

Investigations of Sol-Gel Parameters, Thermal and Optical Properties of Silica Aerogels for Large Scale Production

by

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This is to certify that I have examined this copy of a master's thesis by

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to my lovely mother, Kamer Karayılan...

ABSTRACT

Transparency in thermal insulation systems provides new practical opportunities for insulation industry since transparent insulation materials can replace conventional window glazing. Silica aerogels are promising candidates to be used in such insulation systems because they are transparent and have very low thermal conductivity (10-15 mW/m.K). Silica alcogels are synthesized by sol-gel chemistry, gelled in a mold and dried by supercritical extraction with CO₂ to get highly porous (porosity > 90%), low density (0.1-0.4 g/cm³) aerogels. The purpose of this study is to investigate the effects of synthesis parameters such as types and compositions of solvents on properties of silica aerogel to produce large scale silica aerogels with optimum thermal conductivity and transparency values and to use these large scale silica aerogels in a transparent vacuum insulation panel. Pore diameters, surface areas, and pore size distributions of the synthesized silica aerogels were measured with N₂ adsorption-desorption technique. Optical properties were determined with using UV-VIS spectrophotometer. Transient Hot-Disk plane source and steady-state Guarded Hot Plate methods were used for analyses of thermal transport properties. It was found that decreasing the molar ratios of the solvents to precursor in the sol mixture increases transparency of resulting silica aerogel. Theoretical calculations on thermal conductivity showed that the lowest values can be reached when the density of the aerogel is between 100-200 kg/m³. Based on this information, a large scale (30x30x2.0 cm³) and transparent silica aerogel panel was produced with density of 180 kg/m³. Transparency ratio and thermal conductivity of the aerogel were measured as 88% (at 600 nm) and 16 mW/m.K, respectively.

Keywords: Silica aerogels, supercritical drying, transparency, thermal conductivity, sol-gel chemistry

ÖZ

Isı yalıtımı sağlayan sistemlerde saydamlık yalıtım endüstrisinde yeni ve pratik imkânlar sağlamaktadır çünkü saydam yalıtım malzemeleri geleneksel camlarla değiştirilebilirler. Silika aerojeller bu tip saydam ısı yalıtım sistemleri için gelecek vadeden bir adaydır. Bunun sebebi silika aerojellerin saydam ve düşük ısı iletim katsayısına sahip olmasıdır (10-15 mW/m.K). Silika alkojeller sol-jel kimyası kullanılarak sentezlenir, bir kalıp içerisinde jelleştirilir ve oldukça gözenekli (gözeneklilik > %90) ve düşük yoğunluklu (0.1-0.4 g/cm³) aerojeller elde edebilmek için karbondioksit (CO₂) ile süperkritik ekstraksiyon edilerek kurutulur. Bu çalışmanın amacı çözücü tipi ve oranları gibi sentez parametrelerinin silika aerojelin özellikleri üzerine etkilerini incelemek, en uygun ısı iletim katsayısına ve saydamlığa sahip büyük ölçekli aerojeller üretebilmek ve büyük ölçekli aerojelleri saydam vakum yalıtım panelleri için kullanabilmektir. Sentezlenen aerojellerin gözenek çapları, yüzey alanları ve gözenek boyut dağılımları nitrojen adsorpsiyon-desorpsiyon tekniği ile ölçüldü. Optik özelliklerini incelemek için UV-VIS spektrofotometresi kullanıldı. Termal özelliklerin analizi için zamana bağlı Hot-Disk yüzey kaynağı ve zamandan bağımsız Guarded Hot Plate yöntemleri kullanıldı. Sol karışımındaki çözücü-ön madde molar oranları azaldıkça saydamlığın arttığı bulundu. Isı iletim katsayısı üzerine yapılan teorik çalışmalar gösterdi ki ısı iletim katsayısı en düşük aerjel yoğunluk 100-200 kg/m³ arasında tutulduğu zaman elde edilebilmektedir. Bu bilgilere dayanarak büyük ölçekli (30x30x2.0 cm³) ve saydam, yoğunluğu 180 kg/m³ olan bir silika aerjel panel üretilmiştir. Üretilen aerjelin saydamlık oranı %88 (600 nm’de) ve ısı iletim katsayısı 16 mW/m.K olarak ölçülmüştür.

Anahtar kelimeler: Silika aerojeller, süperkritik kurutma, saydamlık, ısı iletim katsayısı, sol-jel kimyası

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Nomenclature

ATR	Attenuated Total Reflectance Spectroscopy
BET	Brunauer–Emmett–Teller
Etac	Ethylacetoacetate
E/T	EtOH to TEOS Molar Ratio
FTIR	Fourier Transform Infrared
IR	Infrared
K_n	Knudsen Number
K_s	Extinction Coefficient
n	Refractive Index
PHP	Prehydrolyzed precursor
PMMA	Polymethyl Methacrylate
PP	Polypropylene
SA	Silica Aerogel
scCO₂	Supercritical Carbondioxide
TR	Transparency Ratio
TVIP	Transparent Vacuum Insulation Panel
UV-VIS	Ultraviolet-Visible
VIP	Vacuum Insulation Panel
V_s	Sound Velocity
W/T	Water to TEOS Molar Ratio

Greek Letters

λ	Thermal Conductivity (mW/m.K)
β	Constant (1.5-2.0)
δ	Pore Diameter
α	Extinction Coefficient
ρ	Density
σ_{SB}	Stephen-Boltzmann Constant
φ	The thickness of a surface adsorbed layer

Chapter 1

INTRODUCTION

Energy demand is increasing every day and people are dependent on the petroleum products to fulfill these energy requirements. The petroleum products are limited and people use up these supplies rapidly. New and alternative energy sources can satisfy these increasing energy requirements. Also, producing better insulation materials can help people use current energy resources more efficiently. Nowadays, a large part of energy resources are being utilized for heating and cooling of the buildings and private residences. Producing new materials and improving insulation systems with lower thermal conductivity values result in using less amount of the same energy sources for heating and cooling with more efficient way. For example, porous materials with low intrinsic thermal conductivity can be used to create better thermally insulating materials. Eliminating gas conductivity in the porous network can provide lower total thermal conductivity and this can be achieved by covering these porous materials with barrier films under vacuum that is called as vacuum insulation panels (VIP) [1]. Transparent insulation materials are also another requirement when we think that most of the heat is lost from windows. However, current VIPs are not transparent due to non-transparent barrier films and core materials. Hence, it can be concluded that improving transparent vacuum insulation panels (TVIP) is promising and novel research topic. Since thermal insulation performance of the double window glazing systems is not that efficient, TVIP systems can be considered to be used in between double window glazing in foreseeable future and instead of windows in the

buildings in far future. To be able to produce a TVIP, both a transparent barrier film and a transparent core material are needed. Silica aerogel is good candidate for a transparent core material because they have very low thermal conductivity and can be produced as transparent [2]. Therefore, physical and structural properties that provide unique features to silica aerogel should be investigated comprehensively.

1. 1 Problem Statement and Objectives

The main objective of this study was to synthesize a transparent core material for production of a transparent vacuum insulation panel (TVIP). Silica aerogel can be contemplated as a good candidate for the transparent core material because it can be synthesized with high optical transparency [3, 4] and it has very low thermal conductivity between 10-15 mW/m.K at room temperature [5, 6]. Silica aerogel is produced by following sol-gel science and supercritical fluid drying [7-9]. Synthesis parameters such as molar ratios of solvent or co-solvents to precursor, types of constituents, and ageing conditions are directly related to optical transparency and thermal conductivity of silica aerogel [10, 11]. In addition, theoretical relation of thermal conductivity of aerogels with density was shown in the literature [5]. There are recent studies based on theoretical calculations of silica aerogel's thermal conductivity and thermal conductivity in porous media is also associated with pore properties depending on these studies (i.e. pore diameter, porosity, etc.) of the aerogel [6, 12]. Our purpose was to combine that fundamental information and to produce silica aerogels in different scales. Then, we aimed to produce large scale silica aerogel with optimum thermal and optical properties by using the best sol-gel parameters. Afterwards, we sought finding different methods to increase transparency of silica aerogel.

Literature Review is given in Chapter 2. Fundamental information about vacuum insulation panels, sol-gel science, supercritical drying technique, properties of silica aerogels are briefly mentioned in Chapter 2.

Chapter 3 provides experimental methods and characterization techniques. Synthesis methods of two- and single-step catalyzed silica aerogel, silica aerogels with different solvents to precursor molar ratios and with different co-solvents are described in this chapter. And then, Supercritical CO₂ extraction experiments and large scale silica aerogel production are provided. After that, instrumental methods for determination of properties of silica aerogels such as thermal conductivity and transparency are presented.

In Chapter 4, results of the experiments given in Chapter 3 are discussed. How sol-gel parameters, shapes of molds and ageing conditions affect the properties of silica aerogels are presented. Large scale silica aerogel and transparent vacuum insulation panel are given and thermal conductivity and transparency of silica aerogels are discussed in this chapter.

Chapter 5 concludes the results on this study and represents final outcome.

Chapter 2

LITERATURE REVIEW

2. 1 Transparent Vacuum Insulation Panels

People use energy resources not only heat their houses and buildings in winter, but they also cool these places in summer. In order to keep inside temperature stable and use less energy resources, heat lost must be eliminated or decreased by using a good insulation system. Although walls are the largest area that should be effectively insulated, one should notice that warm air is escaping mainly through windows in winter (Figure 2. 1) [13]. So, transparent insulation systems must be developed to prevent this energy loss.



Figure 2. 1 Thermal camera image of a house (*Retrieved from <http://www.imagingnotes.com>; image courtesy of FLIR Systems, Inc.*)

There are few transparent insulation systems. For instance, double window glazing (Figure 2. 2) is one of the options when a transparent insulation system is required. A double window glazing is composed of double panes separated by an air gap and this gap can be filled with a gas which has lower thermal conductivity than still air. Gas filled double window glazing system is used to minimize the heat transport properties of the insulation system. For example, a higher molecular weight gas and a mono-atomic gas compared to polyatomic gases have lower thermal conductivity. For some double window glazing systems, vacuum can be applied in between the panes. However, vacuum is not hold very long time and the insulating gas can leak out through the window in time. A transparent insulating material can be used in between these panes [13, 14] or can replace the double window glazing system. Silica aerogel is a promising candidate as a transparent insulator [14-16]. Silica based materials (e.g. fumed silica, glass fiber) have been used as a core material in a vacuum insulation panel which is defined as " an evacuated foil-encapsulated open porous material as a high performance thermal insulating material" [1, 17, 18].



Figure 2. 2 A double window glazing system

Vacuum insulation panels (VIP) has better insulation property than current insulation materials but still they are not transparent. A VIP (Figure 2. 3) is composed of a barrier film (e.g. aluminum, Al; polymeric films, etc.), a core material (e.g. fused silica, glass fiber, polyurethane foam, etc.), and sometimes a desiccant [1]. To increase the lifetime of the VIPs, desiccants which can adsorb the water vapor are placed in the VIPs. So, the internal pressure of the VIPs can be maintained. One of the major advantages of the VIPs is that the thickness of the insulation material can be reduced compared to traditional thermal insulation materials in building applications due to better thermal insulation performance of VIPs with the same layer thickness [1, 15]. There are a couple of drawbacks of VIPs. For example, they are very fragile because of very brittle core material and their thermal performances may reduce through time because moisture and air may diffuse into the panel. Also, thermal bridge effect (e.g. air gaps between two adjacent VIPs) will decrease thermal performance of the VIP envelope [1, 19].

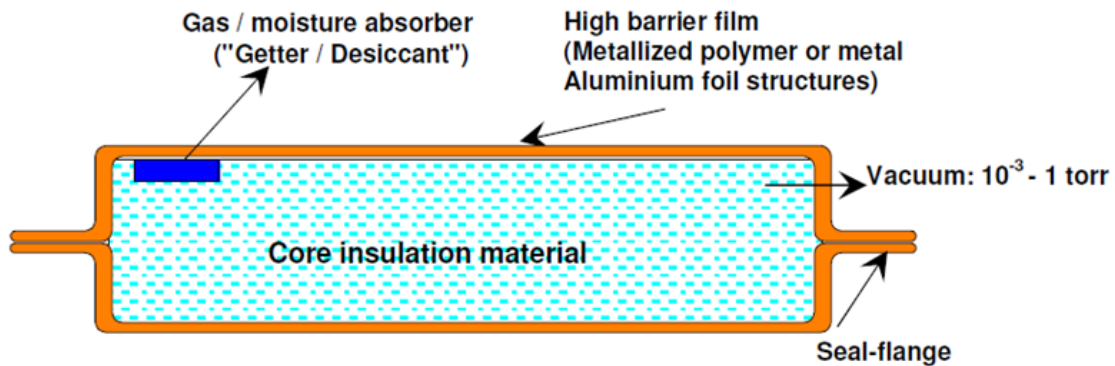


Figure 2. 3 Components of a VIP

Silica aerogel and transparent high barrier films can be used to produce a transparent vacuum insulation panel. The high barrier film is one of the most important components of a TVIP because the vacuum in the panel can be maintained by the help of the envelope.

Although a multi layer of aluminum film is commonly used due to the low atmospheric gas and moisture permeation, the high barrier film must be transparent for TVIP. So, polymeric high barrier films can be developed instead of metal layers to maintain the internal pressure of the panel.

Silica aerogels consist of a crosslinked SiO_2 network in three dimensions and the pore size of aerogel is in mesoporous range (2-50 nm). Silica aerogel is synthesized from organosilicon precursor by sol-gel route and dried by the supercritical extraction method. Silica aerogels are extremely porous materials synthesized through sol-gel chemistry to form a solvent-filled porous solid, which normally is dried under supercritical conditions in order to prevent collapse of the tenuous solid network. Silica aerogel has low thermal conductivity (10-20 mW/m.K), high porosity (80-95 %), small pore size (10-20 nm in diameter), amorphous material, and transparent. However, high porosity, low density and amorphous structure of silica aerogel result in mechanically weak and fragile material and they are not as transparent as glass.

Gels show both solid- and liquid-like properties and they are named based on drying methods such as xerogel or ambigel (evaporative drying at room temperature) [20], aerogel (supercritical drying) [21] and cryogel (freeze drying) [22]; dispersion mediums (DP) of wet gels such as alcogel (DP: alcohol), aquagel or hydrogel (DP: water), acetogel (DP: acetone); being organic or inorganic such as silica gel (SiO_2 network), titania gel (TiO_2 network), resorcinol-formaldehyde or RFA gel (organic network), polyethylene glycol or PEG gel (organic network); different synthesis method such as sonogels (ultrasound assisted synthesis) [23]. After drying, all dried gel can designate as aerogel (DP: air). Aerogels consist of primary particles and pores in the nanometer size range. Numerous unique properties result from their microstructure. Aerogels are known to one of the lowest density, thermal conductivity, dielectric constant and refractive index of any solid material [2]. Aerogels are open-cell foams that have already been shown to be among the best

thermal insulating solid materials known. Low transparency is originated from scattering of light. There are two types of scattering of light for aerogel case. One of them is bulk (Rayleigh) scattering which depends on particle and pore sizes in the aerogel. The other one is surface scattering which is affected by surface roughness of the aerogel [3, 24, 25].

Silica aerogel is highly porous material (up to 99%) and the contribution of gas conductivity will be very important due to the high porosity of the material. On the other hand, silica aerogel is nano-structured material with meso pores. So, a weak vacuum can provide required low thermal conductivity when it is used as a VIP core. Moreover, small pore size (e.g. 10 nm or less) can provide maintaining the internal pressure of the envelope and that increases the lifetime of the VIP. And, only open pore structure makes the evacuation of the gas molecules in the material possible. Silica aerogel has good enough compressive strength for applying vacuum inside a barrier film. Otherwise, the aerogel can be cracked when the panel is evacuated.

2. 2 Synthesis of Silica Aerogels and Their Composites

2. 2. 1 Sol-Gel Science

Sol-gel method provides synthesis of micro and mesoporous, high surface area and high porosity solid materials at low temperature (e.g. room temperature). Silica aerogels are synthesized by following sol-gel route (Figure 2. 4). A precursor is hydrolyzed first in a co-solvent medium. Due to hydrophobic character of the alkoxy groups, silicon alkoxides are not miscible in water. Certain amount of a co-solvent should be added to homogenize TEOS (Tetraethoxysilane)-water mixture. Hydrolyzed TEOS ($\text{Si}(\text{OH})_4$ or $(\text{RO})_{4-n}\text{Si}(\text{OH})_n$, $n \leq 4$) is further condensed and silica alcogels are obtained. Hydrolysis and condensation reactions are performed under acidic and/or basic mediums. After ageing and solvent exchange steps, alcogels are dried under supercritical CO_2 [2, 7, 8].

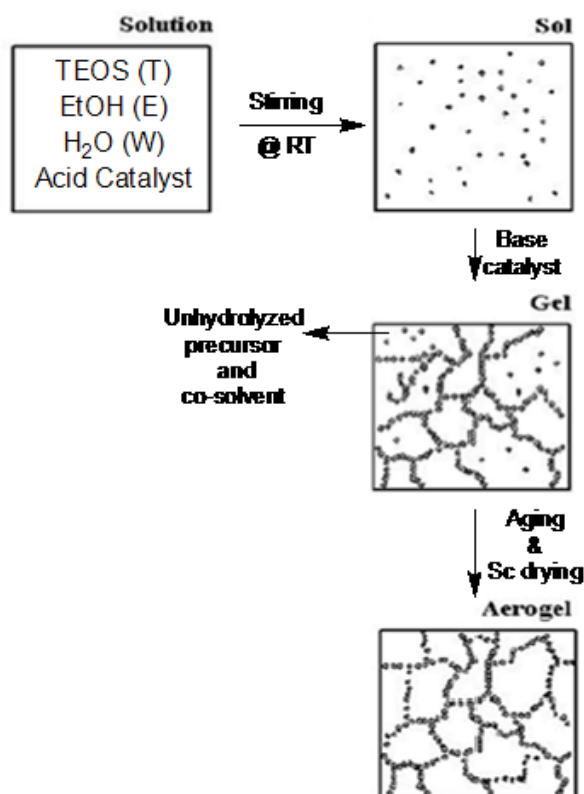


Figure 2. 4 Sol-gel route for silica aerogel synthesis

2. 2. 2 Types of Precursors, Co-solvents, and Catalysts

First silica aerogel was synthesized by using water-glass precursor, sodium metasilicate Na_2SiO_3 by Kistler in 1931[26]. Now, silicon alkoxide precursors $\text{Si}(\text{OR})_4$ are mainly used. R is an alkyl group such as $-\text{CH}_3$ group or $-\text{CH}_2\text{CH}_3$ group. And sometimes, there are one or two alkyl groups linked to silicon atoms instead of four alkoxy groups (Figure 2. 5). Silicon alkoxide precursors are hydrolyzed in an organic solvent and condensation of hydrolysis products occur simultaneously. These reactions are catalyzed with acids or bases or both.

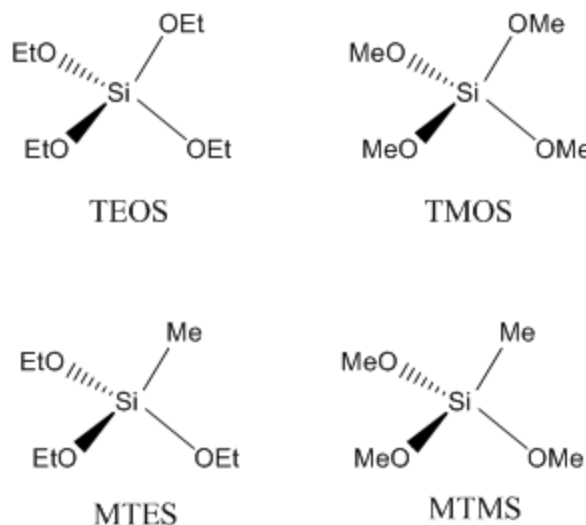


Figure 2. 5 Different silicon precursors

Using different precursors such as TEOS, TMOS, and PEDS (polyethoxydisiloxane) can affect monolithicity, transparency, thermal conductivity, and porosity of the resulting silica aerogels [2, 27]. Moreover, a dangling non-reactive alkyl group in the precursor results in more flexible silica aerogels [28, 29] or hydrophobic silica aerogels can be produced by using one or more non-reactive hydrophobic groups on precursors or co-precursors [30, 31].

The solvents are grouped into non-polar, polar aprotic, and polar protic solvents. TEOS-water mixture is not homogeneous in non-polar solvents. To synthesize silica aerogels, polar protic or polar aprotic solvents must be used such as alcohols, acetone, DMF (Dimethyl formamide) and DMSO (Dimethyl sulfoxide). Types and amount of co-solvents in sol mixture directly affect hydrolysis kinetic, particle size, monolithicity, physical properties and transparency of silica aerogels [32, 33].

Hydrolysis rate can be increased with a catalyst. There are two types of synthesis procedure of silica aerogel which are single-step (with only acid catalysis or with only base catalysis) and two-step catalysis. Types and amount of acid or base catalyst generally affect

gelation time of silica aerogels. However, linear weakly branched and microporous structures can be obtained by single-step acid catalyzed silica aerogel synthesis whereas cross-linked and 3D silica aerogels with larger pore size are obtained under base-catalyzed or two-step processes [2].

2. 2. 3 Hydrolysis and Condensation

First, suspended colloidal particles (sol) (Table 2. 1) are formed in a solvent during hydrolysis. The size of the colloidal particles depends on nucleation and growth mechanisms and the nucleation rate should be much faster than growth rate in order to obtain colloids. These colloidal particles start to connect with each via chemical bonds, hydrogen bonds or van der Waals interactions and form a three dimensional structure in the solvent which is called as a gel. Gelation depends on many factors such as pH, micelle concentration, temperature of the solution. The proposed mechanisms of hydrolysis is nucleophilic attacks from oxygen atoms O, on water molecules to the metal atom M, on the precursor. The nucleophilic attacks depend on the partial positive charge carried out by M. Due to low metallic character of silicon atom Si, Si atoms on tetraalkoxy silicon precursor carry a reduced partial positive charge and hydrolysis reactions need to be catalyzed. Under acidic medium, protonated alkoxy groups bonded to Si atoms can easily leave when Si atoms are exposed to nucleophilic attacks from the O atoms. Hence, alkoxy groups replace with hydroxyl groups. Under basic medium, deprotonated O atoms on hydroxyl groups linked to silicon atoms carry strong negative charge and easily attack to another partially or completely hydrolyzed Si atoms. In Figure 2. 6, relative hydrolysis and condensation rates can be investigated. So, hydrolysis products condensate and form colloidal particles (Figure 2. 7) and finally highly viscous, porous and wet gels. There are still unhydrolyzed precursors remain in the pores, hydrolysis and condensation reactions still continue. That is

why viscous gel can be aged in certain solutions at higher temperature such as 50 °C prior to drying. The appropriate drying results in silica aerogels [34].

Table 2. 1 Different colloidal dispersion systems [34]

Dispersion Phase	Dispersion Medium	Technical Name	Common Name
Solid	Gas	Aerosol	Smoke, dust
Liquid	Gas	Aerosol	Fog
Solid	Liquid	Sol or colloidal sol	Suspension, slurry, jelly
Liquid	Liquid	Emulsion	Emulsion
Gas	Liquid	Foam	Foam, froth
Solid	Solid	Solid dispersion	Alloys and glasses
Liquid	Solid	Solid emulsion	
Gas	Solid	Solid foam	

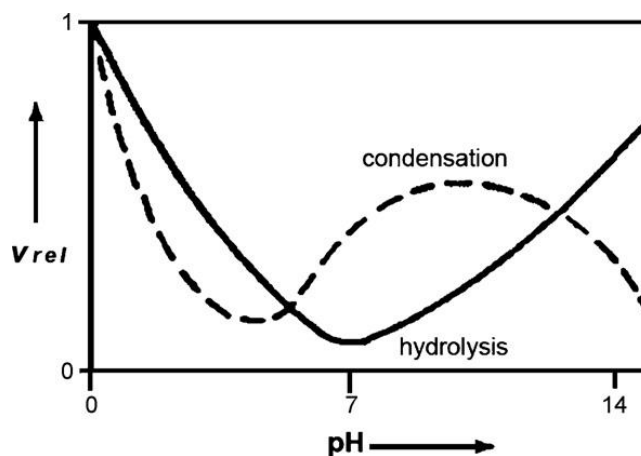


Figure 2. 6 Dependence of the relative hydrolysis and condensation rates on the pH of the solution. Reprinted from [2] with permission from Elsevier

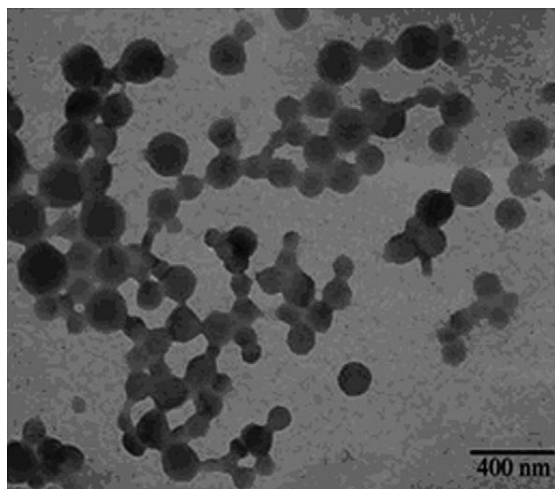


Figure 2. 7 TEM image of silica sol during gelation. Reprinted from [2] with permission from Elsevier

2. 2. 4 Ageing

After gelation, condensation reactions continue in the pores of silica wet gel because there may still remain unreacted alkoxy groups and uncondensated hydroxyl groups in the structure. Syneresis which is the expulsion of pore liquid from wet gel due to the new bond formation through ongoing condensation reactions after gelation can be observed and it is a sign that the condensation reactions are still continuing. Silica wet gel can be placed in certain solutions such as EtOH-water mixture or mother solution (TEOS-EtOH-water solution) at elevated temperature (50 °C) and this process is termed as ageing of the gel. Two different ageing mechanism can be proposed. One of them is the neck growth from reprecipitation of silica particles and the other mechanism is dissolution of smaller silica particles and reprecipitation onto the larger ones [2]. Forming new bonds and Ostwald ripening (or coarsening) occur in the network. The bridging new bonds results in volume shrinkage of the alcogel. So, density of the alcogel increases and the wet gel released from the mold where the gelation occurs. The Ostwald ripening is the dissolution and reprecipitation process of smaller particles on larger particles in the network which is

energetically favorable process. It is certain that ageing process increases the mechanical properties of silica wet gel and that provides monolithical and crack-free silica aerogel after drying.

2. 2. 5 Drying

Liquid in the alcogel pores is removed and replaced with air in drying step. There are three types of drying techniques which are freeze-drying, ambient conditions drying (evaporative drying) and supercritical drying. Since silica alcogels have very small pores (smaller than 50 nm), capillary force is emerged during evaporative drying due to surface tension of liquid in the pores. Silica alcogels are very weak in mechanical strength and they cannot stand this force accumulated in the pore walls so silica alcogel starts to crack during drying. Hence, unique techniques must be used to extract pore liquid without damaging the structure.

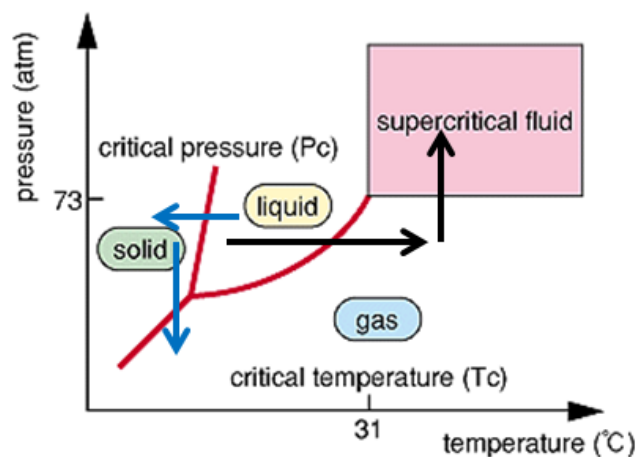


Figure 2. 8 P vs. T graph of CO₂. Black arrows show supercritical drying pathway and blue arrows show freeze drying pathway. Reprinted from [35]

2. 2. 5. 1 Freeze-Drying

Freeze drying is a method to remove generally water or other solvent from a frozen product. This process is called sublimation. Sublimation occurs when a frozen liquid in solid state goes directly to the gaseous state without liquefying. There are three stages for freeze drying process which are prefreezing, primary drying, and secondary drying. In prefreezing step, sample must be completely prefrozen. Samples may be a solute suspended in a solvent system or solid porous network consisting of liquid medium in its pores. These samples are cooled to freeze in a refrigerator or in liquid N₂. Small ice crystals are formed during rapid cooling which is useful in preserving microscopic structures of sample but the resulting frozen product is more difficult to freeze dry. Slower cooling results in larger ice crystals and slower cooling is suggested for the freeze drying process. Temperature and pressure should be arranged in which solid content such as ice to be removed is sublimed. Primary drying under low T and P results in dry and structurally intact product. Selected optimum T must both maintain the sample frozen and provide maximum vapor pressure of the sample because the lower the T of sample, the longer the time required to complete primary drying. To reduce the pressure of the environment around the product, a vacuum pump is needed in freeze drying system. A collecting system which consists of a cold trap collects the moisture leaving from the frozen product. As a result, the collecting system can remove all condensable gases while the vacuum pump collects all other non-condensable gases. Secondary drying is required to dry the sample completely and to remove possible residual moisture is still present in the product. Pressure and collector temperature remain the same while product temperature increases higher than ambient. By this drying, bound moisture can be desorbed from the product [36].

2. 2. 5. 2 Ambient Temperature and Pressure Drying

Silica alcogels are dried at room temperature due to high cost of other drying techniques. However, silica alcogels cannot resist capillary pressure during evaporative drying. So, silica alcogels should be hydrophobic before drying step. H atoms on the hydroxyl groups on the surface of the silica alcogels are replaced with hydrophobic groups. Silylation agents such as hexamethyldisilazane (HMDZ) [20, 37], hexamethyldisiloxane (HMDS) and tetramethylchlorosilane (TMCS) [2] are used to make silica alcogels hydrophobic. After ageing step, pore liquid is exchanged with water-free solvent. A. P. Rao et al. showed that physical and hydrophobic properties of ambient pressure dried hydrophobic silica aerogels depend on the nature of the exchanging solvent [37].

2. 2. 5. 3 Supercritical Drying

Supercritical drying method is the most popular and preferred technique to extract pore liquid without damaging silica alcogels. Supercritical fluids are single phase and have no liquid-vapor interface (Figure 2. 9); as a result, there is no surface tension, capillary pressure (Eqn. 2. 1) [2] is eliminated, and silica alcogel texture is maintained after drying. Supercritical CO₂ is mostly used for the removal of pore liquid because CO₂ has very mild critical pressure and temperature, 73.8 bar and 31.1 °C, respectively [38]. Besides, CO₂ are non-flammable, unreactive and non-toxic gas. These properties of CO₂ make it very attractive, useful and preferred gas for the supercritical drying process. In this process, supercritical CO₂ reaches the pores and dissolves the pore liquid. The liquid inside the pores diffuses to the supercritical fluid phase and the capillary pressure due to surface tension does not exert stress on the alcogel structure. One should pay attention that the pore liquid has to be exchanged with water-free solvent for more efficient drying because supercritical CO₂ does not dissolve water.

$$P_c = (-\gamma l_v)/(r_p - \phi) \quad \text{Equation 2. 1}$$

P_c : Capillary pressure

γl_v : Surface tension of the pore liquid

r_p : the pore radius

ϕ : the thickness of a surface adsorbed layer

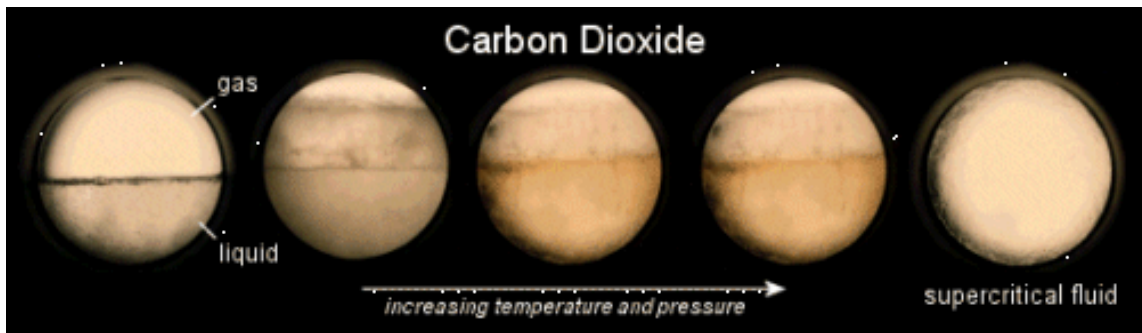


Figure 2. 9 CO₂ phase change upon heating a closed vessel. While liquid CO₂ has a liquid-vapor meniscus, supercritical CO₂ is single phase.

2. 2. 6 Silica Aerogel Composites

Because of more powerful, combined and desired properties of composites, new hybrid materials are developed [39]. For example, silica aerogels are fragile material and organic or inorganic entities would be integrated in the silica aerogel matrices to increase mechanical strength of the resulting material [40, 41]. Also, some additives can be added into a transparent silica aerogel structure that can eliminate radiative thermal conductivity of the material and increase the thermal performance at high temperature.

The second components of the silica aerogel composite materials can be added in sol before or after hydrolysis of the silicon precursor [41] and for some processes, other components can be incorporated into the silica structure after gelation or after drying. A number of particles can be deposited and functional materials can be chemically or physically adsorbed on the silica aerogel surface by supercritical CO₂ deposition method. Silica aerogel composites can be synthesized generally with organic or inorganic molecules and specifically with a precursor different from the silica precursor (e.g. titania precursors), a metallic solid (e.g. Au, Pd), organometallic compounds, powders (e.g. carbon black), functional molecules or polymers (e.g. PMMA) [42].

2. 3 Properties of Silica Aerogels

2. 3. 1 Surface and Pore Properties

"Mesopores" are defined the pores with diameter between 2 and 50 nm. If the diameter of the pores is less than 2 nm, then it will be "micropores" and that of the pores is higher than 50 nm, the pores are termed as "macropores". Silica aerogels have pores of all types and they are composed of the pores with size between 5 and 100 nm. However, pore size of silica aerogels is mainly in mesoporous range. BET surface area of silica aerogels is mentioned between 600 and more than 1000 m²/g in the literature. When silica aerogels are synthesized by using regular sol-gel route and TMOS or TEOS as precursor, hydroxyl terminated hydrophilic surface is obtained. Silica aerogels are highly porous material and porosity can be reached up to 99%. Porosity and pore volume of silica aerogels can be calculated according to Eqn. 2.2 and Eqn. 2. 3, respectively. Silica aerogels have open-pore structure and fluid inside the pores can travel through in the network. Mercury intrusion porosimetry (MIP), thermoporometry (TPM), and nitrogen adsorption/desorption (NAD) techniques are used to determine surface and pore properties of silica aerogels. Although

sample preparation for analysis is difficult due to electrostatic loading on the aerogel powder and electrically insulated property of silica aerogel, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can be used to get more information about particle size and pore size of the silica aerogel [2].

$$\text{Porosity} = (1 - \rho_b / \rho_s) \times 100 \quad \text{Equation 2. 2}$$

$$\text{Pore Volume (cm}^3\text{/g)} = (1 / \rho_b - 1 / \rho_s) \quad \text{Equation 2. 3}$$

ρ_b : the bulk density of the silica aerogel

ρ_s : the skeletal density of the silica aerogel

2. 3. 2 Thermal Properties

Radiation, conduction through solid skeleton and gas conductivity constitute the total thermal conductivity in porous media (Eqn. 2. 1). Gas conductivity inside the material can be divided in two heat transfer processes which are gas conduction and gas convection [1, 5].

$$\lambda_T = \lambda_S + \lambda_R + \lambda_G + \lambda_{CV} \quad (\text{Equation 2. 4})$$

λ_S describes the solid conduction through solid skeleton, λ_R the radiative heat transfer between pore surfaces, λ_G the gas conduction within the material pores and λ_{CV} the gas convection due to air inside the pores. Solid conduction can be decreased by using a solid material with low intrinsic solid conductivity. Gas conduction in porous medium can be eliminated by applying vacuum. Reducing the gas pressure inside a porous material is the most effective way of reduction of the gas conduction. When the pore diameter of the material is less than the average mean free path of the gas molecules inside the pores (The

mean free path of air l_m at 25 °C and 1 atm is 70 nm), the collisions between the air molecules will be eliminated and convective gas conductivity will be suppressed due to energy transfer by the elastic collisions of the gas molecules.

Lawrence W. Hrubesh and Richard W. Pekala [5] examines the three major contributions to thermal transport through porous materials, solid, gaseous, and radiative, to identify how to reduce the thermal conductivity of air-filled aerogels. This paper analyzes the density dependence of the conductivities to determine the optimum density for minimum total thermal conductivity and to identify where reductions in the thermal conductivity of aerogels are possible. For example, solid conductivity in porous media is given in the following

$$\lambda_s' = \rho' \cdot V' [\lambda_s / (\rho_s \cdot V_s)] \quad (\text{W/m.K}) \quad \text{Equation 2. 5}$$

where ρ' and ρ_s are the densities of the aerogel and the solid SiO_2 and V' and V_s are their sound velocities. λ_s is the thermal conductivity of the solid.

There is a substantial contribution to total thermal conductivity from the gas within the pores due to very high porosity nature of the silica aerogel. Small pore size can suppress the convective heat transfer or vacuum should apply to diminish the gas conductivity. The gas conductivity is as follows [1, 5]:

$$\lambda_g' = (\lambda_{g,o} \cdot V_g) / (1 + 2\beta \cdot \text{Kn}) \quad (\text{W/m.K}) \quad \text{Equation 2. 6}$$

where $\lambda_{g,o}$ is the thermal conductivity of the gas in the pores, V_g is the porosity of the aerogel and Kn is the Knudsen number, given by the ratio of the mean-free path for gas molecules, and the average pore size of the material. β is a constant depending on the gas

type, the solid and the temperature (between 1.5 and 2.0) and it characterizes the efficiency of energy transfer as gas molecules within the pores hit the solid structure of the material.

The radiative thermal conductivity in silica aerogel can be given as:

$$\lambda_r' = 16/3 (n^2 \cdot \sigma_{SB} \cdot T_r^3) / (\rho' \cdot K_s / \rho_s) \quad (\text{W/m.K}) \quad \text{Equation 2. 7}$$

where

σ_{SB} : the Stephan-Boltzmann constant,

n : the refractive index (approximately 1.0 for aerogels),

T_r : the temperature within the material, and

K_s : the extinction coefficient for the solid

Each of the heat transfer mechanisms contributing to the total thermal conductivity of the silica aerogel depends on density. The solid conductivity contribution increases monotonically as the density increases, while the gaseous and radiative thermal conductivities decrease with increasing density [5]. As a result, an optimum silica aerogel density for minimum total thermal conductivity can be determined from total thermal conductivity vs. density plot.

2. 3. 3 Optical Properties

Silica aerogels have very low thermal conductivity that provides very high thermal insulation properties and have very high transparency in the visible region (Figure 2. 10). These properties make the silica aerogels strong candidate for double window glazing [13, 14]. Heating after drying [2], using silylating agent [27], the exchanging solvents for ambient pressure drying process [37], and especially sol-gel parameters [3, 10] affect

optical transparency of silica aerogel. The silica aerogel microstructure, pore size and particle size are comparable to the wavelength of the visible light. SiO₂ does not absorb the visible light and silica aerogel has a high transmittance of radiation in the visible range. However, transparency decreases because of the scattering of light which are bulk (Rayleigh) scattering and surface scattering [24, 25]. Silica aerogels become hazy appearance due to the scattering of the light. The Rayleigh scattering occurs when size of particles is less than wavelength of the incident light and the attenuation of the light intensity due to the Rayleigh scattering is defined by the Rayleigh-Gans Theory (Eqn. 2. 8). Inhomogeneities and scattering centers in a material cause the Rayleigh scattering. The pores and the aggregated particles within silica aerogel are the scattering centers in this case and both size of the pores and that of the particles are smaller than the wavelength of the visible light. Size of the corresponding scattering centers can be controlled by sol-gel parameters. The surface scattering is mainly caused by roughness of the silica aerogel surface which depends on roughness of the mold in which gelation occurs .

Rayleigh-Gans Theory [3]

$$\alpha = 32\pi^4 \frac{d_{ap}}{d_{SiO_2}} \frac{a^3}{\lambda^4} \left(\frac{n^2-1}{n^2+2} \right)^2 \quad \text{Equation 2. 8}$$

α : the extinction coefficient (The attenuation of the light intensity I_0 down to I)

d_{ap} : the apparent or bulk density of the silica aerogel

d : the true density of amorphous silica: 2.2 g/cc

a : the particle scattering center

n : the relative refractive index n_1/n_2

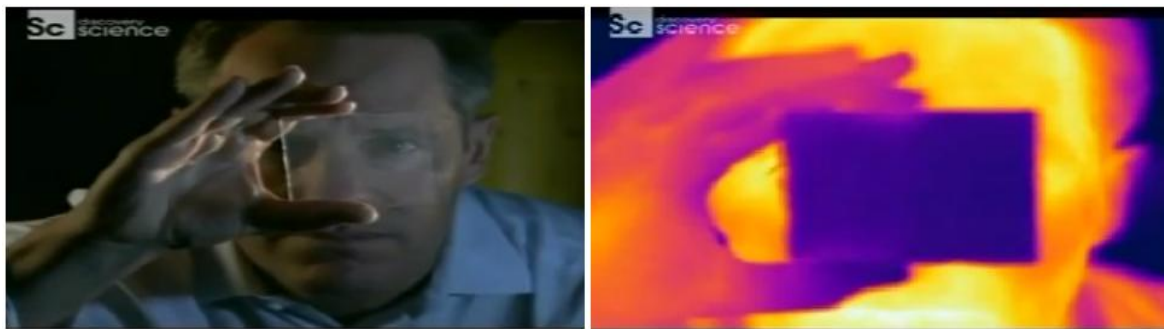


Figure 2. 10 Transparency and thermal conductivity correlation of silica aerogel

2. 3. 4 Mechanical Properties

Silica aerogels are very attractive materials due to their unique properties such as low density and high porosity. However, these properties result in mechanically weak structure. For some cases, it is very difficult to handle a silica aerogel without causing a damage on the structure. Silica aerogels were aged in their mother solution (Precursor-co-solvent-water mixture) [43], composite silica aerogels were synthesized by adding bi- or tri-functional compounds or polymers in the structure [44, 45], fiber-reinforcement were performed [46] and so forth in order to increase mechanical strength of the silica aerogels [47, 48].

Hardness, compression behavior, tension young modulus, shear tests and fracture tests of silica aerogels can be investigated and three-point bending method and dynamic mechanical analyzer (DMA) can be used to determine mechanical properties of silica aerogels.

2. 4 Applications

Silica aerogels can be considered to be applied in different areas [49] because they have low density, high porosity, mesoporous structure, low refractive index, high thermal and

sound insulation performance [50] and they are transparent if it is desired. Thus, silica aerogels can be used as a thermal insulator [15], an adsorbent, a catalyst or catalyst support, as a sensor or as Cherenkov detectors [8]; used in double plane windows [4, 51] or vacuum insulation panels [16-18].

Chapter 3

EXPERIMENTAL METHODS AND CHARACTERIZATION TECHNIQUES

3. 1 Materials

Tetraethoxysilane (Tetraethylorthosilicate; TEOS $\geq 99\%$ purity; Merck and commercial TEOS; Xiameter, Dow-Corning), ethanol (EtOH $\geq 99.8\%$ purity; Sigma-Aldrich), tetrahydrofuran (THF $\geq 99.9\%$ purity; Sigma-Aldrich), acetone ($\geq 99\%$ purity; Sigma-Aldrich), ethyl acetoacetate (Etac $\geq 99\%$ purity; Sigma-Aldrich), hydrochloric acid (HCl, 37% purity; Riedel-de Haen), and ammonia (NH₃, 2.0 M in ethanol; Aldrich) were used as received. Carbondioxide (CO₂) was obtained from Messer Aligaz and had a stated purity of 99.9%. Deionized and distilled water was used in all the experiments.

3. 2 Equipments

Supercritical (Sc) drying experiments, nitrogen (N₂) adsorption-desorption analyses and thermal conductivity measurements with transient plane source were performed in our research laboratory, the Energy Technologies and Supercritical Fluids Research Laboratory. Small scale supercritical drying experiments were performed with the Applied Separation high pressure drying system (Spe-ed SFE-2). Large scale panel drying were performed with a 35-liters high pressure drying vessel made by Natex. For both small and large scale drying systems, the applied separation pump unit connected to a CO₂-deep tube was used. N₂ adsorption-desorption analyses (BET surface area, BJH isotherm, pore size

distribution, average pore diameter, and pore volume) were carried out on Micromeritics ASAP 2020-surface area and porosity analyzer. Hot Disk thermal constants analyzer with software version 6.0 was used to determine thermal conductivities of small scale silica aerogel samples (e.g. $5.0 \times 5.0 \times 1.0 \text{ cm}^3$). Spectroscopy measurements (UV-VIS, IR and Raman), at Koç University Surface Science and Technology Center (KUYTAM). Transmission, transparency ratios, and haze measurements were recorded using the Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600). Silica aerogels were analyzed after synthesis using the Thermo Scientific Nicolet Avatar 360 E.S.P. FTIR spectrophotometer with Horizontal Attenuated Total Internal Reflectance (ATR) Accessory. Renishaw Invia Raman Microscope was used to determine hydrolysis kinetics. Guarded Hot Plate analyses were done at Arçelik.

3. 3 Silica Aerogel Synthesis

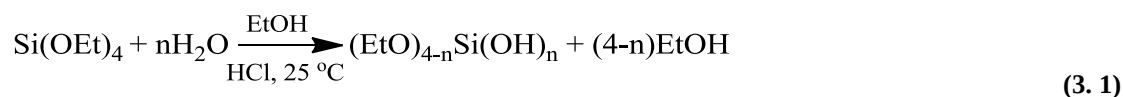
Silica aerogels (SAs) are synthesized by following the sol-gel route. Based on this route, an organosilicon precursor, TEOS, is hydrolyzed with certain amount of water in a co-solvent medium, generally EtOH, under continuous stirring. Hydrolysis takes place about 30 minutes under acidic conditions. So, HCl solution is used to make the sol mixture acidic. After hydrolysis, ammonium hydroxide (NH_4OH) solution can be added into the sol to accelerate the condensation reactions. Prior to gelation, the liquid sol mixture is placed in a mold that gives final shape of the gel. Gelation occurs in the mold and a wet gel is obtained. Hydrolysis and condensation reactions are performed at room temperature. The liquid inside the pores of the gel is trapped in the network formed during gelation and it does not flow away but the network is not strong enough to remove the wet gel from the mold in a single piece as a monolith and to be handled without damaging the structure. Thus, an aging solution is added on the wet gel which shrinks and releases from the mold by itself without any external force during aging. The wet gel is aged at high temperature

(i.e., 50 °C) about 24 hours. The aging step is followed by a solvent exchange step. Pore liquid is replaced with a solvent which is soluble and easily extractable by supercritical CO₂ (scCO₂). The aged wet gel is placed and waited for 2-3 days in pure EtOH that is changed with new one twice or three times during these 3 days. The wet gel is now called as alcogel because the dispersion medium in pores is alcohol. The final step is drying. EtOH in pores is replaced with air by scCO₂ extraction process. The drying step results in SiO₂ aerogel. Further heat treatment can be applied to take out any possible residual EtOH inside pores. Finally, after these several consecutive processes, SiO₂ aerogel is ready to be characterized.

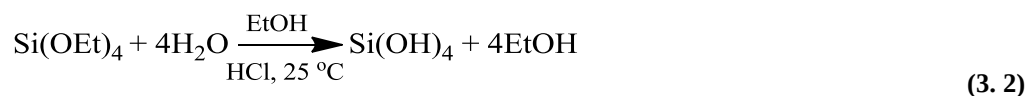
3. 3. 1 Two-Step Catalyzed Silica Aerogel Synthesis

TEOS is hydrolyzed in a co-solvent. For complete hydrolysis reaction (Eq. 3. 2), H₂O/TEOS (W/T) molar ratio should equal to 4. An acid catalyst is added to TEOS-Co-Solvent-H₂O mixture to increase the hydrolysis reaction rate. Partial and complete hydrolysis reactions are in the following:

Partial hydrolysis:



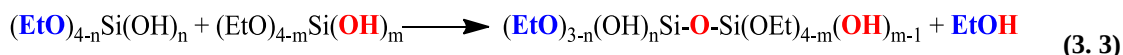
Complete hydrolysis:



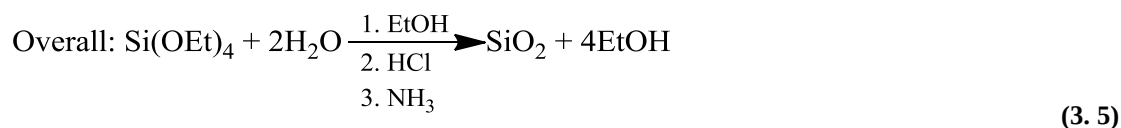
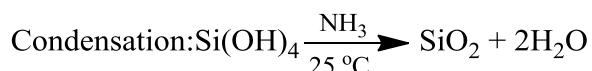
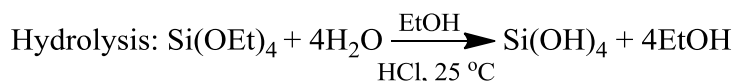
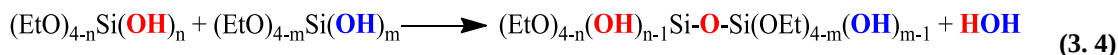
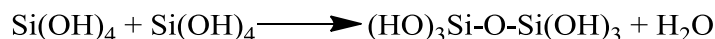
Hydrolysis and condensation reactions take place simultaneously. There are two types of condensation reactions that are alcohol (Eq. 3. 3) and water condensations (Eq. 3. 4) in which alcohol or water is the condensation product. Both condensation reactions occur in

reaction medium. As a result, water is produced during condensation reaction so it should be paid attention that when initial W/T molar ratio at least equals to 2, all TEOS molecules react to produce SiO₂ network (Eq. 3. 5). If acid catalyzed hydrolysis reaction is followed by base catalyzed condensation reaction; the complete process is called as two-step catalyzed SA synthesis. Unless otherwise is mentioned, EtOH was used as a co-solvent and two-step catalyzed SA synthesis method was performed. Alcohol and water condensation reactions and overall reactions are in the following:

Alcohol condensation:



Water condensation:



1.0 g TEOS was used for the smallest scale synthesis. We call it as unit synthesis and a 4.80×10^{-3} mole (n) of TEOS was used (Eqn. 6). Moles and amount of other constituents were calculated based on TEOS amount. Gelation of the unit synthesis was done in an injection syringe. Head of the syringe is cut and taken out. Sol mixture is poured in the syringe and mount of the syringe is closed and sealed with a cork or stopper to prevent

evaporation of solvent from gels. After gelation, gels are pushed and removed from the mold and placed in an ageing solution. In the Table 3. 1, molecular weights and densities of the constituents which were used in the synthesis are given.

Table 3. 1 Molecular weights and densities of the compounds used in silica aerogel synthesis

	MWt*, g/mol	Density, g/mL
TEOS (T)	208.33	0.933
EtOH (E)	46.07	0.789
H ₂ O (W)	18.02	1.00
HCl (A)	36.46	
NH ₃ (B)	17.03	

*MWt: Molecular weight

$$1.0 \text{ g} / 208.33 \text{ g/mol} = 4.80 \times 10^{-3} \text{ mol (n)} \quad (3.6)$$

3. 3. 2 Single-Step Catalyzed Silica Aerogel Synthesis

In the single-step catalyzed SA synthesis, instead of consecutive additions of acid and base catalysts, either acid or base catalyst is added to sol to accelerate the gelation. Four different sol mixtures were prepared with different acid concentrations without adding any further base catalyst. Only added acid volume was changing while keeping amount of other constituents same (Table 3. 2). Sol mixtures were stirred in vials about an hour at room temperature. The vial mounts were closed tightly to prevent solvent evaporation and then they were placed in oven at 50 °C. Gelation occurred in the vials #1A and #2A in 10 days at 50 °C. The wet gels were highly transparent. Even after 10 days at 50 °C, #3A and #4A were still viscous liquid.

Table 3. 2 Single-step acid catalyzed SA synthesis by adding different volume (V) of the acid solution

Samples	TEOS (g)	EtOH (g)	H ₂ O (g)	HCl (mL)
# 1A	1.0	1.0	0.34	0.1
# 2A	1.0	1.0	0.34	0.2
# 3A	1.0	1.0	0.34	0.5
# 4A	1.0	1.0	0.34	0.7

After observing synthesis of the single-step acid catalyzed SA and the effects of acid catalyst volume in sol mixture on gelation time, different amount of co-solvent and water were added into sol mixture in order to decrease the gelation time. While amount of co-solvent was decreased, that of water was increased in miscible region (Table 3. 3). The gelation time was decreased to 3 days at 50 °C by changing the amount of co-solvent and water.

Table 3. 3 Single-step acid catalyzed SA synthesis with different amount of the constituents

TEOS	EtOH	H ₂ O	HCl
1.0 g	0.83 g	0.43 g	0.1 mL

Similarly, four different sol mixtures were prepared with different base concentrations without any pre-addition of acid catalyst. At 50 °C, these solutions were gelled in 3 days but they were completely opaque and weak.

Table 3. 4 Single-step base catalyzed SA synthesis by adding different V of base solutions

Samples	TEOS (g)	EtOH (g)	H ₂ O (g)	NH ₄ OH (mL)
# 1B	1.0	1.0	0.34	0.1
# 2B	1.0	1.0	0.34	0.2
# 3B	1.0	1.0	0.34	0.5
# 4B	1.0	1.0	0.34	1.0

3. 3. 3 Synthesis of Silica Aerogel with Different Molar Ratios of H₂O/TEOS and EtOH/TEOS

Different SAs were synthesized by changing water to TEOS and EtOH to TEOS molar ratios. Effects of water and EtOH amounts in sol mixture on properties of SAs were investigated. SAs with different molar ratios were synthesized in spray lid and plexiglass molds. In order to have identical alcogel samples, sol mixtures were prepared in same batch and base solution was added into these mixtures and then the solution was separated into two or more spray lids or plexiglass molds. For the unit synthesis, 1.0 g (n: 4.80×10^{-3} moles) of TEOS was used. In

Table 3. 5, required moles of water were given for different water to TEOS molar ratios using in the unit synthesis. Amounts of water Table 3. 6 and EtOH (

Table 3. 7) were calculated for different molar ratios while keeping amount of other constituents constant.

Table 3. 5 Moles of water for certain water/TEOS (W/T) molar ratios

H ₂ O/TEOS (W/T)	Moles of H ₂ O
2	$2 \times n = 0.0096$ moles
3	0.0144
4	0.0192
6	0.0288
8	0.0384

Table 3. 6 Amounts of compounds as only W/T ratio is changing (at constant E/T*: 4)

W/T	2	3	4	6	8
Amount					
TEOS (T)	1.0 g	1.0 g	1.0 g	1.0 g	1.0 g
EtOH (E)	0.885 g	0.885 g	0.885 g	0.885 g	0.885 g
H ₂ O (W)	0.173 g	0.259 g	0.346 g	0.519 g	0.692 g
HCl (A)	0.2 mL	0.2 mL	0.2 mL	0.2 mL	0.2 mL
NH ₄ OH (B)	0.5 mL	0.5 mL	0.5 mL	0.5 mL	0.5 mL

* E/T: EtOH/TEOS molar ratios

Table 3. 7 Amounts of compounds as only E/T ratio is changing (at constant W/T: 3)

E/T	2	3	4	6	8
Amount					
T	1.0 g	1.0 g	1.0 g	1.0 g	1.0 g
E	0.442 g	0.663 g	0.885 g	1.33 g	1.77 g
W	0.259 g	0.259 g	0.259 g	0.259 g	0.259 g
A	0.2 mL	0.2 mL	0.2 mL	0.2 mL	0.2 mL
B	0.5 mL	0.5 mL	0.5 mL	0.5 mL	0.5 mL

Amount of constituents must be proportionally increased to fill the molds up to desired height and to obtain silica alcogels with intended thickness or dimensions. For example, one spray lid mold was filled with a sol mixture which is composed of a threefold amount of the unit synthesis (Table 3. 8). Diameter and height of the spray lid are 3.2 cm and 2.1 cm, respectively. Alcogel thickness would be 1-1.5 cm with the threefold amount. Plexiglass mold dimensions are 10 cm x 5.5 cm x 1.2 cm. To fill one plexiglass mold up to 5-6 cm and to obtain a SA with 5 cm x 5 cm x 1 cm dimensions, the unit synthesis amount must be multiplied with 14. Since two identical silica alcogels were prepared from same

batch, 24-fold amount of each constituents must be added into the mixture. Based on these calculations, SAs gelled in both spray lid and plexiglass molds were synthesized with different W/T and E/T molar ratios (Table 3. 9 and Table 3. 10).

Table 3. 8 Different E/T molar ratios for synthesis in the spray lid

EtOH/TEOS	2	3	4	6	8	10
TEOS (g)	3.0	3.0	3.0	3.0	3.0	3.0
EtOH (g)	1.33	1.99	2.65	3.98	5.31	6.63
H ₂ O (g)	1.04	1.04	1.04	1.04	1.04	1.04
HCl (mL)	0.5	0.5	0.5	0.5	0.5	0.5
NH ₄ OH (mL)	1.0	1.0	1.0	1.0	1.0	1.0

Table 3. 9 Amount of constituents required to synthesize two identical SAs with changing W/T in the plexiglass mold (5.5 cm x 5.5 cm x 1.2 cm)

W/T	2	2x	3	2x	4	2x	5	2x
T	14.0 g	28.0 g	14.0 g	28.0 g	14.0 g	28.0 g	14.0 g	28.0 g
E	12.4 g	24.8 g	12.4 g	24.8 g	12.4 g	24.8 g	12.4 g	24.8 g
W	2.42 g	4.84 g	3.63 g	7.26 g	4.84 g	9.68 g	6.01 g	12.11 g
A	2.5 mL	5.0 mL	2.5 mL	5.0 mL	2.5 mL	5.0 mL	2.5 mL	5.0 mL
B	6.0 mL	10 mL	6.0 mL	10 mL	6.0 mL	10 mL	6.0 mL	10 mL

Table 3. 10 Amount of constituents required to synthesize two identical SAs with changing E/T in the plexiglass mold (5.5 cm x 5.5 cm x 1.2 cm)

E/T	3	4	5	6	8
T	28.0	28.0	28.0	28.0	28.0
E	18.58 g	24.77 g	30.96 g	37.15 g	49.53 g
W	7.26 g	7.26 g	7.26 g	7.26 g	7.26 g
A (mL)	5.0	5.0	5.0	5.0	5.0
B (mL)	10	10	10	10	10

3.3.4 Synthesis of Silica Aerogels with Different Types of Co-Solvents

In this study, SAs are almost always synthesized by using EtOH as co-solvent. To compare the effects of co-solvents types on properties of SAs (e.g. transparency, density, etc.), acetone and THF were used to synthesize different SAs. Water to TEOS (W/T: 3) and co-solvents to TEOS (E/T, Acetone/T, and THF/T : 4) molar ratios were kept constant. Required amounts of all constituents are given in the Table 3. 11 for the unit syntheses and for the syntheses in the spray lid molds. Then, SAs with different co-solvents were synthesized in the plexiglass mold. Amounts of each constituent used for the syntheses in the plexiglass mold can be seen in the

Table 3. 12.

Table 3. 11 Amount of constituents required to synthesize SAs with different co-solvents in the spray lid mold

	Alcogel		Acetogel		THF-gel	
	Unit Synthesis: x	3x	x	3x	x	3x
T	1.0 g	3.0 g	1.0 g	3.0 g	1.0 g	3.0 g
Co-solvent	0.885 g	2.65 g	1.12 g	3.35 g	1.39 g	4.16 g
W	0.259 g	0.777 g	0.259 g	0.777 g	0.259 g	0.777 g
A (mL)	0.2	0.5	0.2	0.5	0.2	0.5
B (mL)	0.5	1.0	0.5	1.0	0.5	1.0

Table 3. 12 Amount of constituents required to synthesize SAs with different co-solvents in the plexiglass mold (6 cm x 5.5 cm x 1.5 cm)

	Alcogel	Acetogel	THF-gel
T	17 g	17 g	17 g
Co-solvents	15.04 g	18.96 g	23.55 g
W	4.40 g	4.40 g	4.40 g
A (mL)	3.0	3.0	3.0
B (mL)	5.0	5.0	5.0

3. 3. 5 Prehydrolyzed Precursor Synthesis

When sol mixtures are prepared with EtOH, THF and acetone, the solution would be homogeneous if sufficient amount of the co-solvents are added. On the other hand, TEOS-Etac (Ethyl acetoacetate)-Water mixture is not homogeneous. So, Etac cannot be used as a co-solvent in regular synthesis method. Synthesis procedure was changed to be able to use Etac and to see effects of Etac on the properties of SA. W/T and E/T molar ratios in sol mixture were decreased to 1.8 and 1.6, respectively. For that case, W/T molar ratio is less than stoichiometric ratio (substoichiometric ratio) for synthesis of SiO_2 from TEOS. First, half amount of EtOH that is used in synthesis is mixed with TEOS. Other half is taken from the solution which is prepared with 0.5 mL HCl stock solution diluted to 100 mL with EtOH. This EtOH-HCl solution (Solution B) is added into TEOS-EtOH mixture (Solution A) drop wise under continuous stirring and TEOS-EtOH-HCl solution (Mixture C) is obtained. Then, the mixture C is placed in a cold water bath and desired amount of water is added on it slowly with vigorous stirring. After adding water, the solution is continued to be stirring for a few more minutes for completion of hydrolysis reactions. After that, while heating the mixture, it was connected to a vacuum pump to ease the evaporation of EtOH (Figure 3. 1). Most of the added and produced EtOH was distilled off the mixture. The resulting mixture is called as prehydrolyzed precursor (PHP). There are some EtOH and hydrolysis product, $(\text{EtOH})_{4-n}\text{Si}(\text{OH})_n$ in the prehydrolyzed precursor. Now, Etac and base solution can be added into the PHP solution and an etac-gel (dispersion medium in the wet-gel pores is mostly Etac) is obtained. There is no need further water addition.

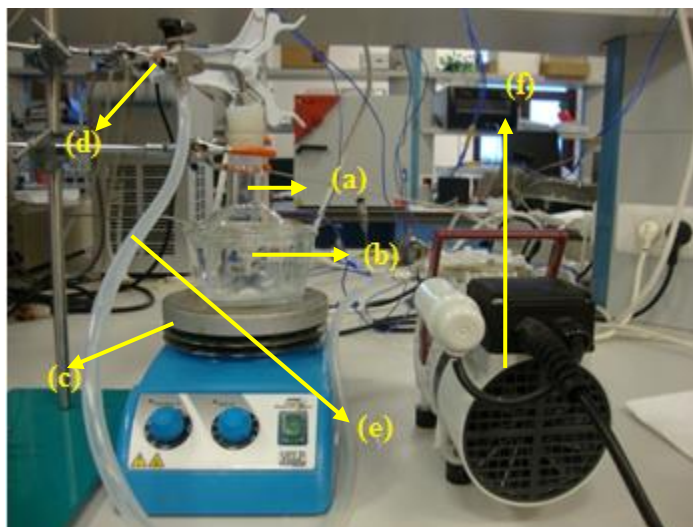


Figure 3. 1 EtOH evaporation experimental set-up: (a) the solution in a round bottom flask, (b) hot water bath, (c) hot plate and stirrer, (d) valve, (e) polymeric tube connects the solution to the vacuum pump, (f) the vacuum pump

First, 1.76 g EtOH was added into 9.82 g TEOS (Solution A). A mixture (Solution B) prepared with 1.764 g EtOH and 0.5 mL HCl solution was added drop wise into the solution A. Then, the final solution was placed in a cold water bath and water was added into the final solution slowly under continuous stirring. The solution was stirred for 30-60 minutes more after adding water. For distillation of EtOH, the evaporation set-up in Figure 3. 1 was used and 6-6.5 g EtOH was evaporated. The remaining solution is the PHP. Etac-gel was synthesized as in the following. 4.0 PHP, 1.2 g Etac (30% amount of PHP) and 0.2-0.3 mL 2.0 M ammonia in EtOH was mixed and stirred about 30 seconds and poured in a mold. Polypropylene (PP) test tubes were used as a mold. Gelation occurred in half an hour. For large amount of PHP and large scale of Etac-gel synthesis, amounts given in Table 3. 13 can be multiplied with desired integers and same procedure can be followed.

Table 3. 13 Amount of constituents for synthesis of prehydrolyzed precursor

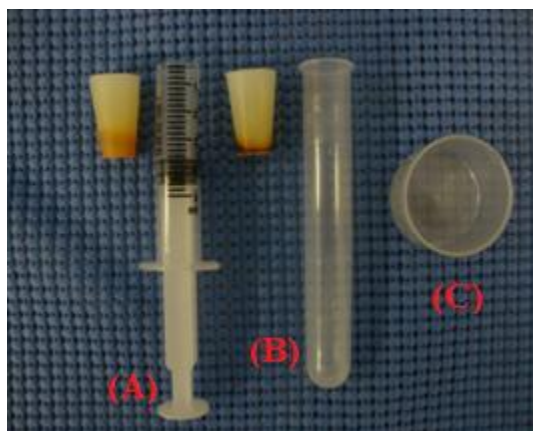
TEOS	EtOH	H ₂ O	HCl
9.82 g	3.53 g	1.53 g	0.5 mL

Table 3. 14 Amount of constituents for synthesis of Etac-gel

PHP	Etac	NH ₃
4.0 g	1.2 g	0.2 - 0.3 mL

3. 3. 6 Gelation in Different Types and Shapes of Molds

Gelation of the unit synthesis was performed in syringes (Figure 3. 2-A) and PP test tubes (Figure 3. 2-B). After gelation in syringes, wet gels can be easily pushed outside without damaging the gels. Wet gels can slide down from PP test tubes when the test tubes are turned upside down. For very small scale trials, those two molds are very appropriate. Cylindrical SA samples with 2.5 cm in diameter were produced in spray lid molds (Figure 3. 2-C).

**Figure 3. 2** A syringe (A), a PP test tube (B) and a spray lid (C) molds

For larger scale syntheses, planar-rectangular prism SAs were synthesized in glass, Teflon, and PP molds. Monolithical SAs in glass molds were not be able to be synthesized.

Commercial storage container type PP molds are useful but PP and Teflon (Figure 3. 3) molds are difficult to be manufactured because processed PP and Teflon molds have quite rough surfaces that affect transparency of SA and their bottom surfaces get bended due to heat evolution during production.



Figure 3. 3 Manufactured Teflon mold

All SAs synthesized in regular rectangular molds (e.g. Teflon molds in Figure 3. 3) were not flat so different shape of mold were considered to be used. This shape mold can be manufactured with using plexiglass material because it can be produced by sticking flat plexiglass parts onto each other. Moreover, wet gels are not stick to plexiglass surfaces and are taken out easily. There are two drawbacks of plexiglass mold (Figure 3. 4). The first problem is that plexiglass mold cannot be put and waited for a while at high temperature (50 °C) if there is an organic solvent inside because it gets soften at high T in an organic solvent. Hence, wet gel cannot be put aging at 50 °C if it is in plexiglass mold. Wet gel should be removed from the mold first and then the aging step can be done at high T. In plexiglass mold, aging is being done at 25 °C. After 24 hours in aging solution in the plexiglas mold at 25 °C, alcogel shrinked and released by itself. It seems to be handled. Then, the alcogels placed in the aging solution and put in the oven at 50 °C. Then, it is taken out and placed in pure EtOH. At 25 °C, EtOH does not affect the plexiglass surface

but other solvents such as acetone and THF dissolve and damage the plexiglass mold even at 25 °C which is the second problem. In other words, there should be found different types of molds with same shape in order to synthesize SAs with different co-solvents. Hence, drawings of a brass mold were prepared (Figure 3. 5) and then brass parts were purchased, machined, and Teflon film covered (Figure 3. 6). Leakage problem could not be solved for brass mold. That is, when sol mixture was filled in the brass mold, it flew away from the mold. Later, Teflon film covered plexiglass mold were tried. As plexiglass mold is covered with a film, it is not possible to stick plexiglass parts onto each other by using an adhesive which is actually liquid methyl methacrylate monomer. So, plexiglass parts were drilled in some point to screw them together (Figure 3. 7). SAs with different co-solvents were synthesized in the Teflon film covered plexiglass mold (Figure 3. 8).



Figure 3. 4 Plexiglass molds

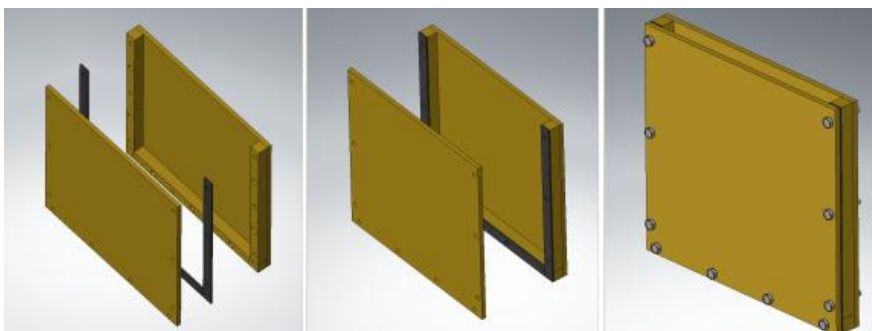


Figure 3. 5 Drawings of brass mold



Figure 3. 6 Teflon film covered brass mold

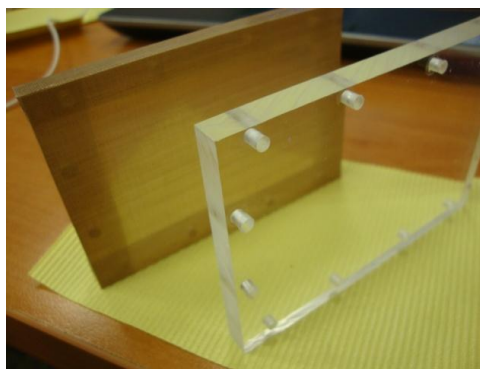


Figure 3. 7 Drilled and covered plexiglass part

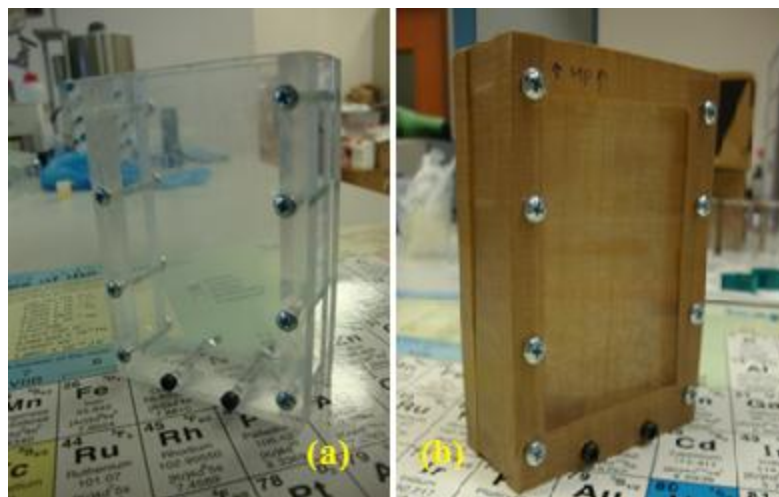


Figure 3. 8 Without (a) and with (b) Teflon film covered screwed plexiglass mold

3. 4 Ageing Silica Alcogels at Different Conditions

Condensation reactions keep continuing even after gelation. So, ageing step increases the strength of wet gel and ageing of wet gel is very crucial to obtain monolithic SA. Wet gels were aged in pure EtOH both at 25 °C and at 50 °C. Ageing in pure EtOH eases or eliminates solvent exchange step because no more water applies to wet gel and water content in pores of wet gel does not rise. However, bulk shrinkage is higher for wet gels aged in pure EtOH and they tend to crack. Accordingly, SAs were always aged in water:EtOH mixture (1:1 in volume) at 50 °C.

To increase the strength of wet gel more, TEOS-EtOH-Water (mother solution) ageing solutions were prepared with different proportions. Different amounts of TEOS and water were added into ageing solution (Constant T/W volume ratios: 4) and wet gels were aged in different mother solution (Constant total volume: 300 mL). Besides, while keeping amount of TEOS in ageing solution constant, ageing T (50 °C and 80 °C) and time (24 hours, 2 and 4 days) were changed and effects of TEOS concentrations, T and time on properties of SAs

were investigated. Wet gels were synthesized in plexiglass mold and W/T and E/T molar ratios were 3 and 4, respectively (Table 3. 15). After gelation, Water-EtOH solution was added on wet gels in plexiglass molds and these gels were waited in this solution about 2-3 hours for spontaneous release from the mold. Afterwards, ageing of those wet gels were performed in desired mother solution and under desired ageing conditions.

Table 3. 15 Amount of each constituent for syntheses of SAs aged in the mother solution

Components	Amount	
	For one sample	For two samples
T	13.59 g	27.19 g
E	12.05 g	24.10 g
W	3.53 g	7.06 g
A	2.5 mL	5 mL
B	5 mL	10 mL

Table 3. 16 Different ageing solution concentrations and ageing conditions

	Ageing Solution	Ageing T	Ageing Duration
Age#1	80 mL T:20 mL W: 200 mL E	50 °C	1 day
Age#2	100 mL T:25 mL W:175 mL E	50 °C	1 day
Age#3	120 mL T:30 mL W:150 mL E	50 °C	1 day
Age#4	100 mL T:25 mL W:175 mL E	80 °C	1 day
Age#5	100 mL T:25 mL W:175 mL E	50 °C	2 days
Age#6	100 mL T:25 mL W:175 mL E	50 °C	4 days

3. 5 Solvent Exchange and Supercritical CO₂ Extraction

In course of condensation of hydrolysis products, water produces. Water content in the pores of wet gel increases when ageing is performed in W-E mixture. Water is not soluble and easily extractable in ScCO₂. So, solvent exchange step is essential to obtain a

completely dried monolithical SA. That is why wet gel is placed in pure EtOH after ageing, stayed there in 2-3 days and EtOH is changed with new one each day. After solvent exchange, silica alcogel is placed in a special design high pressure vessel which is filled with EtOH until level of EtOH exceeds top of the alcogel to prevent possible evaporative drying. The vessel inlet is connected to a pump which can charge the vessel with liquid CO₂ via controllable valve system and temperature of the vessel is increased up to 40-50 °C. After the intended vessel temperature is reached, the inlet valve is opened and the vessel is pressurized to 85-90 bars. Then, the outlet valve is opened and the flow rate is adjusted. In this study, supercritical drying is continuous process and CO₂ in supercritical phase is continuously flown over wet gel. Firstly, EtOH around the gel is collected and then EtOH inside the pores is extracted by scCO₂. Drying process lasts about 6-7 hours with very fast flow rate. Applied Separation extraction unit (Figure 3. 9) was used for all small scale drying. Silica alcogels which were synthesized in the syringe and the PP test tube molds were dried in the cylindrical 30 mL vessel (Figure 3. 10 and Figure 3. 11) (Diameter: 1.5 cm and height: 17 cm). Silica alcogels which were synthesized in the spray lid and plexiglass molds were dried in the larger (500 mL) cylindrical Applied Separation vessel (Figure 3. 12). Six silica alcogels with dimensions of 5 cm x 5 cm x 1 cm can be dried in the larger vessel at the same time.

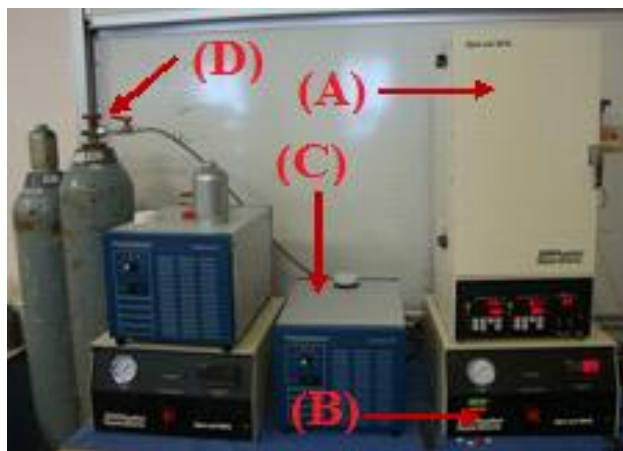


Figure 3. 9 Applied Separation extraction unit: Applied separation oven (A), pump (B), circulator (C) and deep tube CO₂ cylinder

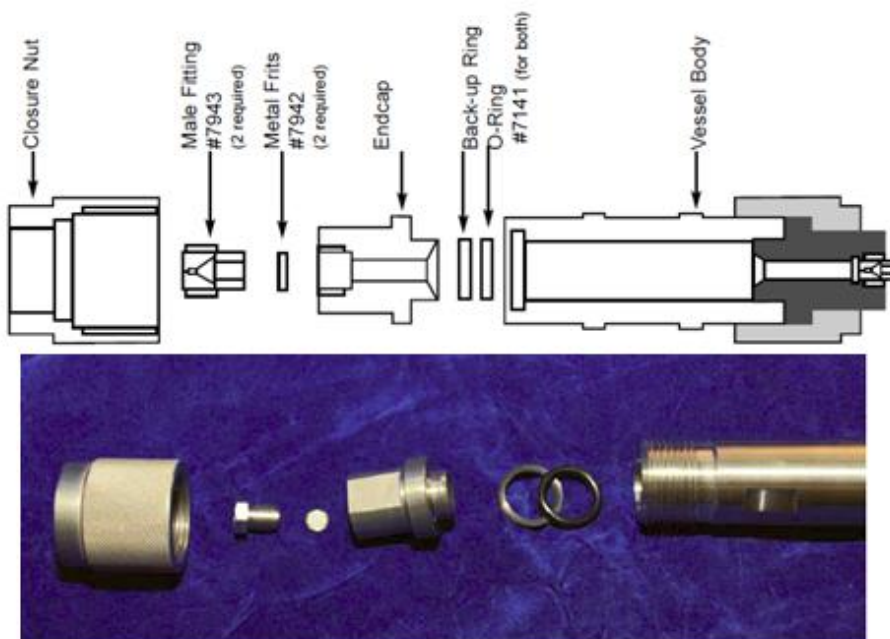


Figure 3. 10 Applied Separation smaller extraction vessel parts



Figure 3. 11 Applied Separation smaller vessel in the oven



Figure 3. 12 Applied Separation larger extraction vessel (D: 7.5 cm and H: 12 cm)

3. 6 Synthesis of Large Scale Silica Aerogels

Prior to large scale synthesis, different sol-gel parameters, ageing solutions, co-solvents, and molds were tried. So, the effects of those parameters and conditions on the properties of SAs were observed and optimum conditions were determined. Based on these experiences on small scales, the collected information was used for large scale synthesis and large scale silica wet gels were synthesized at 25 °C as W/T and E/T molar ratios equal to 3 and 4, respectively. The wet gels were aged in Water-EtOH solution (50% water and

50% EtOH in the solution in volume) at 25 °C and 6-7 days. Then, solvent exchange step was performed in 5.0 L pure EtOH which was renewed twice. Finally, silica alcogels were dried in the Natex large scale extraction system.

3. 6. 1 Sol-Gel Synthesis for Large Scale Aerogels

918.45 g TEOS was used for large scale silica aerogel synthesis. E/T and W/T molar ratios were 4 and 3, respectively. Since total amount was too much, it would be a mixing problem. So, total amount of each compound was divided into three separate batches in 1.0 L bottle. Three separate mixtures of 306.15 g TEOS, 271.23 g EtOH, 79.43 g water and 50 mL HCl solution were stirred about 2 hours. 5.0 mL stock base solution was diluted to 100 mL with EtOH and three of them were prepared 300 mL in total. Three separate sol mixtures were poured in same glass jar. 300 mL base solution was added into the jar slowly with continuous vigorous stirring. Then, the final solution was poured in a large plexiglass mold (Height: 50 cm, length: 37 cm and aperture: 2.2 cm) (Figure 3. 13) with help of a large funnel quickly. Gelation occurred in about 30 minutes and the alcogel released from the mold in about another 30 minutes. Gelation occurred slowly and that let us fill the mold in proper time. Required amount of each compound is given in Table 3.

Table 3. 17 Amount of each compound for large scale SA synthesis

	Three separate batches	Total desired amount
TEOS	3 x 306.15 g	918.45 g
EtOH	3 x 271.23 g	813.69 g
Water	3 x 79.43 g	238.29 g
HCl	3 x 50 mL	150 mL
NH ₄ OH	300 mL	300 mL



Figure 3. 13 Large scale plexiglass mold

3. 6. 2 Large Scale Extraction System

Prior to ScCO_2 extraction, solvent exchange step was done in pure EtOH. Large scale alcogel (H: 35 cm, L: 35 cm, T: 2 cm) was placed in a large PP container with 5.0 L pure EtOH which was changed with new one once again (Figure 3. 14). Large scale alcogels were dried in the Natex large scale extraction unit. Volume of the vessel is 35 L and there are too much empty dead volume (Figure 3. 15) that wastes time and excessive amount of EtOH and CO_2 . Hence, two-half cylindrical Al-steel blocks were placed inside the vessel to decrease this dead volume and to provide more efficient extraction. There is enough room for only one alcogel in between the blocks. Top view of the vessel with the Al-steel blocks and silica aerogel in between them can be seen in Figure 3. 16.

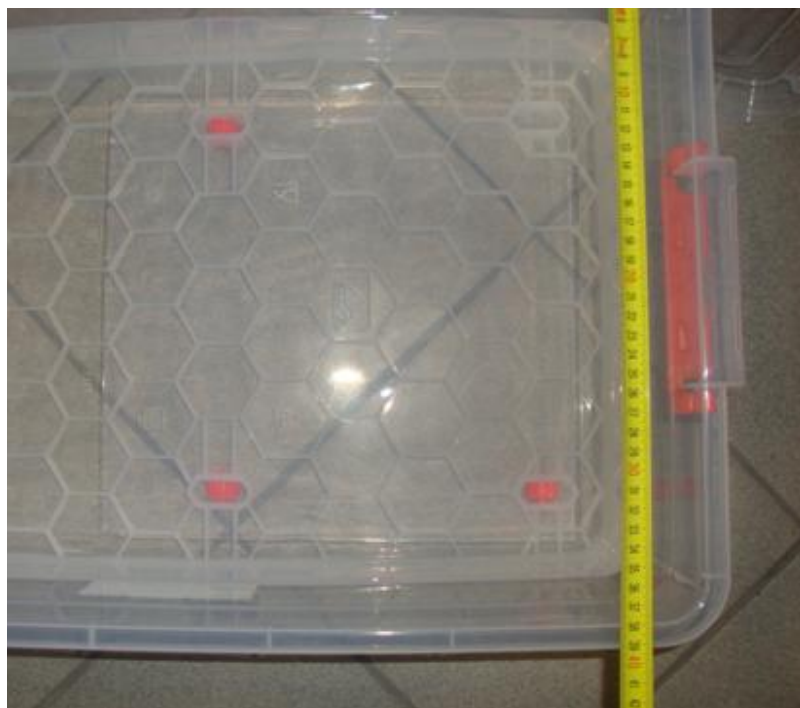


Figure 3. 14 Large scale silica alcogel placed in pure EtOH in a PP container

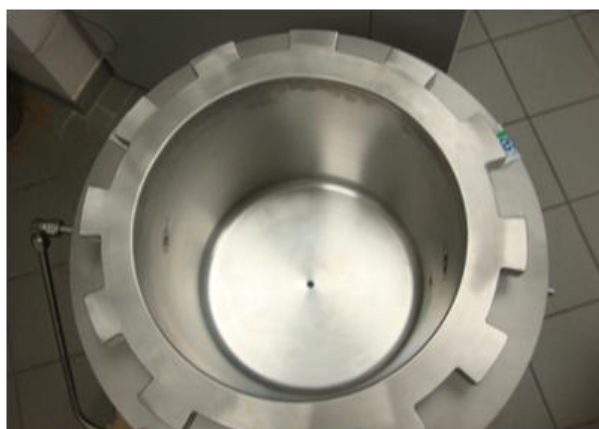


Figure 3. 15 Top view of empty Natex large scale extraction vessel

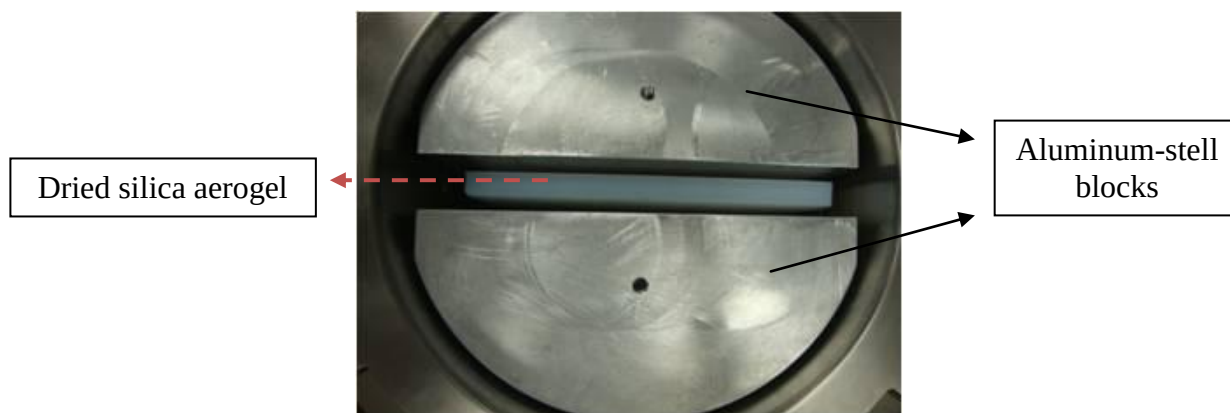


Figure 3. 16 Top view of Natex large scale extraction vessel with two-half cylinder Al-steel blocks and dried flat silica aerogel

First, the vessel was filled with EtOH. Then, an alcogel was placed in the vessel between two blocks vertically. EtOH level should be higher than top of the alcogel. The cover and the bayonet ring were moved with a crane on top of the vessel. The ring was brought to closed position by rotating it and the safety plug was placed and screwed. The Natex large scale extraction unit can be seen in Figure 3. 17. Hot water was pumped into the jacket of the vessel via a hot water circulator. Temperature of the vessel was increased up to 50 °C. Inside pressure of the vessel raised a bit due to evaporation of EtOH in the closed system. After that, the vessel was charged with liquid CO₂ from one side of the vessel by using the Applied Separation pump system. EtOH inside the vessel can be collected before reaching the critical P in order to prevent mixing of CO₂ and EtOH. CO₂ was pumped to the vessel until the inside P of the vessel reached to 80-85 bars. Figure 3. 18 represents schematic of the Natex large scale vessel. The extraction process continued for 8 days. The extraction lasted that long time to be sure that the alcogel was certainly dried. Finally, the vessel was depressurized by turning off the inlet valve and with slow outlet flow. The depressurization rate was between 0.15-0.20 bar/min.



Figure 3. 17 Side view of Natex large scale extraction unit with cover, bayonet ring and safety plug

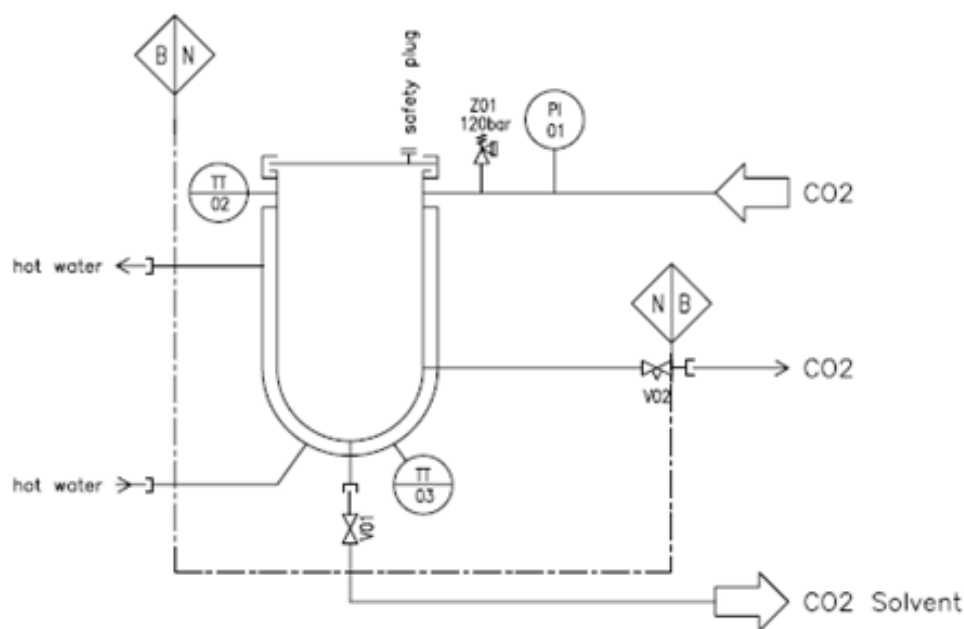


Figure 3. 18 Side view of schematic of Natex large scale extraction system

3. 7 Determination of Properties of SA and Instrumental Analyses

3. 7. 1 Monolithicity, Bulk Shrinkage, Density, and Porosity

Monolithic samples showed good transparency and thermal conductivity. Silica aerogel can only be used in market if it is monolithic without any crack or broken pieces. Monolithicity was determined by observation. Bulk shrinkage affects density and final dimensions of aerogel. Bulk shrinkage can be calculated directly from difference between volume of the mold in which gelation is done and volume of the synthesized silica aerogel. Density is calculated from mass of a silica aerogel which is weighed by a balance and volume of the aerogel calculated from dimensions of certain shape of silica aerogels which is determined by a caliper. Porosity is calculated from the equation in the following:

3. 7. 2 N₂ Adsorption-Desorption Analysis

N₂ adsorption-desorption analysis is performed in Micromeritics ASAP 2020 instrument (Figure 3. 19). First, sample is degassed before analysis. The instrument degas dewer is filled with liquid N₂ and should be refilled in 3-4 days. Micromeritics' sample tube with glass rod and lid are weighed while it is empty (Figure 3. 20). About 100 mg sample is weighed for the analysis. Crashed sample is filled in the sample tube which is placed degas port 1 or 2 on the instrument. The tube is covered with the instrument heating jacket. Then, sample information is entered from instrument software. Degas conditions are 300 °C hold temperature and 300 minutes as hold time for silica aerogel. Finally, degas can be started and followed from degas schematic from software. Pressure inside the sample tube should drop to a few $\mu\text{m Hg}$ from a few mm Hg. After degas, the sample tube is taken from degas port and weighed. Weight of the empty sample tube is subtracted from weight the sample tube filled with sample and weight of the sample is calculated. Then, the sample tube is covered with a polymeric jacket to keep temperature same throughout the tube. The tube is placed on analysis port. The instrument analysis dewer should be filled up to desired level and checked before each analysis. Weight of the sample is entered to software and analysis is started.

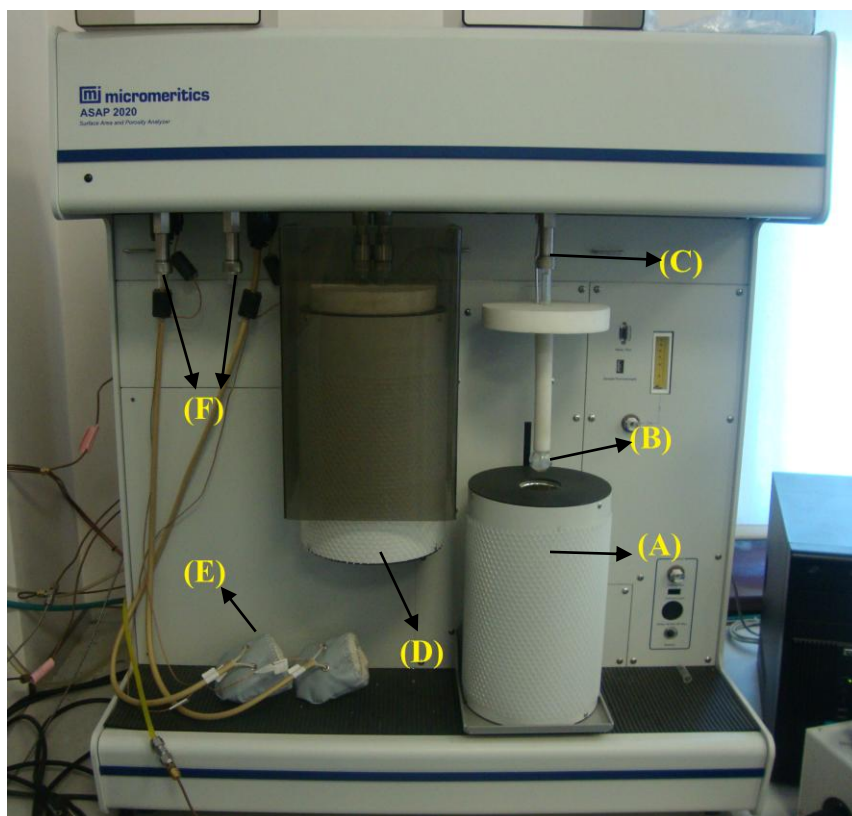


Figure 3. 19 Micromeritics ASAP 2020 N₂ Adsorption-Desorption Analysis instrument; Analysis dewar (A), sample tube (B), analysis port (C), degas dewar (D), heating jacket (E), and degas ports (F)

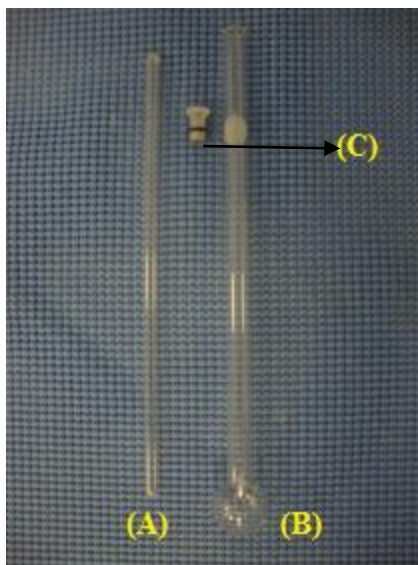


Figure 3. 20 Glass rod (A), sample tube (B), and lid (C)

3. 7. 3 ATR-FTIR and UV-VIS Spectrophotometers

Thermo Scientific Nicolet Avatar 360 E.S.P. FTIR spectrophotometer with Horizontal Attenuated Total Internal Reflectance (ATR) Accessory was used for IR analyses of silica aerogel samples (Figure 3. 21). FTIR is used to investigate the nature of molecular bonds and to identify the functional groups among a molecule. A transmission cell or a KBr pellet is not required for ATR-FTIR analysis. The IR beam travels through a sample and is reflected back internally to the ATR crystal. This happens several times and the IR beam reaches to detector (Figure 3. 22). For analysis of sample, surface of the ATR crystal is cleaned and the first measurement is done without a sample for blank analysis. Then, crashed silica aerogel sample is placed on surface of the ATR crystal and is pressed against the crystal. Finally, IR analysis of a silica aerogel sample is taken and saved as transmittance versus wave number.



Figure 3. 21 Thermo Scientific Nicolet Avatar 360 E.S.P. FTIR spectrophotometer with Horizontal Attenuated Total Internal Reflectance (ATR) system

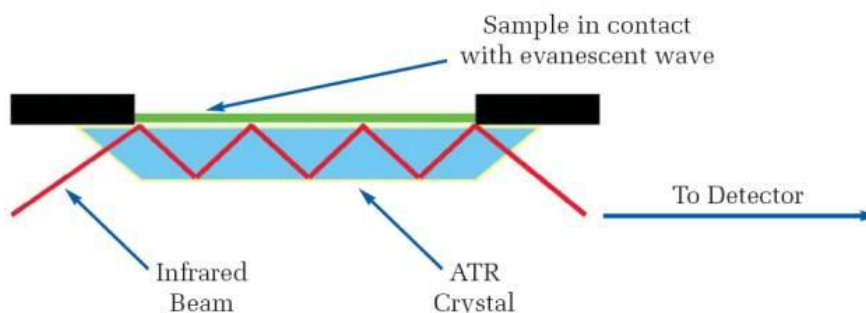


Figure 3. 22 A multiple reflection in ATR crystal (Taking from Perkin-Elmer FTIR-ATR technical note document,

http://las.perkinelmer.com/content/TechnicalInfo/TCH_FTIRATR.pdf)

UV-VIS Spectrophotometer with integrating sphere apparatus (Figure 3. 23) can be used for analysis of transparency of silica aerogel. The Integrating system is comprised of UV-VIS-NIR light source, sample holder, detector at the center of the system, two BaSO₄ powder to reflect the incoming light and reference beam (Figure 3. 24). Analysis range is 200 nm-900 nm. Scan speed is arranged as medium. Sampling interval (nm) is set as 1.0

and auto mode is selected for sampling mode. Measuring mode is always transmittance and slit width is selected as 20 nm. External 2 detector (Not direct) is selected for detector unit.

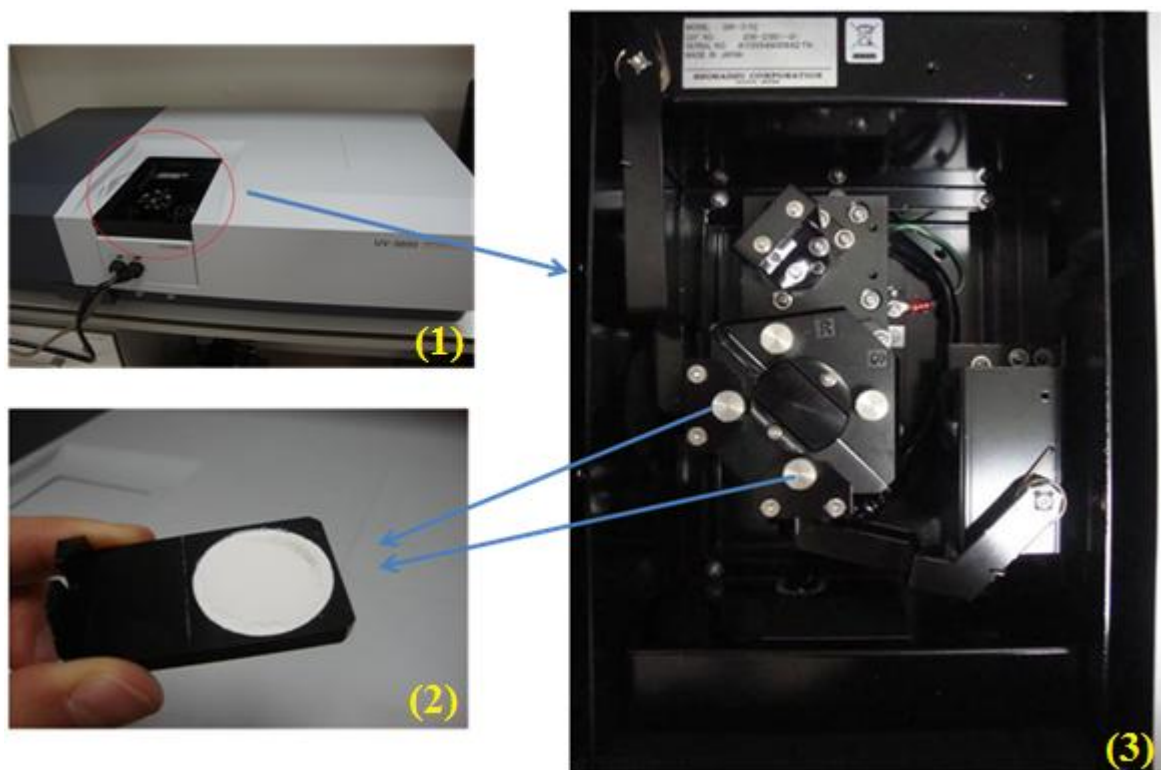


Figure 3. 23 UV-VIS Spectrophotometer with integrating sphere system; Shimadzu UV-VIS spectrophotometer, the integrating sphere apparatus (2), BaSO₄ (3)

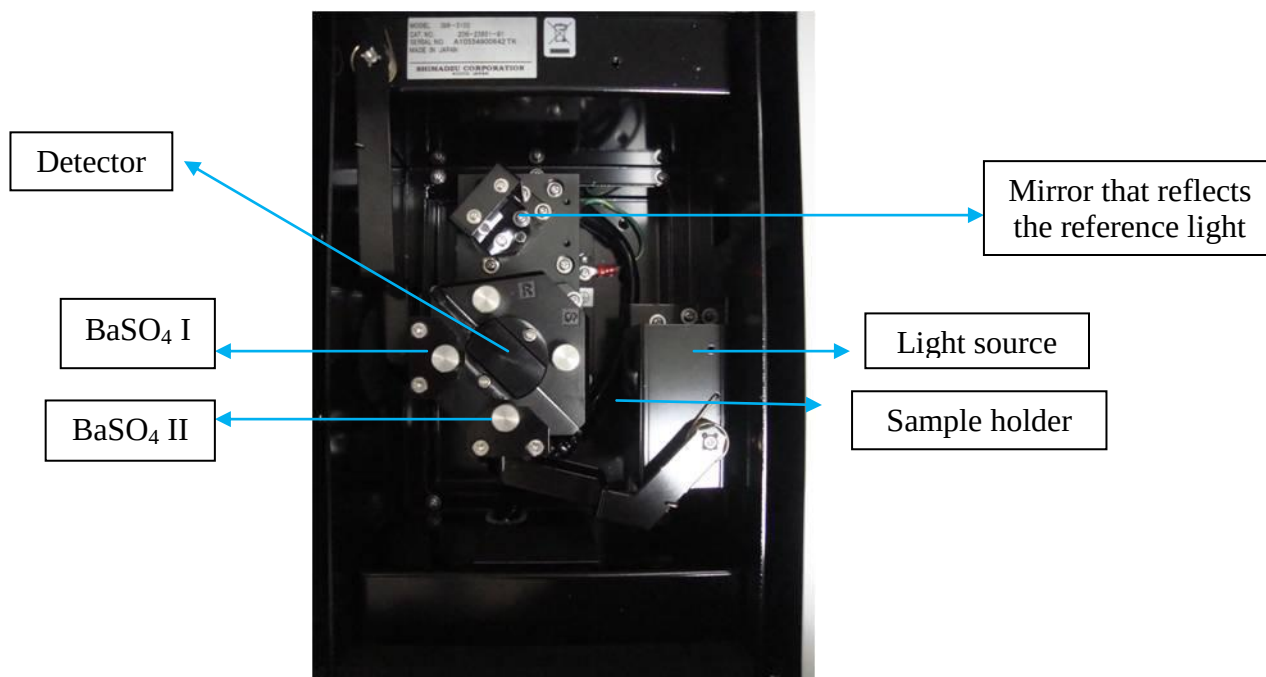


Figure 3. 24 The integrating sphere parts

In order to determine haze value or transparency ratio of a sample, both total and diffuse transmittances should be analyzed by following three consecutive steps. First measurement should be done without sample for baseline correction (Figure 3. 25-A). After baseline correction, sample is placed inside the integrating sphere and total transmittance is measured. For diffuse transmittance, BaSO₄ I is removed from the integrating sphere and only forward scattered light is measured. Ratio of diffuse to total transmittance gives haze value for a certain material (Eqn. 3. 8).

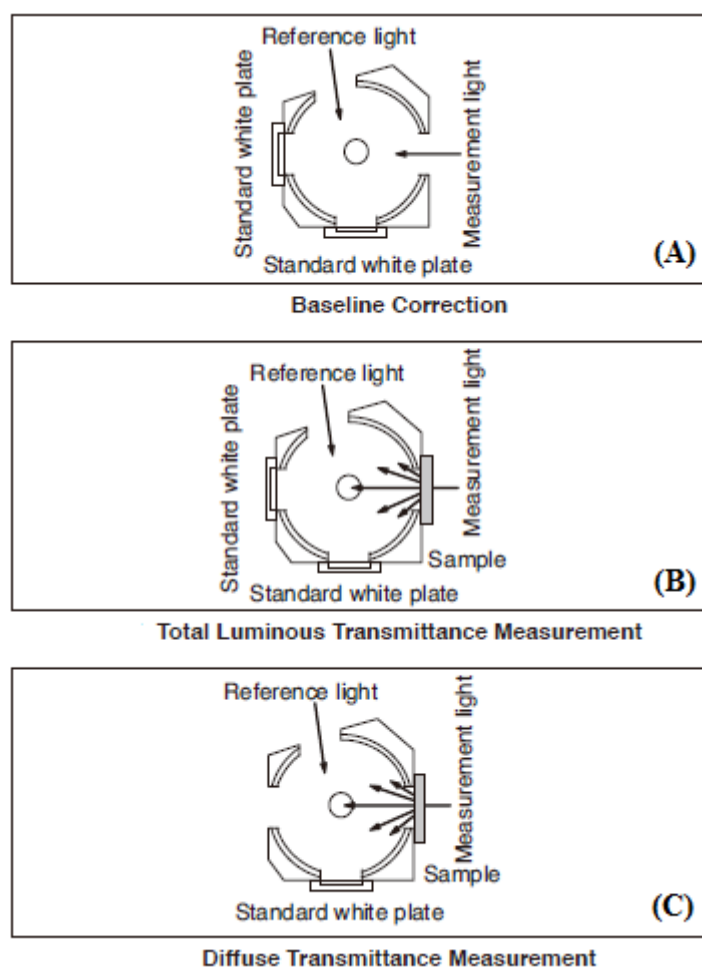


Figure 3. 25 Transparency analysis method with integrating sphere; baseline correction (A), total transmittance measurement (B), diffuse transmittance measurement (C)

$$(\text{Difusse/ Total Transmittance}) \times 100 = \text{Haze} \quad (3. 7)$$

$$(\text{Total -Diffuse})/\text{Total Transmittance} \times 100 (1\text{-Haze}) = \text{Transparency Ratio} \quad (3. 8)$$

3. 7. 4 Hot Disk Transient Plane Source

Thermal transport properties (thermal conductivity, thermal diffusivity, heat capacity) can be determined by using Hot-Disk method which is a transient (time dependent) technique. Plane heating source that is also detector in the system is used (Figure 3. 26). This heating source is made of double spiral thin Nickel metal foil covered with an insulation polymer, Kapton. To be able to determine the thermal properties of a material, two identical samples which should have at least one flat surface to directly contact with the heating source are required. The heating source is placed and pressed between two identical samples and any air gap between the heating source and sample must be prevented (Figure 3. 27). A cylindrical cover is placed on the sample support (Figure 3. 28) to prevent system from temperature disturbance through air draft to the sample during the transient recording.

Hot Disk analysis software is started and from experiment type selection dialog box, isotropic and low density/high insulating checkbox are selected and Bulk (Type I) is clicked for silica aerogel samples. Before analysis, room temperature value must be entered to software of the Hot-Disk instrument which is essential for calculating temperature coefficient of resistivity of the sensor (TCR). Heating power and analysis time are chosen by user. These parameters can be selected from database of the instrument or be determined after many experiments. Since there is no database for silica aerogels; heating power, analysis time, and required time between two successive measurements were determined as a result of many trials. Based on these trials, 10 mW as heating power and 40 sec or 80 sec as analysis time gave very consistent results. 30 minutes or more time is appropriate for waiting period. A transient graph of heating profile (T difference, K vs. time, sec) is obtained by heating the sample with the selected heating power and time and recording 200 data points of the T increase of the sensor. From calculation settings, start and end point can be changed, time correction and T drift compensation can be done, and heat capacity of

the sample can be entered if known. Thermal conductivity, thermal diffusivity and heat capacity can be calculated simultaneously.

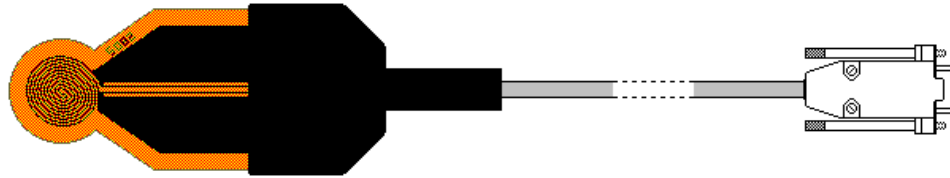


Figure 3. 26 Hot-Disk plane source instrument heating source (and detector)

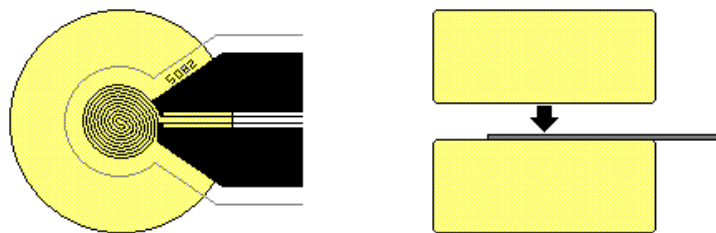


Figure 3. 27 The heating source position between two identical samples



Figure 3. 28 Room T sample support and cylindrical cover

Chapter 4

RESULTS AND DISCUSSION

4. 1 Effects of Sol-Gel Parameters on Properties of Silica Aerogels

Silica aerogels are synthesized by following sol-gel route and using supercritical CO₂ (scCO₂) extraction method. To be able to synthesize transparent, flat, low density, and monolithic silica aerogel in large scale, sol-gel parameters must be investigated thoroughly [10, 11, 52, 53].

4. 1. 1 Single-Step and Two-Step Silica Aerogel Syntheses

Single step base catalyzed silica wet gels were opaque in all proportions (Figure 4. 1). So, this synthesis method is not useful for further study. Single step acid catalyzed silica aerogel synthesis resulted in transparent silica alcogels (Figure 4. 2). Gelation occurred when low amount of acid was added. For example, sample #1A composed of 1.0 g TEOS, 1.0 EtOH, 0.34 g water and 0.1 mL HCl showed the fastest gelation (10 days at 50 °C) among four different sol mixtures with different acid volumes (e.g. 0.2 mL, 0.5 mL). The main reason is that increasing amount of acid solution in sol mixture decreases pH of the sol and increases rate of hydrolysis reactions but also decreases rate of further condensation reactions. As amount of EtOH was decreased and amount of water was increased in sol mixture for single-step acid catalyzed SA synthesis, gelation time decreased to 3 days at 50 °C. Gelation time is changing from a few minutes to half an hour for two-step silica aerogel

synthesis. Transparency of silica aerogels which were synthesized by following two-step catalyzed method is changing depending on sol-gel parameters. Hence, two-step catalyzed synthesis method was focused on due to controllable gelation time and sol-gel parameters were investigated to determine optimum conditions for better transparency and thermal conductivity of SA.



Figure 4. 1 Single step base catalyzed silica wet gels

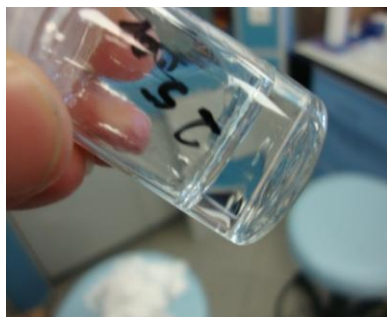


Figure 4. 2 Single step acid catalyzed silica wet gel

4. 1. 2 Effects of Molar Ratios

In advance of large scale SA synthesis, effects sol-gel parameters on transparency and thermal conductivity of SAs were investigated in small scales. SAs with different W/T and E/T molar ratios were synthesized in PP (synthesized aerogel dimensions: 0.93 ± 0.03 cm in

thickness and 2.71 ± 0.03 cm in diameter) and plexiglass (synthesized aerogel dimensions: H: 5.0 cm, L: 5.0 cm and T: 1.0 cm) molds. As W/T molar ratios (keeping amount of other substance constant) increases; density, gelation time and transparency (Figure 4. 3, Figure 4. 4 and Figure 4. 5) of SAs decrease. Density of SA decreases when amount of water increases in sol mixture because while amount of SiO_2 produced remains constant at the end of reactions (TEOS is limiting reactant), volume of the aerogel increases. Reason of increasing volume is unreacted water forms dispersion medium inside aerogel pores when excess amount of water is added. Addition of W/T less than 4 resulted in SAs with better transparency. Cracked SA was obtained when W/T: 2 and E/T: 3 molar ratios were used to synthesize a SA (Figure 4. 6).



Figure 4. 3 Effect of W/T molar ratios on transparency of silica alcogels (E/T: 4)

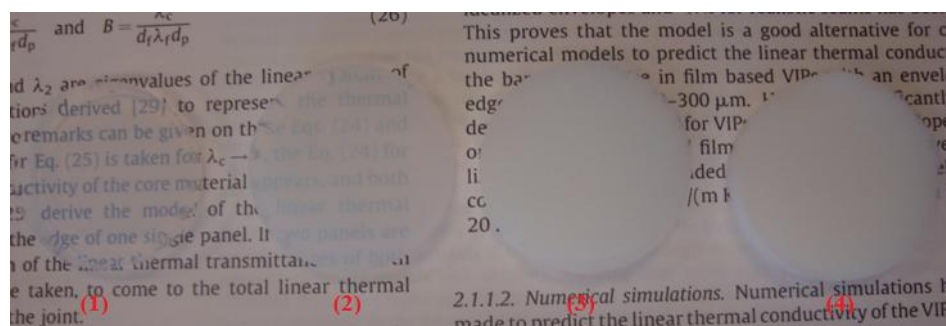


Figure 4. 4 Silica aerogels with different W/T molar ratios; W/T: 2 (1), W/T: 4 (2), W/T: 8 (3), and W/T: 10 (4) (E/T: 4)

Based upon ^{55}Cr , (1) indicates the mass number of the most stable isotope											
3	4	5	6	7	8	9	10	11	12		
IIIB	IVB	VB	VIB	VII	VIII	VIII	VIII	IB	IIB		
21 Sc Scandium 44.95591 [Ar]3d ¹ 4s ² 2.12	(a) 22 Ti Titanium 47.88 [Ar]3d ² 4s ² 1.79	23 V Vanadium 50.9415 [Ar]3d ³ 4s ² 1.76	24 Cr Chromium 51.9961 [Ar]3d ⁵ 4s ¹ 1.74	(b) 25 Mn Manganese 54.938044 [Ar]3d ⁵ 4s ² 1.75	26 Fe Iron 55.934936 [Ar]3d ⁶ 4s ² 1.83	27 Co Cobalt 58.933195 [Ar]3d ⁷ 4s ² 1.88	(c) 28 Ni Nickel 58.6934 [Ar]3d ⁸ 4s ² 1.91	29 Cu Copper 63.546 [Ar]3d ¹⁰ 4s ¹ 1.90	30 Zn Zinc 65.38 [Ar]3d ¹⁰ 4s ² 1.92		
39 Y Yttrium 88.90584 [Kr]4d ¹ 5s ² 2.27	40 Zr Zirconium 91.224 [Kr]4d ² 5s ² 1.73	41 Nb Niobium 92.90638 [Kr]4d ⁴ 5s ¹ 1.76	42 Mo Molybdenum 95.94 [Kr]4d ⁵ 5s ¹ 1.78	43 Tc Technetium 98.90625 [Kr]4d ⁵ 5s ² 2.20	44 Ru Ruthenium 101.07 [Kr]4d ⁷ 5s ¹ 2.26	45 Rh Rhodium 102.90550 [Kr]4d ⁸ 5s ¹ 2.28	46 Pd Palladium 106.363156 [Kr]4d ¹⁰ 2.20	47 Ag Silver 107.8682 [Kr]4d ¹⁰ 5s ¹ 2.28	48 Cd Cadmium 112.411 [Kr]4d ¹⁰ 5s ² 2.28		
72 Hf Hafnium 178.49 [Xe]4f ¹⁴ 5d ² 6s ² 2.20	73 Ta Tantalum 180.94788 [Xe]4f ¹⁴ 5d ³ 6s ² 2.24	74 W Tungsten 183.84 [Xe]4f ¹⁴ 5d ⁴ 6s ² 2.26	75 Re Rhenium 186.207 [Xe]4f ¹⁴ 5d ⁵ 6s ² 2.28	76 Os Osmium 190.23 [Xe]4f ¹⁴ 5d ⁶ 6s ² 2.28	77 Ir Iridium 192.222 [Xe]4f ¹⁴ 5d ⁷ 6s ² 2.28	78 Pt Platinum 195.083 [Xe]4f ¹⁴ 5d ⁹ 6s ¹ 2.28	79 Au Gold 196.966569 [Xe]4f ¹⁴ 5d ¹⁰ 6s ¹ 2.20	80 Hg Mercury 200.59 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 2.20	81 Tl Thallium 204.38 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 2.28	82 Pb Lead 207.2 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 2.28	
104 Rf Rutherfordium 261 [Rn]5f ¹⁴ 6d ² 7s ²	105 Db Dubnium 262 [Rn]5f ¹⁴ 6d ³ 7s ²	106 Sg Seaborgium 266 [Rn]5f ¹⁴ 6d ⁴ 7s ²	107 Bh Bohrium 264 [Rn]5f ¹⁴ 6d ⁵ 7s ²	108 Hs Hassium 277 [Rn]5f ¹⁴ 6d ⁶ 7s ²	109 Mt Meitnerium 268 [Rn]5f ¹⁴ 6d ⁷ 7s ²	110 Ds Darmstadtium 271 [Rn]5f ¹⁴ 6d ⁸ 7s ²	111 Rg Roentgenium 272 [Rn]5f ¹⁴ 6d ⁹ 7s ²	112 Uu Ununbium 285 [Rn]5f ¹⁴ 6d ¹⁰ 7s ²	113 Uuh Ununhennium 288 [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	114 Uuq Ununquadium 289 [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	
116 Lv Livermorium 293 [Og]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	117 Ts Tennessine 294 [Og]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵	118 Og Oganesson 294 [Og]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶									

Figure 4. 5 Silica aerogels with different W/T molar ratios; W/T: 2 (a), 4 (b), 6(c) (E/T: 3)

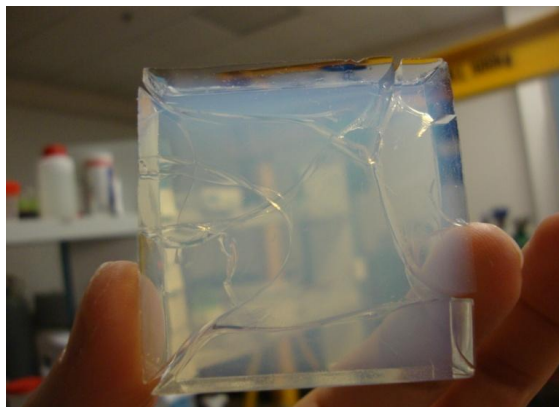


Figure 4. 6 Cracked silica aerogel (W/T: 2 and E/T: 3)

Transparency is lost when W/T molar ratio is equal to 5 or more in sol mixture because excess water forms white precipitates with NH_3 (Figure 4. 7 and Figure 4. 8-A) and these white precipitates in solution results in completely opaque aerogel (Figure 4. 8-B).

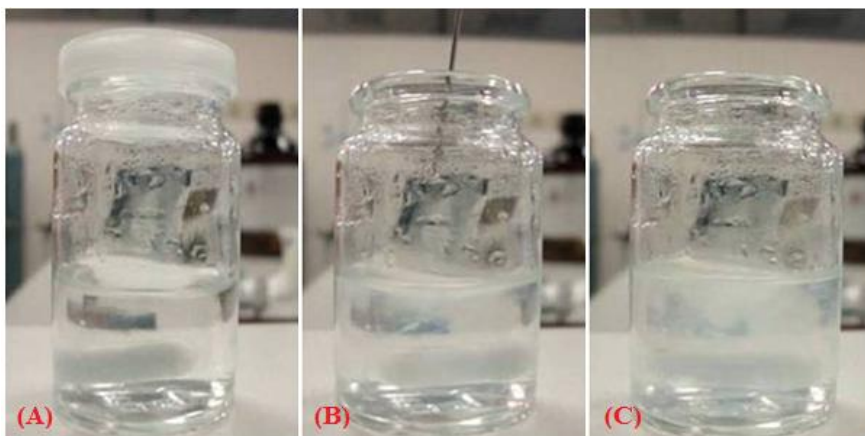


Figure 4. 7 Addition of NH_4OH into sol mixture with high amount of water (W/T: 5)

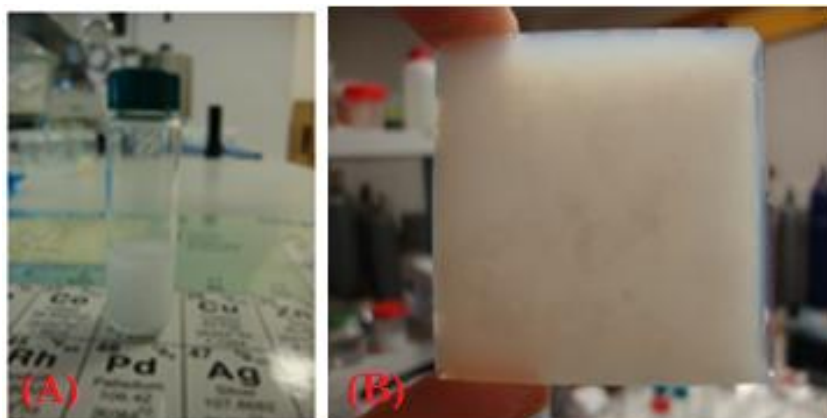


Figure 4. 8 Water-NH₃ mixture (A) and a silica aerogel sample with W/T: 6 and E/T: 4 (B)

Thermal conductivity is directly related to density of SA and as W/T molar ratio increases in sol mixture, thermal conductivity of the resulting SAs decreases. The heating profiles (Figure 4. 9) of the SAs with different W/T molar ratios show that temperature increase on the surface of the SA with higher W/T molar ratio is greater which means that heat flow is more restrictive for the SA with higher amount of water and low density. Accordingly, the SA synthesized with W/T: 4 has lower thermal conductivity than the SAs with W/T: 2 and 3.

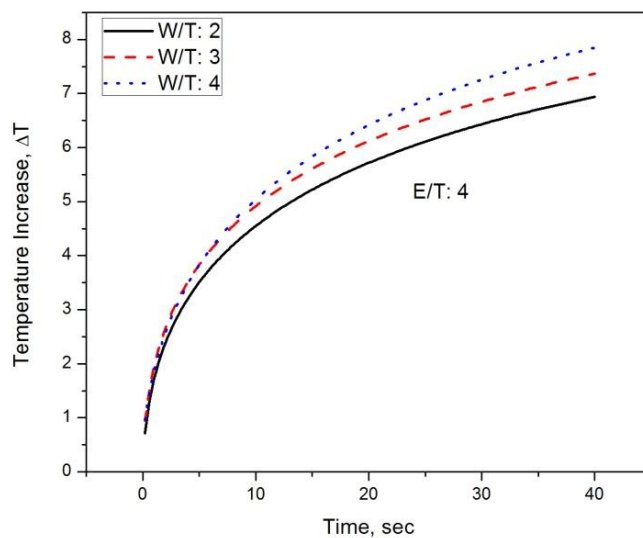


Figure 4. 9 Heating profile of silica aerogels with different W/T molar ratios
(constant E/T: 4)

Although increasing amount of water decreases thermal conductivity of the SA which means better insulation property, higher W/T molar ratio results in worse transparency and more hazy material. While total transmittance of the SA decreases, diffuse transmittance of the SA increases when SA is synthesized with higher W/T molar ratio (Figure 4. 10). The best transparency was obtained with W/T: 2 and E/T: 3. The problem is that it is very difficult to get monolithic and crack-free SA with these proportions.

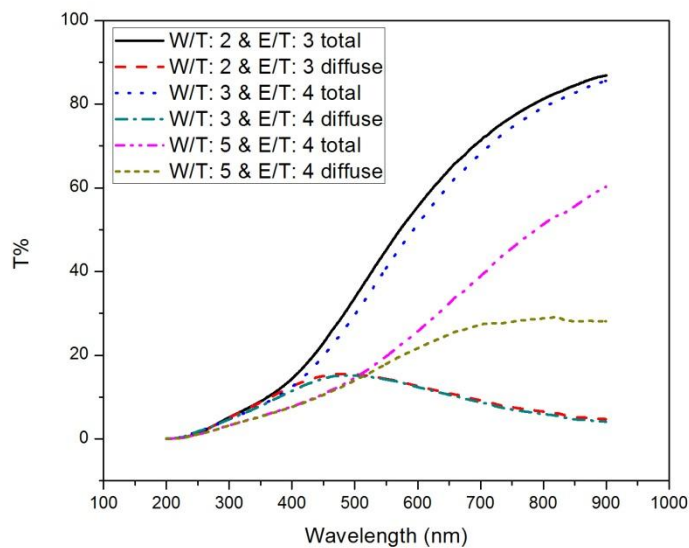


Figure 4. 10 Total and diffuse transmittance of silica aerogels with different W/T molar ratios

Different SAs were synthesized by changing E/T molar ratio while W/T molar ratio was kept constant. Transparency of SAs decreases as E/T molar ratio increases in sol mixture (Figure 4. 11 and Figure 4. 12) because both particle size (size of aggregates that form larger clusters and gel network) increases and homogeneity decreases as E/T molar ratio increases so that results in worse transparency and higher haze value.

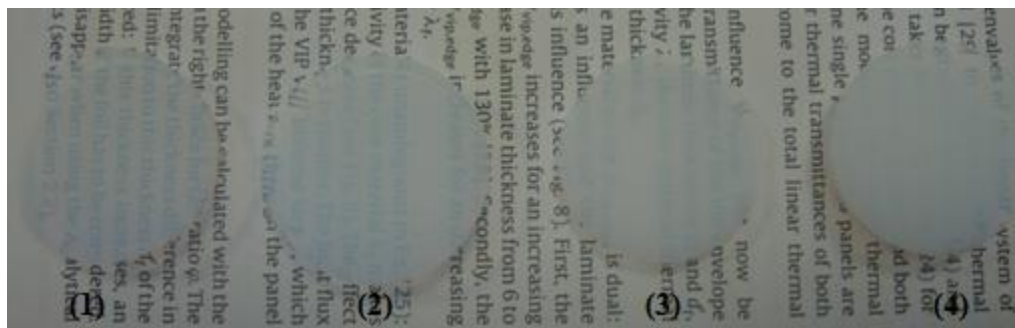


Figure 4. 11 Silica aerogel samples with different E/T molar ratios; E/T: 2 (1), 3 (2), 4 (3), and 6 (4) (W/T: 4)

Based upon ¹²C, () indicates the mass number of the most stable isotope.

4	5	6	7	8	9	10	11
VB	VB	VIB	VII	VIII	VIII	VIII	IB
22 ³ F ₂ Ti Titanium 47.867 [Ar]3d ² 4s ² 6.8281	23 ⁴ F _{3/2} V Vanadium 50.9415 [Ar]3d ³ 4s ² 6.7462	24 ⁷ S ₃ Cr Chromium 51.9961 [Ar]3d ⁵ 4s 6.7665	25 ⁶ S _{5/2} Mn Manganese 54.938049 [Ar]3d ⁵ 4s ² 7.4340	26 ⁵ D ₄ Fe Iron 55.845 [Ar]3d ⁶ 4s ² 7.9024	27 ⁴ F _{9/2} Co Cobalt 58.933200 [Ar]3d ⁷ 4s ² 7.8810	28 ³ F ₄ Ni Nickel 58.6934 [Ar]3d ⁸ 4s ² 7.6398	29 ² S _{1/2} Cu Copper 63.546 [Ar]3d ¹⁰ 4s 7.7264
40 ³ F ₂ Zr Zirconium 91.224 [Kr]4d ² 5s ²	41 ⁶ D _{1/2} Nb Niobium 92.90638 [Kr]4d ⁴ 5s ¹	42 ⁷ S ₃ Mo Molybdenum 95.94 [Kr]4d ⁵ 5s ¹	43 ⁶ S _{5/2} Tc Technetium (98) [Kr]4d ⁵ 5s ²	44 ⁵ F _{5/2} Ru Ruthenium 101.07 [Kr]4d ⁷ 5s ¹	45 ⁴ F _{9/2} Rh Rhodium 102.90550 [Kr]4d ⁸ 5s ¹	46 ¹ S ₀ Pd Palladium 106.42 [Kr]4d ¹⁰	47 ² S _{1/2} Ag Silver 107.8682 [Kr]4d ¹⁰ 5s ¹

EtOH/TEOS

6

5

3

Figure 4. 12 Silica aerogel samples with different E/T molar ratios (W/T: 3)

Density of SAs decreases (Figure 4. 13) as E/T molar ratio increases in sol because even though more shrinkage occurs with higher E/T molar ratio, higher amount of EtOH in sol increases volume of SA. Hence, depending on density of SA, thermal conductivity of SA decreases as amount of EtOH in sol increases (Figure 4. 14). Relations of thermal conductivity and density with E/T molar ratios are given in Table 4. 1 and Figure 4. 15

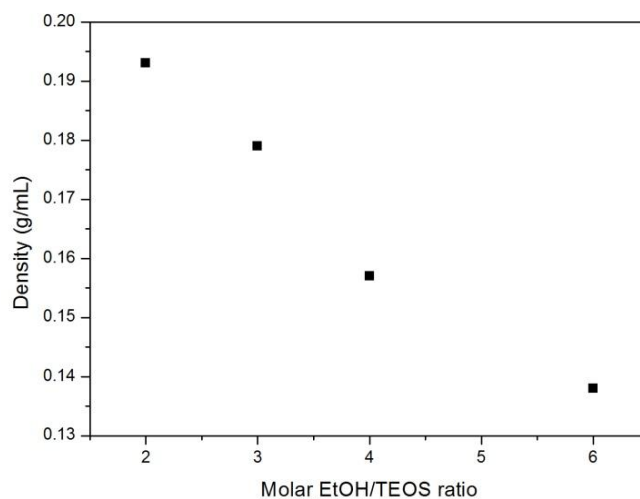


Figure 4. 13 Density of silica aerogels with respect to different E/T molar ratios

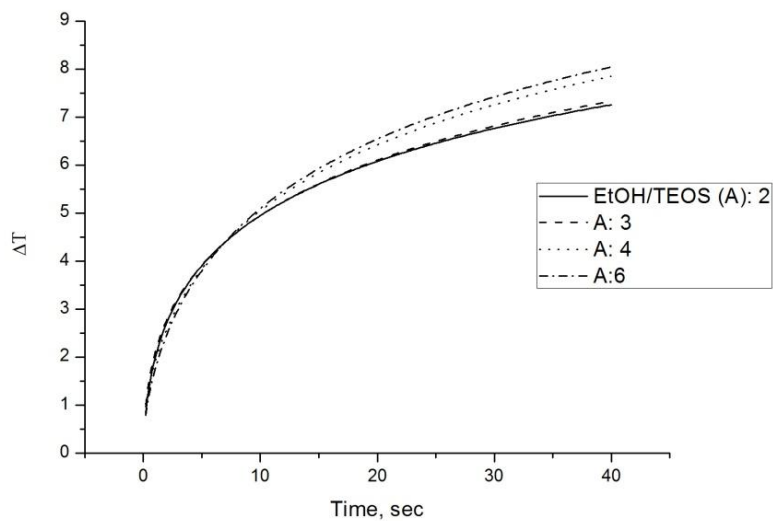


Figure 4. 14 Heating profile of SAs as E/T molar ratios changing from 2 to 6 (W/T: 4)

Table 4. 1 Density and thermal conductivity (Hot Disk results) values of SAs synthesized using different E/T molar ratios (W/T: 4)

EtOH/TEOS	Density (g/cc)	Thermal Conductivity
2	0.193	0.036 W/mK
3	0.179	0.033 W/mK
4	0.157	0.029 W/mK
6	0.139	0.028 W/mK

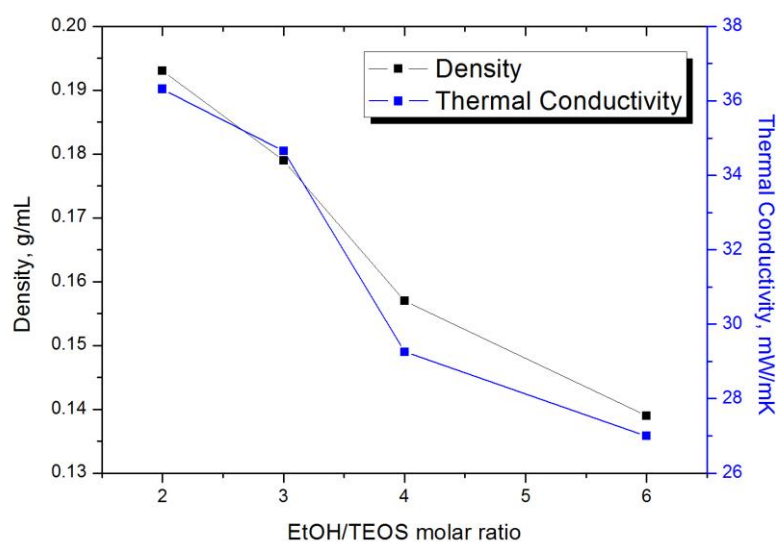


Figure 4. 15 Density and thermal conductivity relation with respect to different E/T molar ratios

The lower the E/T molar ratio were used, the more transparent SAs were obtained. While total transmittance of SAs increases with decreasing E/T molar ratios, diffuse transmittance decreases (Figure 4. 16) and that results in more transparent SAs. Haze values and transparency ratios of SAs with different E/T molar ratios at 600 nm are given in Table 4. 2. Based on this information, the SA synthesized by using E/T: 3 and W/T: 3 is most transparent among others (Figure 4. 17).

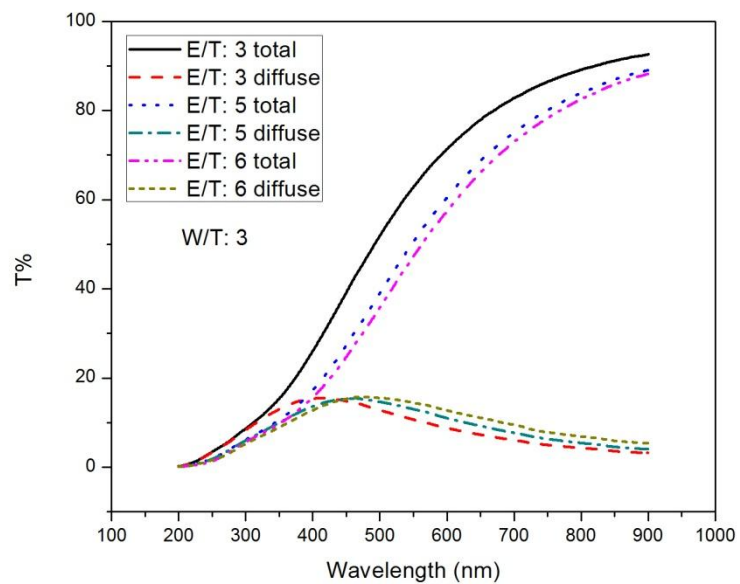


Figure 4. 16 Total and diffuse transmittance of the SAs with changing E/T molar ratios

Table 4. 2 Haze and transparency ratio value for SAs synthesized with different E/T molar ratios

E/T Ratio	Haze (@ 600 nm)	TR% (@ 600 nm)
3	12.3	87.7
5	18.2	81.8
6	22.2	77.8



Figure 4. 17 Transparent silica aerogel samples (E/T: 3 and W/T: 3)

Decreasing amount of acid catalyst increases hydrolysis time. Decreasing amount of base catalyst increases gelation time. Increasing or decreasing amount of acid or base catalyst does not show obvious effect on transparency of silica aerogel.

4. 1. 3 Effects of Types of Co-Solvents

Different co-solvents were tried to produce more transparent SAs. Polar aprotic co-solvents such as acetone and THF were used instead of polar protic EtOH. When acetone was used as co-solvent to synthesize a SA, more transparent SA than regular SA which is synthesized using EtOH as co-solvent was obtained. The major drawback of acetone and THF is that they damage and deface the plexiglass mold (Figure 4. 18). TEOS-THF-Water mixture (THF/TEOS: 4 and W/T: 3) was not homogeneous just after preparing the solution (Figure 4. 19-A) but hydrolysis reactions could continue in the solution and the solution turned into clear mixture (Figure 4. 19-B). It means that even if TEOS-water mixture is not completely soluble at that proportion in THF; hydrolysis products, $\text{Si}(\text{OEt})_{4-n}(\text{OH})_n$ ($n \leq 4$),

are soluble in THF. Thus, this inhomogeneity observed in the beginning does not affect transparency of resulting SA.

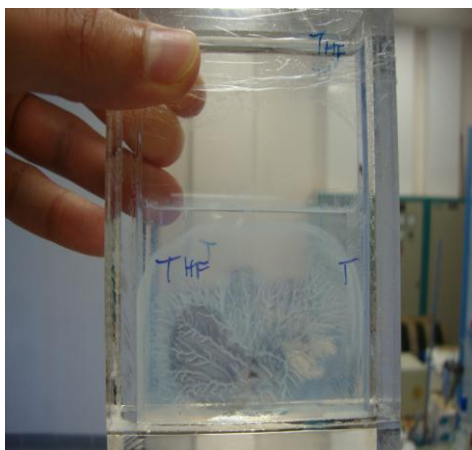


Figure 4. 18 Effect of THF on surface of plexiglass mold after gelation

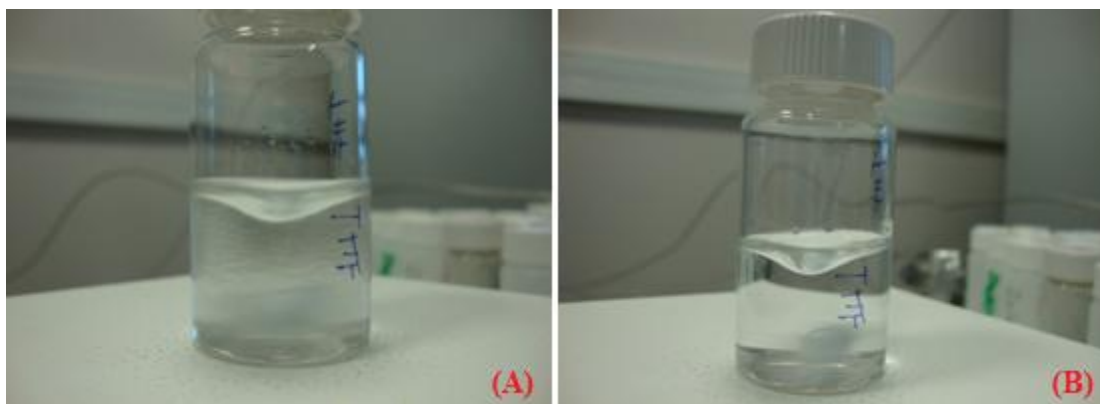


Figure 4. 19 Sol mixture prepared with THF; non-homogeneous sol mixture just after mixing the components (A) and after certain time (B)

To synthesize SAs with different co-solvents, completely same procedure was followed. Only difference was the co-solvent used in sol mixture. SAs which were synthesized in plexiglass molds were produced by changing co-solvents (Figure 4. 20).

There is small differences between densities of the produced SAs. The SA synthesized by using THF as co-solvent is more transparent than that synthesized by using EtOH. When acetone was used as co-solvent, the most transparent SA was obtained (Figure 4. 21 and Figure 4. 22). Hence, it can be easily said that co-solvent is an important factor that affects transparency.

Boltzmann constant k $1.3807 \times 10^{-23} \text{ J K}^{-1}$

¹Based upon ¹²C. () indicates the mass number of the most stable isotope.

3	4 (1)	5	6	7	(2) 8	9	10	11 (3)	12
IIIB	IVB	VB	VIB	VII B	VIII	VIII	VIII	IB	IIB
1 Sc Scandium 44.955910 [Ar]3d ¹ 4s ² 6.5115	22 Ti Titanium 47.867 [Ar]3d ² 4s ² 6.8281	23 V Vanadium 50.9415 [Ar]3d ³ 4s ² 6.7462	24 Cr Chromium 51.9961 [Ar]3d ⁵ 4s ¹ 6.7665	25 Mn Manganese 54.938045 [Ar]3d ⁵ 4s ² 7.4354	26 Fe Iron 55.845 [Ar]3d ⁶ 4s ² 7.8024	27 Co Cobalt 58.933195 [Ar]3d ⁷ 4s ² 8.10	28 Ni Nickel 58.6934 [Ar]3d ⁸ 4s ² 7.5398	29 Cu Copper 63.546 [Ar]3d ¹⁰ 4s ¹ 7.204	30 Zn Zinc 65.38 [Ar]3d ¹⁰ 4s ² 7.3912
9 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411

Figure 4. 20 SAs synthesized in different co-solvents; in acetone (A), d: 0.204 g/cm³; in THF (B), d: 0.186 g/cm³; in ethanol (C), d: 0.197 g/cm³

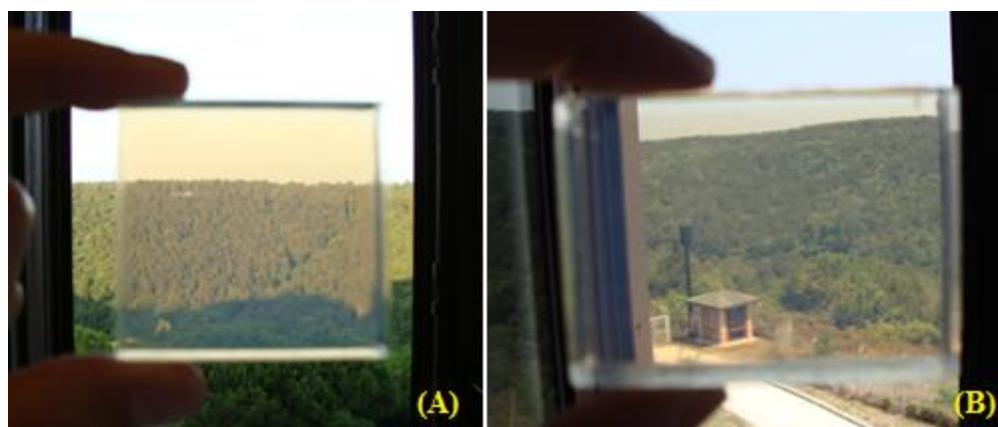


Figure 4. 21 Silica aerogels synthesized using different co-solvents; co-solvent: ethanol (a) and acetone (b)

3	4	5	6
IIIF	IVB	VB	VIB
1 Scandium 44.955910 [Ar]3d ¹ 4s ² 6.566	22 Titanium 47.867 [Ar]3d ² 4s ² 6.8281	23 Vanadium 50.9415 [Ar]3d ³ 4s ² 6.7462	24 Chromium 51.9961 [Ar]3d ⁵ 4s ¹ 6.776
9 Yttrium 88.90585 [Kr]4d ¹ 5s ² 6.36	40 Zirconium 91.224 [Kr]4d ² 5s ² 6.88	41 Niobium 92.90638 [Kr]4d ⁴ 5s ¹ 6.95	42 Molybdenum 95.94 [Kr]4d ⁵ 5s ¹ 7.13

Figure 4. 22 Silica aerogel synthesized using acetone as co-solvent

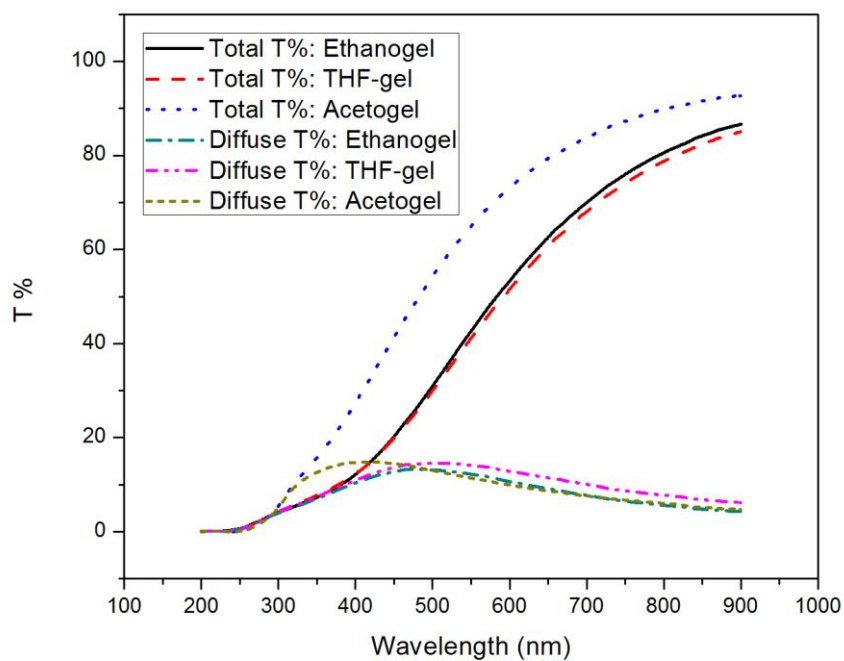


Figure 4. 23 Total and diffuse transmittance plots of different silica aerogels synthesized by using different co-solvents

4. 1. 4 Silica Aerogel Synthesis from Prehydrolyzed Precursor and Etac

It is determined that decreasing amount of co-solvent and water in the sol increases transparency. Stiochiometric ratios of water/TEOS for hydrolysis to $\text{Si}(\text{OH})_4$ and polycondensation of $\text{Si}(\text{OH})_4$ to SiO_2 network are 4 and 2, respectively. Working in between these molar ratios (Between $\text{H}_2\text{O}/\text{TEOS}$: 2 and 4) or lower than the stiochiometric ratio to produce SiO_2 ($\text{H}_2\text{O}/\text{TEOS}$: 2) are contemplated to result in better transparency. Very transparent SA was obtained with W/T: 2 and E/T: 3. SAs synthesized with less than these molar ratios were cracked after gelation or drying. In order to produce more transparent SAs, different synthesis method was tried. A sol mixture was prepared when E/T molar ratio and W/T molar ratio are equal to 1.6 and 1.8, respectively. This is substiochiometric molar ratio for water. Most of the hydrolysis product, EtOH, was distilled off the solution. Almost 40% of the total volume of sol mixture was evaporated. The resulting solution is called as prehydrolyzed precursor (PHP). If more than this volume is evaporated, very viscous solution would be obtained and get gelled quickly. Certain volume of PHP and 20-30% of that volume ethyl acetoacetate (Etac) were mixed and then a base catalyst was added. There is no need to add any more water to PHP for gelation. So, after addition of high amount of base catalyst, the PHP-Etac-base solution does not get whiten or hazy because it does not remain any excess water in the solution. Hence, highly transparent silica wet gels were obtained (Figure 4. 24 and Figure 4. 25)

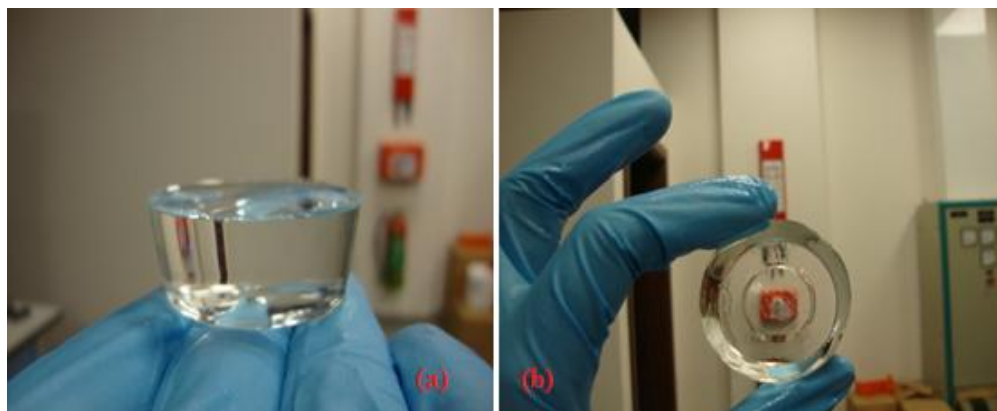


Figure 4. 24 A silica wet gel sample synthesized from PHP and Etac



Figure 4. 25 PHP-Etac silica wet gels

Four different co-solvents were used to synthesize SAs which are EtOH, THF, acetone, and Etac. Chemical structures can be seen in Figure 4. 27. EtOH, THF, and acetone can form homogeneous solution with TEOS-water mixture if they are added in required proportion whereas TEOS-water-Etac solution is not homogeneous. So, Etac cannot be used directly instead of other co-solvents to hydrolyze TEOS. Gelation of PHP does not occur because of addition of water in substiochiometric ratio even if 30-40% of EtOH is evaporated.

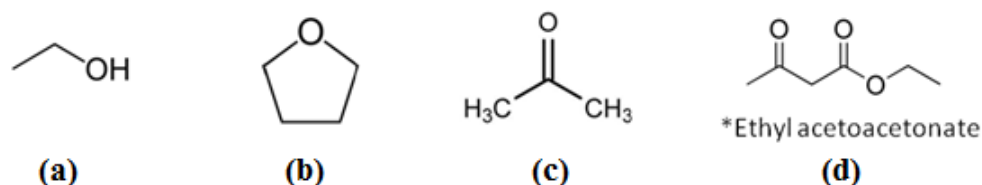


Figure 4. 26 Different co-solvents used to synthesize SAs; ethanol (a), THF (b), acetone (c), and Etac (d)

The silica aerogel synthesized from PHP-Etac-base solution is the most transparent one among other silica aerogels synthesized by other co-solvents (Figure 4. 27 and Figure 4. 28). In Figure 4. 27, it can be seen that there is no hazy appearance for the sample (d).

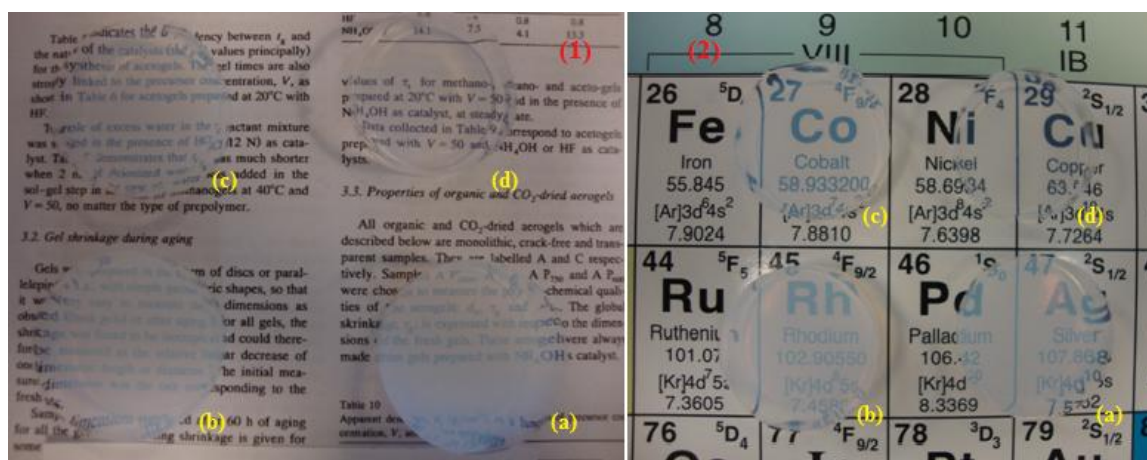


Figure 4. 27 SA samples synthesized with different co-solvents; ethanol (a), THF (b), acetone (c), and Etac (d)

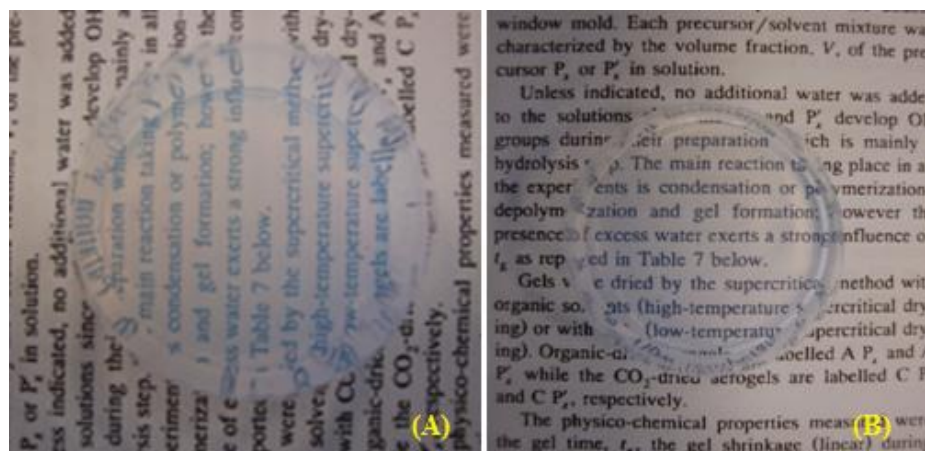


Figure 4. 28 SAs synthesized by using acetone as co-solvent (A) and PHP-Etac (B) solution

The SA synthesized from PHP-Etac-base solution is very dense and transparent and whitish appearance in the aerogel is not seen (Figure 4. 29). However, it is not very durable material at room T. Cracks formed when it stayed at ambient conditions (Figure 4. 30). Most of the SAs synthesized from PHP-Etac mixture cracks during scCO₂ extraction.



Figure 4. 29 A SA sample synthesized by using PHP and Etac

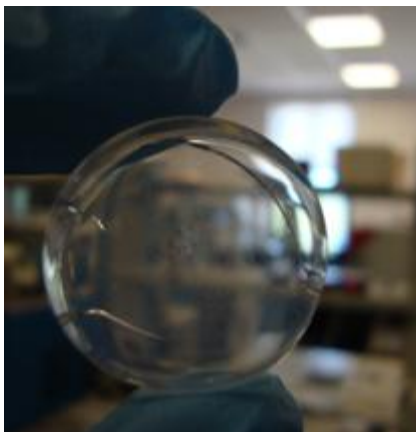


Figure 4. 30 Cracked PHP-Etac SA

4. 2 Effects of Types and Shapes of Molds

Type and shape of a mold are important for getting monolithic, transparent, and flat aerogel. PP syringes and spray lids are appropriate for synthesis of silica aerogels in small scales (e.g. 2.5 – 3 cm in diameter and 1 – 1.5 cm in thickness). In case of large scale production, using PP mold is not that easy. Our first attempt was to use PP mold for large scale synthesis. The first large scale aerogel was synthesized in a commercial PP which could find in some supermarkets. But there exist curvatures at the edges, corner and bottom surface of the mold that affects shape of SA. This curvature on the surface of the mold causes bending on the wet gel structure. If the wet gel is already bended after the aging step, the bending improves during drying due to further shrinkage. So, a mold should be ordered and manufactured in desired size and shape. PP and Teflon molds were ordered but these molds had already curvature on the surface which occurred during production due to heat evolution and they had very rough surfaces that affect surface scattering from SA; hence affect its transparency. Glass molds were tried and again it failed because glass and silica aerogels have same surface terminated groups. SAs stacked to the glass mold and it did not allow the aerogel to release without any cracks (Figure 4. 31). Accordingly, the

alcogel had irregular and non-flat shape after synthesis. These irregularities and bending (Figure 4. 32) are based on both mold surface and shrinkage of the alcogel during releasing from mold (Figure 4. 33) and drying. Thus, it is considered that there should be 90° between intercept of the edge and the bottom surface of the mold and both large surfaces of the alcogel should contact with mold surfaces. Bending on the aerogel structure must be eliminated because flat and regular shape silica aerogel panel is required to produce vacuum insulation panel. Plexiglass (polymethyl metacrylate) (Figure 4. 34) can be produced in definite shape and size by cutting and sticking the parts together with glue which is its liquid form of the monomer, MMA. Plexiglass mold has no obvious effect on transparency of SA and an alcogel can release from the plexiglass mold as monolithic. As a result, a plexiglass mold was prepared with internal size of $50 \times 35 \times 2.2 \text{ cm}^3$.

$35 \text{ cm} \times 35 \text{ cm} \times 2.2 \text{ cm}$ large scale silica alcogels were synthesized at first. After shrinkage of the gel, the alcogel sizes became $31 \text{ cm} \times 30 \text{ cm} \times 2 \text{ cm}$. About 15% shrinkage by length occurred during aging. The target density without any shrinkage is between $0.08 - 0.11 \text{ g/mL}$. Water to TEOS ratio was 3 and EtOH to TEOS ratio was 4 in these large scale syntheses.



Figure 4. 31 Silica wet gel synthesized in a glass mold



Figure 4. 32 Bended silica wet gel due to mold shape

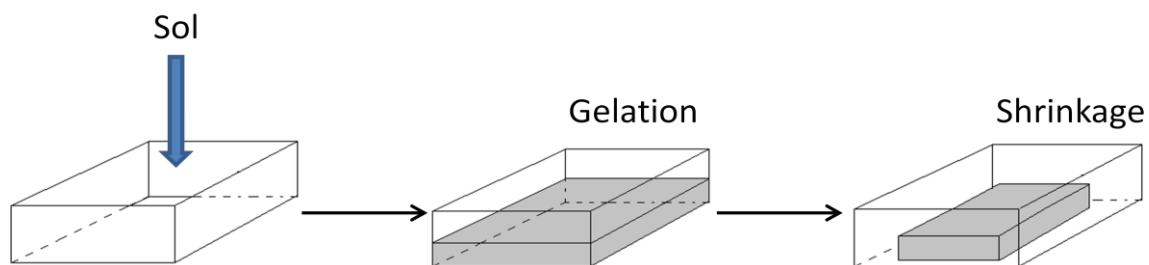


Figure 4. 33 Gelation, shrinkage and release steps of a wet gel in a regular shape mold



Figure 4. 34 Plexiglass mold with different shape to eliminate bending

The aging step is performed in EtOH-Water solution at 50 °C before a wet gel releases from mold. Plexiglass mold surface is affected from EtOH at high T and gets soften. Other

co-solvents deface the surface of plexiglass mold even at room T. So, aging in EtOH-water solution at 50 °C and silica alcogel synthesis with THF, acetone and Etac co-solvents at room T are not convenient. In order to produce SAs with other co-solvents in large scale, Teflon film covered brass and plexiglass molds were prepared. And aging silica wet gel in EtOH-water solution was started to be performed at room T for 24 hours.

4. 3 Effects of Ageing Conditions

The aging step is crucial because condensation reactions continue after gelation and a wet gel can gain strength. Aging medium/solution, aging temperature, and aging time were investigated. For example, when pure EtOH was used as aging solution, monolithical or crack free SAs could not be obtained (Figure 4. 35 and Figure 4. 36). Using pure ethanol as aging solution is useful because EtOH exchange step can be eliminated. In other words, silica wet gel is not aged in EtOH-Water aging solution and the wet gel is not exposed to more water so EtOH exchange step is not required. However, resulting silica alcogels were very weak in strength and during drying, the structure could not stand volume shrinkage and they got broken.



Figure 4. 35 Cracked silica aerogel aged in pure EtOH

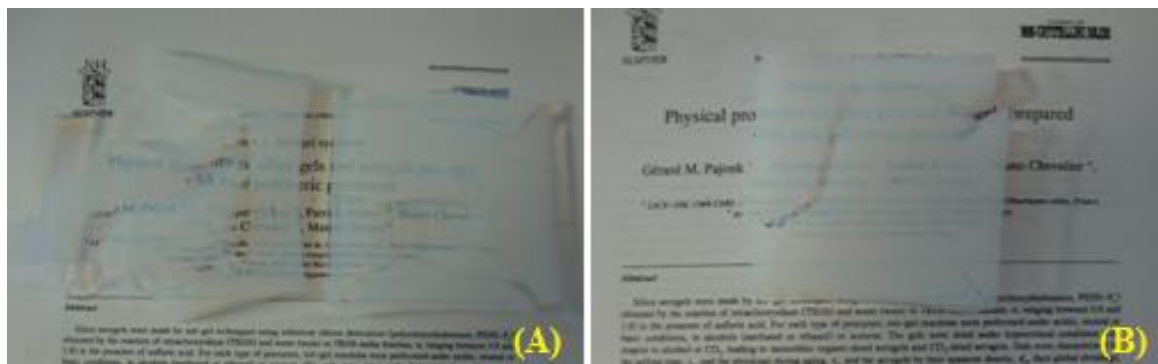


Figure 4. 36 Aging of SAs in pure EtOH at room T; W/T: 3, E/T: 5 (A) and W/T: 3, E/T: 6 (B)

Regular aging conditions are EtOH-Water mixture (1:1 in volume) at 50 °C and 24 hours. In order to strengthen silica aerogel structure further, the precursor, TEOS, was added into aging solution. TEOS-EtOH-Water mixtures were used as aging solution in different proportions. Moreover, two different aging temperatures and three different aging times were used while using same TEOS-EtOH-Water aging solution. TEOS to water volumetric ratio (T/W volume ratio: 4) and total volume of the aging solutions (V_T : 300 mL) were kept constant as for all the aging solutions. First, while keeping total volume of the ageing solution constant, 80 mL, 100 mL and 120 mL TEOS were used to prepared the ageing solution. The silica aerogels which were aged in these ageing solutions can be seen in Figure 4. 37 and Figure 4. 38. Densities of the resulting silica aerogels are increasing when TEOS volume, ageing temperature or ageing time increase (Table 4. 3 and Table 4. 4). This density increase affect thermal conductivity (Table 4. 5) and transparency (Figure 4. 41, Figure 4. 42 and Figure 4. 43) of the silica aerogels negatively. As expected, transparency of regular silica aerogel shows better transparency than all of the silica aerogels which were aged in the mother solution.

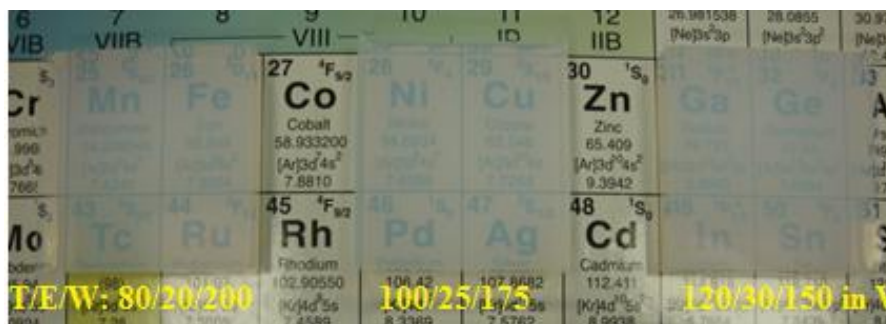


Figure 4. 37 Different silica aerogels aged in different ageing solutions

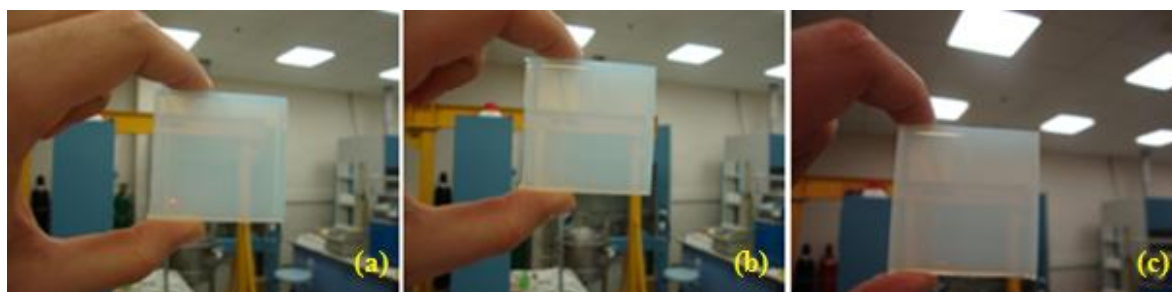


Figure 4. 38 Pictures of silica aerogel aged in different ageing solutions; 80 mL TEOS (a), 100 mL TEOS (b), 120 mL TEOS (c) in ageing solutions

Table 4. 3 Mass, volume, dimensions and density values of the silica aerogels which were aged in the different ageing solutions

	Mass, g	Volume, cm ³	Density, g/mL	L/H/T* in cm
80 mL -1	6.269	27.93	0.225	4.87/5.03/1.14
80 mL-2	6.066	27.00	0.225	4.865/4.89/1.135
100 mL -1	6.369	28.11	0.227	4.91/5.00/1.145
100 mL-2	6.336	27.98	0.226	4.91/5.00/1.14
120 mL-1	6.858	28.31	0.242	4.955/4.99/1.145
120 mL-2	7.016	29.03	0.242	4.95/5.10/1.15

Table 4. 4 Silica aerogels aged in the different ageing conditions and resulting average densities and average volumetric shrinkage values

Ageing Conditions (T/E/W in V)	Aging time	Aging T (°C)	Avg. Density (g/mL)	Avg. V Shrinkage (%)
80/20/200* (80T)	1 day (1 D)	50	0.225	16.12
100/25/175 (100 T)	1 day	50	0.227	15.01
120/30/150 (120 T)	1 day	50	0.242	13.89

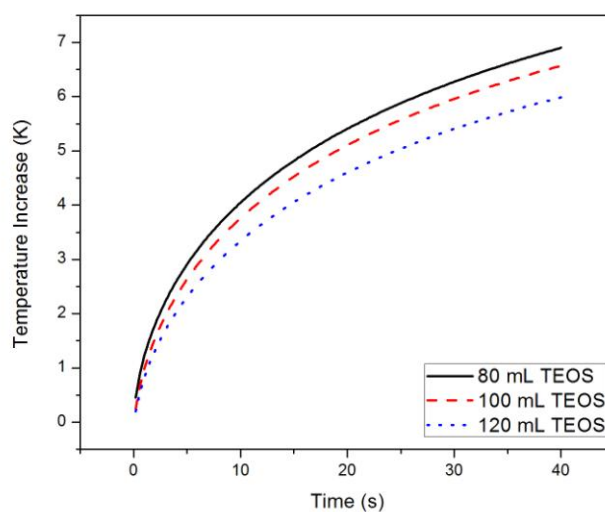


Figure 4. 39 Hot-Disk plane source results of the silica aerogels aged in the different ageing solutions with different TEOS concentration

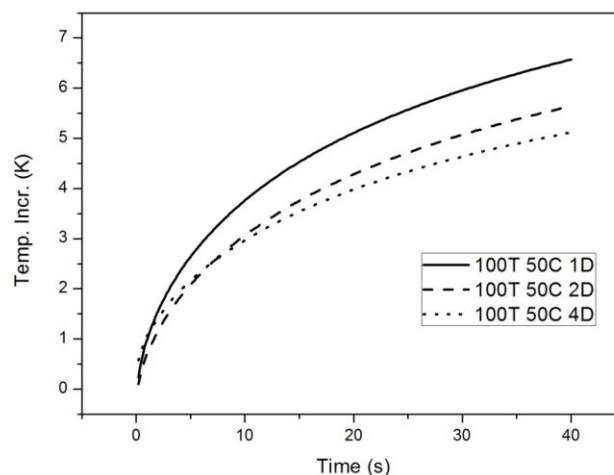


Figure 4. 40 Hot-Disk plane source results of the silica aerogels aged in the same ageing solution with different ageing time

Table 4. 5 Densities and thermal conductivity results of the silica aerogels aged in different ageing conditions

Aging Conditions	Density, g/mL	Thermal Conductivity*, W/m.K
80T 50°C 1D	0.225	0.0258
100T 50°C 1D	0.227	0.0264
120T 50°C 1D	0.242	0.0284
100T 50°C 2D	0.260	0.0290
100T 50°C 4D	0.313	0.0350
100T 80°C 1D	0.260	0.0308

*Hot Disk results: Heating power: 10 mW and Time: 40 sec

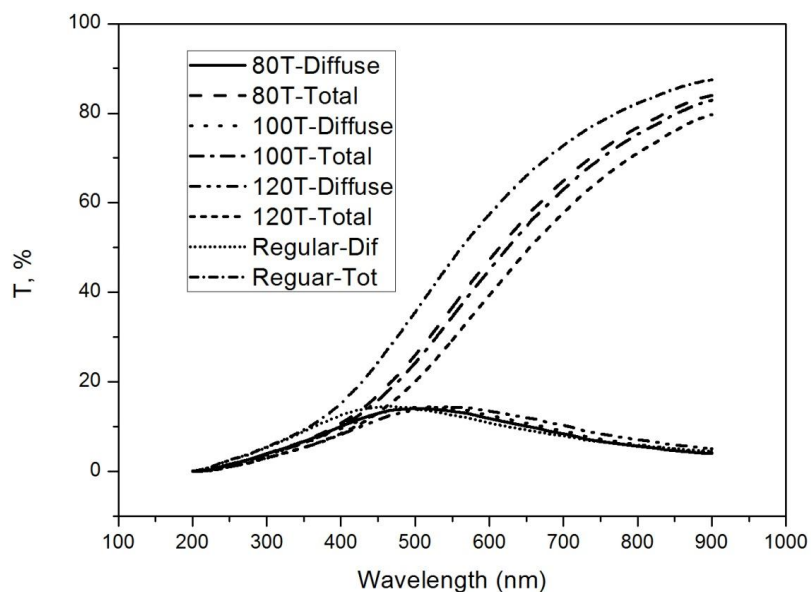


Figure 4. 41 Total and diffuse transmittance plots of a regular silica aerogel and the silica aerogels aged in the solutions with different TEOS concentration

Table 4. 6 Haze values of regular silica aerogel and the silica aerogels aged in the solutions with different TEOS concentration

Sample	Haze, %
Regular	12.804
80T 50°C 1D	17.875
100T 50°C 1D	18.277
120T 50°C 1D	19.261

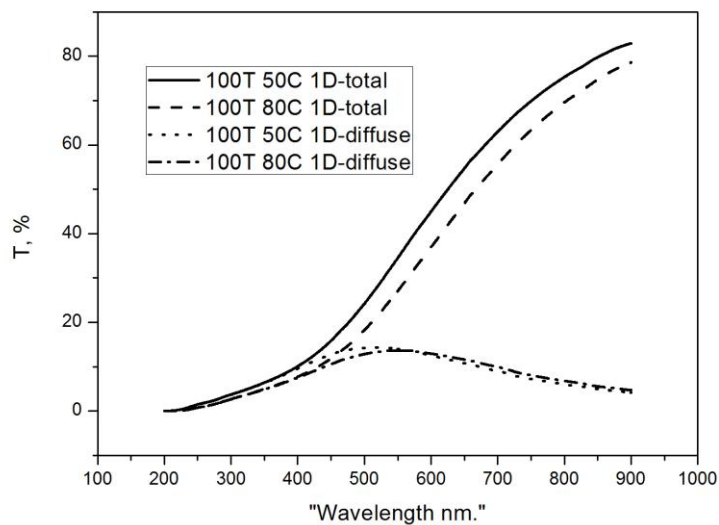


Figure 4. 42 Total and diffuse transmittance plots of the silica aerogels aged in different temperatures and in same composition of TEOS-EtOH-water ageing solution

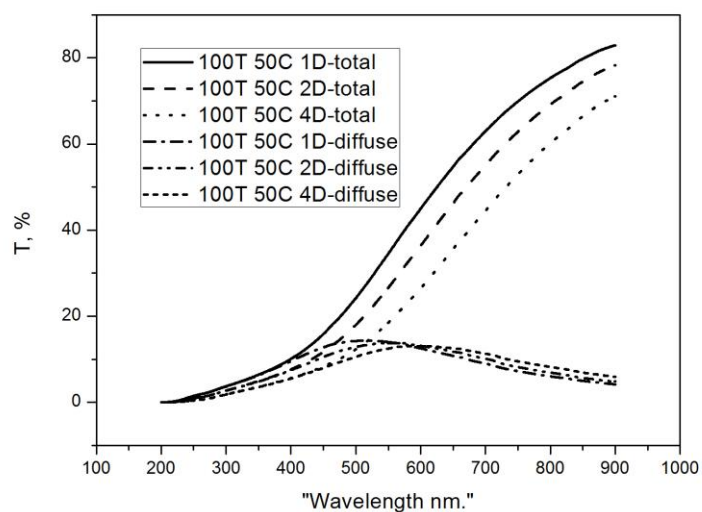


Figure 4. 43 Total and diffuse transmittance plots of the silica aerogels aged in same composition of TEOS-EtOH-water ageing solution and along different ageing durations

4. 4 Solvent Exchange Step and Supercritical Drying

To be able to dry the alcogel (dispersion medium in the pores is alcohol), one has to exchange water remaining in the pores with ethanol. While supercritical carbon dioxide (ScCO₂) can dissolve EtOH, water is not miscible in ScCO₂. Exchange of water with EtOH is important to have monolithic aerogel after drying. The EtOH exchange was done in three times in 5 liter pure EtOH. Remaining water content in the pores was calculated as about 0.5% after the exchange step. In the aging step, silica alcogel is being placed in water/ethanol solution (1:1 in volume) just after synthesis. Although there are 5% of water inside the pores, water percent rises to about 20% after the aging. The aging is done at room temperature and it is very crucial to have an alcogel with good strength.

Drying vessel is about 35 liters. Drying of an alcogel in this volume requires too much time, EtOH, and CO₂. Two half cylinder of aluminum-stainless steel metal blocks were sent to us from Arçelik in order to decrease dead (unused) volume inside the vessel. These blocks were put in the vessel and there remained enough room to be able to be placed the alcogel inside the vessel.

To be able to dry the alcogel, water has to be exchanged which remains in the pores with ethanol. While supercritical carbon dioxide (ScCO₂) can dissolve EtOH, water is hardly miscible in ScCO₂. Exchange of water with EtOH is important step to have monolithic completely dried silica aerogel after scCO₂ extraction. The solvent exchange was done in three times with 5 liter pure EtOH. Remaining water content in the pores was calculated as about 0.5% after the solvent exchange step. The aging is putting an alcogel in water/ethanol solution (1:1 in volume) just after synthesis. Although there are 5% water inside the pores, water percent rises to about 20% after the first aging. The first aging is done at room temperature and it is very crucial to have an alcogel with good strength.

Drying vessel is about 35 liters. Drying of an alcogel in this volume requires too much time, EtOH, and CO₂. Two half cylinder of aluminum-stainless steel metal blocks were

sent to us from Arçelik in order to decrease dead (unused) volume inside the vessel. These blocks were put in the vessel and there is enough room to be able to be placed the alcogel inside the vessel. Now, we have been dealing with drying steps (Figure 4. 45).

4. 5 Large Scale Silica Aerogel Production

After synthesis of the small scale silica aerogels, a large scale silica aerogel (28 cm x 28 cm x 1.0 cm) were synthesized (E/T: 4 and W/T: 3) in the polypropylene mold and aged in TEOS-EtOH-water mixture (25:65:10 in volume) in three days at 50 °C (Figure 4. 44). Then, it was dried in the Natex large scale high pressure and temperature extraction unit at 50 °C and 80 bar.

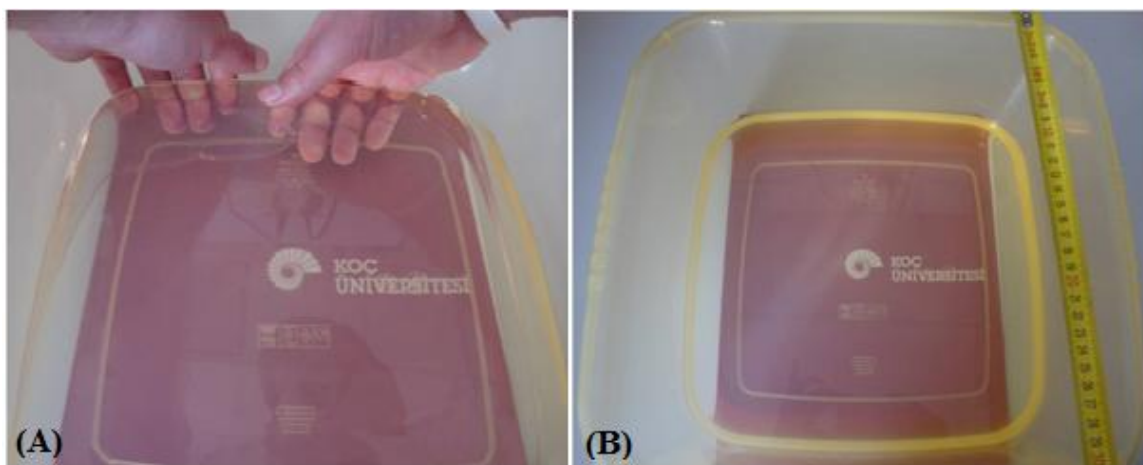


Figure 4. 44 First large scale silica alcogel sample (28 cm x 28 cm)

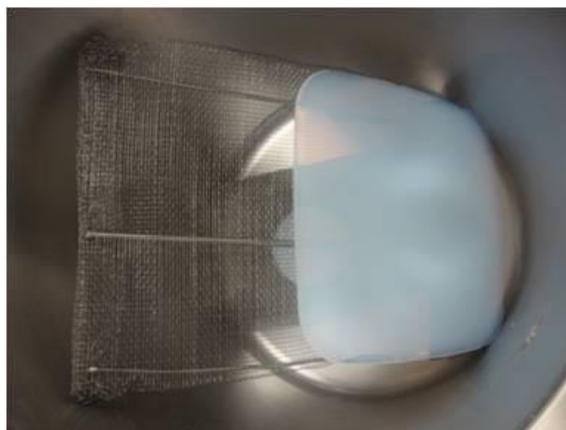


Figure 4. 45 First large scale silica aerogel

The first synthesized silica aerogel was enveloped in the transparent high barrier films under vacuum (Figure 4. 46) and thermal conductivity of the silica aerogel (λ : 17 mW/m.K) and the TVIP (λ : 19 mW/m.K) were measured with the guarded hot plate method. Even if the silica aerogel was aged in the mother solution, it could not stand compression and it got broken during applying vacuum due to being non-flat shape.



Figure 4. 46 First TVIP produced by Arçelik

After the first large scale silica aerogel synthesis, the second silica aerogel was synthesized in the plexiglass mold without ageing in the mother solution. Moreover, two half cylindrical aluminum-steel metal blocks were placed in the extraction vessel to

increase drying efficiency. 30 cm x 30 cm x 2.0 cm silica alcogel was dried about one week but this drying time was not sufficient to obtain completely dried, monolithical and crack free silica aerogel (Figure 4. 47).

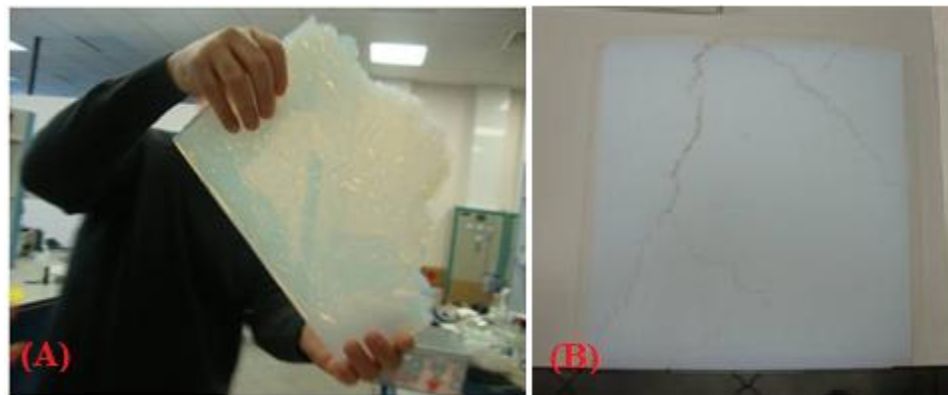


Figure 4. 47 Non-dried flat and large scale silica aerogels with full of cracks due to continuing evaporative drying after taking off from the extraction vessel (30 cm x 30 cm)

Finally, another silica alcogel was synthesized in the plexiglass mold with 35 cm x 35 cm x 2.2 cm in dimensions. E/T and W/T molar ratios were 3 (TEOS:H₂O:EtOH:HCl:NH₄OH; 1:3:4:1.62x10⁻³:6.28x10⁻³) and the silica alcogel was aged in EtOH-Water ageing solution in one week at room temperature. It was dried in the extraction vessel along almost two weeks and 31 cm x 30 cm x 1.9 cm large scale silica aerogel was obtained. Density of the silica aerogel was 0.183 g/cm. It was send to Arçelik immediately and they measured its thermal conductivity and produced a TVIP by using the silica aerogel. Thermal conductivity of the silica aerogel and the TVIP were 16 mW/m.K and 12 mW/m.K, respectively.

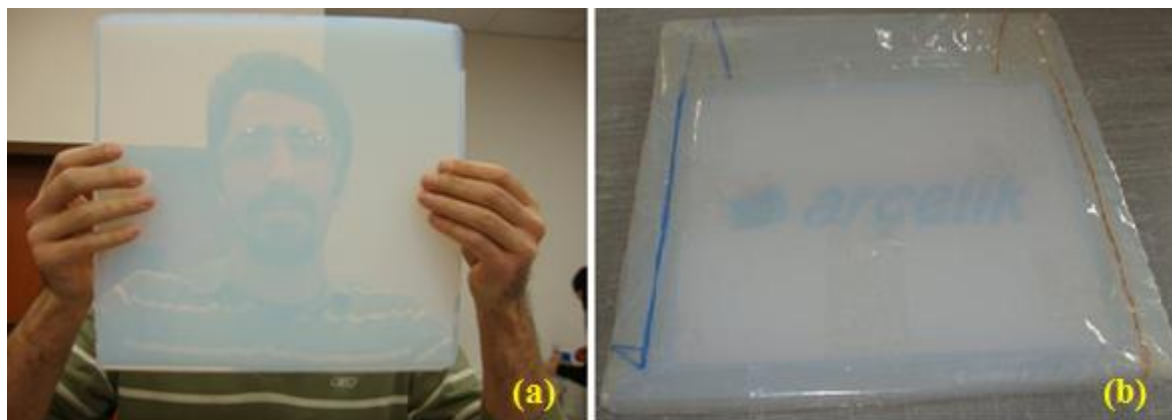


Figure 4. 48 First large scale and flat silica aerogel (a) and TVIP (b). (30 cm x 30 cm x 2.0 cm) (density: 0.180 g/mL and λ_T : 16 mW/m.K for silica aerogel and λ_T : 12 mW/m.K for TVIP)

4. 6 Theoretical Calculations and Experimental Results of Thermal Conductivity of Silica Aerogel

Radiative, gaseous, solid and total thermal conductivities vs. density graphs were plotted based the literature studies [5, 6, 12]. Minimum total thermal conductivity values can be obtained when density of the silica aerogel is between 0.1-0.2 g/cm³ (Figure 4. 49). Hence, depending on these information and sol-gel parameters that substantially affect transparency of the silica aerogel, large scale silica aerogels were synthesized. It can be seen that there is a close correlation between experimental results and theoretical calculations for the silica aerogel which was synthesized in the plexiglass mold as perfectly flat and monolithical (Figure 4. 50).

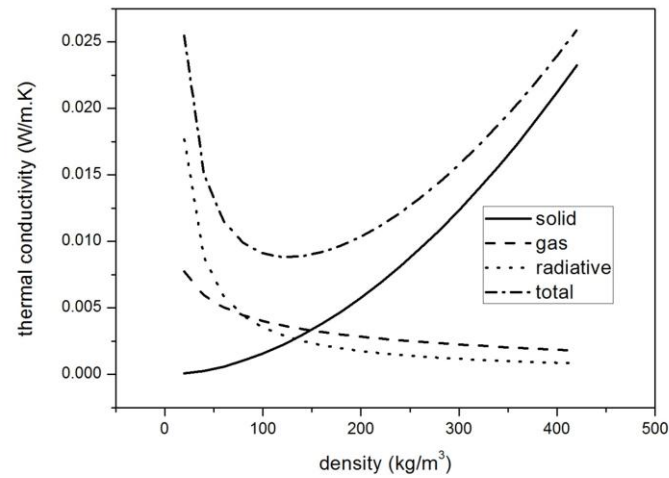


Figure 4. 49 Radiative, gaseous, solid and total thermal conductivity graphs plotted from theoretical calculations based the literature [5]

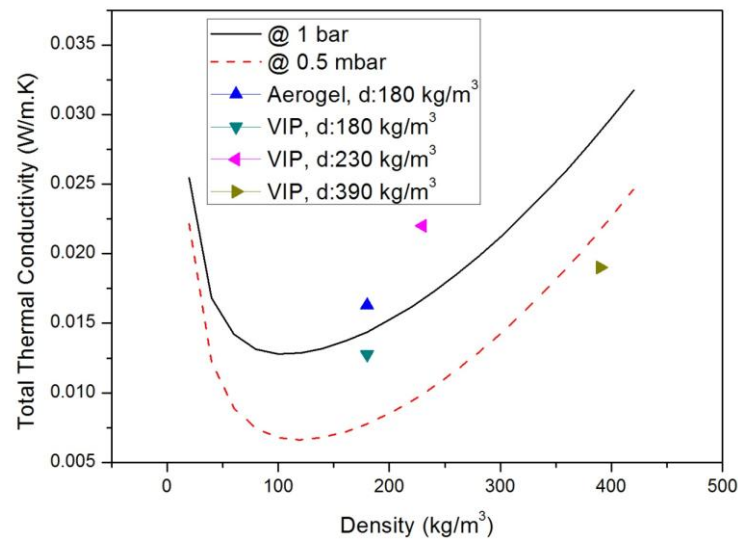


Figure 4. 50 Experimental results of thermal conductivity of VIPs determined by Guarded Hot Plate method

Chapter 5

CONCLUSION

Silica aerogels are highly porous (porosity: 90-95%), low density ($0.1\text{-}0.3\text{ g/cm}^3$), very transparent (up to 95% transparency ratio) and very low thermal conductivity ($10\text{-}15\text{ mW/m.K}$) materials. So, they can be considered to be used in insulation industry due to their unique properties. Transparent vacuum insulation panel (TVIP) systems with using transparent high barrier films and silica aerogels as core materials are novel systems. In this study, silica aerogels were tried to synthesized with optimum transparency and thermal conductivity in large scale for transparent vacuum insulation production. Silica aerogels are synthesized by sol-gel chemistry and supercritical fluid extraction method. Sol-gel parameters are massive impact on properties of silica aerogels such as density and transparency. Therefore, different silica aerogels were synthesized with different synthesis parameters to observe effects of sol-gel parameters on the properties of silica aerogels and to produce a silica aerogel panel in large scale with optimum thermal conductivity and transparency. Silica aerogels were synthesized with different water-to-TEOS (W/T: 2 to 6) and EtOH-to-TEOS (E/T: 3 to 8) molar ratios. Decreasing the E/T and W/T molar ratios increase transparency and density of the resulting silica aerogels. Density is directly proportional to thermal conductivity and the lowest thermal conductivity values can be reached when the density of the aerogel stay between $100\text{-}200\text{ kg/m}^3$ based on theoretical calculations. Besides sol-gel parameters, it is seen that types of co-solvent affect transparency. THF and acetone were used instead of EtOH as co-solvent and new silica aerogels were synthesized. The silica aerogel were produced with using acetone was the

most transparent one among others. Then, new experiments were conducted to both decrease the E/T and W/T molar ratios and use another co-solvent, Etac. By evaporating EtOH in sol mixture which is hydrolysis product, prehydrolyzed precursor (PHP) was produced. PHP-Etac-base solution resulted in more transparent silica aerogel than the one produced with acetone as co-solvent. However, these PHP-Etac silica aerogels did not have good durability and they cracked. Different shapes and types of mold materials were used to obtain flat and crack-free silica aerogels with low surface roughness. Plexiglass is contemplated as the best option for the large scale silica aerogel panel production. As a result, a large scale (Height: 30 cm, length: 30 cm and thickness: 1.2 cm), transparent silica aerogel panel was synthesized by using EtOH as co-solvent and when both E/T and W/T molar ratios were 3 and 3. Density, transparency ratio, and thermal conductivity of the aerogel were 180 kg/m^3 , 88% (at 600 nm), and 16 mW/m.K , respectively. Our industrial collaborator, Arçelik, produced a TVIP by using the silica aerogel panel that was synthesized at Koç University and high barrier films that were produced in Fraunhofer and Amcor. Thermal conductivity of the TVIP was mentioned as 12 mW/m.K .

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APPENDIX

Preparation of Hydrochloric Acid (HCl) Solution

0.40 mL is taken from 37% purity HCl stock solution and diluted to 100 mL with EtOH.

Molarity of the stock solution can be calculated as follows:

$$M = \frac{\% \cdot d \cdot 1000}{M_w}$$

M: Molarity

%: Percentage of the stock (0.37)

d: density (specific gravity is commonly used, SG= $d_{\text{sample}}/d_{\text{water}}$ = 1.19 g/mL)

M_w : Molecular weight of the corresponding acid (M_w of HCl = 36.5 g/mol)

$$M = \frac{0.37 \times 1.19 \frac{\text{g}}{\text{mL}} \times 1000 \text{ mL/L}}{36.46 \text{ g/mol}} = 12 \text{ mol/L}$$

Specific gravity = $d_{\text{sample}}/d_{\text{H}_2\text{O}}$

SG of HCl = 1.19 g/mL

Mwt of HCl = 36.46 g/mol

$0.37 \times 1.19 \text{ g/mL} \times 1000 \text{ mL/L} = 440.3 \text{ g/L}$

$(440.3 \text{ g/L})/(36.5 \text{ g/mol}) = 12.063 \text{ mol/L} = 12 \text{ M}$ our stock solution

Molarity of the prepared acid solution is as follows

$M_1 \times V_1 = M_2 \times V_2$

$$12 \text{ M} \times 0.4 \text{ mL} = M_2 \times 100 \text{ mL}$$

$$M_2 = 0.048 \text{ M} \quad \text{pH} = 1.32$$

Preparation of Ammonium Hydroxide (NH₄OH) Base Solution

0.50 mL is taken from 2.0 M NH₃ in EtOH solution and diluted to 10 mL with EtOH.

Molarity of the base solution is 0.1 M.

Table A- 1 Amount of constituents used to synthesize two identical SAs with different W/T molar ratios in the plexiglass mold (6 cm x 5.5 cm x 1.5 cm)

W/T	2	3	4	6	8	10
T (g)	31.69	31.69	31.69	31.69	31.69	31.69
E (g)	28.08	28.08	28.08	28.08	28.08	28.08
W (g)	5.478	8.217	10.96	16.43	21.91	27.39
A (mL)	6.0	6.0	6.0	6.0	6.0	6.0
B (mL)	10	10	10	10	10	10

Table A- 2 Amount of constituents used to synthesize two identical SAs with different E/T molar ratios in the plexiglass mold (6 cm x 5.5 cm x 1.5 cm)

E/T	2	3	4	6	8
T (g)	31.69	31.69	31.69	31.69	31.69
E (g)	14.01	21.01	28.08	42.02	56.02
W (g)	10.96	10.96	10.96	10.96	10.96
A (mL)	6.0	6.0	6.0	6.0	6.0
B (mL)	10	10	10	10	10

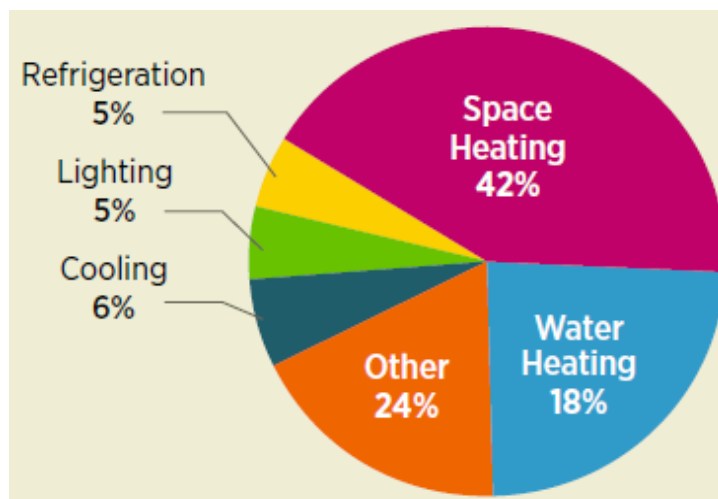


Figure A- 1 Average energy usage in a house in U.S.

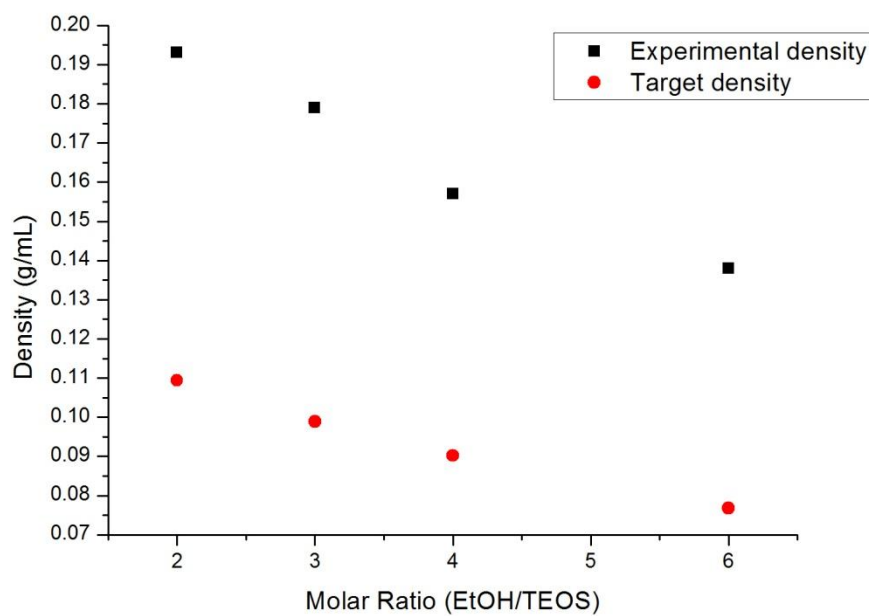


Figure A- 2 Target and experimental densities of silica aerogels with different E/T molar ratios. Volumetric shrinkage causes this difference.

Table A- 3 Effect of hydrolysis time on gelation time

Hydrolysis Time (min)	Gelation Time (sec)
5	No Gelation
15	264
30	242
60	219
90	227

**Figure A- 3** A silica aerogel with high transparency (TR%: 88) (E/T: 3 and W/T: 3)

3	4	5	6	7	8	9	10	11	12
IIIB	IVB	VB	VIB	VIIIB	VIIIB	VIIIB	VIIIB	IB	IIIB
1 Sc Scandium 44.955910 [Ar]3d ¹ 4s ² 6.5615	22 Ti Titanium 47.88 [Ar]3d ² 4s ² 6.5615	23 V Vanadium 50.9415 [Ar]3d ³ 4s ² 6.5615	24 Cr Chromium 51.9961 [Ar]3d ⁵ 4s ¹ 6.7665	25 Mn Manganese 54.938045 [Ar]3d ⁵ 4s ² 7.4330	26 Fe Iron 55.845 [Ar]3d ⁶ 4s ² 7.4330	27 Co Cobalt 58.933195 [Ar]3d ⁷ 4s ² 7.8810	28 Ni Nickel 58.6934 [Ar]3d ⁸ 4s ² 7.8810	29 Cu Copper 63.546 [Ar]3d ¹⁰ 4s ¹ 8.3942	30 Zn Zinc 65.408 [Ar]3d ¹⁰ 4s ² 8.3942
9 Y Yttrium 88.90585 [Kr]4d ¹ 5s ² 6.2173	40 Zr Zirconium 91.224 [Kr]4d ² 5s ² 6.2173	41 Nb Niobium 92.90638 [Kr]4d ⁴ 5s ¹ 6.2173	42 Mo Molybdenum 95.94 [Kr]4d ⁵ 5s ¹ 7.0924	43 Tc Technetium [98] [Kr]4d ⁵ 5s ² 7.28	44 Ru Ruthenium 101.07 [Kr]4d ⁷ 5s ¹ 7.3605	45 Rh Rhodium 102.90550 [Kr]4d ⁸ 5s ¹ 7.4589	46 Pd Palladium 106.42 [Kr]4d ¹⁰ 8.3368	47 Ag Silver 107.8682 [Kr]4d ¹⁰ 5s ¹ 7.5762	48 Cd Cadmium 112.411 [Kr]4d ¹⁰ 5s ² 8.9926

Figure A- 4 Silica aerogels with different E/T molar ratios (W/T: 3): 6 (a), 5 (b) and 3 (c)

window mold. Each precursor/solvent mixture was characterized by the volume fraction, V , of the precursor P_x or P'_x in solution.

Unless indicated, no additional water was added to the solutions P_x and P'_x develop OH groups during their preparation which is mainly a hydrolysis step. The main reaction taking place in all the experiments is condensation or polymerization-depolymerization and gel formation; however the presence of excess water exerts a stronger influence on t_g as reported in Table 7 below.

Gels were dried by the supercritical method with organic solvents (high-temperature supercritical drying) or with CO_2 (low-temperature supercritical drying). Organic-dried aerogels are labelled A P_x and A P'_x while the CO_2 -dried aerogels are labelled C P_x and C P'_x , respectively.

The physico-chemical properties measured were the gel time, t_g , the gel shrinkage (linear) during

Figure A- 5 Silica aerogel synthesized by using PHP and Etac

IIIb Si 14 Titanium 22 Vanadium 23 Chromium 24 Yttrium 39 Zirconium 40 Niobium 41 Molybdenum 42	IVb Ti 22 V 23 Cr 24 Zr 40 Nb 41 Mo 42	Vb V 23 Cr 24 Nb 41 Mo 42	Vb Cr 24 Mo 42	VIIIb Mn 25 Fe 26 Co 27 Tc 43 Ru 44 Rh 45	VIIIb Fe 26 Co 27 Ru 44 Rh 45	VIIIb Co 27 Rh 45	IB Ni 28 Cu 29 Pd 46 Au 47	IB Cu 29 Pd 46 Au 47	IB Zn 30 Ag 48 Cd 48
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Figure A- 6 Acetogel (A), THF-gel (B) and EtOH-gel (C) Acetogel

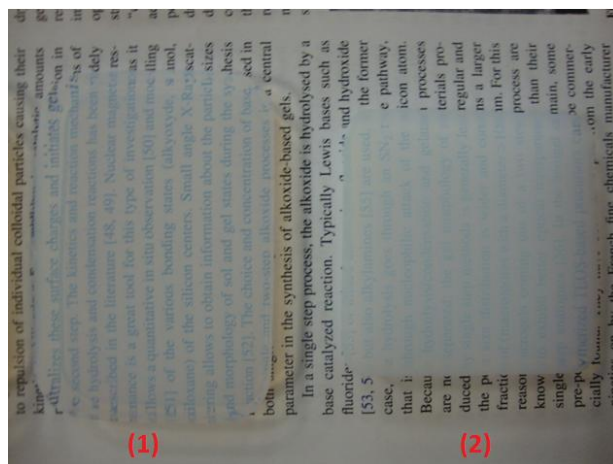


Figure A- 7 Silica aerogels synthesized in different molds: commercial PP mold (1), manufactured Teflon mold (2)

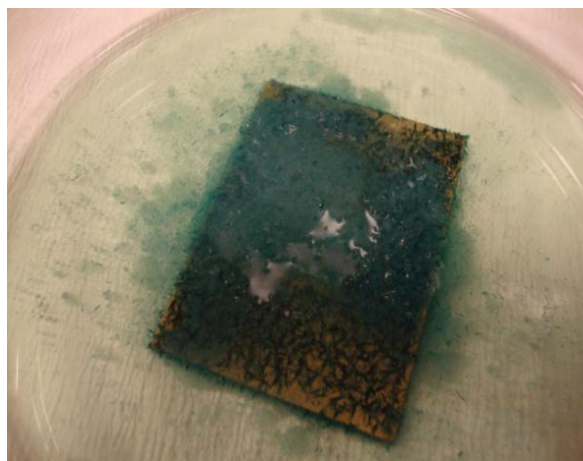


Figure A- 8 A brass piece stayed in Etac

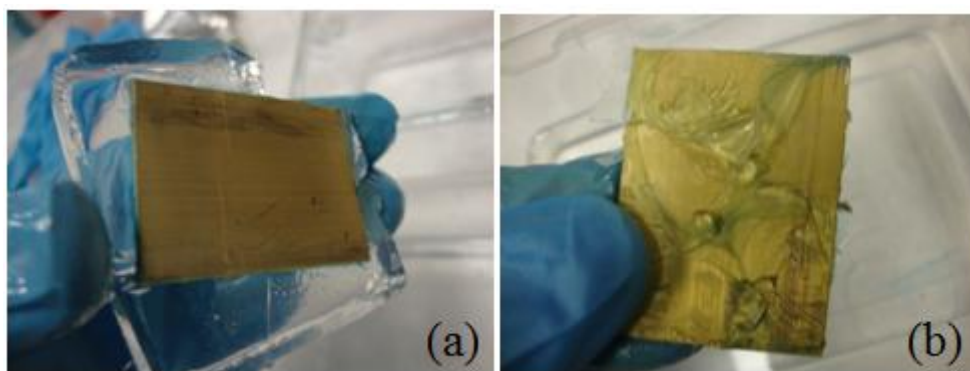


Figure A- 9 Silica wet gel sticking on the brass piece



Figure A- 10 Effect of brass on surface of a PHP-Etac silica wet gel

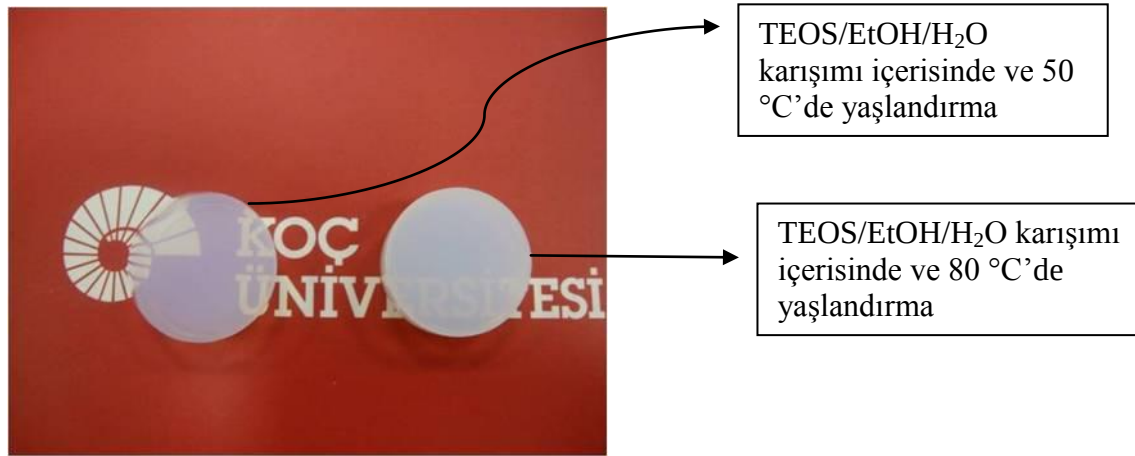


Figure A- 11 Effect of aging temperature on transparency of silica aerogels (Ageing in TEOS:EtOH:Water mixture, 43:43:14 in V)

Table A- 4 Effects of ageing temperature on physical properties of silica aerogels aged in the T:E:W solution

Sol (T/E/W)	Aging Solution (T:E:W)	Density (g/cm ³)	BET Surface Area (m ² /g)	Pore V (cm ³ /g)	Pore Diameter (nm)
1.0 g/1.0 g/0.34 g	43:43:14* at 50 °C	0.222	812.8	3.12	14.76
1.0 g/1.0 g/0.34 g	43:43:14 at 80 °C	0.358	399.1	1.6	14.48

* 43:43:14 in volume

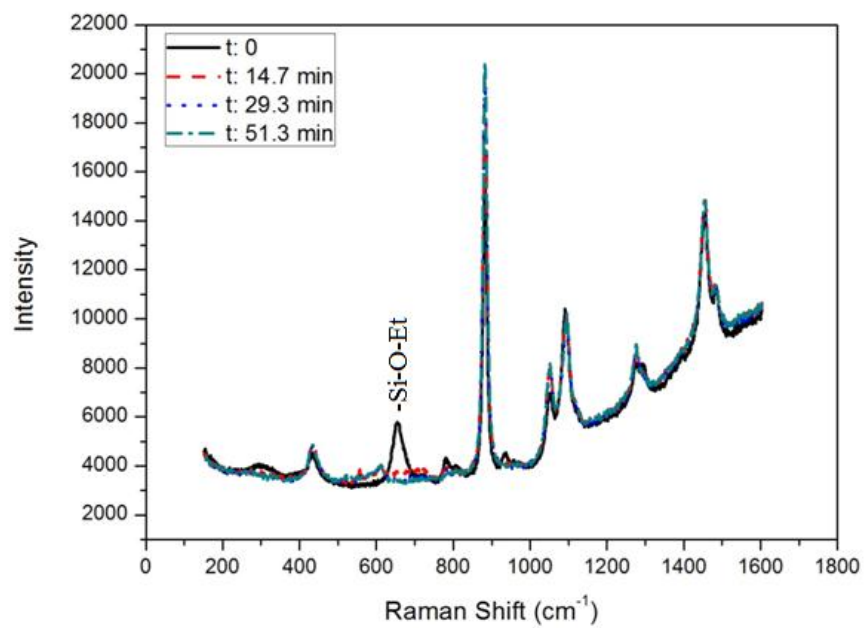


Figure A- 12 Kinetic Raman results at 633 nm of sol mixture during hydrolysis

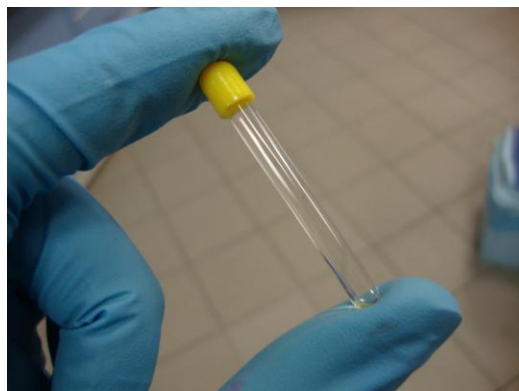


Figure A- 13 Closed lid glass sample holder for Raman analysis

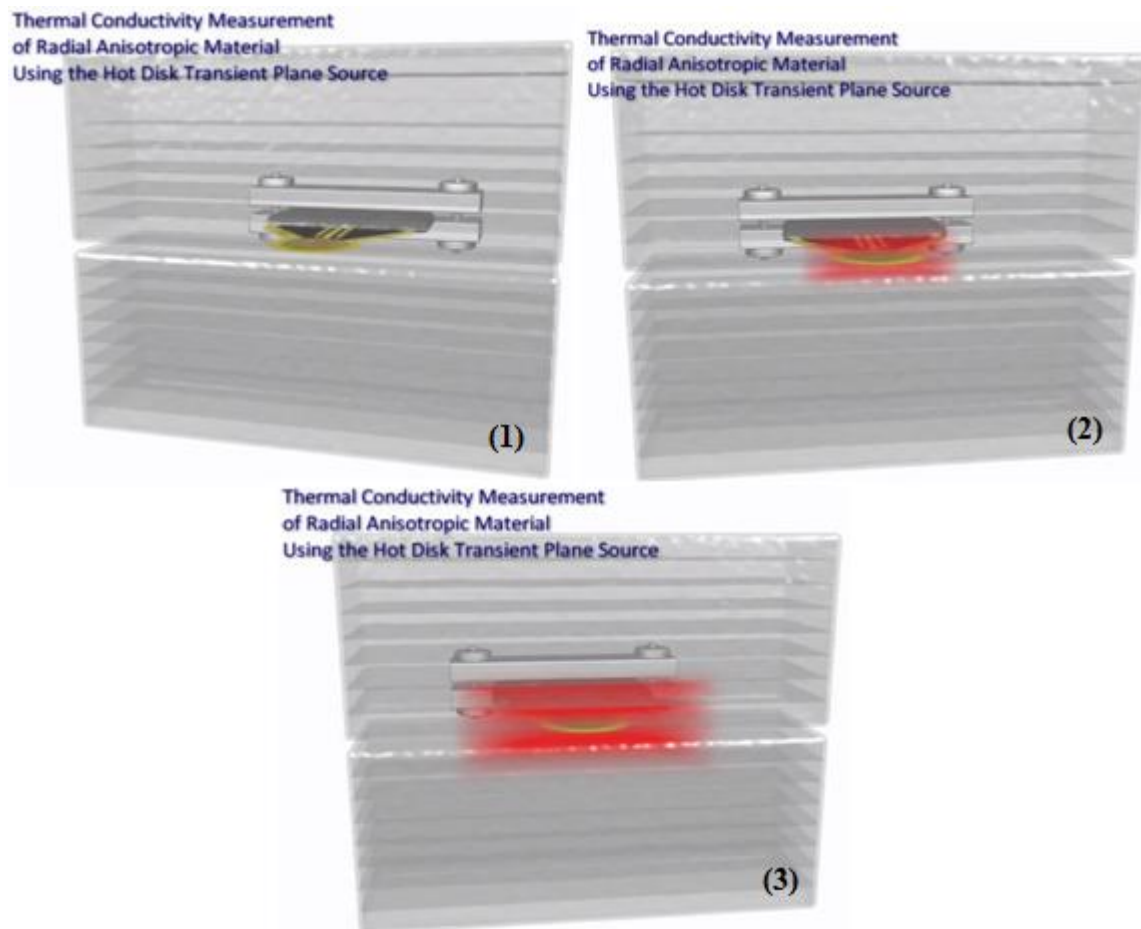


Figure A- 14 Working principle of Hot-Disk plane source

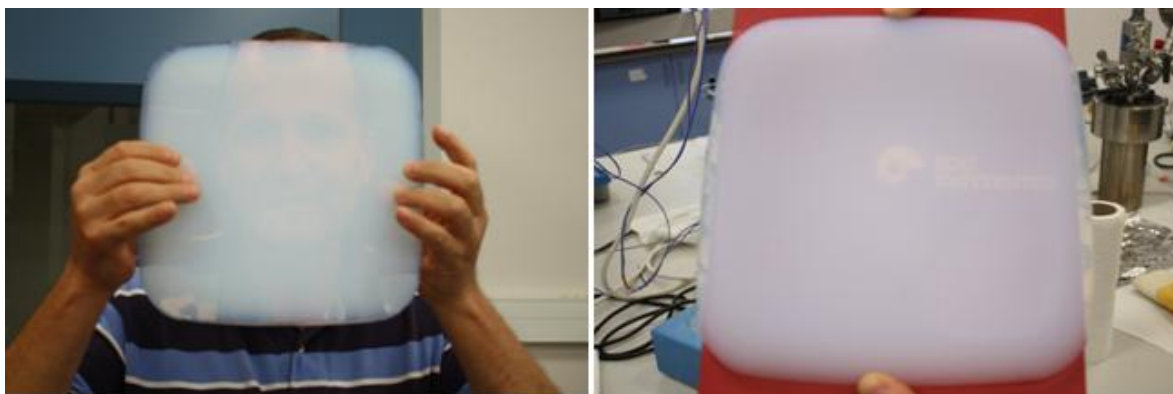


Figure A- 15 First large scale silica aerogel sample



Figure A- 16 First large scale silica aerogel without any bending on the structure

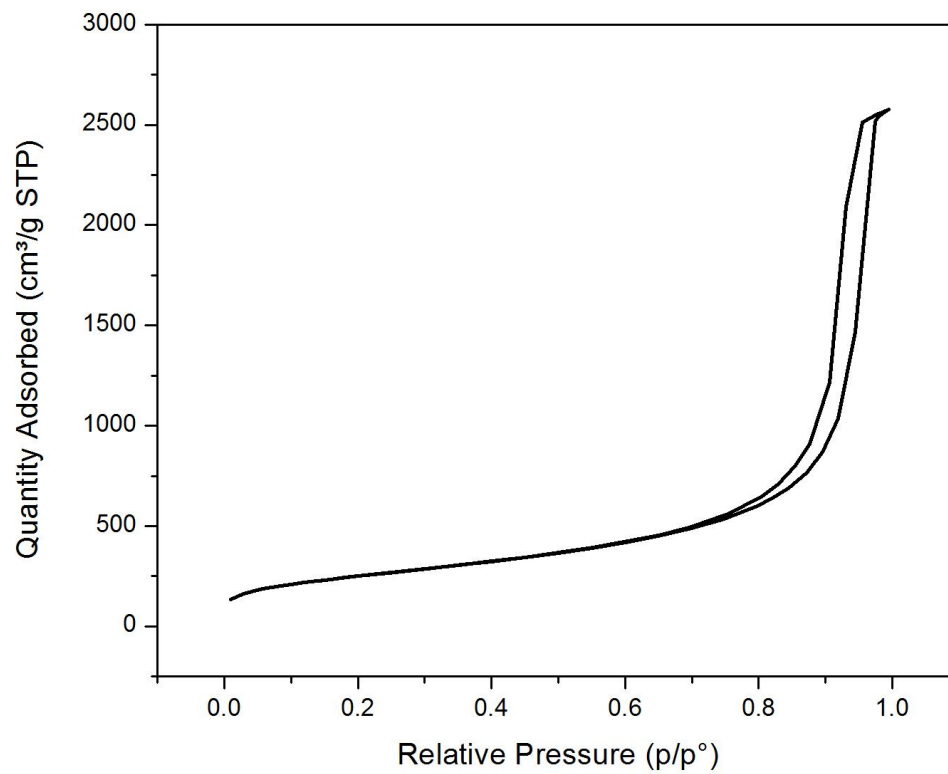


Figure A- 17 N₂ adsorption-desorption (BET) isotherm of silica aerogel

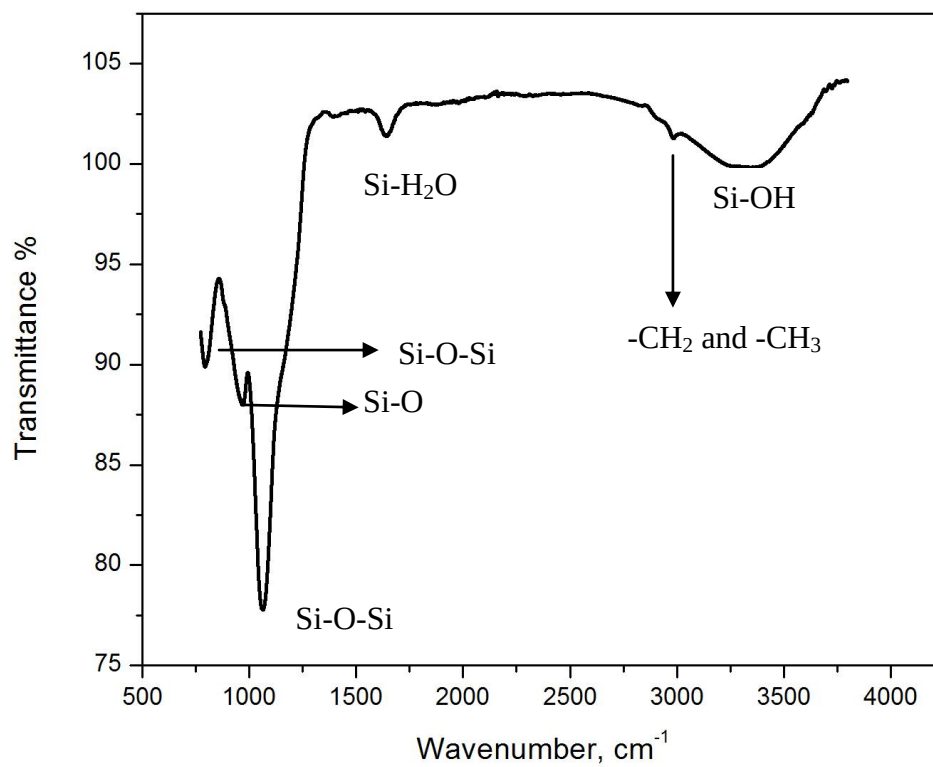


Figure A- 18 IR spectrum of a regular silica aerogel

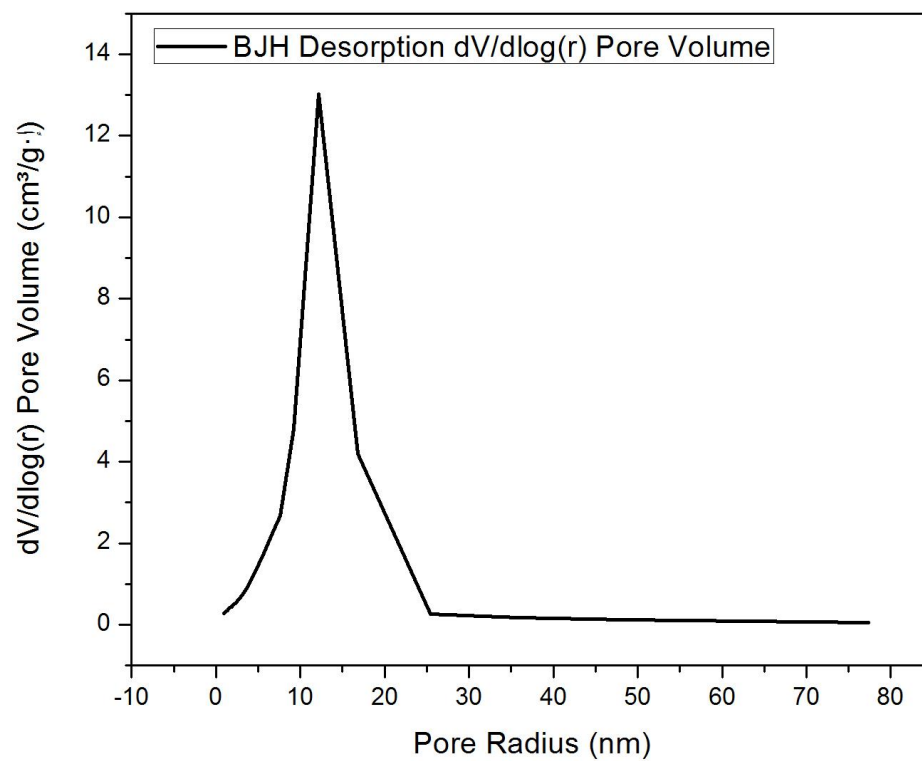


Figure A- 19 BJH pore volume of a regular silica aerogel

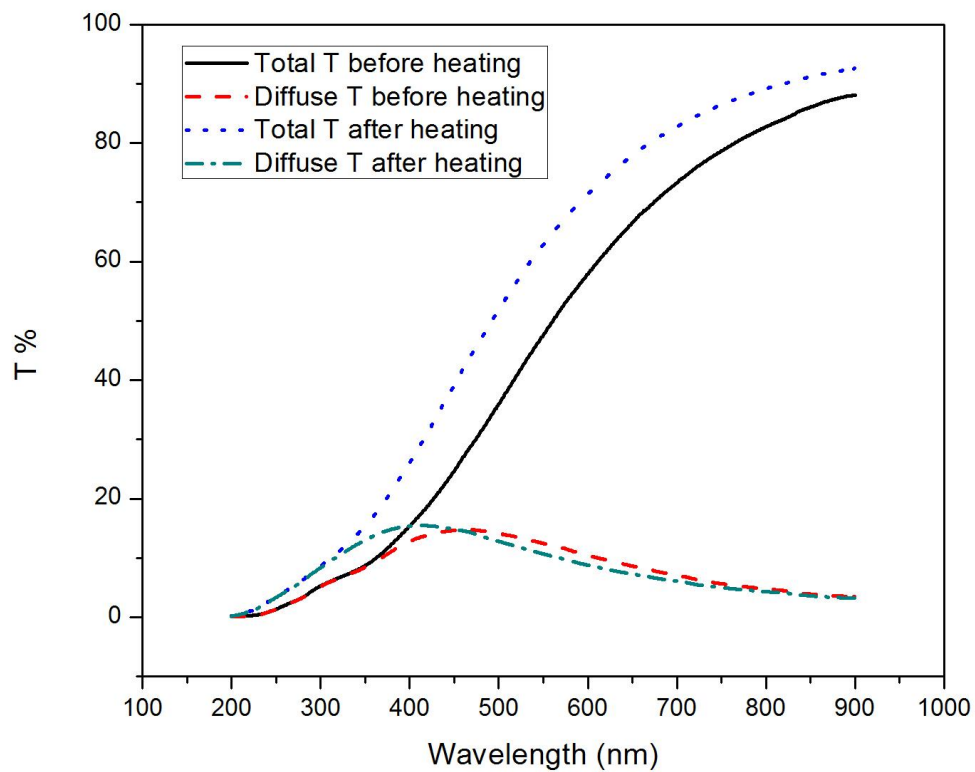


Figure A- 20 Effect of heat treatment on transparency of silica aerogels after drying

VITA

Metin Karayılan was born in Izmir in 1988. He grew up and stayed there until he was 14. He continued his high school education in Istanbul. He received his Bachelor Science Degree on Chemistry from Middle East Technical University, Ankara in 2011. He focused on Organic Chemistry during undergraduate years and worked in the Synthor Research Group. He worked on the synthesis of aminoconduritols, heterocyclic compounds in 2011. He worked as a teaching and research assistant at Koç University, Istanbul between 2011 and 2014 during his M.Sc. study in Chemical and Biological Engineering Department. He worked on “Transparent Vacuum Insulation Panels” project supported by TÜBİTAK in these years.