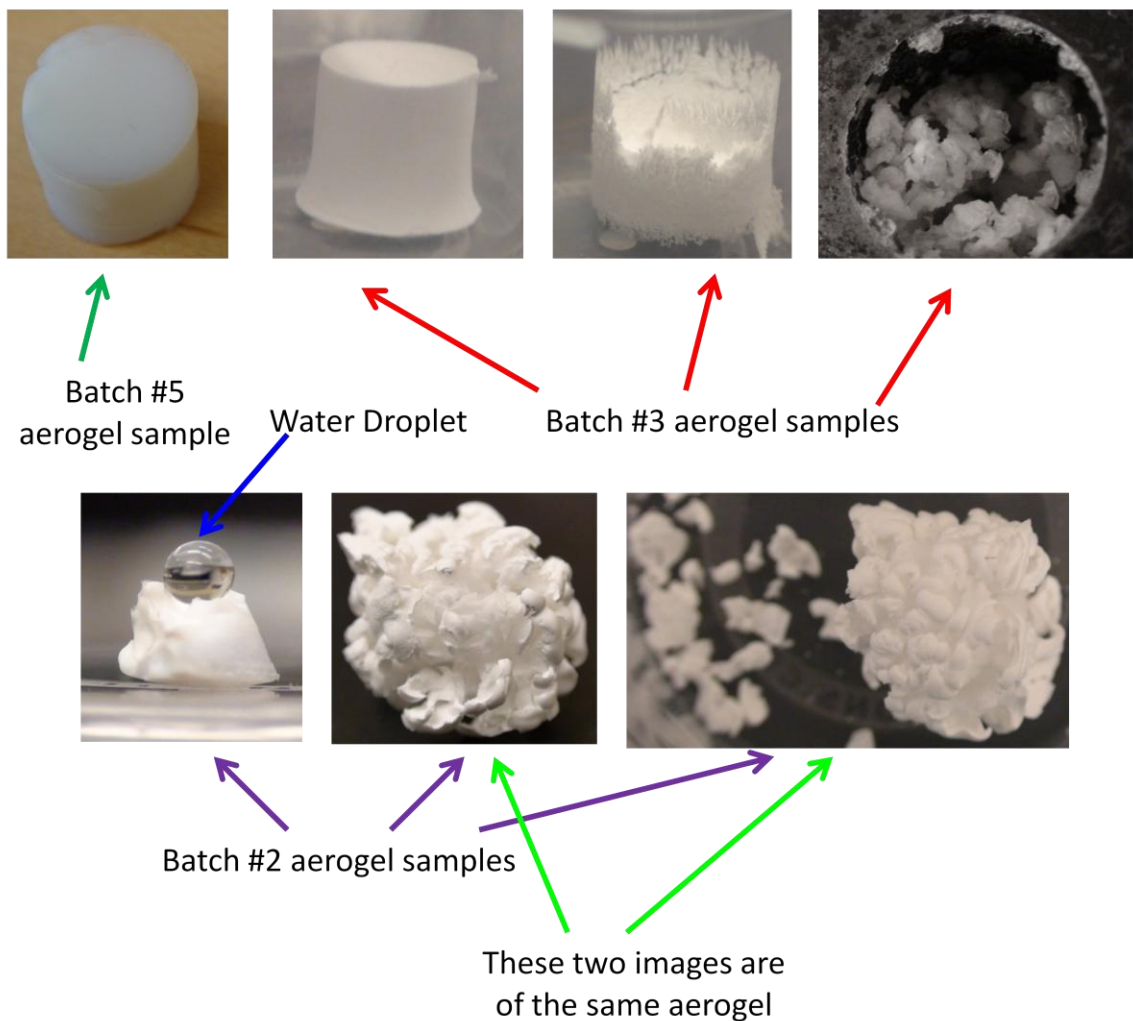
aerogel batches were produced, but it should be noted that no flexible xerogel batches were produced either. Thus, there does not seem to be a good correlation between fine-tuning the xerogel recipe and producing fine-tuned MTES aerogels.

Physical Description and Photographs of MTES Aerogels

MTES-based aerogels were fabricated using Union's RSCE process. About half the MTES aerogels remained monolithic; others were fragmented or in small grains of the material nucleating around a hard core. The MTES aerogels ranged from whitish/mostly opaque to somewhat translucent (crystalline looking pieces). None of the MTES aerogels were found to be flexible, even though they are found to be flexible when fabricated by other methods, such as the two-step acid-base catalyzed method performed by Nadargi.¹⁷ Seen below in Figure 3-13 are digital photographs taken of some of the MTES aerogel batches fabricated during winter 2011. Many of the samples have a bluish tint or are white.

As seen in the MTES aerogel photographs, there is considerable batch-to-batch variation, as well as variation within the batches. Some of the samples turned out soft and fluffy, while others were shrunken like a xerogel, but had visual characteristics that more closely resembled TEOS aerogels. Other samples looked crystalline and yet others, such as the two images from Batch #2 that are noted by the green arrows, look like popcorn, where the soft fluffy part is facing out and the hard, crystalline looking parts are on the inside.

Figure 3-13: Photographic Images of Various Batches of MTES Aerogels



Fourier Transform-Infrared Spectroscopy (FT-IR)

An IR spectrum for an MTES RSCE aerogel from Batch #5 can be seen in Figure 3-14, where silica peaks are noted as well as a -CH stretch peak and two Si-C peaks. The IR spectrum of the MTES-based aerogel samples displayed peaks at about 3000 cm^{-1} , 1271 cm^{-1} , 1119 cm^{-1} , 1025 cm^{-1} , 769 cm^{-1} and 410 cm^{-1} . It can be inferred from the data obtained for the RSCE TEOS aerogels that the silica peaks present at 1119 and 1025 cm^{-1} show the internal and external O-Si-

O framework, respectively. The -CH stretch at about 3000 cm^{-1} and the Si-C peaks at 1271 and 769 cm^{-1} prove that the aerogels are organically modified because the Si- CH_3 is still present in the aerogel framework. No -OH signal was observed in the IR meaning that no significant amount of water has been adsorbed into the aerogel. Only the expected silica peaks and methyl groups appear in the IR spectra.

Optical Transmission

Optical transmission spectra of eight monolithic MTES-based aerogels can be seen in Figure 3-15 along with some representative % optical transmission data in Table 3-5. The monolithic aerogels tested were from both recipes used in Batch #5. The samples tested were opaque in the visible region (scattered visible light), but had some optical clarity in the near-infrared region. The aerogel samples had up to 23% transmission in the Near-IR with the best sample having between 16 and 23% transmission. Therefore, the monoliths scatter visible light, but transmit in the near-infrared. There is considerable sample-to-sample variation even within batches. This could be due to slight variations in path lengths due to cracking of the samples. MTES aerogels are generally opaque.²¹

Figure 3-14: MTES-based Aerogel IR Spectrum from Batch #5

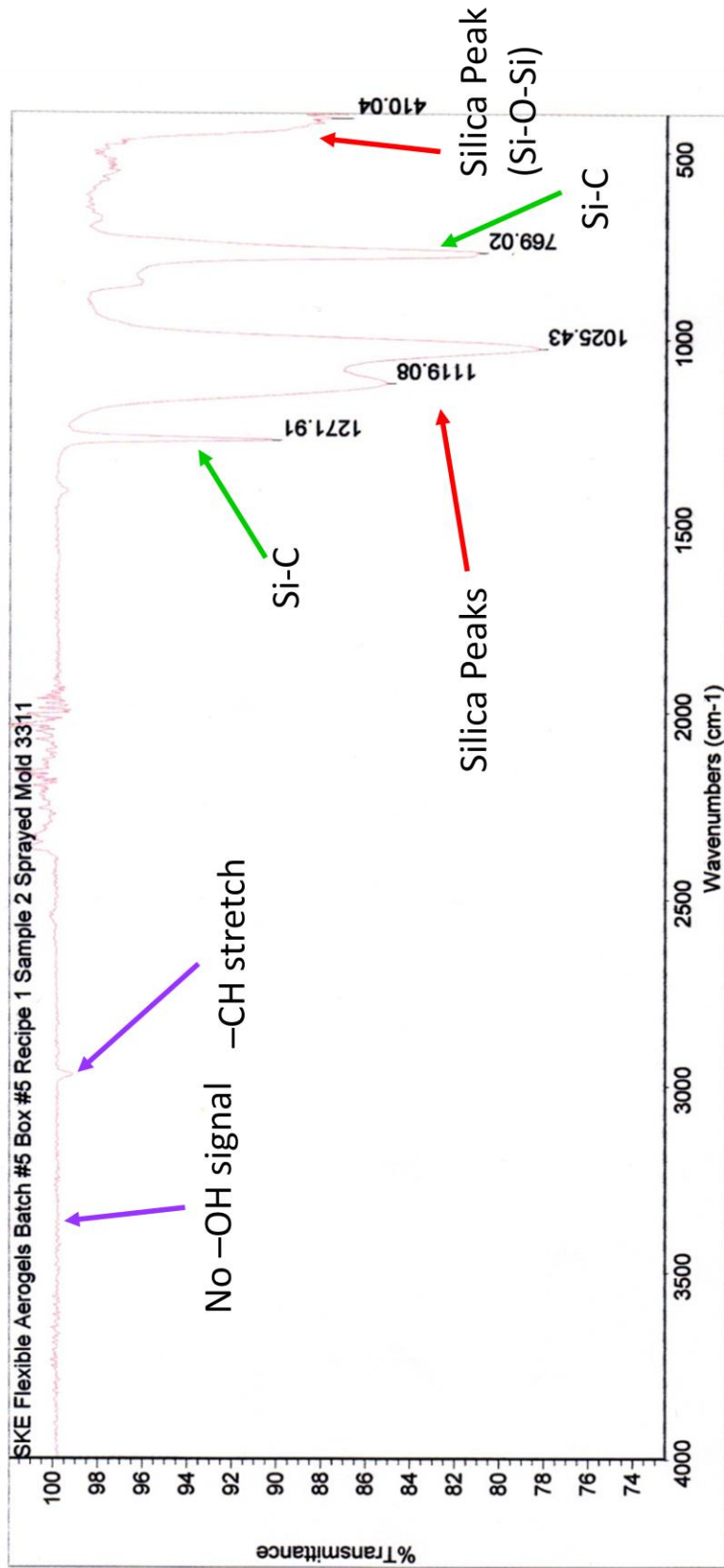


Figure 3-14: An MTES aerogel IR spectrum from Batch #5 is shown, where the specific silica peaks are noted at 1119, 1025 and 410 cm⁻¹. The Si-C peaks are noted at 1271 and 769 cm⁻¹. There is a -CH stretch at about 3000 cm⁻¹ and there is no -OH signal present. The spectrum was taken with a resolution of 4 cm⁻¹ and 32 scans.

Figure 3-15: Optical Transmission Spectra

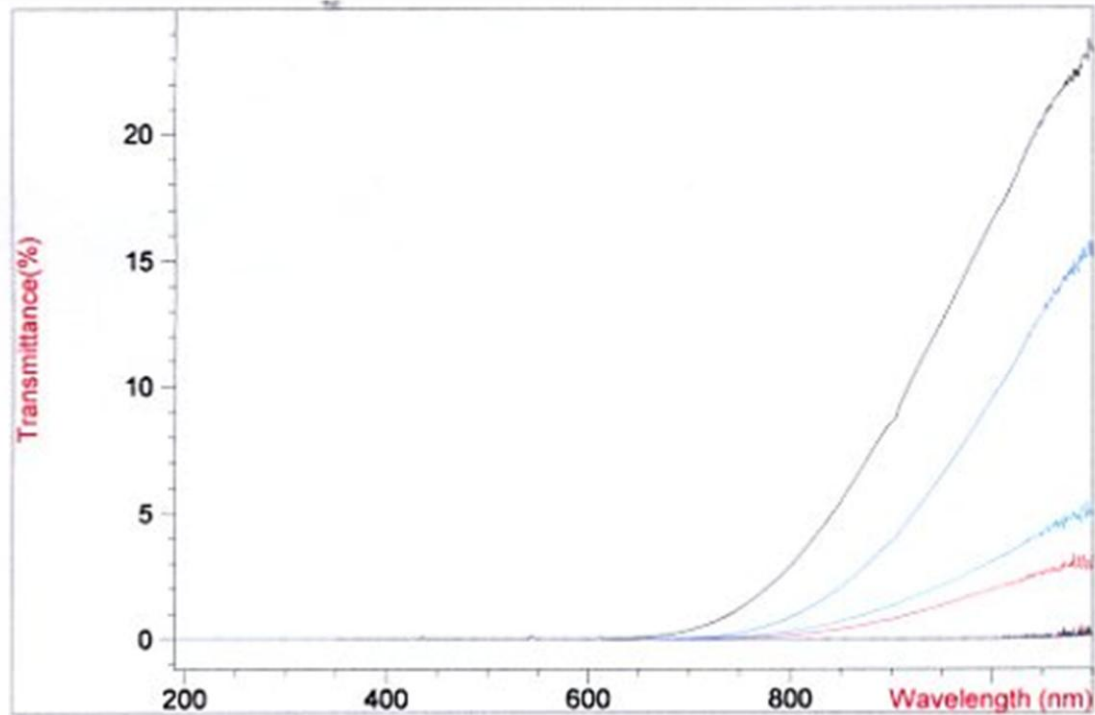


Figure 3-15: Eight optical transmission spectra were taken of aerogels from Batch #5. The spectra were acquired over the range of 600-1100 nm with path length = height of cylindrical monolith = 1.5 cm.

Table 3-5: Representative % Optical Transmission (MTES)

Sample Name (Recipe 2)	Wavelength (nm)	
	1000	1100
Batch #5 Sample #3	16.5	23.4
Batch #5 Sample #4	1.9	3.1
Batch #5 Sample #5	9.5	15.9
Batch #5 Sample #6	3.1	4.7

Contact Angle

Contact angles less than 90° indicate a hydrophilic surface and contact angles greater than 90° indicate a hydrophobic surface. Superhydrophobic surfaces have contact angles greater than 150°.

Contact angle measurements show that all of the aerogels tested are hydrophobic as can be seen in Figure 3-16 and Table 3-6. Contact angles between 126 and 153° were measured. Most of the contact angles are over 137°. MTES aerogels made by a two-step acid-base catalyzed sol-gel method using methanol as the solvent had a contact angle of 160° for one sample.¹⁷ Thus, the MTES aerogels are hydrophobic and some are even superhydrophobic (those with contact angles greater than 150°).

For comparison, I attempted to make contact angle measurements for the TEOS RSCE aerogels. The drops of water were immediately adsorbed by the aerogel, indicating that the TEOS RSCE aerogels are hydrophilic.

Figure 3-16: Contact Angle Measurements

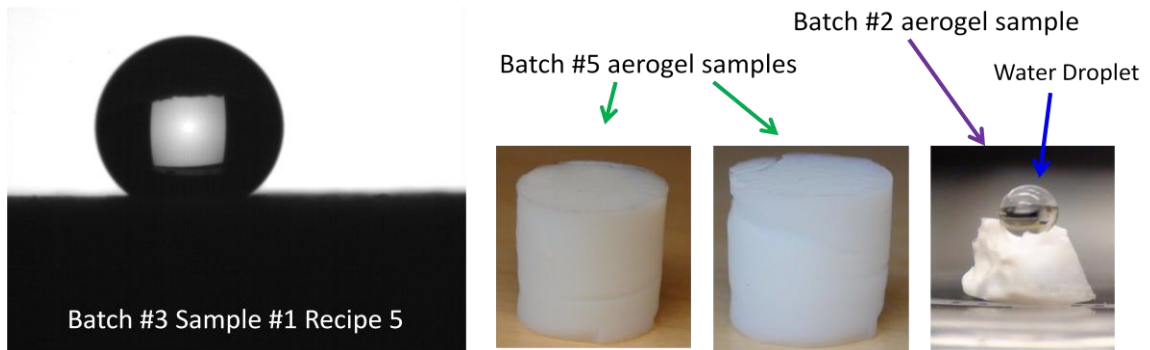


Table 3-6: Contact Angles of MTES Aerogels

Sample Recipe #	Contact Angle (°) for Replicate Measurements		
Recipe 1	132	132	-
Recipe 2	126	141	-
Recipe 3	128	139	129
Recipe 4	135	137	141
Recipe 5	151	-	-
Recipe 6	152	151	153

Further Characterizations and Optimizations

Although I was successful in fabricating MTES RSCE aerogels, these materials are not flexible and have limited optical transmission. Both flexibility and optical transmission are necessary for optically or laser controlled soft robots.

The MTES aerogel recipe needs to be optimized to achieve flexibility as one of the aerogels' properties, as well as tailoring the MTES aerogels to be more optically transparent. Moreover, we do not yet have batch-to-batch reproducibility for the MTES aerogels.

3.3 Future Work

Other characterizations to be performed on the TEOS aerogel samples include pore size (porosity) using the BJH settings on the Tristar instrument, thermal conductivity, skeletal densities with the pycnometer and atomic force microscopy (AFM). Other characterizations to be performed on the MTES aerogel samples include surface area and pore size (porosity) using the Tristar instrument, thermal conductivity, skeletal densities with the pycnometer, scanning electron microscopy (SEM), atomic force microscopy (AFM), surface area analysis, Raman spectroscopy, bulk density, and mechanical strength testing.

The porosity of the TEOS aerogels should be studied to obtain a more accurate range of pore sizes than can be estimated using the SEM and the porosity of the MTES aerogels should be studied to obtain an accurate range of pore sizes, which can be compared to the TEOS aerogel pore sizes.

Thermal conductivity should be tested to ascertain how good an insulator the TEOS aerogels are since they are proposed to be used as thermal insulation for windows. The thermal conductivity of the MTES aerogels should be tested to ascertain how good an insulator the MTES aerogels are so they can be compared to the TEOS aerogels.

The skeletal densities should be studied to see if the TEOS RSCE silica aerogels differ from the TMOS RSCE silica aerogels and the MTES RSCE modified silica aerogels, although it is not expected that the TEOS and TMOS aerogel skeletal densities will differ greatly.

The AFM can be used to study the surface morphology of the aerogels in the nanometer range more effectively than the SEM, thus the nanometer range morphology of the aerogels can be studied in more detail. The SEM and AFM give complementary and more detailed data in their various ranges of optimal operation because the SEM gives the best images between 1 mm and 1 μm and the AFM gives the best images between 5 μm and 200 nm.

Bulk densities of the MTES aerogels should be studied to be compared to other types of aerogels, such as the RSCE TEOS aerogels.

The surface area of the MTES aerogels should be studied to see how the surface area compares to other aerogels, since aerogels are high surface area materials.

Raman microscopy of the MTES aerogels should be studied because it gives complementary data to that obtained by IR, which could help to identify the peaks in the spectra.

Mechanical strength of the MTES aerogels should be studied because flexibility is one of the characteristics being optimized for in the MTES aerogels. Finally, testing the mechanical strength of the MTES aerogels studies the stress-strain curve of the material, which will show how elastic (flexible) the MTES aerogels are.

Chapter 4: Conclusions

Reproducible, monolithic, translucent TEOS-based aerogels have been fabricated and optimized using Union's RSCE method. The TEOS aerogels have high surface areas, low bulk densities, moderate optical transmission, are very porous, are hydrophilic and have unique acoustic properties.

Monolithic MTES-based aerogels have been fabricated using Union's RSCE method. The MTES aerogels have yet to be tailored for optical clarity, reproducibility and flexibility, but they have adequate optical transmission in the near-IR and are hydrophobic with high contact angles.

By using Union's RSCE method both types of aerogels are fabricated more quickly than by conventional methods because conventional methods for silica aerogels take days to a week or more to complete for aerogels made in an autoclave with a CO₂ drying process.

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