

TRANSPARENT AND CRACK-FREE SILICA AEROGELS

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ABSTRACT

The process of making silica aerogels has been studied in detail over the past two decades due to its usage in a wide range of low end applications such as thermal insulators, super-capacitors etc., as well as high end applications like particle physics, space explorations. These applications call for control over the properties of aerogels, such as their transparency, density, porosity, pore size, and integrity. However, despite all the past research, controlling properties of aerogels is still not a fully developed science, a lot more research needs to be done.

The literature on silica aerogels does not cover the study of the relation between transparency and cracks in aerogels – which can be a key factor in making aerogels for many applications. Hence, optimization of the transparency and integrity of the aerogels in order to obtain high transparency and low cracks was attempted in this thesis.

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CHAPTER 1. LITERATURE REVIEW

1.1 Introduction

The process of making silica aerogels has been studied in detail over the past two decades due to its usage in a wide range of low end applications such as thermal insulators, super-capacitors etc., as well as high end applications such particle physics, space explorations, etc. (Refer Section 1.1.1 – Applications). And these applications call for control over the properties of the aerogels, such as their transparency, density, porosity, pore size, and integrity.

The typical aerogel making process consists of the following steps: forming a solution (*sol*), gelation (*gel*), aging, and drying. The gel making involves preparing a silica based gel using precursors that act as the source of silica and polymerizing the precursor to form an intricate nano-scale network of silica molecules and agglomerates, whose voids are filled with a liquid (could be water, solvents like ethanol, methanol, acetone, etc.), thus forming a gel. The gel drying process involves supercritically drying the liquid in the gel. This is done because under normal conditions, when the gel is dried, it shrinks due capillary pressure applied on its pores by the liquid in the gels. This capillary pressure leads to mechanical damage of the gel as the tension can reach up to 100-200 MPa [1].

1.1.1 What is an aerogel?

Aerogels can be transparent, opaque, and colorless or have different colors such as red, black etc. depending on the precursors and additives used to make it. The most common type of aerogel is silica aerogel which is transparent and colorless, while another common type of aerogel is carbon aerogel which is completely opaque and black. An aerogel has a porous structure similar to a sponge, except the pores are in the range of 2-100nm [2] in size and much more densely

packed resulting in the aerogels being extremely light weight (see Figure 1). Aerogels are usually very brittle.

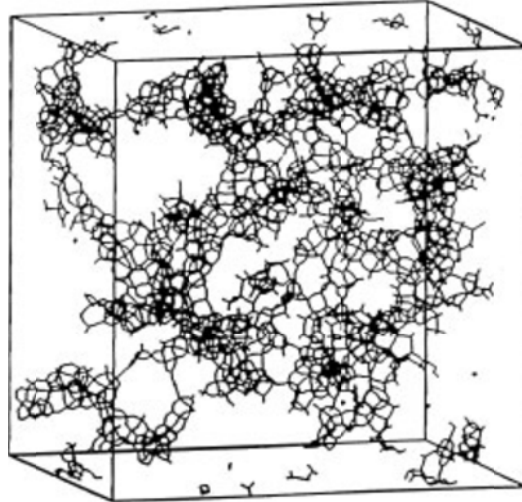


Figure 1. Schematic structure of a silica aerogel [3]

1.1.2 Unique properties of aerogels

Aerogels are not naturally occurring materials and have very unique properties compared to any other type of materials. They have very high porosity (as high as 99%), and pore sizes in the range of 2 to 100nm, with the pores being open. Because of such a porous structure, they have extremely large surface areas (as high as 1000 m²/g) [2]. Some aerogels like silica aerogels also have very good thermal insulation properties due to very low heat transfer. The detailed physical properties of silica aerogels is given in Table 1.

1.1.3 Application

Due to their unique properties, aerogels have been used in a wide variety of applications. These applications of aerogels have been categorized according to the major type of property of the aerogel being used.

Table 1. Physical properties of silica serogels [4]

Property	Value	Comments
Apparent density	0.003-0.5 g/cm ³	Most common density is 0.1g/cm ³ ($\rho_{air} = 0.001\text{g/cm}^3$)
Inner surface area	500-1500 m ² /g	As determined by nitrogen adsorption/desorption A cubic centimeter of an aerogel has about the same surface area as one soccer field)
Solid percentage in volume	0.13-15 %	Typically 5 % (95 % free space)
Mean pore diameter	20-150 nm	As determined by nitrogen adsorption/desorption (varies with density)
Primary particle diameter	2-5 nm	Determined by transmission electron microscopy
Index of refraction	1.007-1.24	Very low for solid material ($n_{air} = 1.004$)
Thermal tolerance	Up to 500 °C	Shrinkage begins slowly at 500 °C, increases with increasing temperature. Melting point is ~1200°C
Poisson's ratio	0.2	Independent of density, similar to dense silica. Determined using ultrasonic methods.
Young's modulus	0.1-300 MPa	Very small (<10 ⁴) compared to dense silica
Tensile strength	16 kPa	For density of 0.1 g/cm ³
Fracture toughness	0.8 kPa.m ^{1/2}	For density of 0.1 g/cm ³ . Determined by 3-point bending
Dielectric constant	1.1	For density of 0.1 g/cm ³ , very low for a solid material ($k_{air} = 1$)
Acoustic impedance	10 ⁴ Kg/m ² .s	Determined using ultrasonic methods al KHz frequency.
Sound velocity through the medium	20-800m/s	100 m/s for density of 0.07 g/cm ³ , one of the lowest velocities for a solid material
Optical property	Transmittance>90% (630nm)	Transparent-blue haze
Thermal conductivity	0.02 W/mK (20°C)	Very low thermal conductivity. 2 cm slab provides the same insulation as 30 panes of glass

Aerogels have very high surface area due to their high porosity and open pore structure.

Which makes them ideal as catalysts in chemical reactions [5, 6, 7]. The high porosity and surface area of aerogels has also lead to its application as filters [8] and desiccants [9].

Carbon aerogels are electrically conductive and have high surface area, which lead to their application as energy storing devices known as 'aerocapacitors'. These aerocapacitors have high-energy density and uses an electrochemical double-layer capacitor made of carbon aerogels [10]. Such capacitors can release energy much faster than conventional batteries.

Carbon aerogels have also been used in capacitive deionization process, in which stacked carbon aerogel electrodes are used to purify contaminated water by generating an electric field between the carbon aerogel electrodes. This process is cost-effective, since it uses only electricity and no other additional chemicals to operate. [11]

The transparency of silica aerogels along with their extremely high thermal insulation has made them very attractive for use in providing additional insulation in double walled windows where the silica aerogels could be inserted between the two panes in the window [12, 13].

Silica aerogels can also be used to prepare very pure silica based glass by the process of sintering [8].

Modern research (starting from 1980s) on silica aerogels was accelerated by the need for silica aerogels in Cherenkov detectors. Cherenkov detectors are used in particle physics related experiments where Cherenkov light passing through transparent materials is measured. The best way to do this is called 'threshold' type Cherenkov detector which requires the transparent material to have a very low refractive index (1.007 – 1.03). And silica aerogels were found to be the best fit this purpose due to their low refractive indices.

Aerogels have been found to exhibit some of the lowest thermal conductivities among all solids. This is because of the unique structure of the aerogel which forces the heat to travel through a very narrow and labyrinth chain of the solid skeleton to reach the other side. Silica

aerogels have a thermal conductivity as low as 0.013W/m.K to 0.004W/m.K. This makes it very attractive for a wide variety of insulation applications such as insulation in architecture, refrigerators, vessels etc. [14, 15]

Aerogels also have very unusual acoustical and mechanical characteristics because of their unique structure. The velocity of sound in an aerogel can be as low as 30m/s which are much lower than the velocity of sound in air (343 m/s). Since aerogels have very low density as well as very low sound velocity in the material, they have the lowest mechanical impedance of all solids (mechanical impedance is a product of density and velocity of sound in the material). This low value of mechanical impedance of aerogels is used in air-coupled piezoelectric transducers, where lower impedance results in better performance of the transducers [16, 17]. Aerogels are also used for sound absorption [17].

Silica aerogels are very good electrical insulators and also have the lowest dielectric constant for a solid material (dielectric constant $k = 1.1$), which makes it useful in electronics where the signal propagation speed increases with the decrease in the dielectric constant of the surrounding electrical insulation [18]. Silica aerogels can also be used as high voltage insulator in bulk form [18]. Carbon aerogels can be used in batteries and super-capacitors [10].

Aerogels have been used to capture micron sized space dust in Space Shuttle experiments [19]. Aerogels were also used as insulators in the Mars Rover [20]

1.2 Synthesis of aerogels

1.2.1 Sol-Gel chemistry

Synthesis of aerogel starts with forming a gel that has porous structure whose pores are filled with liquid. When the liquid in the pores are replaced with air without altering the network structure of the gel, an aerogel is obtained.

Nicola et al. [3] explains how the gel is formed from a 'sol'. In a sol, particles of 1-1000 nm diameter are dispersed in a liquid. The gel is formed from a sol by hydrolysis and then condensation of the particles on the sol. The resulting gel has a sponge-like porous structure with the polymerized particles forming a skeletal network and the pores formed by the skeletal network filled with liquid.

1.2.2 Silica alcogel

The original process of making silica gels developed by S.S. Kistler in 1931 used to take weeks to produce each sample of aerogel which was too long a period when research on aerogels was rekindled decades later in 1962 by a French group working with S.J. Teichner. This led to the nervous breakdown of one of his students who was working with him on this project, as he was worried that it would take years to finish his thesis at that rate. However, by the time he recovered a new and much quicker method was developed that used Tetramethoxysilane (TMOS), which was dissolved in methanol and hydrolyzed with water to form a silica gel [21].

The gels prepared to make silica aerogels, is most commonly derived from tetraalkoxysilanes $\text{Si}(\text{OR})_4$ precursors [3] which are hydrolyzed (a reaction in which H_2O molecule splits into H^+ cations and OH^- anions and reacts with a different molecule by breaking it down, in this case - the reaction of Si-OR with water to form Si-OH and ROH) and then condensed (a

reaction in which two molecules react with each other to form a single large molecule and smaller residual molecule, which is usually H₂O. e.g. the reaction of Si-OH and Si-OH to produce Si-O-Si polymer and H₂O) in a solution of water, alcohol and catalysts (acidic and/or basic). The chemical reactions occurring during the gel formation are shown in Figure (2).

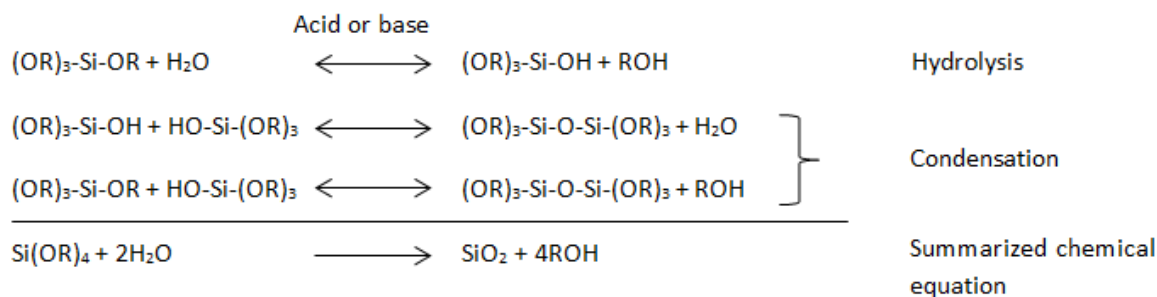


Figure 2. Chemical reactions during alcogel formation [3]

Tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) are two of the most common precursors used for making silica aerogels. Wagh et al. [22] compared silica aerogels derived from TMOS and TEOS and found that TMOS based silica aerogels had higher transmittance than TEOS based aerogels. Also, TMOS based aerogels had narrower pore size distribution and larger pore radii than TEOS based aerogels. Methytrimethoxysilane (MTMS) was used by Rao et al. [23] as a co-precursor along with TMOS to study the optical properties of the resulting hydrophobic silica aerogels, and it was found that the transmittance of silica aerogels decreased with increase in MTMS concentration with respect to TMOS. Xu et al. [24] used polyethoxydisiloxanes (PEDS) as precursor to produce ultralow density silica aerogels.

Two-step process is a slightly different process of gel preparation in which the precursor is partially hydrolyzed and partially condensed in the first step with sub-stoichiometric amount of water and acidic catalyst. In the second step, the precursor is fully hydrolyzed with water and

basic catalyst [25]. Bhagat et al. [26] studied the effect of processing parameter on silica aerogels produced by two-step process and found that higher acid concentrations and lower basic concentrations increased transparency of the aerogel, but also resulted in cracking of the aerogel. Increase in ethanol/TEOS molar ratio also resulted in increased transparency of the aerogel.

Evaggelos et al. [27] studied effect of different types of Tetraalkylammonium fluoride catalysts on the properties of silica aerogels. It was found that tetrabutyl and tetraoctyl ammonium fluoride provides highest transparency of the silica aerogel.

It has been found that aging solutions and aging periods affect the properties of aerogels by affecting the Oswald ripening of the silica structure in the gel [2]. Oswald ripening is a phenomenon in which silica particles are transferred within the gel to be deposited on the necks in the silica structure. Einarsrud et al. [28] studied the effect of aging conditions on the effect of silica aerogel properties and found that, aging in water and water+ethanol solutions result in increased stiffness, strength and permeability of aerogels, which in turn result in crack-free aerogels after supercritical drying.

1.2.3 Supercritical drying

Supercritical drying is one of the most common methods of producing aerogels from gels by replacing the liquid in the pores of the gel with air. When the liquid in the pores of a gel is evaporated under normal conditions, the capillary forces acting on the skeletal network of the gel by the liquid leads to mechanical failure of the skeletal network (See Figure 3). In order to avoid this failure, the capillary forces applied by the liquid would have to be eliminated. This can be achieved by bringing the liquid in the gel to a supercritical state (see Figure 4) by increasing temperature and pressure of the liquid (the temperature and pressure required to bring a liquid to supercritical state depends on the type of liquid).

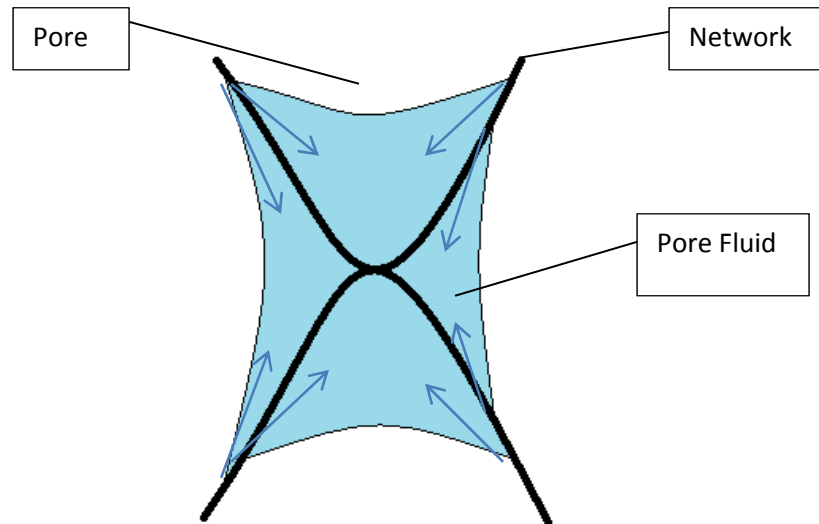


Figure 3. Representation of the contracting surface forces in pores during drying

Supercritical fluid is a phase which occurs when a liquid is compressed and heated above its critical point (See Figure 4). At this state, the fluid displays properties of both a liquid as well as gas. The supercritical fluid has solubility properties similar to that of a liquid while at the same time it exhibits no capillary forces, just like a gas. Also, any type of supercritical fluid can be dissolved in any other type of supercritical fluid; just any type of gas can mix with any other type of gas.

The liquid in a gel (used for producing silica aerogels) mostly consist of water and alcohol. The temperatures and pressures required to bring either water or alcohol (mostly ethanol or methanol) are extremely high – supercritical condition for water is 374°C and 22063.22 Kpa (3200 psi), ethanol is 190.9°C and 6140.264 Kpa (890.57 psi), and methanol is 189.6°C and 8085.758 Kpa (1172.74 psi). In the case of water the conditions required are too high, requiring very robust and expensive autoclaves, whereas the conditions required to bring ethanol and methanol to supercritical state simply makes it dangerous (In 1984, a 3000 liter autoclave at the laboratory of

Airglass using alcohol based supercritical drying process exploded - destroying the entire facility). To avoid such dangerous and expensive methods of performing supercritical drying, the liquid in the gels could be replaced with liquid CO₂ whose supercritical conditions are 31.1°C and 7384.285 Kpa (1071 psi), which is much safer and cheaper to achieve [29]. Tewari et al. [30] first came up with this process of replacing methanol in the aerogel with liquid CO₂ in order to drastically reduce dangers involved in the supercritical drying process.

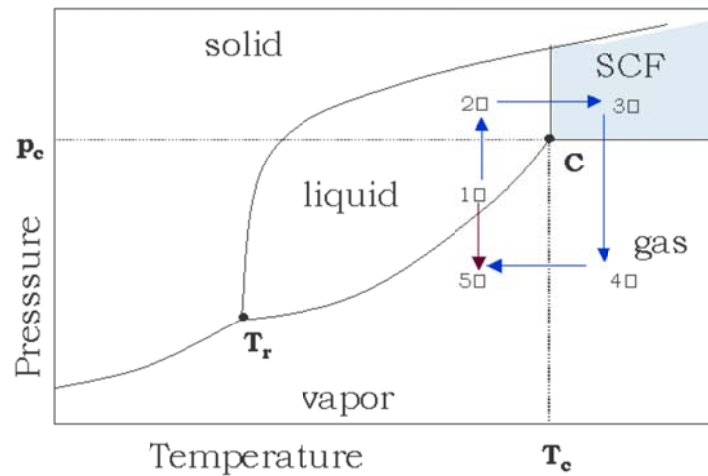


Figure 4. Scheme of the pressure and temperature variation on the solvent phase diagram during a gel supercritical drying process. The shaded area represents the supercritical region (SCF), where C is the critical point; T_r represents the triple point, and 1 to 5 are random points in the phase diagram [4]

While ethanol and methanol are miscible with liquid CO₂, water is not [29]. Hence the liquid in the gel would first have to be fully replaced with very pure ethanol (ethanol being cheaper than methanol) in an ethanol bath and then the ethanol in the gel can be replaced with liquid CO₂ inside the autoclave

Rogacki et al. [1] studied the effect of diffusion rate of ethanol into liquid CO₂ on cracking of silica aerogel. In the experiment they performed the gel solution was prepared with TEOS:H₂O:EtOH:NH₄OH molar ratio of 1:6:6:(5 X 10⁻⁵), aged for 80 days and placed in an autoclave with a volume of 60 ml. The gel size was 36 X 10 X 10 mm³. The starting temperatures were 20°C and 25°C. Once the gel was placed in the autoclave, the excess ethanol was removed in the first 15 min. Then the slow draining of ethanol+liquid CO₂/siphoning of liquid CO₂ was done with varying durations ranging between 15-90 min. Then the system was heated up to 40°C for 15 min, which brought the CO₂ to supercritical state. Next the pressure in the autoclave was reduced to atmospheric pressure over a period of 15 min.

Zoran et al. [31] studied the effect of diffusion rate of methanol into liquid CO₂ on cracking of silica aerogel. In the experiment they performed, the gel solution was prepared with TMOS:H₂O:MeOH:NH₄OH molar ratio of 1:4:6:0.01, aged for 10 days and placed in an autoclave with a volume of 100 ml. The gel size was diameter 14mm and 40mm height. The starting temperatures were 20°C and 25°C. Once the gel was placed in the autoclave, the excess ethanol was removed in the first 30 min. Then the slow draining of ethanol+liquid CO₂/siphoning of liquid CO₂ was done with varying durations ranging between 30-120 min. Then the system was heated up to 40°C for 15 min, which brought the CO₂ to supercritical state. Next the pressure in the autoclave was reduced to atmospheric pressure over a period of 15 min.

The resulting aerogels consist of transparent zone and damaged zone. The damaged zone is caused due to unsteady-state diffusion of solvent (ethanol or methanol) and liquid CO₂. The unsteady state diffusion occurs when solvent and liquid CO₂ mixture is below the binary critical curve where they are not miscible and exist in two separate phases, which leads to capillary forces inside the gel during the diffusion of solvent and liquid CO₂.

When the diffusion rate is too high, some of the ethanol/methanol still remains inside the aerogel and if its concentration is >5%, the mixture would not reach supercritical state when heated to 40°C (which is required for 5% concentration [1, 31]). The place where the ethanol/methanol concentration remains >5% forms the damaged zone.

The damaged zone depends on the distribution of concentration in the gel during the diffusion of CO₂. For simple geometries, the shape and size of the damaged zone can be predicted as a function of diffusion time. The papers [31, 1] however do not precisely define what a damaged zone is nor do they mention how they have been measured.

1.3 Objective

1.3.1 Problem statement

During initial attempts at making silica aerogels in order to gain some expertise, it was noticed that almost all aerogels were cracked. It was also seen that the concentration of catalysts and ethanol during the gel making (TEOS based) seemed to affect the cracking and transparency of the aerogels (Refer to section 3.3). However there seems to be no literature available to relate the level of cracking with molar ratios of starting chemical mixtures, which makes it impossible to make an educated estimate of what combination of the starting chemicals needs to be used to produce crack-free aerogels with maximum possible transparency.

1.3.2 Research objective

In applications such as Cherenkov detectors the Cherenkov light passing through silica aerogel is measured which requires the silica aerogel to be very transparent and at the same time have no cracks either, so that the light passing through the aerogel is not disturbed and thus affect their measurement. In space shuttle experiments the silica aerogels are used to capture space

dust because when the dust gets stuck in the aerogel, it leaves a trail behind it inside the aerogel thus making it easy to locate the dust particles and remove them from the aerogel. Obviously the aerogel would have to be very transparent in order to locate the dust particle and at the same time it should also be crack-free so that dust particles striking the aerogels don't alter their trajectory and depth of penetration. The literature on silica aerogels, however, does not cover the study of the relation between transparency and cracks in aerogels. Hence, optimization of the transparency and integrity of the aerogels in order to obtain high transparency and low cracks was attempted.

1.3.3 Research tasks

The literature on production of silica aerogels has already shown clear relationship between transparency of aerogels and the molar ratio of starting material. Initial attempts at making silica aerogels had shown that the level of cracking in aerogels is also affected by the molar ratio of starting materials. In order to find a relationship between transparency and integrity of the aerogels, control of the transparency of aerogels by controlling the molar ratios of the starting materials was attempted, and its effect on the cracks of the resulting aerogels was observed. Thus the relationship between transparency and cracks in the aerogels were observed as well.

It has been observed that diffusion rate of liquid in gel with liquid CO₂ affects the level of cracking in aerogels [1, 31]. One of the research tasks in this work is to see how the diffusion rate affects cracking and transparency of the aerogels.

CHAPTER 2. TMOS BASED AEROGELS

2.1 Phase 1: Slow and quick diffusion

2.1.1 Aim of experiment

In this experiment, the study the effects of Methanol:TMOS ratio and NH_4OH :TMOS ratio on the transparency and integrity of the aerogels is done. Also the effect of diffusion rate of ethanol inside the gel into liquid CO_2 after the gels are placed in the autoclave is also verified.

2.1.2 Background

While there has been a lot of research done on how to control transparency, density, porosity and pore size of silica aerogels, very little research could be found on the factors affecting the formation crack-free/monolithic silica aerogels with any useful quantitative data. The information that has been gathered from literature survey about monolithic/crack-free aerogels suggest that diffusion rate of solvent in the gel into supercritical fluid can affect cracking of the aerogel. This implies, when diffusion rate is very quick (all the solvent is drained out 15 min after liquid CO_2 has been siphoned into the autoclave over a period of another 15 min) the resulting aerogels were found to be completely damaged, and when the diffusion rate of the solvent is slow (all the solvent is drained out 15 min after liquid CO_2 has been siphoned into the autoclave over a period of another 90 min) the aerogel was found to be monolithic without any cracks [1]. Another factor to be taken care of in order to obtain crack-free aerogels is the autoclave pressure before its heating for supercritical phase so that the liquid does not turn into vapor before achieving supercritical state (if the autoclave pressure is too low, the liquid CO_2 might directly turn into gas before turning into supercritical state) [32]. It was also observed that narrower pore size distribution reduces differential pressures during the extraction of solvent in supercritical phase

[33]. The permeability of the gel was also found to be a factor influencing the monolithicity of the aerogel, as higher permeability leads to lesser cracking [34].

The best solvent for TMOS would be methanol, as it is miscible with both TMOS and H₂O, thus facilitating the reaction between TMOS and H₂O [35].

The effect of molar ratio of TMOS:H₂O:MeOH:NH₄OH on the properties of silica aerogels has been studied to some extent in the past, and it has been found that the molar ratios of methanol:TMOS and NH₄OH:TMOS affect the properties of the aerogel such as transparency, density, integrity, porosity etc. [33]. But the exact relationship between the molar ratios and integrity of the aerogels is still unclear, although it can be said from our own experiments in the past that NH₄OH concentrations directly affect the transparency of the aerogel.

While the molar ratio of TMOS:H₂O have been observed to be consistent at - 1:4, the molar ratios of methanol:TMOS and NH₄OH:TMOS would have to be further investigated. The molar ratio of TMOS:H₂O:MeOH:NH₄OH suggested by some sources for achieving good transparency and integrity of the aerogels are shown in Table 2.

Table 2. Molar ratios of starting solutions for good transparency and integrity of silica aerogels

TMOS	H₂O	MeOH	NH₄OH	
1	4	8.75	0.058	[32]
1	3.3	7.3	0.01	[2]

There are two major types of catalysts that are used in the gel making process – acidic and basic. These acidic and basic catalysts help hydrolysis of the precursor [33, 32]. Only the basic catalyst which in case of TMOS precursor would be NH₄OH was used. NH₄OH was used because it has been well established in the aerogel making process, thus providing a large database to

compare the results of the current experiments with (if necessary). While, the other types of catalysts that have been used/studied have not yielded any significant improvement in the strength or transparency of the silica aerogels [2, 36, 35].

In the present case it was decided to not pursue any research in effect of aging as past experiments on aging solutions have provided insufficient evidence to suggest any relationship between the aging solution and the transparency or integrity of the aerogels.

The aging solution was fixed to be methanol and the optimum aging period set at 48 hours [2]. Further research might be done in the future on the effect of aging while studying the permeability, porosity and pore size of the aerogels.

2.1.3 Design of experiment

The most important factors affecting the transparency and integrity of the aerogels that were investigated upon are - the molar ratios of methanol:TMOS and NH_4OH :TMOS, and the diffusion rate of the liquid in the gel and liquid CO_2 . Hence a set of experiments studying the effects of these factors on the transparency and integrity of the aerogels were conducted.

It was decided to conduct an experiment in which 3 molar ratios of methanol:TMOS and 3 molar ratios of NH_4OH :TMOS was used, which would require making 9 gels with all the combinations of the molar ratios. Another set of 9 gels with the same combination of molar ratios were made to check for consistencies in the gel making, and supercritically dry all 18 gels at once with a slow rate of diffusion (removing the solvent in the autoclave gradually over a period of 6 – 10 hours) of the liquid in the gels. The same experiment was repeated again to check for consistency in the drying process and reproducibility.

The precursor used was TMOS, molar ratio of TMOS:H₂O was 1:4, aging solution was methanol, and the aging time was 48hrs. Table 3 shows the molar ratio combinations of TMOS, methanol, NH₄OH and H₂O used. (Refer to Section A5.2 in the Appendix for details of chemicals used)

Table 3. Molar ratio combinations of TMOS, Methanol, NH₄OH, H₂O used for the slow diffusion experiment

Gel No.	Molar Ratios			
	TMOS	H ₂ O	Methanol	NH ₄ OH
1	1	4	8	0.005
2	1	4	12	0.005
3	1	4	16	0.005
4	1	4	8	0.025
5	1	4	12	0.025
6	1	4	16	0.025
7	1	4	8	0.05
8	1	4	12	0.05
9	1	4	16	0.05

Next, 4 sets of gels with 2 molar ratios (highest and lowest molar ratios used in the previous set of experiments) of methanol:TMOS and NH₄OH:TMOS were made. After placing them in the autoclave, the liquid in the gels was quickly diffused into liquid CO₂ (removing all the solvent in the autoclave right at the beginning). This experiment is done to observe the effect of diffusion rate on the monolithicity and transparency of the gels. Table 4 shows the molar ratio combinations of TMOS, methanol, NH₄OH and H₂O used.

2.1.4 Experimental procedure

Silica alcogels were prepared by mixing TMOS, water, methanol and NH₄OH (as discussed in the Design of experiments section) in syringes such that a total of 5 ml of solution is formed. Once the sol-gel solidified into a gel, methanol was poured on top of the gel for aging. The aging

process was 72 hours long. After aging the gels were removed from their syringes and placed in ethanol bath for complete replacement of liquid in the gels with pure ethanol. The ethanol bath was replaced twice a day for 3 days, at the end which, the gels were placed in the autoclave. The autoclave was then filled with ethanol until the ethanol level rose above the gels inside the autoclave. The autoclave was then filled with liquid CO₂ and then ethanol-liquid CO₂ exchange was done. For quick diffusion, the buffer ethanol in the autoclave was immediately removed within 1.5 hours, whereas for the slow diffusion the buffer ethanol was removed over a period of 8 hrs. After the removal of buffer ethanol, the liquid CO₂ in the autoclave was replaced twice a day until no more ethanol was recovered, and then two extra liquid CO₂ exchanges were done (to ensure not even a small amount of ethanol remains in the gels). Then supercritical drying of the gels was done to obtain the aerogel samples.

Table 4. Molar ratio combinations of TMOS, Methanol, NH₄OH, H₂O used for the quick diffusion experiment

Gel No.	Molar Ratios			
	TMOS	H ₂ O	Methanol	NH ₄ OH
1	1	4	8	0.005
2	1	4	16	0.005
3	1	4	8	0.05
4	1	4	16	0.05

The transparency of the gels were measured using a UV-Visible light spectrophotometer (see Figure 5 and 6) (UV-2501PC, by Shimadzu). The specifications of the spectrophotometer used are given in Table A2, in Appendix.



Figure 5. UV-VIS Spectrophotometer

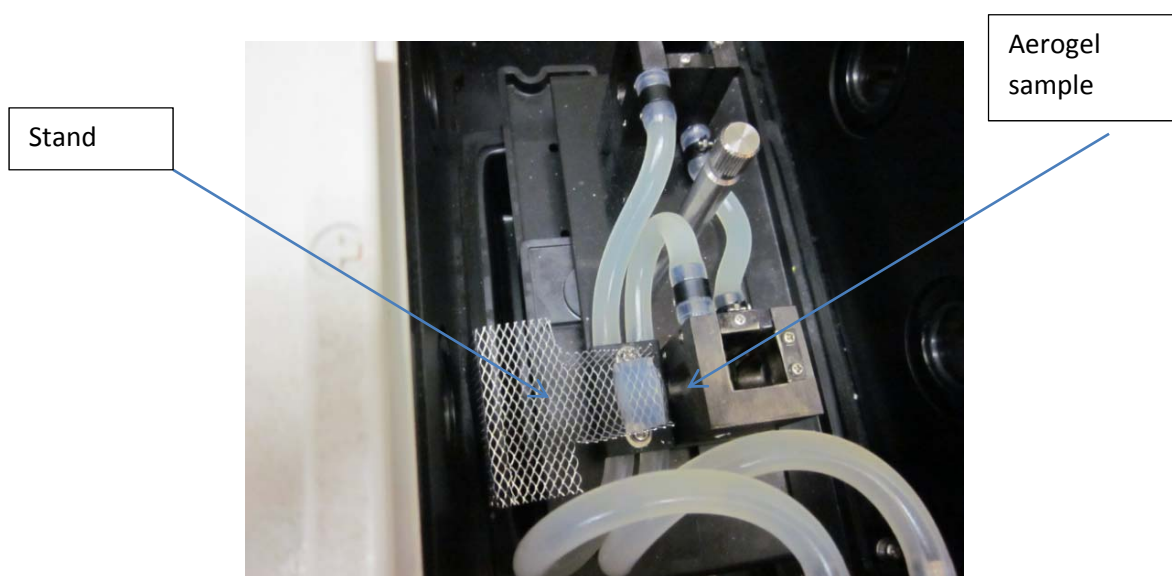


Figure 6. Inside view of UV-VIS spectrophotometer

The integrity of the aerogels is measured by quantifying the cracks in the aerogels. This is done by first taking pictures of the aerogels. Then Corel Photo-Paint® software package is used to convert the pictures to black and white – which highlights the cracks in the aerogels in black. Next,

software package known as Pixcavator[®] by Dr. Saveliev which is designed to analyze images and extract meaningful information from it is used to measure the black pixels in the aerogels.

The UV-VIS spectrometer used to measure the transparency of the aerogels uses light at varying wavelengths from 200 nm to 800 nm at an increment of 0.5 nm and measures the absorbance of the aerogel at each of the 1200 wavelengths. The formula to convert absorbance to transmittance is given by Equation 1.

$$\text{Absorbance} = -\log_{10}(I_o/I) = -\log_{10}(\text{transmittance}) \quad (1)$$

where,

$$\text{Transmittance} = \text{output intensity}/\text{input intensity} \quad (2)$$

An example of one of the transparency measurement data obtained for one of the aerogels is given in Figure 7.

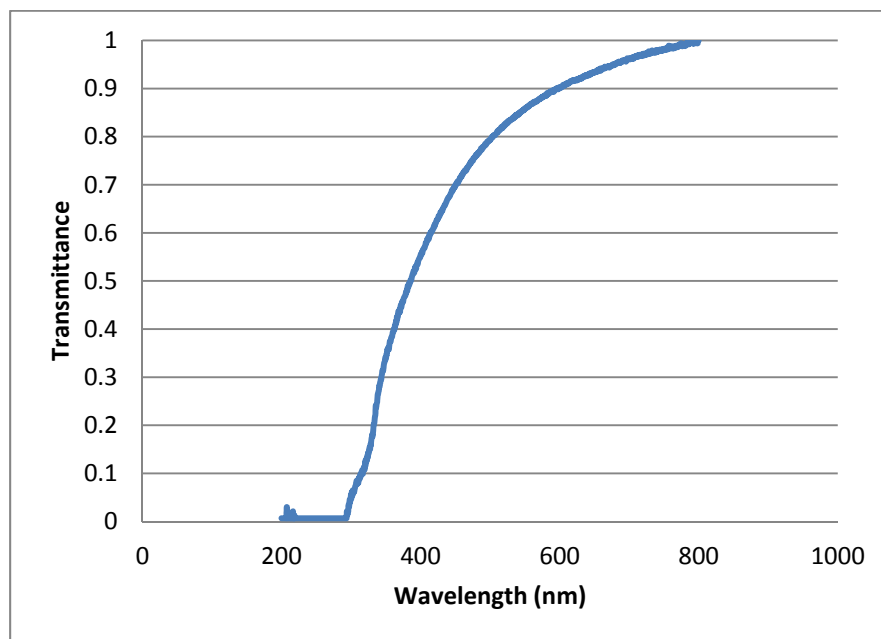
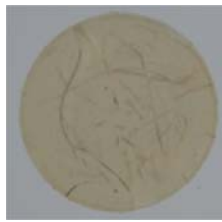


Figure 7. Example of transmittance measurement obtained by UV-VIS spectrophotometer

The average transmittance (see Equation 3) is calculated by integrating the area under the curve of transmittance between the wavelengths of 35nm to 750nm (which is the visible range of light) and dividing it by (750-350). The integration for area under the curve is done by doing a summation of (transmittance at each wavelength X 0.5 nm). The 0.5nm is the interval between each wavelength at which the transmittance is measured.

$$\text{Average transmittance} = (\sum \text{transmittance at each wavelength} * 0.5) / (750 - 350) \quad (3)$$

In order to quantify the cracks in aerogels, pictures were taken for each aerogel sample from 3 angles as shown in Figures 8 (a), (b) and (c)



(a)



(b)



(c)

Figure 8. (a) Top view; (b) Side view; (c) Side view with 90 degree rotation

The setup for taking the pictures is shown in Figure 9.

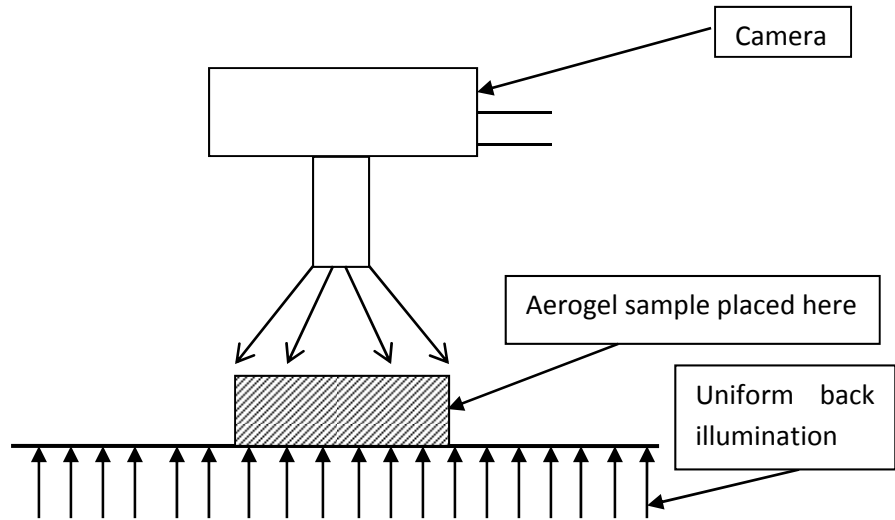


Figure 9. Schematic diagram of the setup for taking pictures of aerogel samples

Once the pictures of all the samples were taken, they were opened in Corel Photo-Paint X5®, where the pictures were shrunk to 25% of its original size. Next the images were cropped into a 15"x15" square and saved. Then the images were converted to Black and White-> Line Art -> line art intensity was set as required for each picture so that the resulting black and white picture represents the cracks as closely as possible. Then all those parts of the black and white image which do not represent the cracks were erased, and the file saved under a different name (See Figure 10). Then the file was saved in a .bmp file.

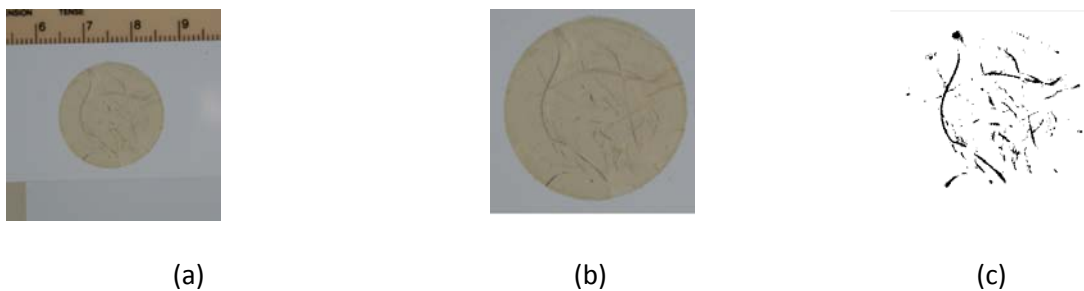


Figure 10. (a) Image from the camera, (b) Image after cropping, (c) Image after converting to Black and White

The .bmp file was then opened in Pixcavator®, whose settings were set as shown in Table

5.

Table 5. Pixcavator® settings

Size	0	Average Contrast	0
Maximal Contrast	0	Intensity, Dark	255
Border Contrast	0	Intensity, Light	0

The area of the dark objects was recorded, while excluding the light objects (see Figure 11). And for each aerogel, the average surface area from the images of the three angles were calculated in an excel file and saved.

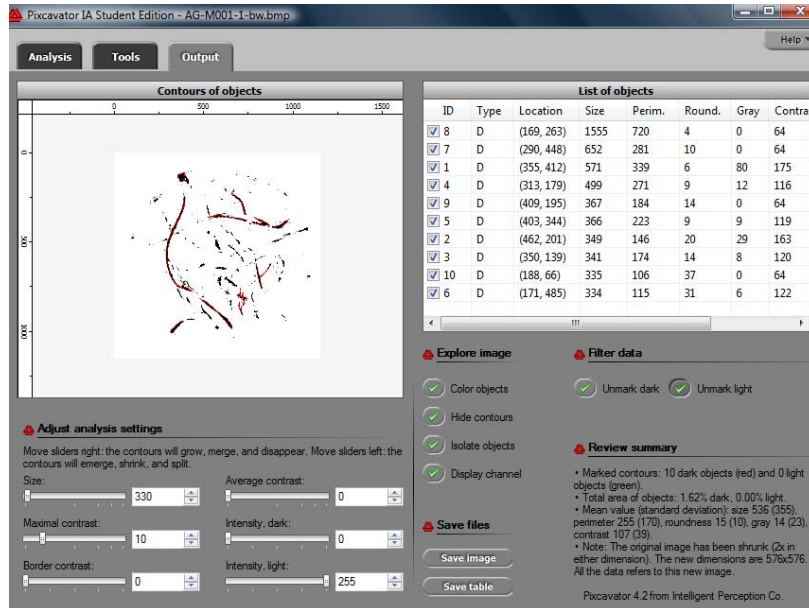


Figure 11. Analysis of a Black and White image of an aerogel sample by Pixcavator®

2.1.5 Experimental results and discussion

The transparency values aerogels for each combination of $\text{NH}_4\text{OH}:\text{TMOS}$ and methanol:TMOS molar ratio obtained by slow diffusion are shown in Table 6 and for each combination of $\text{NH}_4\text{OH}:\text{TMOS}$ and methanol:TMOS molar ratio obtained by quick diffusion are shown in Table 7.

Table 6. Transparency values for aerogels obtained by slow diffusion

Molar Ratios		Transmittance*				Normalized over 350– 750 nm on the scale from 0 to 1
NH ₄ OH:TMOS	MeOH:TMOS	Run 1	Run 2	Run 3	Average	
0.005	8	319.3917	317.6231	314.6603	317.225	0.3965
0.005	12	292.3113	299.2922	308.0545	299.886	0.3749
0.005	16	261.1733	291.1731	285.763	279.3698	0.3492
0.025	8	357.4568	364.7199	365.0088	362.3952	0.4530
0.025	12	348.0946	344.3134	352.5252	348.3111	0.4354
0.025	16	324.7555	332.5778	334.1206	330.4846	0.4131
0.05	8	369.5774	369.9453	368.318	369.2802	0.4616
0.05	12	360.5553	358.962	361.4996	360.339	0.4504
0.05	16	347.5419	344.1985	339.3877	343.7094	0.4296

* 'Transmittance' value of an aerogel sample is calculated by integrating the transmittance value of the sample measured at each wavelength of light from 350nm to 750nm as shown in Equation 3. The units for this kind of transmittance measurement would be 'nm' (the transmittance is simply a ratio, hence it has no units)

Table 7. Transparency values for aerogels obtained by quick diffusion

Molar Ratio		Transmittance*					Normalized over 350– 750 nm on the scale from 0 to 1
NH ₄ OH:TMOS	MeOH:TMOS	Run 1	Run 2	Run 3	Run 4	Average	
0.005	8	313.4705	329.3278	317.2092	318.535	319.6356	0.3995
0.005	16	295.6713	291.8336	301.7675	294.4932	295.9414	0.3699
0.05	8	365.0223	360.5706	360.5224	365.5727	362.922	0.4537
0.05	16	341.759		354.5269	347.6308	347.9722	0.4350

*'Transmittance' value of an aerogel sample is calculated by integrating the transmittance value of the sample measured at each wavelength of light from 350nm to 750nm as shown in equation 3. The units for this kind of transmittance measurement would be 'nm' (the transmittance is simply a ratio, hence it has no units)

The aerogels obtained by quick diffusion were observed to be extremely cracked as compared to slow diffusion, which negates the necessity to analyze those cracks, as the purpose of making the aerogels with quick diffusion was simply to verify whether there is any significant difference between the cracks occurring in the quick diffusion-aerogels and the slow diffusion-aerogels. The crack measurements for each aerogels obtained by slow diffusion are shown in Table 8.

Table 8. Crack values for slow diffusion

Molar Ratio		Crack Area*			
NH4OH:TMOS	MeOH:TMOS	Image 1	Image 2	Image 3	Average
0.005	8	11244	15852	15121	14072.33
0.005	12	15896	17635	6475	13335.33
0.005	16	4991	4876	4824	4897
0.025	8	6299	21158	27853	18436.67
0.025	12	5407	3686	3181	4091.333
0.025	16	3890	3261	4343	3831.333
0.05	8	9805	11118	6116	9013
0.05	12	3328	7514	5492	5444.667
0.05	16	5822	2069	1750	3213.667
0.005	8	4086	2583	4297	3655.333
0.005	12	2064	4417	7777	4752.667
0.005	16	1677	2786	3368	2610.333
0.025	8	1455	4043	8907	4801.667
0.025	12	8009	5631	9508	7716
0.025	16	667	8618	1974	3753
0.05	8	2963	5504	2908	3791.667
0.05	12	4156	2960	6252	4456
0.05	16	8956	6710	1954	5873.333
0.005	8	4362	5132	10927	6807
0.005	12	3967	2165	3084	3072
0.005	16	2307	1986	589	1627.333
0.025	8	2239	13995	8955	8396.333
0.025	12	7845	5956	5918	6573
0.025	16	4880	32	4366	3092.667
0.05	8	17028	9324	8388	11580
0.05	12	7356	5792	3344	5497.333
0.05	16	5505	5873	3776	5051.333

* Crack area of each sample of aerogel is calculated by averaging the crack area measured from the 3 angles as shown in Figure 7 (a), (b) and (c). The crack measurement is done by counting the dark pixels of the cracks in the sample on Pixcavator®

The interaction plot of methanol:TMOS and NH_4OH :TMOS values for the transparency of the aerogels is shown in Figure 12. The interaction plot of methanol:TMOS and NH_4OH :TMOS values for the cracks (the crack values of samples with same molar ratios were averaged) in aerogels is shown in Figure 13.

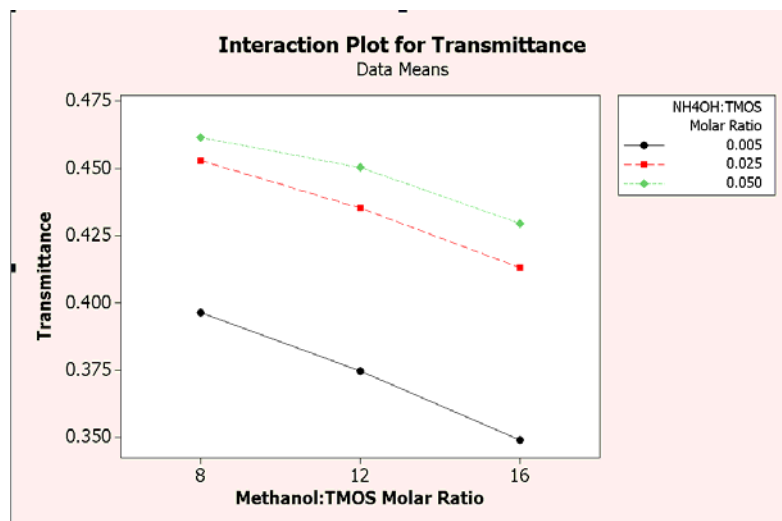


Figure 12. Interaction plot of methanol:TMOS and NH_4OH :TMOS molar ratios for transparency values

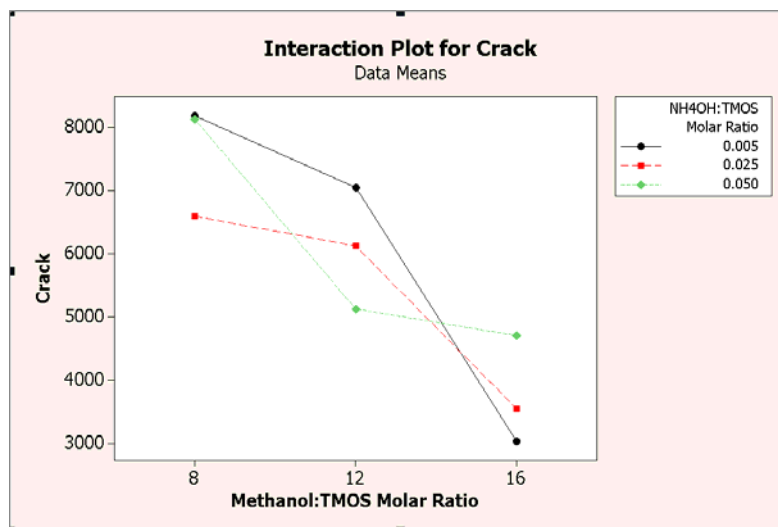


Figure 13. Interaction plot of methanol:TMOS and NH_4OH :TMOS molar ratios for Crack sizes

Figures 12 and 13 show that there is a clear pattern of relationship between transparency v/s methanol:TMOS molar ratio and transparency v/s NH_4OH :TMOS molar ratio. But there is little interaction between NH_4OH :TMOS and methanol:TMOS molar ratios of the aerogels. It can be seen that transparency increases with increase in concentration of NH_4OH , but it decreases with increase in concentration of methanol. However, the relationship between cracks v/s methanol:TMOS molar ratio and cracks v/s NH_4OH :TMOS molar ratio is not as clear as it was with transparency. Still it can be observed that, cracks seem to decrease with increase in concentration of methanol, whereas the effect of NH_4OH on cracks is not obvious. This conclusion is also substantiated by ANOVA analysis done on the data in Minitab® (Refer Appendix). The ANOVA analysis also reveals that there is significant interaction between methanol:TMOS and NH_4OH :TMOS molar ratios on the crack measurements in the aerogels.

The correlation between the transparency values and crack measurements for each aerogel was calculated on Minitab® and the Pearson-Correlation coefficient was found to be 0.199, which means that there is very little correlation between the transparency and integrity of the aerogels.

One possible explanation for the lack of clarity in the effect of methanol:TMOS and NH_4OH :TMOS molar ratios on the crack values is the inherent limitation in accurately measuring the cracks in each aerogel. Also cracking in aerogels occurs due to structural failure of the extremely intricate and complex structure of the aerogels, which makes the effect of methanol:TMOS and NH_4OH :TMOS molar ratios on the intensity of cracking imprecise. Whereas transparency of the aerogels is directly related to the initial chemistry of the solution used to make the aerogels, which leads to very little deviations in the transparency of the aerogels.

Also there isn't any significant difference between the transparency values of the aerogels obtained by slow diffusion and the aerogels obtained by quick diffusion. This shows that the rate of diffusion of ethanol from the gels into liquid CO₂ does not affect the transparency of the aerogels.

2.2 Phase 2: Optimization

2.2.1 Aim of experiment

In order to further optimize the transparency and integrity of aerogels using TMOS precursor, another set of 15 aerogels are prepared to further optimize the transparency by more closely studying the effect of NH₄OH:TMOS and methanol:TMOS molar ratios.

2.2.2 Design of experiment

It was decided to make 15 aerogels with 3 replications, which means 5 aerogels of different of NH₄OH:TMOS and methanol:TMOS molar ratio combinations repeated 3 times. The molar ratio combinations are shown in Table 9.

Table 9. Molar ratios of starting solutions for phase 2 experiments

Molar Ratio		Sample Numbers*		
NH ₄ OH:TMOS	Methanol:TMOS	Run 1	Run 2	Run 3
0.025	16	11	12	13
0.025	20	21	22	23
0.030	18	31	32	33
0.035	16	41	42	43
0.035	20	51	52	53

* The sample numbers is the numbers assigned for each sample of gel prepared – with the first digit of the sample number representing the individual combination of NH₄OH:TMOS and Methanol:TMOS molar ratios of the gels and the second digit representing the replication of each of the combination of NH₄OH:TMOS and Methanol:TMOS molar ratios of the gels

It was also decided to randomize the order in which the 15 aerogels was divided into 2 batches during the gel making process. A random order of the gels to be prepared in each batch was generated and is shown in Table 10.

Table 10. Gel sample distribution in random order for the 2 batches

1 st batch	2 nd batch
13	51*
53	23
33	11
31	41
32	43
21	22
12	42
	52

* The sample numbers is the numbers assigned for each sample of gel prepared – with the first digit of the sample number representing the individual combination of NH₄OH:TMOS and Methanol:TMOS molar ratios of the gels and the second digit representing the replication of each of the combination of NH₄OH:TMOS and Methanol:TMOS molar ratios of the gels

2.2.3 Experimental procedure

The sample preparation was done the same way as in Phase 1, except there is no quick diffusion of buffer ethanol after the gels are placed in the autoclave.

The characterization of cracks and transparency of the aerogels is also exactly the same as it was done in Phase 1.

2.2.4 Experimental results and discussion

The transparency values of aerogels for each combination of NH₄OH:TMOS and methanol:TMOS molar ratio are shown in Table 11.

Table 11. Transparency measurements for phase 2 experiment

Molar Ratio		Transmittance*				Normalized over 350– 750 nm on the scale from 0 to 1
NH ₄ OH:TMOS	MeOH:TMOS	Run1	Run2	Run3	Average	
0.025	16	N/A	312.18	310.81	311.495	0.3894
0.025	20	297.28	306.93	N/A	302.105	0.3776
0.03	18	322.34	323.32	321.09	322.25	0.4028
0.035	16	330.36	327.95	331.23	329.8467	0.4123
0.035	20	321.91	321.56	318.08	320.5167	0.4006

* 'Transmittance' value of an aerogel sample is calculated by integrating the transmittance value of the sample

measured at each wavelength of light from 350nm to 750nm.

The results from crack measurements for each aerogel are shown in Table 12.

Table 12. Crack measurements for phase 2 experiment

Molar Ratio		Crack value*			
NH ₄ OH:TMOS	MeOH:TMOS	Run1	Run2	Run3	Average
0.025	16	N/A	3824.333	3093	3458.667
0.025	20	706	3153	N/A	1929.5
0.03	18	2377.333	4093	4226.667	3565.667
0.035	16	2614	6501	1563.667	3559.556
0.035	20	3669.667	2516.333	2564.667	2916.889

* Crack area of each sample of aerogel is calculated by averaging the crack area measured from the 3 angles as shown in

Figure 7 (a), (b) and (c). The crack measurement is done by counting the dark pixels of the cracks in the sample on

Pixcavator®

From the results derived from Minitab® (refer Appendix), a relationship between crack values and methanol:TMOS and NH₄OH:TMOS molar ratios was derived (Eq. 5), similarly a relationship between transparency values and methanol:TMOS and NH₄OH:TMOS molar ratios was derived (Eq. 4). Also it should be noted that the R² value for the ANOVA analysis on crack values indicate that the model explains only 18.05% of the crack data. This means any further analysis based on the model derive from such a data is not reliable.

Transparency =

$$0.4028 - 0.0058(\text{MeOH}) + 0.0115(\text{NH}_4\text{OH}) - 0.0078(\text{MeOH})^2 + 0.000019(\text{MeOH}) * (\text{NH}_4\text{OH}) \quad (4)$$

Crack =

$$3565.67 - 542.96(\text{MeOH}) + 272.07(\text{NH}_4\text{OH}) - 599.514(\text{MeOH})^2 + 222.625(\text{MeOH})(\text{NH}_4\text{OH}) \quad (5)$$

Using Eq. 4 and 5, optimum values of methanol:TMOS and NH₄OH:TMOS molar ratios were derived using a mathematical solver – Gams[®]. For the optimization, transparency was given a range between 0.3937 to 0.4185 and crack value was minimized. The resulting optimum solution provided by Gams[®] was – transparency = 0.3937, MeOH:TMOS = 20, NH₄OH:TMOS = 0.032, crack = 2621.504.

2.3 Phase 3: Glycerol

2.3.1 Aim of experiment

Since the previous experiments on TMOS based aerogels have failed to eliminate cracking in aerogels, it was decided to use glycerol as a drying control chemical additive (DCCA) which has proved to be effective in preventing cracking of silica aerogels [37]. It has been found that using small amounts of Glycerol (Glycerol:TMOS molar ratio = 0.025) has resulted in aerogels with lower density, lesser shrinkage, transparency and monolithicity. Glycerol also resulted in narrower and more uniform pore size distribution (PSD) [38], which is known to result in lesser cracking of aerogels due to reduced differential pressures during solvent (liquid CO₂) extraction in supercritical phase [33].

2.3.2 Design of experiments

18 aerogels were made with TMOS:methanol:H₂O:NH₄OH molar ratio kept constant at 1 : 12 : 4 : 0.05 and 6 levels of glycerol:TMOS molar ratio varying from 0 to 0.001 with 3 replications of the whole set (see Table 13).

Table 13. The molar ratios and sample numbers of sol-gel solutions for phase 3 experiments

Molar Ratio					Sample Numbers		
TMOS	H ₂ O	MeOH	Glycerol	NH ₄ OH	Run 1	Run 2	Run 3
1	4	12	0	0.05	11	12	13
1	4	12	0.05	0.05	21	22	23
1	4	12	0.2	0.05	31	32	33
1	4	12	0.4	0.05	41	42	43
1	4	12	0.6	0.05	51	52	53
1	4	12	0.8	0.05	61	62	63

2.3.3 Experimental procedure

The sample preparation in this experiment is the same as in Phase 2, with the addition of Glycerol in the sol-gel preparation.

Only the transparency values of the aerogels were measured using a spectrophotometer in the same way as it was done in Phase 1 and Phase 2 experiments, but not the cracks, because most of the aerogels obtained had no cracks at all.

2.3.4 Experimental results and discussion

The aerogels that were produced had negligible cracks in 7 of the 18 made, while the rest had no cracks at all. The transparency values for each of the 18 aerogels is shown in Table 14, along with a graph representing the glycerol:TMOS molar ratio vs. transparency value (see Figure 14).

Table 14. Transparency measurements of aerogels obtained from phase 3 experiment

Molar Ratio	Transmittance*					
	Glycerol:TMOS	Run1	Run2	Run3	Average	Normalized over 350– 750 nm on the scale from 0 to 1
0		359.2399	361.7681	361.7448	360.9176	0.4511
0.05		363.0626	364.7539	363.9961	363.9375	0.4549
0.2		358.1896	351.8159	339.9305	349.9787	0.4375
0.4		354.846	341.9036	342.4334	346.3943	0.4330
0.6		356.6857	336.3333	329.065	340.6947	0.4259
0.8		349.2127	326.0041	303.9639	326.3936	0.4080

* 'Transmittance' value of an aerogel sample is calculated by integrating the transmittance value of the sample measured at each wavelength of light from 350nm to 750nm.

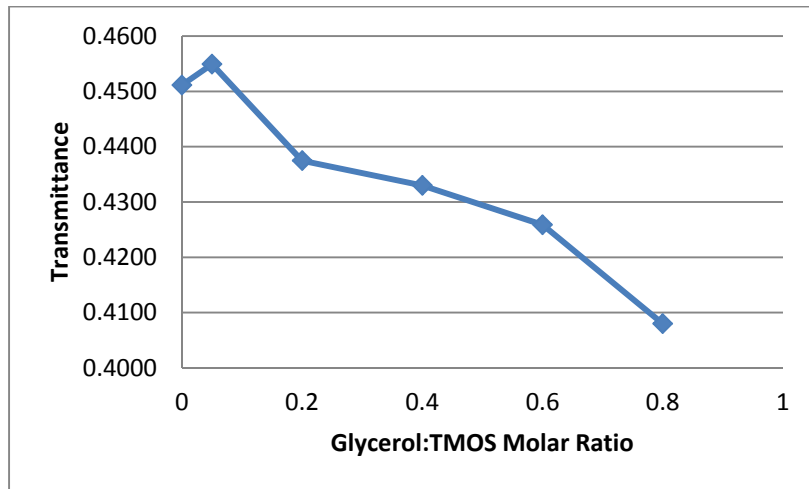


Figure 14. Transmittance versus Glycerol:TMOS molar ratio

The transmittance of the silica aerogels has increased initially and then continues dropping (although not by much) with increase in the Glycerol:TMOS molar ratio. The shape of the graph shown in Figure 14 is very similar to that observed by Kulkarni et al [38].

CHAPTER 3. TEOS BASED AEROGELS

3.1 Introduction

TEOS was used as the precursor for making aerogels at the beginning, since it was much cheaper than TMOS and it was not toxic either

3.2 Using cubical mold

In the initial attempt to make aerogels, a cubical mold made of detachable aluminum walls open on one side was used. Also the walls were lined with 1/16" Teflon® on the inside. The chemical composition for preparing the gel was derived from the gel making procedures shown for TEOS based aerogels in www.aerogel.org

3.2.1 Experimental procedure

To make the aerogels, a catalyst stock solution was first prepared by, mixing 1.852g of NH_4F in 100ml of water, and then adding 18.45ml of 30% concentration NH_4OH to the solution. An alkoxide solution was then prepared by mixing 15ml of TEOS with 33ml of 200-proof ethanol in a beaker. And a catalyst solution was prepared by mixing 21ml of de-ionized water with 33ml of ethanol and 1.1ml of catalyst from stock solution added to the solution. The catalyst solution and the alkoxide solution were poured into the cubical mold. After the gel was set, the entire mold was placed in an ethanol bath. The ethanol bath was then exchanged once every 24hrs for 3 days. Next, the bottom of the mold was removed and replaced with a mesh plate made of steel and the set-up was transferred to an autoclave. Then ethanol was poured into the autoclave until the mold was submerged in ethanol and liquid CO_2 was siphoned into the autoclave. Approximately 50 ml of ethanol was drained twice a day until no more ethanol was drained. Then supercritical drying was done.

3.2.2 Result and discussion

A white silica powder was derived, with no signs of any aerogel (cracked or otherwise)

3.3 Using Teflon® mold

In order to be able to remove the gel from the mold without damaging the gel, a Teflon® mold was used. The Teflon® mold consisted of 2" inside diameter, 2" high Teflon® cylinder and a 2" diameter plunger.

3.3.1 Experimental procedure

The gel solution prepared the same way as was done in section 3.2.1, except all quantities were decreased to 1/3rd and mixed in the Teflon® mold. After the gel was set, ethanol was poured over the gel in the mold for aging. The gel was aged for 24hrs. After the aging, the gel was removed by pushing the plunger from the bottom and then sliding the gel from over the plunger. Next, the gel was placed in an ethanol bath and the bath was exchanged twice a day for 6 days. Then the gel was placed in an autoclave after which all procedures were performed similar to what has been mentioned in section 3.1.1.

3.3.2 Result and discussion

A translucent aerogel was obtained, which had a few large cracks through its body.

3.4 Silbond® based aerogels

Silbond H-5® is a commercially available readymade gel precursor made of pre-polymerized TEOS. The gels prepared by such pre-polymerized TEOS are known as 'two-step' acid-base catalyzed gels (since the pre-polymerized TEOS is made from ethanol, sub-stoichiometric amount of water and an acid catalyst, which is later dissolved in ethanol and water in basic

conditions) [39]. The usage of Silbond® was also found to result in smaller and narrower pore size distribution.

3.4.1 Aim of experiment

This experiment is performed to study the effect of concentration of NH₄OH, aging solutions, polyethylene glycol (PEG) on the transparency, porosity, and integrity of the aerogels. PEG was used because it is known to increase the strength of the solid structure of the aerogel when added in small quantity in the initial solution used to make gels [40].

3.4.2 Design of experiment

The combinations of different levels used to make the 18 gels are shown in Table 15.

Table 15. Volume of chemicals used to make each of the 18 gels for Silbond® based experiment

	Sample Number	Silbond H5® (ml)	EtOH (ml)	H2O (ml)	NH4OH (ml)	PEG 5000 (mg)	Aging Solution/conditions
1	AG-E006	1.25	1.25+0.875	1.875	0.003	0	Ethanol for 72 hrs
2	AG-E007	1.25	1.25+0.875	1.875	0.003	0	20% H ₂ O/Ethanol for 27 hrs
3	AG-E008	1.25	1.25+0.875	1.875	0.003	0	20% H ₂ O/Ethanol for 72 hrs
4	AG-E009	1.25	1.25+0.875	1.875	0.013	0	Ethanol for 72 hrs
5	AG-E010	1.25	1.25+0.875	1.875	0.013	0	20% H ₂ O/Ethanol for 27 hrs
6	AG-E011	1.25	1.25+0.875	1.875	0.013	0	20% H ₂ O Ethanol for 72 hrs
7	AG-E012	1.25	1.25+0.875	1.875	0.025	0	Ethanol for 72 hrs
8	AG-E013	1.25	1.25+0.875	1.875	0.025	0	20% H ₂ O /Ethanol for 27 hrs
9	AG-E014	1.25	1.25+0.875	1.875	0.025	0	20% H ₂ O /Ethanol for 72 hrs
10	AG-E015	1.25	1.25+0.875	1.875	0.003	25	Ethanol for 72 hrs
11	AG-E016	1.25	1.25+0.875	1.875	0.003	25	20% H ₂ O /Ethanol for 27 hrs
12	AG-E017	1.25	1.25+0.875	1.875	0.003	25	20% H ₂ O /Ethanol for 72 hrs
13	AG-E018	1.25	1.25+0.875	1.875	0.013	25	Ethanol for 72 hrs
14	AG-E019	1.25	1.25+0.875	1.875	0.013	25	20% H ₂ O /Ethanol for 27 hrs
15	AG-E020	1.25	1.25+0.875	1.875	0.013	25	20% H ₂ O /Ethanol for 72 hrs
16	AG-E021	1.25	1.25+0.875	1.875	0.025	25	Ethanol for 72 hrs
17	AG-E022	1.25	1.25+0.875	1.875	0.025	25	20% H ₂ O /Ethanol for 27 hrs
18	AG-E023	1.25	1.25+0.875	1.875	0.025	25	20% H ₂ O /Ethanol for 72 hrs

3.4.3 Experimental procedure

The aerogels were prepared the same way as it was done in the TEOS based experiments, except, the precursor used in this case was Silbond®.

The pore sizes were to be measured by equipment called *Autosorb* by Quantachrome (Model – AS1 Win Version 1.55). The transparency and integrity of the aerogels were rated visually on a scale of 1 to 5. For transparency 1 being completely opaque and 5 being completely transparent and similarly for integrity, 1 being very cracked and 5 being no-cracks. This type of visual rating was done because the differences in the transparency and cracks of each of the 18 aerogels were very drastic. Also this was only a preliminary experiment to see the approximate effects of aging period, aging solution, catalyst concentration and PEG, and hence a precise measurement of transparency and cracking of the aerogels was not required. Whereas, in the Phase 1, 2 and 3 experiments based on TMOS, the optimum values of transparency and cracks were being predicted, which required precise measurements of the transparency and crack values of each aerogel produced.

3.4.4 Results and discussion

The results from characterizing the 18 aerogel are shown in Table 16.

It was decided to not measure pore sizes as it was decided that transparency and integrity of the aerogels need to be optimized first.

Table 16. Transparency and crack ratings for the aerogels obtained from the Silbond® based experiments

	Sample Number	Density(Kg/m3)	Transparency	Cracks
1	AG-E006	112.4415994	2	5
2	AG-E007	121.5137343	1	4
3	AG-E008	102.406076	3	3
4	AG-E009	92.77496948	3	4
5	AG-E010	87.73583418	4	2
6	AG-E011	90.49633432	1	4
7	AG-E012	76.38978195	5	4
8	AG-E013	85.81123047	5	2
9	AG-E014	78.3837627	5	2
10	AG-E015	99.23615357	1	4
11	AG-E016	93.14966948	4	5
12	AG-E017	89.8111303	1	5
13	AG-E018	90.90792558	4	4
14	AG-E019	88.46869203	2	4
15	AG-E020	80.27808299	4	3
16	AG-E021	76.69414799	4	4
17	AG-E022	87.47506654	5	3
18	AG-E023	81.07405094	5	3

CHAPTER 4. CONCLUSIONS

Requirements for the design of autoclave needed to make silica aerogels were derived based the needs of the current research and by studying the autoclave specifications from other publications [1, 2, 33]. The autoclave was then successfully manufactured based on these requirements.

4.1 TEOS based

In the first set of experiments that used a cubical mold, the ethanol exchange done on the gels to remove water from the gels might not have worked because of the gel was being surrounded by the mold on 5 sides, which led to crushing of the aerogel structure during supercritical drying. This means the gels will have to be removed from the mold before ethanol exchange could be done, in order to facilitate complete water/ethanol exchange in the gels by providing more outer surface area for the exchange to take place. This could also lead to a better ethanol/liquid CO₂ exchange in the autoclave, in case the exchange was not being completed when the gel was in the mold.

In the Teflon® based mold, the water from the gel was completely removed during ethanol exchange because of the gel being completely exposed to the ethanol bath from all sides, allowing easy diffusion of the water from the gel. This led to a solid aerogel being formed after supercritical drying, without any of the white powder observed in the first experiment due to residual water in the gel during supercritical drying. The few cracks that were observed in the aerogel could be attributed to the quick diffusion of ethanol from the gel into liquid CO₂ in the autoclave and extreme rate of pressure reduction during removal of CO₂ from the autoclave after supercritical drying, leading to pressure differentials between the inner and outer parts of the aerogel in both cases.

Finally when Silbond® was used, the data collected from the experiment showed that NH_4OH concentrations clearly affect the transparency of the aerogels. With increase in NH_4OH concentration, the transparency of the aerogel also increases. However, no clear patterns of the effect of aging conditions or PEG could be seen on the transparency or the integrity of the aerogels.

4.1.1 Phase 1: Slow and quick diffusion

While there was a clear pattern visible for the effect of methanol:TMOS and NH_4OH :TMOS molar ratios on the transparency of the aerogels, the effect of methanol and NH_4OH :TMOS molar ratios on the cracks produced in the aerogels is not very clear. The transparency of the aerogel tends to increase with increase in NH_4OH :TMOS molar ratio, while it tends to decrease with increase in methanol molar ratio. The rate of increase of transparency value with increase in NH_4OH :TMOS molar ratio tends to decrease between 0.025 to 0.05 (molar ratio of NH_4OH :TMOS). While there does seem to be a general trend of decrease in cracking of the silica aerogels with increase in methanol:TMOS molar ratio and an increase in the cracking of silica aerogels with increase in NH_4OH :TMOS molar ratio. However these patterns are not very accurate. These results are a significant improvement compared to the monolithicity studies done by Rogacki et al [1] and Zoran et al [31], which have been the best study done on cracking of silica aerogels so far. Also it has been verified that the quick diffusion of ethanol from gels into liquid CO_2 leads to increased cracking as was observed by Rogacki et al [1] and Zoran et al [31], but does not affect transparency of the aerogels.

It had been decided to conduct another set of aerogels to further optimize the transparency and integrity of the aerogels made from TMOS.

4.1.2 Phase 2: Optimization

The molar ratios of methanol:TMOS and NH_4OH :TMOS that gave optimum value of transparency and cracks were 20 and 0.032 respectively. I.e. at a methanol:TMOS molar ratio = 20 and NH_4OH :TMOS molar ratio = 0.032 an optimum transparency of 0.3937 and crack value of 2621.504 could be achieved. However, the model used to predict the crack values is not very reliable; hence the optimum value is not reliable either.

4.1.3 Phase 3: Glycerol

During the supercritical drying of the samples, the decompression rate of CO_2 was decreased from the usual 138 Kpa (20 psi/min) to 69 Kpa (10 psi/min) (in an attempt to be extra careful), which resulted in crack free aerogels in 11 of the 18 aerogel samples, which included the ones that had no glycerol in them. This shows that although using a DCCA like glycerol might be helpful in producing crack-free aerogels, the same might be achieved by simply decreasing the rate of pressure release in the autoclave. It can also be observed that glycerol concentration affects the transparency of the aerogels slightly as was observed by Rao et al. [41].

4.2 Future work

In the last set of experiments conducted using TMOS precursor, it was found that most of the aerogels had none or negligible cracks, however it is not clear whether it was the result of decreased decompression rate of CO_2 , or because of the use of glycerol or both. Hence there is a scope for further investigation to take place in order to determine how cracking of aerogels can be completely eliminated. The future experiments could first study the exact effect of decreased rate of CO_2 on the aerogels without using glycerol.

REFERENCES

1. Diffusion of ethanol - liquid CO₂ in silica aerogel. G. Rogacki, P. Wawrzyniak.: Journal of Non-Crystalline Solids, 1995.
2. www.aerogel.org. [Online]
3. Nicola Husing, Ulrich Schubert. Aerogels.: Wiley-VCH Verlag GmbH & Co., 2005.
4. Gerona, Magda Moner i. Silica Aerogels: Synthesis and Characterization. 2002.
5. Application of Alumina Aerogels as Catalysts. Hiroshi Hirashima, Chihiro Kojima and Hiroaki Imai. Yokohama : Journal of Sol-Gel Science and Technology, 1997, Vol. 8, pp. 843-846.
6. Novel carbon aerogel-supported catalysts for PEM fuel cell application. Smirnovaa, X. Dongb, H. Harab, A. Vasiliev, N. Sammesa. : International Journal of Hydrogen Energy, 2005, Vol. 30, pp. 149 – 158.
7. Application of silica aerogel encapsulated lipases in the synthesis of biodiesel by transesterification reactions. Olivier Orcaire, Paulette Buisson, Alain C. Pierre. : Journal of Molecular Catalysis B: Enzymatic, 2006, Vol. 42, pp. 106-113.
8. SiO₂-aerogels: Modifications and applications. Fricke, J. 1-3, : Journal of Non-Crystalline Solids, 1990, Vol. 121, pp. 188-192.
9. Humidity sensors based on silica nanoparticle aerogel thin films. Chien-Tsung Wang^a, Chun-Lung Wu^a, I-Cherng Chen^b, Yi-Hsiao Huang^c. : Sensors and Actuators B, 2005, Vol. 107, pp. 402–410.

10. The Aerocapacitor - An Electrochemical Double-Layer Energy-Storage Device. S. T. Mayer, R. W. Pekala, and J. L. Kaschmitter. 2, : Journal of the Electrochemical Society, 1993, Vol. 140, pp. 446-451.
11. Capacitive deionization of NH_4ClO_4 solutions with carbon aerogel electrodes. J.C. Farmer, D.V. Fix, G.V. Mack, R.W. Pekala, J.F. Poco. 10, : Journal Of Applied Electrochemistry, 1996, Vol. 26, pp. 1007-1018.
12. Transparent silica aerogels for window insulation. Michael Rubin, Carl M. Lampert. 4, : Solar Energy Materials, 1982, Vol. 7, pp. 393-400 .
13. Development of windows based on highly insulating aerogel glazings. K.I. Jensen, J.M. Schultz , F.H. Kristiansen. : Journal of Non-Crystalline Solids, 2004, Vol. 350, pp. 351-357.
14. Applications for silica aerogel products. M. Schmidt, F. Schwertfeger. : Journal of Non-Crystalline Solids, 1998, Vol. 225, pp. 364–368.
15. Aerogel-based thermal insulation. Douglas M. Smith, Alok Maskara, Ulrich Boes. : Journal of Non-Crystalline Solids, 1998, Vol. 225, pp. 254–259.
16. Acoustic Impedance Matching of Piezoelectric Transducers to the Air. Alvarez-Arenas, Tom´as E. G´omez. : IEEE transactions on ultrasonics, ferroelectrics, and frequency control, 2004, Vol. 51, pp. 624-633.
17. Acoustic properties and potential applications of silica aerogels. V. Gibiat a, O. Lefevre, T. Woinier, j. Pelous, j. Phalippou. : Journal of Non-Crystalline Solids, 1995, Vol. 186, pp. 244-255.
18. Aerogels for Electronics. Hrubesh, L. W. Washington D.C. : s.n., 1994.

19. Silica aerogel captures cosmic dust intact. Tsou, Peter. : Journal of Non-Crystalline Solids, 1995, Vol. 186, pp. 415-427.
20. Aerogel: Space exploration applications. Jones, Steven M. : Journal of Sol-Gel Science and Technology, 2006, Vol. 40, pp. 351-357.
21. Materials Chemistry and Physics. Physics, Materials Chemistry and. 8, : Journal of American Ceramic Society, 1992, Vol. 75, pp. 2027-2036.
22. Comparison of some physical properties of silica aerogel monoliths synthesized by different precursors. P.B. Wagh, R. Begag, G.M. Pajonk, A. Venkateswara Rao, D. Haranath. : Materials Chemistry and Physics, 1999, Vol. 57, pp. 214-218.
23. Effect of methyltrimethoxysilane as a co-precursor on the optical properties of silica aerogels. A. Venkateswara Rao, G.M. Pajonk. : Journal of Non-Crystalline Solids, 2001, Vol. 285, pp. 202-209.
24. Ultralow density silica aerogels prepared with PEDS. Xu Chao, Shen Jun, Zhou Bin. : Journal of Non-Crystalline Solids, 2009, Vol. 355, pp. 492-495.
25. Transparent ultralow-density silica aerogels prepared by a two-step sol-gel process. Hrubesh, T.M. Tillotson and L.W. : Journal of Non-Crystalline Solids, 1992, Vol. 145, pp. 44-50.
26. Synthesis and physical properties of TEOS-based silica aerogels prepared by two step (acid–base) sol–gel process. A. Venkateswara Rao, Sharad D. Bhagat. : Solid State Sciences, 2004, Vol. 6, pp. 945-952.

27. Synthesis of transparent silica aerogels using tetraalkylammonium fluoride catalysts. Evaggelos Economopoulos, Theophilos Ioannides. : Journal of sol-gel science technology, 2009, Vol. 49, pp. 347-354.
28. Strengthening of silica gels and aerogels by washing and aging processes. M.A Einarsrud, E. Nilsen, A. Rigacci, G.M. Pajonk. : Journal of non-crystalline Solids, 2001, Vol. 285, pp. 1-7.
29. Drying of silica aerogel with supercritical carbon dioxide. M.J. van Bommel, A.B. de Haan. : Journal of Non-Crystalline Solids, 1995, Vol. 186, pp. 78-82.
30. Ambient-temperature supercritical drying of transparent silica aerogels. Param H. Tewari, Arlon J. Hunt, Kevin D. Lofftus. 9-10, : Materials Letters, 1985, Vol. 3, pp. 363-367.
31. Diffusion of methanol–liquid CO₂ and methanol–supercritical CO₂ in silica aerogels. Zoran Novak, Zeljko Knez. : Journal of Non-Crystalline Solids, 1997, Vol. 221.
32. Dependence of monolithicity and physical properties of TMOS silica aerogels on gel aging and drying conditions. G.M. Pajonk, A. Venkateswara Rao, B.M. Sawant, N.N. Parvathy. : Journal of Non-Crystalline Solids, 1997.
33. Effect of Sol-Gel Processing Parameters on Optical Properties of TMOS Silica Aerogels. A. Venkateswara Rao, G. M. Pajonk, D. Haranath, P. B. Wagh. 1, : Journal of Materials Synthesis and Processing, 1998, Vol. 6.
34. Highly porous aerogels of very low permeability. J. Phalippou, T. Woignier, R. Sempéré, P. Dieudonné. 1, : Materials Science, 2002, Vol. 20.
35. Synthesis, Characterisation and Applications of Silica Aerogels. Luc Van Ginneken, René E. Van de Leest, Louis Willems, Kathy Elst, Herman Weyten.

36. Thermal and Temporal Aging of Two Step Acid-Base Catalyzed Silica Gels in Water/Ethanol Solutions. S. Hæreid, E. Nilsen, V. Ranum and M.A. Einarsrud. : Journal of Sol-Gel Science and Technology, 1997, Vol. 8.
37. Influence of DCCAs on Optical Transmittance and Porosity Properties of TMOS Silica Aerogels. D. Haranath, A. Venkateswara Rao and P.B. Wagh. : Journal of Porous Materials, 1999, Vol. 6, pp. 55-62.
38. Effect of glycerol additive on physical properties of hydrophobic silica aerogels. A. Venkateswara Rao, Manish M. Kulkarni. : Materials Chemistry and Physics, 2002, Vol. 77, pp. 819-825.
39. Group, Lawrence Berkeley Laboratories: Microstructured Materials. Silica Aerogels.
40. Mechanical and acoustical properties as a function of PEG concentration in macroporous silica gels. J. Martin, B. Hosticka, C. Lattimer, P.M. Norris. : Journal of Non-Crystalline Solids, 2001, Vol. 285, pp. 222-229.
41. Effect of glycerol additive on physical properties of hydrophobic silica aerogels. Rao, A. Venkateswara. : Materials Chemistry and Physics, 2002, Vol. 77, pp. 819-825.

APPENDIX

Equipment

Autoclave

The autoclave is mainly required for the supercritical drying of gels to form aerogels. Before the supercritical drying, the gels also require the liquid (usually ethanol) in them to be replaced with liquid CO₂. Liquid CO₂ exists in pressures > 4826.332 KPa (700 psi) at room temperature, while the pressures during supercritical drying can go as high as 11376.35 KPa (1650 psi) and temperatures as high as 65°C.

Design specification

The design of the autoclave was done based on the requirements to be fulfilled by the autoclave. The details of the design requirement and their solutions are shown in Table A1.

Table A1. Autoclave design requirements and solutions

Requirement	Solution
The loading of the gels requires an easily accessible opening in the autoclave, which can later be sealed safely.	This requires the autoclave to have large enough space to load the gels and a simple non-permanent mechanism to seal the autoclave
After the gels are placed in the autoclave, they have to be submerged in ethanol before liquid CO ₂ is siphoned into the autoclave, to avoid drastic diffusion of the ethanol in the gels into the liquid CO ₂ .	This requires an opening near the top of the autoclave to pour the ethanol, and a window from which to observe the ethanol level to ensure the gels are properly covered
After the liquid CO ₂ is siphoned, the liquid mixture (liquid CO ₂ + ethanol) in the autoclave has to be exchanged with liquid CO ₂ by draining the liquid mixture from the bottom, while simultaneously siphoning liquid CO ₂ from top.	This requires an inlet valve connected to the top of the autoclave from which liquid CO ₂ can be siphoned in a controlled manner. Also a drain valve at the bottom of the autoclave is needed
For supercritical drying, the liquid CO ₂ has to be heated in a controlled manner until it reaches supercritical state.	To heat/cool the liquid CO ₂ , the autoclave has to be heated/cooled evenly, while temperature inside the autoclave is measured and controlled
Next the CO ₂ has to be released from the top, while making sure the CO ₂ in the autoclave stays in supercritical state, to avoid any capillary pressures on the solid network of gel.	For the depressurization, a pressure release valve is required at the top (of the autoclave

Description of the autoclave

Figure A1 shows the autoclave set up used to make aerogels



Figure A1. Autoclave

1. Autoclave Inside diameter = 4.5", depth = 3"
2. Temperature control, with maximum temperature of 65°C, and minimum temperature of 5°C
3. Pressure control valve set to a maximum pressure of 11721.09 KPa (1700 psi)
4. Glass window for observation
5. Opening near the top to pour ethanol to cover the gels
6. Inlet valve to siphon CO₂ into the autoclave
7. Pressure release valve near the top for depressurization
8. Pressure gauge for observing pressure
9. Drain valve at the bottom

Materials required

1. Tetramethoxysilane (TMOS) 99% purity – Sigma Aldrich

2. Tetraethoxysilane (TEOS) 99% purity– Sigma Aldrich
3. Ethanol 200 proof, Absolute, anhydrous – Pharmco-AAPER
4. Methanol HPLC – Mallinckrodt Chemicals
5. Ammonium Hydroxide 28-30% Conc. – VWR
6. Ammonium Fluoride 96% purity – Alfa Aesar
7. Liquid Carbon dioxide, Bone dry – Airgas
8. De-ionized water

Molds for the gels

Requirement

A mold is used to make gels in them and remove the gels without damaging the gels. Since gels might stick to the walls of the mold, the inner sides of the mold walls need to be made of Teflon®, so that the gels would not stick to them and break up.

Description of different molds designed

The cubical mold

The cubical mold is an aluminum cube that is open on one side. The walls of the mold are detachable by unscrewing the screws used to assemble the cube. The inner sides of the mold walls have a Teflon® layer so that the gels don't stick to the walls when they are removed from the cube.

Teflon® mold

The Teflon® mold has two main parts (made from Teflon®) – a cylinder 2" high, 2" internal diameter and circular plunger with 2" diameter. During gel making, the plunger is inserted at the bottom of the cylinder and when the gel needs to be removed, the plunger is pushed up from the bottom until the gel rises out of the cylinder.

Syringe mold

The syringe mold has two main parts. The first part is a plastic cylinder derived from the cutting the top part of a syringe of 1" diameter. The second part is a Teflon® plunger of 1" diameter. It works similar to a Teflon® mold.

Transparency characterization: Spectrophotometer

The specifications for the spectrophotometer (UV-2501PC, by Shimadzu) used to measure the transparency are shown in Table A2.

Table A2. UV-2501PC Spectrophotometer specifications

Property	Details
Wavelength range	190 – 900 nm
Monochromator system	Double monochromator with a high-performance double-blazed holographic grating in the aberration corrected Czerny-Turner mounting.
Resolution	0.1 nm
Spectral bandwidth	0.1, 0.2, 0.5, 1, 2 and 5nm
Wavelength repeatability	±0.1nm.
Wavelength accuracy	±0.3nm.
Wavelength scanning speed	FAST, MEDIUM, SLOW and SUPER SLOW.
Light source	50W halogen lamp (2,000 hours life) and D2 lamp (500 hours life).
Light source lamp switching	Selectable between 282nm and 393nm.
Stray light	Less than 0.0003% at 220nm and 340nm.
Power requirements	100V, 120V, 220V, 240V, switch-selectable; 50/60Hz; 250 VA.
Dimensions and weight	Main spectrophotometer 570W X 660D X 275Hmm; about 36kg.

Gel making procedure

Gel solution preparation

A gel needs to be prepared from which aerogels can be made. The following steps need to be taken in order to create the best possible gels which in turn can give aerogels with consistent properties:

1. Calculate the volumes of the chemicals to be mixed to form the gel

2. Clean the syringe-mold and plungers to be used to prepare the gels using lint-free wipes + ethanol
3. Insert the plunger into the syringe-mold all the way to the bottom and test for leakage with ethanol
4. Prepare the catalyst stock solutions for each combination of molar ratios of precursor:H₂O:solvent: catalyst initially decided upon.
 - a. Note: The stock solution should contain half of the calculated volume of solvent (ethanol, methanol etc.) + water + catalyst
5. First pour the required amount of solvent into the syringe-mold (over the plunger) using a pipette
6. Next add the required amount of precursor into the syringe-mold
7. Then add the required amount of catalyst mixture (from the catalyst stock solution) into the syringe mold
8. Immediately stir the mixture thoroughly without causing any splatter using the pipette (with its tip), blow a few holes with the pipette for good mixture. Wipe out any tiny bubbles that form along the walls of the syringe in the gel solution using the pipette tip
9. Wait for gelation. Check if gelation has occurred by slightly moving the syringe across the table and observe if the surface of the gel solution is shaking or not. (Gelation can take anywhere from 5 min to 9-10 hrs depending on the molar ratio of catalyst and solvent used)

Aging

Pouring the aging solution over the gel without damaging the gel is a bit tricky. The following steps describe how to avoid damaging the gels while pouring the aging solution:

1. Once the gel solution has solidified, pick up the syringe-mold; hold it under a light source such that the light is reflected off the surface of the gel.
2. Then tap the side of the syringe-mold wall with a finger nail to see how much the surface wobbles.
3. Wait until the wobbling is as low as possible before pouring the aging solution over the gel. Take care not to wait too long, or else the gel surface could get cracked. (To get an idea of what is the level of wobbling to look for before pouring the aging solution, make a test-gel and keep checking its level of wobbling every 10 min all the way until it cracks – the test-gel solution for TMOS based gels can have a molar ratio combination of TMOS:H₂O:MeOH:NH₄OH = 1:4:16:0.025)
4. Pour the aging solution along the inner wall of the syringe-mold over the gel slowly using the pipette, until the level of the aging solution is slightly below the top of the syringe mold

Ethanol exchange

The following steps describe how ethanol exchange of the gels needs to be done:

1. Place the aluminum mesh base along with its handles in a container and pour 200-proof absolute anhydrous ethanol up to a height of 1.5”
2. Empty the aging solution inside the syringe mold into the chemical waste disposal bin
3. Hold the syringe-mold over the ethanol bath and slowly push out the plunger from the syringe-mold using the marker with duct tape over it that matches the inside diameter of the syringe.
4. Push the plunger until the top of the plunger slightly comes out of the top of the syringe mold

5. Then slide the gel off the plunger and into the ethanol bath using a glass slide, while making sure that the glass slide makes complete contact the full width of the gel.
6. Position the gels over the mesh base in the ethanol bath as required/planned
7. Carefully place the aluminum mesh cage over the gels samples without damaging them
8. Exchange the ethanol bath at least 6 times – twice a day
9. While exchanging the ethanol bath, carefully lift the entire set of(Al mesh base + gels + cage) with the handles on either side of the mesh base and place them outside the bath container
10. Dispose the ethanol bath in the container
11. Pour new bath of ethanol into the container (up to 1.5” height)
12. Make sure to not change the orientation of the aluminum mesh set up while placing it back in the fresh ethanol bath

Aerogel making

Autoclave purging

Before the gels can be loaded into the autoclave, it has to be purged with ethanol + liquid CO₂ in order to remove any impurities in the autoclave. The purging steps are as follows:

1. Put a new O-ring on the lid of the autoclave
2. Seal the lid of the autoclave
3. Remove the screw from the opening near the top of the autoclave
4. Close the drain valve and open the pressure release valve
5. Pour 600 ml of ethanol into the autoclave through the opening at the top

6. Wrap Teflon® tape over the threading of the screw removed from the top of the autoclave
 - make sure the direction of the wrapping is along the direction of friction force on the threads while screwing it back into the opening
7. Screw the screw back into the opening tightly
8. Siphon liquid CO₂ into the autoclave, until the level of the liquid mixture rises above the top of the autoclave window
9. Wait for 10 min
10. Drain the liquid mixture
11. Repeat the purging cycle 2 more times

Gel loading

The following steps describe how gels need to be loaded into the autoclave and how to start the CO₂ exchange:

1. After the purging, remove the lid and spray silicone lubricant on the O-ring of the lid
2. Remove the gels along with the aluminum mesh + cage from the ethanol bath
3. Remove the handles from the aluminum mesh base
4. Place the steel base (3" X 2" X 0.5" or 3" X 3" X 0.5" whichever is suitable) into the autoclave
5. Place the gels along with the aluminum mesh + cage over the steel base in the autoclave
(Make note of the orientation in which the gels are placed)
6. Seal the lid of the autoclave
7. Remove the screw from the opening near the top of the autoclave
8. Close the drain valve and open the pressure release valve

9. Pour ethanol into the autoclave until the ethanol level rises above the aluminum cage covering the gels (Make note of the volume of ethanol poured)
10. Wrap Teflon® tape over the threading of the screw removed from the top of the autoclave – make sure the direction of the wrapping is along the direction of friction force on the threads while screwing it back into the opening
11. Screw the screw back into the opening tightly
12. Very slowly siphon CO₂ into the autoclave such that the pressure rise in the autoclave is < 103.42 KPa (15 psi)/min
13. Siphon liquid CO₂ until the level of liquid mixture rises to the required level
14. The autoclave may be cooled to 15°C in order to facilitate siphoning of the liquid CO₂, if the siphoning doesn't happen at room temperature. However it needs to be avoided as, after the siphoning is stopped, the level of liquid CO₂ comes down a little over a period of 4 -6 hrs, and if it comes too low, the gels might not be covered by liquid anymore. In which case more liquid CO₂ might have to be siphoned every few hours

CO₂ exchange

The following steps describe how the liquid mixture (liquid CO₂ + ethanol) in the autoclave is to be exchanged with liquid CO₂ siphoned from the CO₂ supply tank:

1. Open the drain valve (#9 in Fig. 1) so that the level of liquid in the autoclave starts dropping slowly
2. Start siphoning liquid CO₂ to keep the liquid level in the autoclave constant
3. Continue the exchanging for 20 min
4. Close the drain valve
5. Stop siphoning once the liquid level in the autoclave has reached the desired level

6. The CO₂ exchange has to be done 2 times a day until no more ethanol is recovered from the draining and then it has to be done 2 more times

Slow ethanol draining

The following steps describe how the buffer ethanol in the autoclave is to be drained for a slow draining cycle, after the gels have been loaded into the autoclave (or whenever ethanol is decided to be drained slowly) :

1. Wait for 30 min after CO₂ siphoning is done
2. Open the drain valve slightly, until ethanol starts dripping drop by drop
3. Keep adjusting the drain valve every 5 – 10 min as the draining tends to slow down
4. Keep checking the liquid level inside the autoclave and whenever it reaches a little above the top of the cage covering the gels, quickly open the inlet valve to siphon a sudden flow of liquid CO₂ into the autoclave, so that it causes turbulence in the liquid in the autoclave and mixes the liquid CO₂ and ethanol
5. The draining might take up to 8 – 10 hrs

Quick ethanol draining

The following steps describe how the buffer ethanol in the autoclave is to be drained for a quick draining cycle, after the gels have been loaded into the autoclave (or whenever ethanol is decided to be drained quickly):

1. Wait for 30 min after CO₂ siphoning is done
2. Open the drain valve until there is a steady flow of ethanol coming out
3. Keep adjusting the drain valve every 5 – 10 min as the draining tends to slow down

4. Keep checking the liquid level inside the autoclave and whenever it reaches a little above the top of the cage covering the gels, quickly open the inlet valve to siphon a sudden flow of liquid CO₂ into the autoclave, so that it causes turbulence in the liquid in the autoclave and mixes the liquid CO₂ and ethanol
5. The draining might take 1 – 2 hrs

Supercritical drying

The following steps need to be taken in order to perform supercritical drying of the gels to form aerogels:

1. Set the temperature on the autoclave temperature control to 28°C (Keep the chiller ON)
2. Once the temperature reaches 28°C, wait for 20 min
3. Then set the temperature to 31°C
4. Once the temperature reaches 31°C, wait for 20 min
5. Then set the temperature to 34°C
6. Once the temperature reaches 34°C, wait for 20 min
7. Then set the temperature to 39°C (Turn the chiller on the temperature controller OFF)
8. Once the temperature reaches 39°C, wait for 20 min
9. If the pressure is > 9652.664 KPa (1400 psi), then depressurize until pressure reaches 8273.712 KPa (1200 psi) [if pressure >10342.14 KPa (1500 psi), depressurize by 2068.428 KPa (300 psi)]. The depressurizing rate should be < 68.95 KPa (10 psi)/min
10. Then set the temperature to 46°C
11. Once the temperature reaches 46°C, wait for 20 min
12. Depressurize until pressure = 8273.712 KPa (1200 psi)
13. Then set the temperature to 53°C

14. Once the temperature reaches 53°C, wait for 20 min
15. Depressurize until pressure = 7928.974 KPa (1150 psi)
16. Then set the temperature to 62°C
17. Once the temperature reaches 62°C, wait for 30 min
18. Start depressurizing completely, while making sure depressurization rate < 103.42 KPa (15 psi). And turn OFF the heating, by setting the temperature control to room temperature (with the chiller OFF)
19. Once pressure reaches 4826.332KPa (700 psi) turn the chiller ON
20. Once depressurization is completed, remove the lid of the autoclave
21. Remove the aerogels from the autoclave and carefully place them in their respective Ziploc (labeled) pouches

Phase 1 Experiment data analysis

ANOVA analysis of the data collected is shown below.

Two-way ANOVA: Transmittance versus Methanol:TMOS Molar Ratio, NH4OH:TMOS

Molar Ratio

Source	DF	SS	MS	F	P
Methanol Molar Ratio	2	0.0095419	0.0047709	76.81	0.001
NH4OH Molar Ratio	2	0.0369784	0.0184892	297.67	0.000
Error	4	0.0002485	0.0000621		
Total	8	0.0467688			

S = 0.007881 R-Sq = 99.47% R-Sq(adj) = 98.94%

Two-way ANOVA: Crack versus Methanol Molar Ratio:TMOS, NH4OH:TMOS Molar Ratio

Source	DF	SS	MS	F	P
Methanol Molar Ratio	2	22704214	11352107	10.95	0.024
NH4OH Molar Ratio	2	767862	383931	0.37	0.712
Error	4	4148156	1037039		
Total	8	27620232			

S = 1018 R-Sq = 84.98% R-Sq(adj) = 69.96%

Phase 2 Experiment data analysis

A response surface regression analysis of the transparency and crack values of the aerogels was performed on Minitab®, yielding the following results:

Response Surface Regression: transparency, crack versus MeOH:TMOS molar ratio, NH4OH:TMOS molar ratio

The following terms cannot be estimated, and were removed.

NH4OH*NH4OH

Response Surface Regression: trans versus MeOH:TMOS molar ratio, NH₄OH:TMOS molar ratio

The analysis was done using coded units.

Estimated Regression Coefficients for transmittance

Term	Coef	SE Coef	T	P
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Constant	322.250	1.6424	196.206	0.000
MeOH	-4.680	0.9181	-5.097	0.001
NH4OH	9.191	0.9181	10.010	0.000
MeOH*MeOH	-6.259	1.8816	-3.326	0.010
MeOH*NH4OH	0.015	0.9181	0.016	0.987

S = 2.84473 PRESS = 228.790

R-Sq = 94.32% R-Sq(pred) = 79.92% R-Sq(adj) = 91.48%

Analysis of Variance for transmittance

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	4	1074.78	1074.78	268.694	33.20	0.000
Linear	2	985.23	1021.19	510.594	63.09	0.000
Square	1	89.55	89.55	89.548	11.07	0.010
Interaction	1	0.00	0.00	0.002	0.00	0.987
Residual Error	8	64.74	64.74	8.093		
Pure Error	8	64.74	64.74	8.093		
Total	12	1139.52				

Unusual Observations for transmittance

Obs	StdOrder	trans	Fit	SE Fit	Residual	St Resid
2	2	297.280	302.105	2.012	-4.825	-2.40 R
7	7	306.930	302.105	2.012	4.825	2.40 R

R denotes an observation with a large standardized residual.

Estimated Regression Coefficients for trans using data in uncoded units

Term	Coef
Constant	322.250
MeOH	-4.68000
NH4OH	9.19083
MeOH*MeOH	-6.25917
MeOH*NH4OH	0.0150000

**Response Surface Regression: crack versus MeOH:TMOS molar ratio ,
NH4OH:TMOS molar ratio**

The analysis was done using coded units.

Estimated Regression Coefficients for crack

Term	Coef	SE Coef	T	P
Constant	3565.7	907.6	3.929	0.004
MeOH	-543.0	507.4	-1.070	0.316
NH4OH	272.1	507.4	0.536	0.606
MeOH*MeOH	-599.5	1039.8	-0.577	0.580
MeOH*NH4OH	221.6	507.4	0.437	0.674

S = 1572.00 PRESS = 50188451

R-Sq = 18.05% R-Sq(pred) = 0.00% R-Sq(adj) = 0.00%

Analysis of Variance for crack

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	4	4354184	4354184	1088546	0.44	0.777
Linear	2	3061131	3540725	1770363	0.72	0.517
Square	1	821524	821524	821524	0.33	0.580
Interaction	1	471529	471529	471529	0.19	0.674
Residual Error	8	19769389	19769389	2471174		
Pure Error	8	19769389	19769389	2471174		
Total	12	24123573				

Unusual Observations for crack

Obs	StdOrder	crack	Fit	SE Fit	Residual	St Resid
9	9	6501.000	3559.556	907.593	2941.444	2.29 R

R denotes an observation with a large standardized residual.

Estimated Regression Coefficients for crack using data in uncoded units

Term	Coef
Constant	3565.67
MeOH	-542.958
NH4OH	272.069
MeOH*MeOH	-599.514
MeOH*NH4OH	221.625