MONOLITHIC AEROGELS AND THEIR APPLICATIONS IN AIRBORNE
NANOPARTICLE FILTRATION

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MONOLITHIC AEROGELS AND THEIR APPLICATIONS IN AIRBORNE
NANOPARTICLE FILTRATION

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Dissertation

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Several interrelated problems were studied in this thesis research involving mesoporous silica aerogels, macroporous δ-form syndiotactic polystyrene aerogels, and their hybrid aerogel systems. In the first part of the study, a rapid manufacturing method was developed for fabrication of aerogel monoliths where the objective was to reduce the fabrication time from several days in conventional methods to less than a day. It was found that the use of high temperature in the steps of aging and chemical modification and the use of ultrasound in washing step are key elements for shortening of the production time.

In the second part of the study, sensitivity of silica aerogel bulk density to pH of the sol in condensation reaction step was investigated. In conjunction a successful method of production of silica aerogel monolith with gradient density was developed. It was found that pH in the range of 7.4 – 8.5 in the condensation step can significantly influence both skeletal density and bulk density values. The bulk density decreases but skeletal density increases with an increase of pH. Silane sols prepared with pH in the range 7.4 – 8.5 and sequentially injected in a mold resulted in a gradient density aerogel with 30 % change in density across a 12 mm long monolith. This method of fabrication of gradient density aerogel is much simpler and easily adaptable to net shape manufacturing process.
The final part of the study focused on the application of aerogel monoliths in airborne nanoparticle filtration. A key objective of the part was to improve filtration efficiency without sacrificing air permeability. It was found that significant macroporosity is needed to handle air permeability, while mesoporosity and electrostatic forces are required for achieving nanoparticle efficiency greater than 99.95 %.
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CHAPTER I

INTRODUCTION

It is widely known that exposures to airborne particles can cause severe health hazards to human being including nausea, breathing difficulties, bronchitis, birth defects, serious developmental delays, weakened immune systems, and even cancers \(^1,2\). World Health Organization (WHO) reported that around 7 million people died in 2012 as a result of air pollution exposure.\(^3\) The significance of the hazards is a function of the size of the airborne particles. For example, smaller particles can easily penetrate into the human body and reach the pulmonary alveoli.\(^4\) Fine particles of size 0.1 \(\mu\)m - 1 \(\mu\)m and ultrafine particles of size < 0.1 \(\mu\)m are more detrimental to human health than the coarse grain particles of size > 1 \(\mu\)m. The health hazards are compounded by the presence of pathogens of size 20-2,000 nm residing in these particles.\(^5\)

Removal of small particles and pathogens by filtration can significantly improve the quality of air and reduce the health hazards. The use of high efficiency particulate absorption (HEPA) filters fabricated from filter media of fiber mats are widely used for the purpose. The filtration efficiencies of HEPA filters are high at 99.95% for removing around 0.3 \(\mu\)m particles as per EN 1822-1:2009 classification at comparably low pressure drops. However, removal of airborne nanoparticles of sizes 100 nm and smaller using fiber mat-based HEPA filters still remains a challenge. Published literature on evaluation
of HEPA filters for removal of airborne nanoparticles of sizes 100 nm and smaller are scarce.

A wide range of industrial applications use porous media for filtration due to their large surface area and pore volume. In this context, monolithic aerogels fabricated from inorganic or organic sources present several attributes as filter media. The aerogel monoliths have low solid contents, high porosity with various pore sizes, and large surface areas. For example, silica aerogels derived from alkoxy silanes offer large surface areas, up to 1,000 m$^2$/g, significant mesopore fractions, and porosities over 90%. The $\delta$-form syndiotactic polystyrene (sPS) aerogels also offer macropores and porosities up to 97%; the nanocavities of crystalline strands of sPS selectively absorb small organic molecules. Despite offering several attractive characteristics, research on filtration of nanometric airborne particles by monolithic aerogels is scarce. A handful of studies used aerogel granules or microspheres in packed beds. Some literature reports are available on the use of aerogels impregnated into HEPA filter media for airborne particle filtration, colonization of bioluminescent organisms inside a monolithic silica aerogel to detect viral particles, and applications of heterogeneous catalyst for removal of pollutants, such as removal of cyanides or combustion gases by monolithic silica aerogel composites containing metal oxides. Literature on direct investigations of filtration of airborne nanoparticles by monolithic aerogels is scarce.

This study established scientific principles behind functioning of monolithic aerogels for filtration of airborne nanoparticles by using macroporous monolithic aerogels of $\delta$-form syndiotactic polystyrene as a baseline material, and other derived aerogels from the baseline material. The scientific principles were established based on
the following hypotheses. (1) There exists an optimum porous structure that balances the two core elements in filtration of airborne nanoparticles - filtration efficiency and air permeability. The filtration efficiency and air permeability are in competition. The porosity and sizes of pores primarily determine the two competing elements. (2) Macropores (diameter > 50 nm) offer high permeability and largely determine the filtration capacity in the regime of depth filtration. Substantial macropores fraction is expected for achieving high air permeability (3) Mesopores (diameter: 2-50 nm) are highly functional for the captures of nanometric particles, as they relate to the diffusional deposition mechanism. (4) The macro-mesopore hybrid aerogels balance the two competitive elements. The mesoporous materials offer high filtration efficiency but low permeability, while the macroporous materials offer high permeability and filtering capacity, but comparatively low filtration efficiency. (5) The gradient density aerogels improve the filtration efficiency with the gradient porosity in the aerogel monoliths and offer high filtration capacity. (6) Static surface charges developed in aerogels increase the capture efficiency of airborne nanoparticles. The validations of the hypotheses are discussed in Chapter VI to Chapter XI.

An efficient processing method for fabrication of monolithic aerogels was invented. This topic is discussed in Chapter IV. An improved rapid production (IRP) method for monolithic aerogels was invented based on one-pot synthesis where the processes of aging, washing, and supercritical drying were carried out sequentially in a newly designed multi-injectable reactor. The relationship between material properties and process parameters were also investigated in this chapter.
Before applying monolithic aerogels in airborne nanoparticle filtration, the aerogel structures and their relationship to properties of aerogels were studied as function of pH in condensation reaction step. This information was later used in controlling the aerogel structures and pores arriving at desired structural formations of aerogels for the application. This topic is discussed in Chapter V.

Chapter VI discusses the potential of macroporous polymer aerogel monoliths in removing airborne nanoparticles. Macroporous monolithic aerogels of δ-form sPS were synthesized for this purpose via thermoreversible gelation of a solution of sPS in a good solvent followed by supercritical drying. The air permeability and airborne nanoparticle removal efficiency were determined as function of the bulk density of aerogels. In addition, gradient density aerogels were produced via sequential injections of sPS solutions to investigate if the gradient density aerogels perform better than single component aerogels. The mode of filtration of airborne nanoparticles in monolithic aerogels was verified also in this chapter.

In Chapter VII, the effect of the skin layers of monolithic aerogels on permeability and their difference in porosity is discussed. For this purpose, monolithic δ-form sPS aerogels with different thicknesses were fabricated, and permeability of the aerogels was measured. A theoretical model for permeability of a multi-layered body was used to investigate the structural differences between the skin layers and the inner bodies. sPS aerogel monoliths thinner than the thickness of the skin layers were also fabricated to confirm the different porosity of the skin layer.
Chapter VIII evaluates the role of mesopore in aerogel monoliths in achieving high efficiency airborne nanoparticle filtration. The diffusional flow in mesopores was expected to be more effective in nanoparticle capture than the viscous flow regime encountered in macropores. However, substantial macropores fraction was also expected for achieving high air permeability. This idea was tested with macro-mesopore hybrid aerogel (sPS-silica hybrid aerogel) monoliths.

Chapter IX discusses the effect of electrostatic surface charges developed in monolithic aerogels on the capture of airborne nanoparticles. For this purpose, polyvinylidene fluoride (PVDF) which has a spontaneous polarity was hybridized with macroporous δ-form sPS aerogels. It was expected that electrostatic force would significantly contribute to the capture of airborne particles if the sizes of the particles are small. This idea was verified by investigating the relationships between the static surface charges of the monolithic aerogels and capture efficiency of airborne nanoparticles.
CHAPTER II

BACKGROUND

2.1 Airborne particles as health hazards

Four categories are defined for pollutants. These are gaseous pollutants, persistent organic pollutants, heavy metals, and particulate matters. SO$_2$, NOx and CO are examples of the gaseous pollutants. The dioxins, produced by incomplete combustion of chlorine containing materials, are examples of persistent organic pollutants. Lead and mercury are examples of the heavy metal pollutants. Particulate matters that are primarily airborne particles or aerosols are pollutants and are hazardous to human body. Nowadays, the airborne particles are a significant issue especially in developing countries and are a frequent subject of news headlines. The particulate matters cause respiratory problems, such as bronchitis and lung cancer. Some particulate pollutants are generated by natural activities, such as volcanos, natural fires and wind blows. Some others are anthropogenic generated by transport vehicles, construction projects, destructions of installation, manufacturing factories, power plants, and fuel combustions, to name a few. The amount of airborne particles produced from natural sources may be tolerable with some natural purification processes in place. However, anthropogenic particles can be more serious for human health via chronic exposures. The chemical composition of particles depends on the source generating them, but it is rather complex. It is known that metals, carbonaceous materials, ions, reactive gases, and biologic materials are major
components of the particles.\textsuperscript{41} The size of airborne particles is critical for human health due to their ability to penetrate into human body. The particulate pollutants are classified in terms of the particle size. The particles larger than 1 $\mu$m are defined as coarse particles, smaller than 1 $\mu$m as fine particles, and smaller than 0.1 $\mu$m as ultrafine particles. It is known that the coarse particles deposit in the upper part of the respiratory tract in human body. However, the fine and ultrafine particles penetrate into the pulmonary alveoli.\textsuperscript{4} Thus, the fine and ultrafine particles are much more harmful than the coarse particles. Apart from the size effect, the hazards of the airborne particles are also derived from the pathogens, e.g., viruses, bacteria and spores.\textsuperscript{5} The pathogens have a wide distribution of size ranging from 0.02 $\mu$m to 20 $\mu$m. The pathogens cause various diseases. The common cold is caused by adenovirus (0.08$\mu$m), coronavirus (0.11$\mu$m), echovirus (0.028$\mu$m), reovirus (0.075$\mu$m) and rhinovirus (0.023$\mu$m) with the respective sizes given in the parenthesis. Flue is caused by influenza (0.1$\mu$m) and parainfluenza (0.22$\mu$m), pneumonia is caused by respiratory scyntical virus (0.22$\mu$m), and legionnaires’ disease is caused by legionella pneumophila (0.6$\mu$m). Farmer’s lung disease is due to micromonospora faeni (1 $\mu$m). Other examples are also abundant.\textsuperscript{36,42} It is reported that exposures to air pollutants contribute to an increase of mortality and hospital admission and can lead to adversary health effects of nausea, difficulty in breathing, birth defects, serious developmental delay, weakened immune system, and even cancer.\textsuperscript{1,2} World Health Organization (WHO) reported that around 7 million people died in 2012 as a result of air pollution exposure.\textsuperscript{3}
2.2 Filtration

Filtration is a unit operation for separating particles or droplets from gaseous and liquid fluids by a filter medium. Particularly, efficient filtration is required for maintaining and cleaning air in facilities, such as hospitals, gymnasiums, classrooms, and offices. There exist two modes of filtration – (1) surface-filtration and (2) depth-filtration. Nets or membranes with pore channels connecting the front and back sides provide surface-filtration, while packed beds of granular or fibrous materials produce the depth-filtration. The filtration efficiency for surface-filtration is independent of the filter thickness, as filtration of larger particles than the size of the perforations is achieved within the front layer. However, the efficiency for depth-filtration is dependent on the filter media thickness. Depth-filtration has the ability to capture smaller particles than the sizes of the open spaces of the filter medium. The filtration efficiency, \( E \), is defined by the ratio of the number of particles retained on a filter medium to the number of incident particles, as given by equation (1).

\[
E = \frac{N_B - N_A}{N_B}
\]  

(1)

In equation (1), \( N_B \) and \( N_A \) are the number of particles before and after filtration respectively in a stream of a gas. Penetration, \( P \) is obtained from efficiency by the relationship, as in equation (2)

\[
P = 1 - E
\]  

(2)

Fiber-based filter media are generally used for airborne particle filtration. An example of a filter, which is an assembly of several fiber-based filter media is HEPA filter. HEPA is acronym for high efficiency particulate absorption. HEPA filter medium
is fabricated from glass fibers with diameters 0.5-2 μm. Several mechanisms are available to explain filtration by fiber-based filter media.\textsuperscript{36,46} Direct interception is a major contributor of filtering particles larger than 1 μm. This mechanism relies on capture of particles by direct contact with a fiber. The particles following streamline of a fluid are captured in this manner. Inertial impaction refers to removal of particles that follow the streamlines and are deviated from the path due to inertia and are captured by the contact with a fiber. Diffusional deposition is a mechanism for filtering particles smaller than the size of the open space in a filter, such as particles smaller than 0.1 μm. In this case, Brownian motion induces the small particles to undergo contact with the fibers. Gravitational settling accounts for particles captured in a filter by the gravitational force. However, the gravitational settling mechanism is negligible for airborne particles. Electrostatic force also helps filtration by removing charged particles when they pass through the filters. This mechanism has not been comprehensively studied, but it is expected that the electrostatic force mechanism will significantly contribute to the captures of particles if the sizes of the particles are small. Among the filtration mechanisms, direct interception, inertial impaction, and diffusional deposition have all been studied for particle filtration. The working principles of these mechanisms are illustrated in Figure 1.

Several mathematical models have been suggested to predict the filtration efficiency for fiber-based filter media. The three mechanisms – (1) direct interception, (2) inertial impaction, and (3) diffusional deposition are taken into account in these models.\textsuperscript{36,42,46-49}
(1) Direct interception  (2) Inertial impaction  (3) Diffusional deposition

Figure 1. Three governing mechanisms for airborne particle filtration.

Inertial impaction is discarded in the case of low fluid velocity in a filter medium. Direct interception is enough to describe the filtration of airborne particles in this regime. The mathematical models are based on definition that the number of particles, \(N\), captured by a filter is proportional to the number of incident particles and the thickness of a filter, \(l\), as in equation (3).

\[
dN = -\alpha N dl
\]  \hspace{1cm} (3)

In equation (3), \(\alpha\) is a proportionality constant. By integration of equation (3) with respect to \(l\), and with the constants of \(L\) as the total thickness of the filter medium in the direction of filtration and \(N_0\) as the number of initial incident particles, one can obtain equation (4).

\[
N = N_0 \exp(-\alpha L)
\]  \hspace{1cm} (4)

Using equation (4), the filtration efficiency which is defined in equation (1) is obtained, as in equation (5).
\[ E = \frac{N_0 - N}{N_0} = 1 - \exp(-\alpha L) \quad (5) \]

The proportionality constant \( \alpha \) in equation (5) is related to fiber diameter, single fiber efficiency, and fiber packing density of the filter medium. The derived efficiency in equation (5) can be rewritten in the more well-known form,\(^4^8\) as in equation (6).

\[ E = 1 - \exp(-E_s S) \quad (6) \]

where \( E_s \) is single-fiber efficiency, and \( S \) is the fiber projected area describing physical characteristics of a filter medium, and defined in equation (7)

\[ S = \frac{4La}{\pi d_f} \quad (7) \]

In equation (7), \( a \) is fiber volume fraction, and \( d_f \) is diameter of single fiber. Equation (7) assumes that the filter has monodispersed fiber diameter. The single fiber efficiency with the two major mechanisms of direct interception and diffusional deposition is given in equation (8).

\[ E_s = E_D + E_R \quad (8) \]

In equation (8), \( E_D \) and \( E_R \) are the efficiency of filtration by diffusional deposition and direct interception respectively. Lee and Liu empirically estimated the efficiency of diffusional deposition,\(^4^2\) as in equation (9)

\[ E_D = 1.6125 \left( \frac{1-a}{Ku} \right)^{\frac{1}{3}} \exp^{-\frac{2}{3}} \quad (9) \]

where \( Ku \) is Kuwabura hydrodynamic factor and is defined in equation (10).
In equation (9), Pe is Peclet number, defined in equation (11).

\[
Pe = \frac{Ud_f}{D}
\]

where \( U \) is the face velocity of a fluid and \( D \) is diffusion coefficient of a particle. Liu and Rubow estimated the efficiency of direct interception for a single fiber\textsuperscript{42}, as in equation (12).

\[
E_R = \frac{1}{\varepsilon} \left( \frac{1-a}{Ku} \right) \left( \frac{R^2}{1+R} \right)
\]

where \( \varepsilon \) is a correction factor describing the homogeneity of a filter with \( \varepsilon \approx 1 \) for a homogeneous filter. In equation (12), \( R \) is an interception parameter, defined as the ratio of diameter for a filtered particle to that of a fiber. Figure 2 shows schematically how the efficiency varies with particle size, as estimated by Kowalski, et al.\textsuperscript{42} based on the governing mechanisms of direct interception and diffusional deposition for fiber-based filter media having monodispersed. As seen in Figure 2, the efficiency of diffusional deposition decreases, and that of direct interception increases with an increase of the size of particles. These two opposing behaviors to the size of particles generate the minimum point of total efficiency. This minimum point indicates that a fiber-based filter has a most penetrable particle with the size ranging from 0.15 to 0.3 \( \mu \)m.\textsuperscript{42} In filter industries, the most penetrable particle size (MPPS) of solid and liquid droplets is considered to be around 0.1 to 1 \( \mu \)m.\textsuperscript{35} Experiments also showed much lower filtration efficiency near the most penetrable particle size. According to the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASJRAE), filters for removal of 60-65%
particles for example, the efficiency is reduced to 20% for particles in the range 0.2 - 0.3 μm. Due to the efficiency dependence on the size of particles, the efficiency of HEPA filters is commonly expressed in the form of efficiency of removal of particles of 0.3 μm size.

Published literature on evaluation of filters for removal of airborne nanoparticles of sizes 100 nm and smaller are scarce. Removal of airborne nanoparticles of sizes 100 nm and smaller using fiber mat-based filters still remains a challenge.

Figure 2. Schematic of filtration efficiency of a fibrous filter medium with two governing mechanisms: direct interception and diffusional deposition.\textsuperscript{42}
Table 1 summarizes the performance of filters as per classifications by European Norm EN 1822-1:2009. The classification is accepted widely as standard for filter performances. The term E10-12 in Table 1 stands for EPA filters. EPA is an acronym for Efficiency Particulate Air filters, while H13-14 stands for HEPA filters. Finally, U15-16 stands for ULPA filters. ULPA is an acronym for Ultra Low Penetration Air filters.

Table 1. Classification of air filters as per EN 1822-1:2009

<table>
<thead>
<tr>
<th>Filter class</th>
<th>Overall values</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Efficiency in %</td>
<td>Penetration in %</td>
</tr>
<tr>
<td>E10</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>E11</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>E12</td>
<td>99.5</td>
<td>0.5</td>
</tr>
<tr>
<td>H13</td>
<td>99.95</td>
<td>0.05</td>
</tr>
<tr>
<td>H14</td>
<td>99,995</td>
<td>0.005</td>
</tr>
<tr>
<td>U15</td>
<td>99.99995</td>
<td>0.00005</td>
</tr>
<tr>
<td>U16</td>
<td>99.999995</td>
<td>0.000005</td>
</tr>
<tr>
<td>U17</td>
<td>99.999995</td>
<td>0.000005</td>
</tr>
</tbody>
</table>

In practice, these filters are not used as a single-stage filter media, but are used in a layered multi-stage form. For example, an EPA/HEPA/ULPA filter stacked in three stages is used for filtration in laboratories or electronic industries. Another important factor that determines the success of filtration process in industry is pressure drop of the
filter system. The pressure drop is directly related to the operating cost, e.g., higher resistance of a filter leads to higher cost of filtration. General thickness for HEPA filters is one inch for home usage, whereas the thickness extends to over 10 inches for filter media in industrial installation. Fiber-based HEPA filters provide high efficiency and comparably low pressure drop. However, if particles start to clog a surface of the HEPA filters, the filtration mode shifts to surface filtration, and pressure drop starts to increase sharply. This regime is known as cake filtration and is disadvantageous for fiber-based HEPA filters. It is known that the pressure drop increases linearly for solid particles, but exponentially for oil droplets in the cake filtration regime. Another disadvantage of HEPA filters is lower efficiency for liquid droplets showing 95% efficiency for 0.3 μm oil droplets.

2.3 Organic aerogels: sPS aerogels

Resorcinol-formaldehyde and melamine-formaldehyde aerogels are two widely known aerogels from organic sources. They are fabricated by sol-gel chemistry similar to silica aerogels. A sol of resorcinol or melamine with formaldehyde in an aqueous solution is polycondensed to form a gel. The solvent is extracted to obtain organic aerogels. The organic aerogels have higher bulk density than that of inorganic aerogels, such as silica aerogels with typical values of 0.38-0.88 g/cm³ compared to 0.05-0.35 g/cm³ for silica aerogels.

Although a large number of aerogels are synthesized via sol-gel chemistry, thermoreversible gelation offers an alternative method to form organic gels. The
technique utilizes the solubility difference of a polymer in a solvent as function of temperature. Polymer solutions exhibiting an upper critical solution temperature (UCST) can undergo spinodal decomposition with reduction of temperature. A polymer-rich phase coexists semi-continuously with a polymer-poor phase leading to formation of a polymer gel.\textsuperscript{52,53} The interconnected polymer-rich phase spanning the entire volume of the dilute polymer solution becomes the body of the gel. Selecting a proper polymer is important because the properties of the gel inherently come from the properties of the polymer itself.

Syndiotactic polystyrene (sPS) is an interesting polymer for aerogel due to its outstanding properties. Good thermal resistance, chemical inertness, and mechanical stiffness of sPS originate from the semi-crystalline structure. sPS is polymerized by radical or anionic polymerization with Ziegler-Natta catalyst to obtain the desired stereo-regularity, which in turn produces the semi-crystalline structure.\textsuperscript{54} The $\alpha$ and $\beta$ crystalline phases in which the conformation of molecular chains is trans-planar zigzag are formed mostly by melt-cold crystallization, while $\delta$ and $\gamma$ crystalline phases in which the conformation of molecular chains is s(2/1)2 trans-trans-gauche-gauche helical are formed mostly by solvent-induced crystallization.\textsuperscript{55} Figure 3 presents the two crystalline phases of the zigzag and helical conformations. These conformations of the molecular chains determine microporosity of sPS gels.\textsuperscript{24,56}

Many sPS/solvent systems were studied for investigation of solvent-induced crystallizations. The studied solvents are benzene, chloroform, toluene, trans-decalin, cis-decalin, chlorobenzene, 1,2-dichlorobenzene, 1,2-dichloroethane, tetrahydrofuran, and o-xylene.\textsuperscript{56-64} These studies showed that the quality of the solvents plays an important role
in determining the molecular conformation in crystalline structure. The helical conformation is thermodynamically favored at low sPS concentration in a good solvent, but the trans-planer zigzag conformation is favored at high sPS concentration in the same solvent. On the other hand, the trans-planar zigzag conformation is obtained at all concentration in a poor solvent.\textsuperscript{31,65}

![Diagram of molecular conformations](image)

**Figure 3.** The molecular conformations in crystalline structure of sPS: (A) Trans-planar zigzag conformation; (B) s(2/1)2 trans-trans-gauche-gauche helical conformation.\textsuperscript{66}

In solvent-induced crystallization process, the helical conformation is stabilized by solvation.\textsuperscript{67} The solvation defines a status whereby the cavities created by adjacent phenyl groups on the sPS molecular chains are filled with a solvent. Micropores in the semi-crystalline strands of sPS gel are created by these solvated cavities.\textsuperscript{24,56,67} Figure 4 presents a schematic of the solvation process. The solvation process stabilizes the helical
conformation and hinders the molecular chains from forming chain-folded lamellar structure. The helical structure further forms semi-crystalline clathrate structures by absorbing a guest molecule in the cavities\textsuperscript{80,88,89}. The guest molecule is generally a low molecular weight substance. The solvents that help form clathrate structures also serve as guest molecules. The clathrate structures are often termed as co-crystals.\textsuperscript{59,68,69} The term $\delta$ in $\delta$-crystalline phase indicates that the crystals are developed by the guest molecules in the cavities.\textsuperscript{70} The crystalline structures free from the guest molecules are termed the $\gamma$-crystalline phase. A $\gamma$-form co-crystal is developed by crystallizing an amorphous sPS without a guest molecule. The amorphous sPS can be prepared by quenching a sPS film before crystallization.

![Figure 4. $\delta$-form co-crystal stabilized by solvation of sPS fibrils. The solvated cavities become to micropores upon drying.\textsuperscript{24}](image-url)
The clathrates can transform between each form. For example, the $\gamma$-form transforms to the $\delta$-form by absorbing carbon disulfide. Likewise, the $\gamma$-form transforms to $\varepsilon$-form by absorbing chloroform.\textsuperscript{69} In reverse order, the $\gamma$-form is obtained by annealing the $\delta$-form at 130 °C.\textsuperscript{69,71} On the other hand, an emptied $\delta$-form ($\delta_e$) structure generated by removing the guest molecules from the $\delta$-form is different from the $\gamma$-form.\textsuperscript{70} The cavities of the $\delta$-form are isolated from each other with each imprisoning a guest molecule. However, the cavities of the $\varepsilon$-form are open to each other forming a channel\textsuperscript{71}. The cavity of the $\varepsilon$-form can accommodate a larger guest molecule than the $\delta$-form. A guest molecule of 0.25 nm$^3$ in volume is accommodated in the $\delta$-form cavity, however a molecule of volume 0.275 nm$^3$ is accommodated prevailingly in the $\varepsilon$-form cavity.\textsuperscript{72} The amount of gas uptake by sPS aerogel monolith also depends on the co-crystalline structure. The $\delta$-aerogel of 91% porosity absorbs 35 cm$^3$/g of N$_2$ at P/P$_0$=0.1, but the $\beta$-aerogel of the same porosity absorbs 14 cm$^3$/g under the same condition.\textsuperscript{72}

sPS aerogel is obtained by solvent extraction from the sPS gel. For solvent extraction, liquid carbon dioxide is widely used, which is then removed under supercritical condition to yield aerogel. The terms, such as $\delta$-form aerogel and $\varepsilon$-form aerogel, come from the co-crystalline structures of $\delta$-form and $\varepsilon$-form respectively. For example, the $\delta$-form aerogel is obtained by solvent extraction from the $\delta$-form of gel. After solvent extraction, the solvent-rich phase turns into macropores.

In the solvent extraction step, the capillary pressure should be minimized, as it can cause collapse of the gel networks.\textsuperscript{73} The capillary pressure is determined from the value of surface tension of a mother liquid inside a gel and the size of pores of the gel. The capillary pressure can be large and can cause collapse of the gel networks if the size
of pores are small. Three methods are widely used for solvent extraction from the gel. First, the solvent is removed by evaporation at ambient pressure, yielding xerogels. Second, the solvent is removed under supercritical condition, leading to aerogels. Third, the solvent is removed by solvent freeze-drying process, thus forming cryogels. Supercritical drying is the best method in terms of preserving the pore structures, as the capillary pressure vanishes under supercritical condition. However, the requirement of high temperature and pressure to reach the critical condition of some of the organic solvents is sometimes untenable. Figure 5 schematically presents the steps involved in supercritical drying process stating with a P-T diagram - (1) an autoclave filled with a solvent, e.g., carbon dioxide is heated to reach the supercritical condition and allowed to stabilize, (2) the autoclave is then depressurized under isothermal condition, and (3) cooled down to room temperature to retrieve an aerogel. Carbon dioxide is universally used as a supercritical fluid due to its non-flammable nature and mild temperature (31.1 °C) to reach the critical condition. The critical temperature of other well-known alcoholic solvents, such as methanol and ethanol are much higher, for example, methanol and ethanol critical temperature are 239.6 and 240.9 °C respectively.

The sPS aerogels can be prepared as follows. A solution of sPS in chloroform is prepared with sPS concentration in the regime of spinodal decomposition, for example, C_{sPS}=0.1g/g. The materials are heated above the boiling point of the solvent to obtain a homogeneous solution. The solution is then cooled down to form sPS gel. The δ-form co-crystal is developed in the gel by solvation. The gel is then solvent exchanged by an alcoholic solvent, such as methanol and ethanol, and dried in supercritical carbon dioxide to obtain the δ-form aerogel. The bulk density and porosity of the fabricated δ-form
aerogel with this procedure were 0.18 g/cm$^3$ and 82% respectively.$^{24}$ Other forms of sPS aerogels can be obtained by the transforming the fabricated δ-form aerogel using the processes discussed earlier. Table 2 summarizes the physical properties of δ-form sPS aerogel obtained from sPS/tetrahydrofuran solution and supercritical drying in carbon dioxide.$^{30}$

Figure 5. Pressure – temperature (P - T) relationship during phase transition.
Table 2. Physical properties of δ-form sPS aerogel obtained from a sPS/tetrahydrofuran solution and supercritical drying in carbon dioxide.$^30$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density</td>
<td>0.032 g/cm$^3$</td>
</tr>
<tr>
<td>Internal surface area</td>
<td>379 m$^2$/g</td>
</tr>
<tr>
<td>Porosity</td>
<td>97%</td>
</tr>
<tr>
<td>Skeletal density</td>
<td>1.056 g/cm$^3$</td>
</tr>
<tr>
<td>Compressive modulus</td>
<td>1.7 MPa</td>
</tr>
<tr>
<td>Linear shrinkage</td>
<td>11%</td>
</tr>
</tbody>
</table>

2.4 Inorganic aerogels: silica aerogels

Silica aerogels are also good candidates in applications of thermal insulation, acoustic barrier, catalysis, storage and filtration because of unique properties of low thermal conductivity, low density, large surface area, and high porosity.$^{74-76}$ Table 3 lists typical properties of silica aerogels. Silica aerogels are characterized as the material of high porosity with significant fraction of mesopores. All the unique properties such as thermal, electrical, and physical properties originate from the characteristics of mesopores in silica aerogels. However, practical applications of silica aerogels in industries are limited due to their fragile nature, slow production process, and difficulty
to form crack-free monoliths. Further research is needed to overcome the limitations such that more widespread industrial applications are obtained.

Table 3. Typical properties of silica aerogels.\textsuperscript{77}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density</td>
<td>0.003-0.35 g/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>Internal surface area</td>
<td>600-1,000 m\textsuperscript{2}/g</td>
</tr>
<tr>
<td>Mean pore diameter</td>
<td>\textasciitilde20 nm</td>
</tr>
<tr>
<td>Primary particle diameter</td>
<td>2-5 nm</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.0-1.08</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.005-0.03 W/mK</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>\textasciitilde1.1</td>
</tr>
<tr>
<td>Sound velocity</td>
<td>100 m/sec</td>
</tr>
</tbody>
</table>

Silica aerogels are obtained following a two-step method – such as formation of gels and extraction of the solvent from the gels. Double-catalyzed acid-base sol-gel reactions are widely used for fabrication of silica gels as the gel time can be short.
Solutions of alkoxy silane in water and an alcohol are hydrolyzed under acidic condition and then condensed under basic condition to obtain faster rate of both hydrolysis and condensation reactions.\textsuperscript{78} The gelation time is an important factor for productivity of silica gels. A study reported that the gelation time holds logarithmic relationship with pH of the condensation reaction step.\textsuperscript{79} Figure 6 shows proposed mechanisms for an acidic hydrolysis and basic condensation reactions of alkoxy silanes.

After the gelation, an aging process is optionally used for strengthening the gel networks.\textsuperscript{73,76,80-85} Aging has three effects on the structures of silica gels. First, the terminal -OR and –OH groups on the surfaces of silica networks undergo further condensation in the aging process. This effect is called syneresis. It was shown that water increases the rate of syneresis.\textsuperscript{80} In view of this, a water/alcohol solution can be used as an aging solution for silica gels. Second, the silane species, if present, can attach to the silica networks and strengthen the networks.\textsuperscript{76,85} Third, structural rearrangement occurs due to the dissolution-redemption reaction in the system. This process renders the structural crevices and necks smooth and flat.\textsuperscript{82} The aging process takes several days, after which an alcoholic solvent exchange step is needed to remove the impurities. The impurities can be residual reactants, catalysts, and water which are undesirable materials for a subsequent solvent extraction step.

Finally, supercritical drying, e.g., carbon dioxide produces silica aerogels. Carbon dioxide is widely used as the supercritical fluid due to low critical temperature. Another reason for using carbon dioxide is to avoid corrosive nature of alcohols at high temperature and pressure and to avoid deteriorating effect on mesoporosity from the soluble nature of silica networks in alcohols.\textsuperscript{86} Nevertheless, the additional step involving
solvent exchange by liquid carbon dioxide and associated production of hydrophilic silica aerogels are considered two disadvantages of supercritical drying sing carbon dioxide. Supercritical drying in an alcohol, on the other hand, reduces processing time and produces hydrophobic silica aerogels due to esterification reaction by alcohol.

Acidic hydrolysis

Basic condensation

Figure 6. Acidic hydrolysis and basic condensation reactions of alkoxy silanes. 87
Alcohol as the supercritical fluid was used by Poco et al. in rapid solvent extraction method. Further improvements of the process were outlined by other researchers. The rapid method is a one-pot synthesis process of sol-to-aerogel conversion in an autoclave. A stainless steel mold filled with a sol of a silica precursor, water, and alcoholic solvent is placed in an autoclave containing excessive amount of the solvent. The autoclave is then heated to bring the temperature and pressure to the critical condition of the solvent. Gelation occurs inside the mold during this heating step. The autoclave is degassed and cooled down to room temperature. The time to produce a monolith by this process was a few hours, which is in stark contrast to several days needed when a conventional method is used. Nevertheless, several limitations are identified for the autoclave method. First, the method does not allow washing of the impurities, which in turn produce inferior properties. Second, the internal surface area, which is an important attribute of silica aerogels, is significantly lowered if the rapid drying process in autoclave process is used. Finally, chemical modification for reinforcement of the gel cannot be exercised in the autoclave method.

Structural development in silica gels were extensively studied using X-ray and rheological techniques in earlier work. Based on these studies, it was concluded that under acidic conditions and especially at low concentration of water, the gel networks are formed by linear strands connections, while under basic condition or at high concentration of water, silica networks of spherical particles are obtained. It was reported that silica gels condensed under basic condition showed mass fractals, while those condensed under acidic condition showed either no fractals at all or only surface fractals. Thus, one can see that the primary factor affecting the structural development
in silica gel synthesis is the catalytic condition. Another factor is the concentrations of water. Silica gels condensed under acidic or basic conditions showed similar structural development when the alkoxy silane was hydrolyzed with small amounts of water, typically at water/alkoxy silane molar ratio of 4.0.\textsuperscript{23,91} Another study showed that large amounts of water of about 20 molar ratio of water/alkoxy silane resulted in the spherical structures, but small amounts of water at molar ratio of water/alkoxy silane of 1.0 resulted in linear structures for the same alkoxy silane hydrolyzed under the same acidic condition.\textsuperscript{23,92,93} These results indicate that the development of structures depends on both the catalytic condition, and the concentrations of water. The effect of concentration of water can be rationalized with the number of hydroxyl groups produced in the hydrolysis step. A large number of hydroxyl groups produced from high concentrations of water lead to spherical particles with highly branched structures of the gels. At low concentrations of water, linear structures are developed due to a small number of hydroxyl groups. This information on the role of molar ratio of water and alkoxy silane can be used in controlling the structure of silica gels and to arrive at desired structural forms.

The physical properties of silica aerogels are determined by several factors. The bulk density is determined from the resistance of the silica networks to compressive stress that originate during drying.\textsuperscript{23} The compressive stress originates from the surface tension force of the receding liquid meniscus. Silica aerogels synthesized at high pH in the condensation reaction step show low bulk density due to low shrinkage. It was reported that linear shrinkage of silica aerogels produced under acidic condition was about 25\%, while those synthesized under basic condition showed only 5 \% shrinkage.\textsuperscript{96}
Figure 7 shows a proposed model of silica gel networks with spherical particles.\textsuperscript{7,97} The skeletal structure of the pearl necklace in Figure 7 contains crevices and necks, in addition to pores generated by the skeletal structures.

![Diagram of silica gel networks with spherical particles](image)

Figure 7. A proposed model of the pearl-necklace structure of silica gels and pores generated by the skeletal structure.\textsuperscript{7,97}

Pore volume, pore size, and surface area of silica aerogels are also primarily dependent on the drying conditions. For example, smaller pore volume and pore size were obtained when the shrinkage was high in drying step.\textsuperscript{98} The aging step also affected the pore structures of silica aerogels. The syneresis of silica gel structures by thermal aging with water led to low bulk density and high porosity due also to low values of
shrinkage.\textsuperscript{84} High porosity and large pore size were also obtained by aging the gel in a solution containing the silane precursor.\textsuperscript{76} The internal surface area also increased with an increase of the volume of pores,\textsuperscript{76,98} but an opposite trend was also reported.\textsuperscript{84} The internal surface area was significantly affected by type of solvents used in the drying step. For example, silica aerogels dried in an alcoholic solvent showed much lower internal surface area than the aerogels dried in carbon dioxide. The structural rearrangement in the alcoholic solvent due to silica dissolution is the primary reason.\textsuperscript{99,100} In summary, the gelation time and bulk density decreased, but skeletal density increased with an increase of pH in the condensation reaction step. An increase of volume and size of pores is also anticipated with an increase of pH.

2.5 Aerogels with advanced structures

A set of hybrid aerogels containing both meso- and macropores were produced by growing silica gel inside the macropores of sPS gel.\textsuperscript{30,31} This field of research, however, is in early stage. The hybrid aerogel showed a synergistic effect on mechanical properties, although monolithic silica aerogels are fragile at low level of stress of about 31kPa.\textsuperscript{7,21} The sPS aerogels are also known to undergo irreversible buckling of the sPS fibrils at low level of stress.\textsuperscript{26,105} However, the hybrid aerogel showed 30 times higher modulus than the silica aerogel. The synergistic effect came from the intertwined silica and sPS networks.\textsuperscript{30} It is known in literature that polymer conformal coating on silica particles can produce greater enhancement of mechanical properties than the factor of 30 reported in the synergistic hybrid aerogel.\textsuperscript{20,22,101-104} However, the route to conformal coating also caused large reduction of porosity and internal surface area. The hybrid aerogel, on the
other hand, retains all the surface properties of silica particles. As an example, the polystyrene cross-linked silica aerogel showed an internal surface area of 213-393 m$^2$/g compared to that of about 1,000 m$^2$/g for silica aerogel.\textsuperscript{101} However, the internal surface area of the sPS/silica hybrid aerogel was maintained at over 540 m$^2$/g.\textsuperscript{30} The hybrid aerogel offered large absorption capacity and high absorption rate at the same time due to the presence of mesoporous silica aerogels residing in the macropores of sPS aerogel.\textsuperscript{30} These characteristics are advantageous for such applications as crude oil removal and particle filtration. The hybrid can also be functional for selective absorption of small organic compounds because nanocavities in sPS fibrils offer the function of selective absorption.\textsuperscript{26,31,105-108}

Gradient density aerogels are an active field of research nowadays with unique applications, such as the interstellar grains collector and acoustic impedance matching materials.\textsuperscript{109,110} The gradient density aerogels can also be applied in filtration due to its unique features in the form of gradient porosity. A representative gradient density aerogel was obtained from a gradient density gel. A gradient gel was prepared by a special type of pumps mixing the sols of different compositions.\textsuperscript{110} Alternative techniques such as layer-by-layer gelation and sol-co-gelation were also used to produce the gradient density aerogel.\textsuperscript{10}

2.6 Previous studies on filtration using aerogels

Porous materials are widely used in industrial applications in particle capture, flow restriction, sound attenuation, and atomization.\textsuperscript{6} For filtration, high porosity with
appropriate sizes of pores and large surface area are desired for maximizing the function of depth filtration. For example, highly activated porous carbons are being used as smoke filters to reduce the particle count in the smoke. In this case, carbon with large surface area of 1,000 m$^2$/g and high microporosity are advantageous. The activated carbons are made of carbon rich materials, such as nutshells. Other factors for efficient filtration are high absorption rate and broad distribution of pore sizes. Aerogels have been frequently listed as materials for effective filtration because they meet these needs. Among aerogels, silica aerogels provide high porosity with various sizes of pores and large surface area. In this context, silica aerogels are among the good candidate materials for filtration. sPS aerogels offer high porosity with significantly developed macropores, and large absorption capacity. This material is also a good candidate for filtration applications. Nevertheless, studies on filtration of airborne particles by monolithic aerogels are scarce. A handful of studies used aerogel granules or microspheres arranged in a packed bed filter.

Permeability and filtration efficiency are two core elements in characterization of filter media. Several studies on air permeability of aerogels have been reported. For example, the value of permeability of monolithic silica aerogels was reported as $10^{-15}$ m$^2$. However, the different value of permeability of the same material was also reported at $10^{-12}$ m$^2$. In the same study, it was reported that permeability of silica aerogel composites with incorporated titanium oxide was lower than that of the unmodified silica aerogel due to decreased porosity of the composite aerogel due to incorporation of titanium dioxide. Silica aerogel spheres arranged in a packed bed showed higher permeability than monolithic silica aerogels with a value of $2.2\times10^{-11}$ m$^2$. For carbon
aerogel, mesopore fractions were a key factor affecting the permeability. Permeability of carbon aerogels was in the range of $10^{-16}$ - $10^{-14}$ m$^2$ with the aerogel bulk density of 0.05-0.44 g/cm$^3$.$^{114}$ The values of permeability followed a power law with bulk density in the study.

The fluid flow through a filter medium is related to permeability, thereby affecting the pressure drop through the filter medium. The fluid flow in aerogels can be viscous, diffusional or a combination of viscous and diffusional flows. Knudsen number (Kn) determines the flow regime.$^{112,115}$ It is defined in equation (13).

$$Kn = \frac{\lambda}{d_p}$$  \hspace{1cm} (13)

In equation (13), $\lambda$ is the mean free path of gases and $d_p$ is the mean size of the pores. If $Kn << 1$, the fluid flow is purely viscous. The viscous flow is driven by the pressure gradient and the viscosity of the fluid as per Darcy’s law, as in equation (14).

$$j = -\frac{k}{\mu} \nabla P$$  \hspace{1cm} (14)

In equation (14), $j$ is the flux with unit m/s, $k$ is permeability, $\mu$ is viscosity and $P$ is pressure. If $Kn >> 1$, the fluid flow is diffusional. Diffusional flow is driven by concentration gradient as Fick’s law describes, as in equation (15).

$$j_D = -D \nabla \psi$$  \hspace{1cm} (15)

In equation (15), $j_D$ is the diffusion flux (mol/m$^2$s), $D$ is diffusivity (cm$^2$/s) and $\psi$ is the concentration (mol/m$^3$). If $Kn \approx 1$, the fluid flow becomes the combination of viscous and diffusional flows. The mean free path of gases should be determined for characterizing
the fluid flows in a monolithic aerogel. The mean free path of gases in free space, $\lambda_{\text{free}}$, is defined by the kinetic theory of gases\textsuperscript{115} as in equation (16).

$$\lambda_{\text{free}} = \frac{1}{\sqrt{2n_g\pi d_g^2}} = \frac{k_B T}{\sqrt{2\pi d_g^2} \rho}$$

(16)

where $n_g$ is the number of molecules in a unit volume, $K_B$ is Boltzmann constant, $T$ is temperature, and $d_g$ is the diameter of the molecule. The mean free path in porous materials, $\lambda_{\text{pore}}$, should be modified because the motion of the gas is restricted by their collisions against the pore walls\textsuperscript{115} as presented in equation (17).

$$\lambda_{\text{pore}} = \frac{1}{\sqrt{2n_g\pi d_g^2} + S_s \rho_b / \Pi}$$

(17)

where $S_s$ is the specific surface area of the pores, $\rho_b$ and $\Pi$ are bulk density and porosity of the porous material respectively. This indicates that the mean free path of gas molecules is reduced in the pores. The mean free path of gases in free space under the condition of 3.7 bar and 296 K is about 20 nm\textsuperscript{115} and this value corresponds to the size of mesopores (2-50 nm). Also, the scale of mean free path of the inside gas becomes similar to the size of mesopores because the gas molecules inside the mesopores are restricted.

For example, $\lambda_{\text{pore}}$ 10 nm is obtained from equation (17) for silica aerogel with $\rho_b=0.1$ g/cm$^3$, $S_s=1,000$ m$^2$/g, and $\Pi=95\%$. The obtained value is in the scale of the sizes of mesopores. In this context, the fluid flow inside a mesoporous material can be the combination of both viscous and diffusional flows. As one can expect, the combined flow was observed in a monolithic silica aerogel at pressure range of 6-200 kPa\textsuperscript{112}. This combination of viscous and diffusional flows is considered advantageous for capturing airborne nanoparticles in relations with diffusional deposition mechanism. The fluid flow
can also be conveniently characterized in terms of conductance. From Darcy’s law in equation (14), flow rate, Q is related to conductance, C, as in equation (18).

\[
Q = j \cdot A = \frac{k A P_{\text{ave}}}{\mu L} \frac{\Delta P}{P_{\text{ave}}} = C \frac{\Delta P}{P_{\text{ave}}}
\]  

(18)

where A is the cross-sectional area of the face normal to the fluid flow, \(P_{\text{ave}}\) is average pressure, and C is conductance \((\text{m}^3/\text{sec})\). For purely viscous flow in which \(Kn \ll 1\), conductance is given by Hagen-Poiseuille law, as in equation (19)\(^{112,116}\)

\[
C = \frac{\pi r_c^4}{8\mu l_c} P_{\text{ave}}
\]  

(19)

where \(r_c\) and \(l_c\) are capillary radius and length respectively. For diffusional flow in which \(Kn \gg 1\), conductance is given as presented in equation (20)\(^{98,104}\)

\[
C = \frac{4}{3} \sqrt{\frac{2\pi R_0 T r_c^3}{M l_c}}
\]  

(20)

In equation (20), \(R_0\) is the gas constant, and \(M\) is the molar mass of the fluid. Note that conductance is proportional to \(P_{\text{ave}}/\mu\) for viscous flow, but proportional to \(M^{-1/2}\) for diffusional flow.

A direct investigation of filtration of airborne particles by monolithic aerogels does not exist to the best of our knowledge. A similar application was reported for titania–silica aerogel.\(^{39}\) Deactivation and destruction of airborne microorganisms were major focus of the above study. The aerogel was able to filter aerosols with very low filtration efficiency about 30%. However, the deactivation of the microorganism was much improved due to high internal surface area offering much photo activity of titanium dioxide. An exposure of 30 min of UV killed 99.9999% microorganisms with the aerogel,
which are much better than commercially available titanium dioxide powders. The permeability of the titania-silica aerogel was lower than that of silica aerogel because of lowered volume of pores. Literature reports exist on the use of silica aerogels impregnated in a fiber mat of a HEPA filter medium for airborne particle filtration.\textsuperscript{36} Penetration of the silica aerogel impregnated HEPA filter medium was 2-3 orders of magnitude lower than that of an untreated HEPA filter medium. On the other hand, permeability of the aerogel impregnated HEPA filter medium was 3 times lower than that of the untreated one. It was found that the particles with the similar sizes to viruses were efficiently captured by the treated HEPA filter medium. A monolithic silica aerogel was studied for a biosensor application.\textsuperscript{37} This study proved that the silica aerogel could colonize bioluminescent cells and detect viral particles. This study did not provide filtration efficiency for viral particles, but showed the function of virus detection. The viral particles could penetrate the silica aerogel. Applications of aerogel monoliths as catalysis for removal of pollutants were reported. Silica aerogels containing metallic oxide for converting combustion gases, such as SO\textsubscript{2}, NO\textsubscript{x}, CO\textsubscript{2}, CO and H\textsubscript{2}S were studied.\textsuperscript{9} The composite aerogels showed higher efficiency for conversion of these gases than the metal oxide powders or agglomerates due to high surface area. Silica aerogels showed SO\textsubscript{2} absorption from 95% to nearly 100% when they contained CaO, MgO. CO\textsubscript{2} adsorption was found to vary between 85% and 100%. CO adsorption was 90% to 98%, and NO adsorption was nearly complete. H\textsubscript{2}S adsorption was 90% in the first stage, but it dropped to 40% after 105 min due to an unknown reason as reported by the authors. TiO\textsubscript{2}-SiO\textsubscript{2} aerogels were also used in removal of cyanides.\textsuperscript{38} Cyanides are hazardous aqueous chemicals from electroplating and metal heat-treating industries. The aerogels
showed higher efficiency than titanium dioxide powders in removal of these pollutants. The high surface area of the monolithic aerogels offered the improvement. Aerogel granules and microspheres arranged in packed bed filters were considered in removal of airborne particles. An invention reported that the aerogel microspheres arranged in packed bed filters could replace fiber-based HEPA filters. The packed bed filter of 3 inches in depth with silica microspheres of diameter of 150-250 μm showed almost 100% efficiency for removal of aerosol particles at low gas velocity. The efficiency for removal of aerosols of 0.3 μm size was about 99.9%, and pressure drop was less than the fiber-based HEPA filters. In another study on packed bed filters, silica aerogel microspheres of 150–250 μm and 250–500 μm diameter, and carbon black granules of 150–250 μm diameter showed filtration efficiency similar to the fiber-based HEPA filters at low gas velocity. Higher efficiency for removal of oil droplets by the packed bed filter with the silica aerogel microspheres of 150–250 μm was reported in the study. High absorption capacity of the silica aerogel microspheres was proposed as the primary reason for better oil droplet filtration. Different hydrophobicity of a filter medium showed different filtration efficiency in the study; hydrophilic fumed silica granules arranged in a packed bed showed poorer filtration efficiency than the hydrophobic granules. In another study, however, the filtration efficiency for silica aerogel microparticles arranged in a packed bed filters was found to be lower than the fiber-based HEPA filters. This study showed that MPPS decreased with an increase of gas face velocity. MPPS was 570, 315, and 300 nm for the velocity 3.4, 20, and 40 cm/s respectively. These authors remarked that diffusional deposition, direct interception, and inertial impaction are three governing mechanisms for filtration by the packed beds filters. In addition, silica gel particles were
reported as an efficient material for removal of free fatty acid from glyceride oils.\textsuperscript{33} For example, peanut oil having an initial free fatty acid at 0.35 wt\% was filtered by spray dried silica aerogels (xerogels are a more appropriate term here). The free fatty acid content after the filtration was dropped to 0.07\% (removal capacity 76\%). The aerogel was 12 μm in diameter with surface area of 300 m\(^2\)/g and pore volume of 1.5 cm\(^3\)/g.
CHAPTER III

MATERIALS AND METHODS

3.1 Materials and synthesis methods

The macroporous δ-form syndiotactic polystyrene (sPS) aerogels were used as the baseline material. In conjunction, gradient density aerogels and hybrid aerogels were synthesized and used.

3.1.1 sPS aerogels

Monolithic δ-form sPS aerogels were fabricated using a two-step process involving thermoreversible gelation and supercritical drying.\textsuperscript{24-31} The thermoreversible gelation of sPS occurred via spinodal decomposition of the polymer-solvent binary system. This method of gelation is known as a simple and convenient technique to obtain organic gels. Various concentrations of sPS in a good solvent were prepared in this work to obtain various porosities of the aerogels. The parameters that affect the microstructure of sPS aerogel are limited. The bulk density, porosity, and volume and size of pores are all dependent on the polymer concentrations. The internal surface area, however, is almost independent of the concentration of sPS in the solution. sPS pellets with 98% syndiotacticity and molecular weight of 300,000 g/mol was provided by Scientific
Polymer Products Inc. (New York, NY). The sPS pellets were converted into powders for easy dissolution in a solvent. Reagent grade tetrahydrofuran (THF) purchased from Fisher Scientific was used as the solvent. The solutions of sPS in THF was turned into δ-form sPS gel via natural cooling.²⁸⁻³¹

Figure 8. Monolithic δ-form sPS aerogels fabricated in this work with 30 mm diameter and 4 mm thickness.

For preparing δ-form sPS aerogel, the sPS powder was dissolved in THF with heating up to the boiling temperature of the solvent in a sealed container. The homogeneous solution was poured into a mold and allowed to gel. The solution contained sPS of the concentrations ranged from 0.01 to 0.05 g/mL. The gels were aged in the
molds for a day. The wet gels were washed and solvent exchanged in EtOH. Ultrasonication was used to expedite the washing and solvent exchange processes. sPS gels were dried by supercritical drying in carbon dioxide by the steps described in Figure 5. For example, sPS gels were placed in a supercritical drying chamber. The solvent exchange for liquid carbon dioxide was carried out first until all original solvent were removed from sPS gels by liquid carbon dioxide. The chamber was then heated and pressurized to reach the supercritical condition of carbon dioxide. In this work, the chamber was heated to 50 °C, and the pressure at the temperature was 10.3 MPa. The materials were kept in the chamber for one hour after which the chamber was depressurized slowly under isothermal condition to atmospheric pressure. Only carbon dioxide was used in the drying step, instead of alcoholic solvents, as sPS melting temperature of 273 °C is very near the critical temperature of alcohols, e.g., ethanol: $T_c=241$ °C. Figure 8 shows a specimen of monolithic δ-form sPS aerogel fabricated in this work with 30 mm diameter and 4 mm thickness.

3.1.2 Silica aerogels

Silica aerogels are fabricated using the steps of sol-gel reaction, aging, washing, and solvent extraction via a suitable drying process.\textsuperscript{76,85} In this work, silica aerogels were fabricated by double-catalyzed sol-gel reactions and supercritical drying steps.

For materials, tetraethyl orthosilicate (TEOS, reagent grade 98%) purchased from Sigma-Aldrich was used as the silane precursor for silica gel. Ethanol (EtOH, 200-proof) purchased from Decon (King of Prussia, PA) was used as the co-solvent of TEOS along
with deionized water to conduct sol-gel reactions. Nitric acid (64-66%, Sigma-Aldrich) and ammonium hydroxide (28-30%, Fisher Scientific) served respectively as the acid and base catalysts in sol-gel reactions.

For the double-catalyzed sol-gel reactions, a silane precursor was hydrolyzed in a water/alcohol solution under acidic condition. Then, the silanes were condensed under basic condition. In this work, pH of the condensation reaction step was varied while maintaining the composition of the sols and the reaction condition of hydrolysis step the same in all cases to produce wet gels. The solution I was prepared by mixing TEOS, EtOH, and deionized water. The solution I was mixed with nitric acid to obtain a sol with pH value about 2.0. The solution II containing EtOH, deionized water, and ammonium hydroxide was then mixed with solution I, so that condensation reaction could take place under basic condition. Different amounts of ammonium hydroxide in solution II produced different silica aerogels in physical and textural property.

Figure 9 shows silica wet gels produced by the double-catalyzed sol-gel reaction in this work. Silica wet gel were aged to harden the silica networks so that crack-free aerogels were obtained. A solution of TEOS, EtOH and deionized water was used as an aging solution. The wet gels were washed with EtOH to obtain silica alcogels in which no impurities, such as residual reactants, water and catalysts are present. Washing was carried out by dipping and rinsing the wet gels in EtOH. The wash liquid was agitated by ultrasound to expedite the washing process. Washing process is important to obtain crack-free aerogels.
Figure 9. Silica wet gel fabricated by the double-catalyzed sol-gel reaction.

Figure 10. Monolithic silica aerogel fabricated in this work with 30 mm diameter and 4 mm thickness.
Silylation step was used to obtain different levels of hydrophobicity of silica aerogels. Silylation is efficient for turning the hydrophilic surface to hydrophobic without much effect on porosity deterioration.\textsuperscript{104} Dimethoxy-methyl (3,3,3-trifluoropropyl) silane (SiF3) is widely used as a silylating agent. Different concentration of SiF3 in an alcohol solvent produce deferent levels of hydrophobicity.\textsuperscript{104}

For supercritical drying of silica gels, both carbon dioxide and ethanol were used as drying solvents. Ethanol also offers an alternative means to obtain hydrophobic silica aerogel promoted by the esterification reaction.\textsuperscript{86,100} However, a reduction of internal surface area and volume of mesopores are two shortcomings of the drying in EtOH. The use of carbon dioxide helps keep the porosity intact. However, the use of carbon dioxide as a supercritical solvent calls for an additional step in solvent exchange and produce hydrophilic silica aerogel. Figure 10 shows silica aerogels fabricated in this work with 30 mm diameter and 4 mm thickness. As presented in Figure 10, silica aerogels were translucent different from sPS aerogels.

3.1.3 Gradient density aerogels

The gradient density aerogels were based on gradient in porosity in a certain direction. Several methods were introduced to produce the gradient density aerogels. These were layer-by-layer gelation, sol-co-gelation, and a method using a gradient density sol.\textsuperscript{10,110} This work used a sequential injection method for producing gradient density of monolithic aerogels.
In case of δ-from sPS, sPS solutions of different solid content were sequentially injected into the mold before or after gelation of the previously injected solution. For example, one gradient density aerogel was obtained by first injecting a solution of 0.05 g/mL sPS into the mold followed by injection of 0.03 and 0.01 g/mL solutions. The time interval of each injection was varied based on the gelation time of each solution. The gelation time of the solution containing 0.05 g/mL sPS was about 4.5 min. Thus, the 0.03 g/mL solution was injected before the 4.5 min mark or shortly afterwards. Two types of gradient density aerogels of δ-from sPS were produced respectively by injecting solutions before and after gelation of the previously injected solutions.

In case of gradient density silica aerogels, this work used the catalytic condition, which was more practical and convenient than the previously used methods. The acidic hydrolysis reaction of TEOS was carried out first using solutions I containing TEOS, deionized water, and EtOH. Solutions II was prepared by mixing EtOH and DIW, but with different amounts of a base catalyst, such that pH was different. Solution I and II were mixed together and the sequential injections of several mixtures of different pH into a mold produced a gradient density wet gel. The injections were completed before the gelation of each mixture; the diffusion of the base catalyst due to concentration gradient induced continuous gradient density in the aerogel monolith. Accordingly, the selection of appropriate pH was important, as the gelation time should be picked in such a way that the desired gradient concentration of the base catalyst was maintained. In this context, slower gelation allowed for homogenization of the base catalyst and gradient aerogels could not be produced.
3.1.4 Hybrid aerogels

The organic-inorganic hybrid aerogels were obtained by combining the two materials - the macroporous δ-form sPS and the mesoporous silica. A large number of hybrid structures could be produced by combining these two materials. The hybrid aerogels obtained by first forming sPS gel followed by impregnation of silica gel worked better than those obtained by the reverse process.\textsuperscript{30,31} In view of this, the sPS gel was formed first by thermoreversible gelation in THF. Then, the double-catalyzed sol-gel reaction was used to impregnate silica gel in sPS macropores in this work. For example, sPS gels filled with ethanol were produced by thermoreversible gelation and solvent exchange for ethanol. TEOS solutions were prepared in a mixture of ethanol and deionized water. TEOS was hydrolyzed to form hydroxysilanes under stirring for one hour at room temperature after the pH of these solutions was adjusted to 2.0 by adding nitric acid. The sPS gel specimens were soaked in hydroxysilane solution for one day and transferred to another container where a solution of ammonium hydroxide was poured over the gel specimen so as to increase the pH to around 9.0 and to promote condensation of hydroxysilanes into silica particle networks. The hybrid gels were aged for a day, washed and solvent exchanged with ethanol, and finally solvent exchanged with liquid carbon dioxide and finally dried under supercritical condition. Figure 11 presents schematic of the method for a fabrication of sPS-silica hybrid aerogel.

Electrostatically active monolithic aerogels were also fabricated in this work as another type of hybrid aerogels. For this purpose, polyvinylidene fluoride (PVDF) was hybridized with δ-form sPS. PVDF chains with the repeat unit CH$_2$-CF$_2$ generate strong molecular dipole moment perpendicular to the axis of the molecular chains due to
stronger electronegativity of fluorine atom than hydrogen atom. Five different crystalline polymorphs are known for PVDF, e.g., α, β, γ, δ and ε with unique electrical properties.\textsuperscript{117-124} The polymer chains in β, γ, and δ crystalline forms are packed to form parallel dipoles and, therefore, are able to have a net spontaneous dipole moment. PVDF with these crystalline phases also possess piezo-, pyro- and ferroelectricity. Of these, the β-phase show the strongest spontaneous polarization. The α-phase is the most stable phase with no-polarity but show para-electricity due to the symmetry of the crystalline unit cell. Formation of the polar crystalline phases in a PVDF film was reported if a polar solvent was used.\textsuperscript{124,125} From the spontaneous polarity, filter media fabricated from PVDF have a potential to have charged surfaces, which are electrostatically active.

\textbf{Figure 11.} Schematic of the method for a fabrication of sPS-silica hybrid aerogel.\textsuperscript{31}
The sPS-PVDF hybrid aerogel monoliths were fabricated by thermos-reversible gelation of sPS from a binary polymer solution of sPS and PVDF followed by supercritical drying of the gels in carbon dioxide. PVDF powders with average molecular weight of 250,000 g/mol was provided by Arkema Inc. (King of Prussia, PA). Reagent grade tetrahydrofuran (THF) purchased from Fisher Scientific was used as a solvent.

3.2 Analysis and characterization techniques

Various characterization techniques were used in this work. Air permeability and filtration efficiency were two key elements in these characterizations.

3.2.1 Air permeability

Air permeability measures how well a material allows the air flow. This is obtained by Darcy’s law in unit of cm$^2$ or m$^2$ as expressed in equation (21) (scalar form of equation (14)).

$$Q = \frac{kA \Delta P}{\mu L}$$

In equation (21), Q is the volumetric flow rate, k is permeability, A is cross-sectional area of the face normal to the fluid flow, $\mu$ is viscosity of the fluid, $\Delta P$ is pressure drop, and L is the length in the direction of the air flow.
In measurement, permeability is obtained from the plots of the pressure drop against fluid superficial velocity, \( v \) (\( v=Q/A \)), as in equation (22). The slope \( v/\Delta P \) is used in evaluation of permeability, \( k \).

\[
\Delta P = \frac{1}{k} v \mu L \tag{22}
\]

Figure 12. The bottom plates for Frazier air permeability tester. 5, 22, 25 mm holes can be used in this test.

An air permeability tester (Frazier Precision Instrument, Hagerstown, MD) was used for this purpose. Disc shaped aerogel specimens were placed at the center of a perforated bottom plate with a central hole which allowed air flow (Figure 12). One of bottom plates (hole sizes: 25, 22, and 5 mm) can be chosen based on the sizes of specimens. Darcy’s law can be modified with the shape factor, \( G \) for holes much smaller than the diameter of the aerogel specimen.\(^{126}\)
A sample holder covered the specimen and prevented lateral flow of air. The gaps between the specimen, the bottom plate, and the sample holder were eliminated using vacuum grease (Figure 13). As seen schematically in Figure 14 a vacuum pump drew air through the aerogel specimen. Finally, the specimen with the assembly was placed inside the Frazier tester to measure the permeability (Figure 14). The power of the vacuum
pump was controlled to obtain several values of pressure drop, $\Delta P$ and volumetric flow rate, $Q$, and the slope $Q/\Delta P$ was used for air permeability, $k$.

![Diagram](image)

Figure 14. Schematic (a) and experimental image (b) of the arrangement in Frazier permeability tester.

3.2.2 Filtration efficiency of airborne nanoparticles

Filtration efficiency measures the fraction of incident particles a filter captures after passing through the filter once. The efficiency, $E[\%]$ is defined by equation (1) in Chapter II. In this work, a TSI-8130 filter tester (TSI Inc., Shoreview, MN) that
generated in situ polydispersed sodium chloride nanoparticles was used. The size distribution of the incident particles is presented in Figure 15.

![Figure 15. The size distribution of particles generated by TSI-8130 filter tester.](image)

Figure 15. The size distribution of particles generated by TSI-8130 filter tester.¹²⁷

![Figure 16. The specimen holders used in TSI-8130 filter tester. A wide-mesh metal net attached at the bottom supports the aerogel specimen](image)

Figure 16. The specimen holders used in TSI-8130 filter tester. A wide-mesh metal net attached at the bottom supports the aerogel specimen
The diameter of generated particles ranged from 25-150 nm with an average diameter of 75 nm. The concentration of particles was about 15.1 mg/m$^3$. The TSI-8130 filter tester was able to measure the filtration efficiency with accuracy up to 99.999%. Specimen holders (Figure 16) were used in this filtration efficiency test. A wide-mesh metal net attached at the bottom of a specimen holder supported the aerogel specimen. The periphery of the aerogel specimen was sealed by a rubber O-ring (Figure 17). The face velocity ($U_f$) of air flow was varied between 25, 40, and 50 cm/sec. For each specimen,
the particles were allowed to go through the specimen 10 times and the value of filtration efficiency corresponding to each incident was measured, and an average value was determined.

3.2.3 Bulk density, skeletal density, and porosity

The value of bulk density, $\rho_b$ was obtained from the weight-to-volume ratio of the specimens. Skeletal density, $\rho_s$ is obtained by pycnometry (Accupyc II 1340, Micromeritics, Norcross, GA) at room temperature. Helium is used for this pycnometry because of its small size. The principle of pycnometry is the simple pressure-volume relations for gases (Boyle’s law). Two chambers whose volumes are already known are used. One of the two chambers is filled with a sample and pressurized first. The pressure is then released extending to another chamber by opening a valve in between the two chambers. With the measured pressure in the two stages, the volume of the sample, $V_{\text{sample}}$ is found from equation (23).

$$P_1(V_{C1} - V_{\text{sample}}) = P_2(V_{C1} + V_{C2} - V_{\text{sample}})$$

where $P_1$ and $P_2$ are the first pressure and second released pressure respectively, and $V_{C1}$ and $V_{C2}$ are the volumes of the two chambers respectively. Thus, $V_{\text{sample}}$ is obtained from equation (24).

$$V_{\text{sample}} = V_{C1} + \frac{V_{C2}}{1 - P_1 / P_2}$$

In practice, the aerogel samples should be completely dried in a vacuum oven to remove any moisture and other liquids, which may influence the measured pressure. In addition,
flushing the samples in the chamber by the measuring gas at least 25 times is recommended for accuracy.

Porosity (П) can be obtained using bulk and skeletal density, as in equation (25).

\[ \Pi = 1 - \frac{\rho_b}{\rho_s} \]  
\[ (25) \]

In the case of sPS aerogels, the skeletal density of sPS aerogels was found to be almost constant, 1.056 g/cm³, regardless of the sPS concentration in the precursor solutions and matched with data reported elsewhere.²⁸-³¹

The total pore volume, \( V_{\text{total}} \) is the sum of volumes of all pores and is also calculated from bulk and skeletal density, as in equation (26).

\[ V_{\text{total}} = \left( \frac{1}{\rho_b} \right) - \left( \frac{1}{\rho_s} \right) \]  
\[ (26) \]

3.2.4 Internal surface area, pore volume and pore size

The internal surface area, \( S_{\text{BET}} \) is obtained from nitrogen sorption isotherms (TriStar II, Micromeritics, Norcross, GA) at temperature about 77 K using Brunauer–Emmett–Teller (BET) method.¹²⁸ If a solid surface is covered by a monolayer of gas, the total surface area of the solid is given, as in equation (27).

\[ S_{\text{BET}} = N_g A_g \]  
\[ (27) \]

where \( N_g \) is the number of gas molecules and \( A_g \) is the cross-sectional area of one gas molecule. BET plots are used to obtain \( N_g \). This method assumes that (1) gas molecules are adsorbed on a solid surface in layers, (2) no interactions occur between adsorption
layers, and (3) Langmuir theory of molecular adsorption in a monolayer is still valid for each layer. Nitrogen adsorption is measured at $0.05 < P / P_0 < 0.35$ where $P$ and $P_0$ are equilibrium and saturation pressure respectively. The volume of the monolayer is estimated with a linear fit of the measured nitrogen adsorption by BET equation (28). \(^{(128)}\)

\[
\frac{1}{V_a (\frac{P}{P_0} - 1)} = \frac{C_{BET}}{V_m C_{BET}} \left( \frac{P}{P_0} \right) + \frac{1}{V_m C_{BET}}
\]

\((28)\)

where $V_a$ and $V_m$ are the volume of the adsorbed gas for total and monolayer respectively and $C_{BET}$ is BET constant. The values of $V_m$ and $C_{BET}$ are obtained with a slope and intercept of the linear fit. Thus, the total surface area, $S_{BET}$ is obtained by equation (29).

\[
S_{BET} = N_A A_g = \frac{V_m N_A}{V_{molar}} A_g
\]

\((29)\)

where $N_A$ is Avogadro’s number and $V_{molar}$ is the molar volume of the adsorbate gas.

Distributions of pore volume as a function of pore size was obtained from nitrogen sorption isotherms using Barrett-Joyner-Halenda (BJH) method. \(^{(129)}\) The pore sizes measured by the BJH method are related mostly to mesopores. The BJH method uses Kelvin equation that correlates pore volume and condensation (or evaporation) pressure to fill the pore volume. Kelvin equation, as presented in equation (30), assumes the shape of pores to be a cylinder,

\[
\ln \left( \frac{P}{P_0} \right) = \frac{2 \gamma_s V}{r_k R_0 T}
\]

\((30)\)

where $\gamma_s$ is surface tension, $r_k$ is Kelvin radius, $R_0$ is the universal gas constant. The actual radius of a pore is the sum of the Kelvin radius for the pore and the thickness of the gas
adsorbed on the wall of the pore. The thickness, $t$ of adsorbed nitrogen on a wall of a pore is obtained from Halsey equation,\textsuperscript{104,130} as in equation (31)

$$t = 3.54 \left( \frac{5}{2.303 \log\left( \frac{P_0}{P} \right)} \right)^{\frac{1}{3}}$$  \hspace{1cm} (31)

Thus, the distribution of pore volume as a function of pore size is obtained with the two equations (30) and (31) using the data of nitrogen adsorption at $0 \leq P/P_0 \leq 1$ where $P$ and $P_0$ are equilibrium and saturation pressure respectively. The cumulative volume of the distribution is the total volume of nitrogen adsorption ($V_{BJH}$), which related mostly to the volume of mesopores. The average ($D_{BJH}$) and dominant sizes of pores are also obtained from the distribution data.

The macropore volume fraction, $\Phi_M$, is computed from the difference of total pore volume and the sum of the volumes of micro- and mesopores. The micropore volume fraction can be obtained by carbon dioxide sorption isotherms. In the case of $\delta$-form sPS aerogels, however, the micropore volume fraction was inferred to be much less than 1 % from the data reported elsewhere.\textsuperscript{24} It was confirmed using carbon dioxide sorption isotherms that sPS aerogels in this work contained micropore volume fraction of $\sim 0.2$ %. In view of this, the contributions of micropores to total pore volume was ignored and nitrogen sorption isotherms was used to determine the value of $\Phi_M$ as per equation (32).

$$\Phi_M = \left( \frac{1/\rho_b - 1/\rho_v}{1/\rho_b - 1/\rho_s} \right) - V_{BJH}'$$  \hspace{1cm} (32)

In equation (32), $V_{BJH}'$ is the specific volume of pores with size less than 50 nm as measured by nitrogen sorption isotherms.
3.2.5 Sizes of condensed particles and fractals

Small angle x-ray scattering (SAXS) provides useful information about the size of condensed particles and fractals. For silica aerogels, the size of condensed particles determines the volume and size of mesopores and the internal surface area as described in Chapter II. The size of condensed particles is obtained from Guinier’s limiting law, \(^9\) as described in equation (33).

\[
I(q) = N_p \Delta \rho_e^2 V_p^2 \exp \left(-\frac{1}{3} R_g^2 q^2 \right)
\]  

(33)

In equation (33), I(q) is the intensity as function of scattering vector q, \(N_p\) is the number of particles, \(\rho_e\) is the electronic density, \(V_p\) is the volume of the particles, and \(R_g\) is the radius of gyration. This approximation is valid for \(qR_g << 1\). \(R_g\) is obtained from plots of \(\log I(q)\) vs. \(q^2\). The radius of a condensed particle, \(R_p\) is obtained by equation (34) if the condensed particles are assumed as a sphere with a radius \(R_p\).

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

(34)

Fractals are defined by variation of mass (mass fractal) or specific surface (surface fractal) as function of the linear dimension. Mass and surface fractals obtained from Porod region give information about the compactness and smoothness respectively. The fractals are obtained at the angle satisfying \(qR_g > 1\) by the power law \(^9\), as described in equation (35).

\[
I(q) \sim q^{-\sigma}
\]

(35)

In equation (35) \(\sigma\) is Porod exponent. The value of Porod exponent for mass fractal is 1-3. The silica aerogel condensed under basic condensation showed mass fractal. The value of
Porod exponent for surface fractal is 3-4. Another dimension, defined for the surface fractal, is \( D_s = 6 - \sigma \). In this definition, the value of \( D_s \) close to 2 means a smoother surface. For SAXS, Rigaku MicroMax-002+ X-ray generator (Rigaku, Tokyo, Japan) with wavelength 1.54Å from Cu source was used.

3.2.6 Structures and chemical composition

The internal structures of monolithic aerogels were examined by scanning electron microscope (JEOL JSM5310) to visually identify the pore structures. For this purpose, aerogel specimens were cut into pieces and a representative piece was mounted on an aluminum stub using carbon tape. The samples were then sputter coated by silver (ISI-5400 Sputter Coater, Polaron) and images were taken at accelerating voltage of 5.0 - 7.0 kV.

Transmitted light microscopy (Olympus SZ-PT, Tokyo, Japan) was used to investigate the filtration mode in monolithic aerogels. For this purpose, images of cross-sectional planes of aerogel specimens after subjecting them to filtration were obtained. The focus was adjusted to obtain images at different depths. The same technique was also used for verifying the existence of the skin layers in monolithic aerogels. For this purpose, a sPS aerogel specimen was notched by a razor blade first and pulled to be cut in half. Then, the cut face crossing the specimen depth was observed by the optical microscope.

Fourier transform infrared spectroscopy (FTIR) is used for quantitative analysis of chemical bonds. A chemical bond has a discrete infrared spectrum of absorption. This technique in this work was used mainly for verifying the residual hydroxyl groups, SiF\(_3\).
attachments or alkoxy groups on the silica networks. Semi-crystalline structures in sPS and PVDF were also analyzed by the same technique. Background was scanned first without a sample for the base line correction. The sample was then scanned with resolution of 6cm\(^{-1}\) at room temperature. A total 60 scans were used for signal averaging. Nicolet IS50 FT-IR (Thermoscientific, Hudson, NH) was used for this purpose.

3.2.7 Static surface charge

Static surface charges of the aerogels were measured by an electrostatic field meter (Simco FMX-003, Hatfield, PA). The electrostatic field meter can measure the static voltage values in the range of ±20kV. The electrostatic field meter was set to zero in ambient air first, and then ten reading from different areas of surfaces of a specimen were made, and the averaged valued was used as a result for each specimen.

3.2.8 Hydrophobicity

The water wettability of a solid surface defines the hydrophobicity of the solid. The water contact angle, \(\theta_c\) quantifies hydrophobicity by Young’s equation of a thermodynamic equilibrium, as in equation (36).

\[
\gamma_{\text{sol-liq}} = \gamma_{\text{sol-liq}} + \gamma_{\text{liq-gas}} \cos \theta_c \tag{36}
\]

where \(\gamma\) with subscript is the interfacial energy and the subscripts indicate each interface made by solid(sol), liquid(liq) and gas(gas). If \(\theta_c\) on a solid surface is smaller than 90°, the surface is defined as hydrophilic, while \(\theta_c\) larger than 90° is defined as hydrophobic.
surface. Highly hydrophobic and super hydrophobic surface are defined for $\theta_c$ larger than 120° and 150° respectively. In this work, the contact angle was measured by a static sessile drop method with a goniometer (Model 500, Rame-Hart instrument, Succasunna, NJ). The hydrophobicity of the material without the effect of porous structures was measured using compressed discs of monoliths.

3.2.9 Mechanical properties

The compressive stress-strain relationships were obtained via ASTM D595 method using Instron 5567 (Canton, MA) machine. For this purpose, cylindrical specimens of aerogels with diameter around 11 mm and height-to-diameter ratio 1:1 were prepared. A 100 N load cell was used and the crosshead speed was 2 mm/min.
CHAPTER IV

AN IMPROVED RAPID METHOD FOR PRODUCTION OF MONOLITHIC SILICA AEROGELS

4.1 Introduction

Silica aerogels are useful in applications involving thermal insulation, acoustic barriers, catalysis, and filtration due to their unique properties such as low thermal conductivity, low density, large surface area, and high porosity.\textsuperscript{74-76} The above mentioned properties originate from nanoscale building blocks that organize into internal solid networks and form the open mesopores. Silica aerogels, however, suffer from fragile nature and lengthy production process. Obtaining crack-free monoliths is still a challenge in silica aerogel research.

Synthesis of silica aerogels follows the steps of formation of gels and extraction of the solvent from the gels in the drying step. A double-catalyzed acid-base sol-gel reaction process is widely used for fabrication of silica gels as the gelation time can be shortened. For example, solutions of alkoxy silane in water-alcohol mixture is hydrolyzed under acidic condition and condensed under basic condition to form the gel.\textsuperscript{78} The gel time is important if one is interested in faster production of silica aerogels. An earlier study reported that the gel time shows logarithmic dependence on pH in the condensation reaction step.\textsuperscript{79}
Structure development in silica gels using x-ray and rheological measurements was studied in earlier work.\textsuperscript{91-95} Under acidic condition and especially at low concentration of water, linear structures develop and form the gel, while highly branched spherical structures are formed under basic conditions or at high concentration of water.\textsuperscript{23} It was also reported that silica gels condensed under basic conditions also produced mass fractals, while those condensed under acidic conditions did not either show fractal nature at all or showed surface fractals.\textsuperscript{94,95} Thus, one can see that the primary factor that affects structure development in silica gels is the pH.

An aging process is optionally followed post gelation for strengthening of the solid networks of the gels.\textsuperscript{73,76,80-85} This process is recommended if crack-free monoliths of silica aerogels are desired. Aging has three effects on the structures of silica gels. First, the terminal alkoxy (\(-\text{OR}\)) and \(-\text{OH}\) groups on the surfaces of silica networks undergo further condensation. This effect is called syneresis. The rate of syneresis increases in the presence of water.\textsuperscript{80} Second, the free silane species in solution can attach to the silica networks and strengthen the structures.\textsuperscript{76,85} Third, the solid networks of the gel continues to evolve due to structural rearrangement via dissolution-redeposition reactions in the system. This process renders the structural crevices and the necks smooth and flat.\textsuperscript{82} The aging process can take up to several days to have any discernible effects after which the impurities are removed via an alcoholic solvent exchange step. The impurities can be residual reactants, catalysts, and water. These are undesirable materials for a subsequent solvent exchange step. Finally, the gels are dried under supercritical conditions, e.g., in carbon dioxide to obtain silica aerogels. The low values of critical temperature and pressure (31.1 °C, and 7.38 MPa) make carbon dioxide attractive as the supercritical fluid.
Direct supercritical drying of silica gels at the supercritical condition of alcohol presents several difficulties, e.g., alcohols are corrosive at high temperature and pressure and the solubility of silica networks in alcohols at high temperature may adversely affect the mesoporosity of silica gels. Nevertheless, the supercritical drying using carbon dioxide requires an additional step involving solvent exchange by liquid carbon dioxide. In addition, only hydrophilic silica networks are produced. Direct supercritical drying in an alcohol, however, shortens the processing time and produces hydrophobic silica aerogels by esterification reactions.

In conventional methods, the processes of gelation, aging, solvent exchange, washing, and supercritical drying require several days. Poco et al. proposed a rapid solvent extraction method based on alcohol as the supercritical fluid. This was further improved by other researchers. The method of Poco et al. involves one-pot conversion of sol to aerogel in an autoclave. A stainless steel mold filled with the sol of a silica precursor, water, and alcoholic solvent is placed in an autoclave containing excess solvent. The autoclave is heated to reach the critical condition of the alcohol. The autoclave is degassed and cooled down to obtain the silica aerogel. The total time to produce a monolith was significantly reduced from several days in a conventional method to a few hours. Despite significant shortening of production time, the process has several limitations. First, the residues remain in the monolith in the absence of the washing step and affect the final properties of an aerogel. Second, the internal surface area is significantly lowered. Third, the process rules out chemical modification schemes, e.g., for reinforcement of the gel.
In this chapter, a rapid method for production of silica aerogel monoliths was developed based on one-pot synthesis as in the work of Poco et al.\textsuperscript{20} in conjunction with the processes of aging, washing, and supercritical drying as in conventional processes. A newly designed multi-injectable reactor was used for the purpose. The reactor also provides scope for chemical modification that was not possible in the process of Poco et al.\textsuperscript{20}

4.2 Preparation of silica aerogels

Silica aerogels are fabricated using the steps of sol-gel reaction, aging, washing, and solvent extraction via a suitable drying process. In this work, silica gels were fabricated by double-catalyzed sol-gel reactions.

4.2.1 Preparation of gel specimens

It was found at the outset that two-step preparation of silica gels would require only a few minutes. Therefore, any effort in shortening the production time of aerogel specimens should focus on the remainder of the steps. Accordingly, silica gels were prepared separately outside the reactor and placed inside the reactor to carry out aging, solvent exchange, and super-critical drying.

Solution I was prepared by mixing tetraethylorthosilicate (TEOS), a quantity of 200-proof ethanol, and deionized water (DIW) in the molar ratio, \text{TEOS:EtOH:DIW = 1:8:5}. Solution I was mixed with nitric acid by stirring for one hour at room temperature. TEOS underwent hydrolysis in this step at pH~2.0 and produced silane solutions.
Solution II containing EtOH and DIW in molar ratio 4:2 and ammonium hydroxide were mixed with the silane solution. A sol was thus obtained with molar ratio TEOS:EtOH:DIW=1:12:7 at pH~8.0. The sol was injected into a polyethylene mold by a syringe and the mold was sealed. The silanes in the sol participated in condensation reactions inside the mold and produced a gel after about 5 min. The gel was kept inside the mold for 1 hour and then placed inside the reactor.

4.2.2 Aging, washing, and drying in the reactor

The silica gel specimens were placed inside the newly designed stainless steel reactor with provision for multiple inlet and outlet ports as seen in Figure 18. A multi-purpose injection port located in the upper part of the reactor could be connected optionally to a liquid pump and gas cylinders. The internal volume of the reactor was 225 mL. A liquid pump (LPP-M Flowrox inc., Linthicum Heights, MD) was used to inject a liquid at a rate of 0.120-290 mL/min. Gas injection was regulated by a pressure regulator, Model 3030, Matheson, Montgomeryville, PA. Two ports were used for venting of gases and drainage of liquids. Pressure and temperature gauges were placed on the top of the reactor. A safety valve that triggers at pressure over 2,000 psi was installed. The reactor assembly was kept inside a shield made of aluminum. Three 500-watt band heaters were used for rapid heating of the reactor.

The previously synthesized gel was allowed to age by soaking in a solution of TEOS, EtOH, and DIW in the volume ratio of respectively 10:75:15. The aging solution was injected at a rate of 150 mL/min after which the autoclave was heated to 70 °C and
the pressure was raised to 1.4 MPa. This condition was maintained for a period of 5 hours after which the heater was turned off, depressurized, and the aging solution was discharged from the reactor. In a conventional process of aerogel preparation, aging is carried out at room temperature over a period of 1-3 days. In this work, the gels were washed by charging EtOH, sonication of the liquid above the gel, and EtOH removal from the reactor.

Figure 18. The reactor setup: (a) schematic, (b) image of the reactor.
Note that complete removal of the impurities from the gels is time-consuming due to slow viscous flow and slow diffusion through the mesopores in the gels.\textsuperscript{112} Thus, the combined action of dipping, agitation of the liquid by ultrasound, and rinsing the gels are desired for removal of impurities. EtOH was sonicated using a bar type ultrasonicator (S-4000, Misonix inc., Farmingdale, NY) at 20 kHz frequency for an hour after which all EtOH was discharged from the reactor. This cycle was repeated five times accounting for a period of 5 hours. In this context, the washing step takes more than 3 days in conventional methods of aerogel preparation.

Ethanol was used in this work as the supercritical solvent for the following reasons. First, it expedited the process as no additional solvent exchange step, such as with liquid CO$_2$, was necessary. Second, supercritical drying in ethanol is known to produce hydrophobic silica aerogels due to esterification reactions.\textsuperscript{86,100} A large majority of studies use carbon dioxide as the supercritical fluid due to its non-flammable nature and lower critical temperature, e.g., 31.1 °C compared to 240.9 °C for EtOH. It is noted that at high temperature alcohols can be corrosive and mesoporosity is affected by the soluble nature of silica networks in supercritical alcohols.\textsuperscript{86}

Anhydrous ethanol with purity over 99.5\% from SIGMA-ALDRICH was used as the drying solvent. For this purpose, EtOH was injected into the reactor at a feeding rate of 150 mL/min. The reactor was then pressurized to 6.9 MPa initially by nitrogen; the critical pressure of ethanol is 6.14 MPa. The drying pressure at or above the critical pressure yields crack-free monoliths.\textsuperscript{131} The reactor was then heated to above the critical temperature and kept at this temperature for several minutes for the condition to stabilize. The solubility of silica in supercritical ethanol is detrimental to mesoporosity and surface
area of silica aerogels.\textsuperscript{99,100} The reactor was slowly depressurized to atmospheric pressure under isothermal condition and then cooled to room temperature. During the cooling step, the reactor was slightly pressurized (1.4 MPa) by injecting nitrogen to avoid condensation of ethanol vapor. Figure 19 presents a chart showing the pressure and temperature used in the entire operation. The total time for supercritical drying step was about 1 hour 15 min, while the total time for fabrication of the aerogels using the method presented in this chapter was 13 hours.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure19.png}
\caption{Pressure and temperature traces in supercritical drying using ethanol as the drying solvent.}
\end{figure}
4.2.3 Chemical modification of the gel

Silica gels were modified by silylation to turn them hydrophobic without affecting the porosity.\textsuperscript{104} For this purpose, dimethoxy-methyl (3,3,3-trifluoropropyl) silane (SiF3) obtained from Sigma-Aldrich was used as the silylating agent in the form of solutions prepared by mixing 15 wt% SiF3 with EtOH and DIW in the ratio 94:6 by volume. The aging step described in Section 5.2.2 was omitted. Instead, the silica gel specimen was placed inside the reactor and the SiF3 solution was injected into the reactor at a rate of 150 mL/min. Before injection ammonium hydroxide was added into the solution to obtain a pH value of about 8.0. After the injection, the reactor was pressurized to 1.4 MPa and heated to 60 °C and kept for 5 hours. Afterwards, the same process of washing and supercritical drying in ethanol as presented in Section 5.2.2 was followed to obtain modified silica aerogels.

4.2.4 Control materials

For comparison purposes, silica aerogels were synthesized following a method reported elsewhere.\textsuperscript{75,76} The total molar ratio of TEOS:EtOH:DIW in the sol was maintained at 1:12:7. The sol was injected into a polyethylene mold by a syringe and allowed to gel for 24 hours. The gel was aged for another 48 hours using the aging solution consisting of TEOS, EtOH, and DIW in the ratio 10:75:15 by volume. The aged gels were washed in EtOH for 3 days to obtain alcogels. The alcogels were placed in an autoclave for solvent exchange and supercritical drying. The gels were dried under supercritical conditions of carbon dioxide and ethanol. In the case of supercritical drying in carbon dioxide, additional solvent exchange was carried out in liquid carbon dioxide.
For supercritical drying, the autoclave was pressurized to 6.2 MPa initially by carbon dioxide. The autoclave was heated to 50 °C and its pressure was raised to 10.3 MPa. The specimen was kept in the autoclave for one hour followed by depressurization under isothermal condition to atmospheric pressure and finally cooling to room temperature. The supercritical drying step with carbon dioxide spanned about 12 hours. In the case of supercritical drying in ethanol, the same process as described in Section 5.2.2 was used. The total time to obtain silica aerogels was 7 days in this method.

Figure 20. Total processing time for production of silica aerogels by the conventional (CON) and IRP methods (IRP).
Silica gels were also modified by silylation. An additional silylation step used SiF$_3$ solution added in between the aging and washing steps. Silica gels were kept for 3 days in SiF$_3$ solution. Figure 20 compares the total time used in production of silica aerogels by each method. The rapid production method needed 13 hours compared to 7 days for the conventional method. The silylation step in conventional method needed another 3 days.

4.2.5 Characterization

The value of bulk density, $\rho_b$ was obtained from the weight-to-volume ratio of the specimens. Skeletal density, $\rho_s$ was obtained by using Helium pycnometry (Accupyc II 1340, Micromeritics, Norcross, GA) at room temperature as described in Chapter III. For this purpose, the aerogel specimens were completely dried in a vacuum oven to remove moisture.

Internal surface area, $S_{BET}$ was obtained from nitrogen sorption isotherms (TriStar II, Micromeritics, Norcross, GA) at temperature of 77 K using Brunauer–Emmett–Teller (BET) method.$^{128}$ Ten (10) adsorption points on the partial pressure (p) in the range $0.05<p/p_0<0.35$ were used for evaluating $S_{BET}$, where $p_0$ is the total pressure. Nitrogen absorption pore volume, $V_{BJH}$, and average pore size, $D_{BJH}$ was obtained from nitrogen sorption isotherms using Barrett-Joyner-Halenda (BJH) method with Halsey–Faas correction$^{129}$ as described in Chapter III.
Morphological study was carried out using scanning electron microscope (JSM5310, JEOL, Tokyo, Japan). SEM samples were prepared by sputter coating silver on pieces of aerogel using sputter coater ISI-5400 Sputter Coater, Polaron.

Small angle x-ray scattering (SAXS) was used for the structural study. The size of condensed particles was obtained from Guinier’s limiting law\(^9\) which is valid for \(qR_g \ll 1\) where \(q\) is the scattering vector and \(R_g\) is the radius of gyration. The fractal dimension, \(\sigma\) was obtained at the angle satisfying \(qR_g > 1\) by the power law\(^9\) as described in Chapter III. For SAXS, Rigaku MicroMax-002+ X-ray generator (Rigaku, Tokyo, Japan) with wavelength 1.54Å from Cu source was used.

Water contact angle, \(\theta_c\) was measured to evaluate the hydrophobicity of silica aerogels. In this work, the contact angle was measured by a static sessile drop method with a goniometer (Model 500, Rame-Hart instrument, Succasunna, NJ) as described in Chapter III. The hydrophobicity of the material without the effect of porous structures was measured using compressed discs of monoliths.

Fourier transform infrared spectroscopy (FTIR) was used for verifying the presence of residual hydroxyl groups, alkoxy groups, and trifluoropropyl groups present on the surfaces of silica particles. All the aerogel samples were dried completely in a vacuum oven under the condition of -15 inch Hg and 60 °C for 24 hours before measurement. Background was scanned first without a sample for the base line correction. The sample was then scanned with resolution of 6 cm\(^{-1}\) at room temperature. A total 60 scans were used for signal averaging. Nicolet IS50 FT-IR (Thermoscientific, Hudson, NH) was used for this purpose.
4.3 Results and discussion

Table 4 lists the values of bulk density, skeletal density, internal surface area, computed total pore volume, nitrogen absorption pore volume, average pore size, average radius of condensed particles, fractal dimension, and water contact angle for the silica aerogels produced by the conventional and the rapid method.

The silica aerogel monoliths produced by the rapid method showed no cracks. We attribute this to the effect of ultra-sonication in the washing step that helped remove the impurities and shortened the processing time. The data in Table 4 showed that the properties of silica aerogels prepared by the rapid method using supercritical drying in ethanol do not differ significantly from the ones produced by the conventional method also with supercritical drying in ethanol. The skeletal density from the rapid method is very close to that of the conventional method despite much shorter time of aging in the former. A slightly lower $S_{BET}$ value in conventional method can be attributed to longer aging time whereby the silanes continued to react on silica particles networks and rendered the structure smooth and flat by the dissolution-redeposition reactions\textsuperscript{76,82,85}. The values of fractal dimension in this work ranged from 2.5 to 2.8, which are typical for silica gels condensed under basic conditions.\textsuperscript{23}

A comparison of the values of water contact angle reveal that hydrophobic surfaces were produced in both rapid method and conventional methods due to esterification reactions when EtOH was used in the supercritical drying step although the water contact angle values were the same, e.g., 100°.
Table 4. Bulk density ($\rho_b$), skeletal density ($\rho_s$), internal surface area ($S_{\text{BET}}$), computed total pore volume ($V_{\text{total}}$), nitrogen absorption pore volume ($V_{\text{BJH}}$), average pore size ($D_{\text{BJH}}$), average radius of the condensed particles ($R_0$), fractals ($\sigma$), and water contact angle ($\theta_c$) of silica aerogels.

<table>
<thead>
<tr>
<th>Property</th>
<th>IRP</th>
<th>IRP/SiF3</th>
<th>CON</th>
<th>CON.CO2</th>
<th>CON.CO2/SiF3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_b$ (g/cm$^3$)</td>
<td>0.106±0.003</td>
<td>0.112±0.001</td>
<td>0.104±0.001</td>
<td>0.116±0.001</td>
<td>0.140±0.002</td>
</tr>
<tr>
<td>$\rho_s$ (g/cm$^3$)</td>
<td>2.148±0.031</td>
<td>2.101±0.021</td>
<td>2.159±0.014</td>
<td>1.814±0.006</td>
<td>1.793±0.006</td>
</tr>
<tr>
<td>$V_{\text{total}}$ (cm$^3$/g)</td>
<td>8.97</td>
<td>8.47</td>
<td>9.18</td>
<td>8.07</td>
<td>6.59</td>
</tr>
<tr>
<td>$S_{\text{BET}}$ (m$^2$/g)</td>
<td>859</td>
<td>863</td>
<td>841</td>
<td>947</td>
<td>735</td>
</tr>
<tr>
<td>$V_{\text{BJH}}$ (cm$^3$/g)</td>
<td>1.49</td>
<td>1.54</td>
<td>1.72</td>
<td>2.26</td>
<td>1.48</td>
</tr>
<tr>
<td>$D_{\text{BJH}}$ (nm)</td>
<td>8.13</td>
<td>8.06</td>
<td>9.30</td>
<td>11.34</td>
<td>10.47</td>
</tr>
<tr>
<td>$R_0$ (nm)</td>
<td>15.3</td>
<td>15.0</td>
<td>15.8</td>
<td>15.1</td>
<td>15.4</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>2.5</td>
<td>2.5</td>
<td>2.4</td>
<td>2.6</td>
<td>2.8</td>
</tr>
<tr>
<td>$\theta_c$ (°)</td>
<td>100±2</td>
<td>123±1</td>
<td>100±1</td>
<td>27±1</td>
<td>121±2</td>
</tr>
</tbody>
</table>
Figure 21. FTIR peak patterns for (a) IRP, (b) IRP/SiF3, (c) CON, (d) CON.CO2, and (e) CON.CO2/SiF3.
Figure 21 presents FTIR spectra of silica aerogels produced by various methods. The Si-O bonds are present in the bands 1,105 and 1050 cm\(^{-1}\), and Si-OH in 3,500 cm\(^{-1}\), 1,634 cm\(^{-1}\) and 960 cm\(^{-1}\). The band at 3,500 cm\(^{-1}\) represents the residual hydroxyl groups. The ethoxy groups are characterized by the peaks at 2,980, 2,935 and 2,905 cm\(^{-1}\). Trifluoropropyl group (CF\(_3\)CH\(_2\)CH\(_2\)-) from the silylating agent appears at 1,316, 1,267, 1,215, 905, and 808 cm\(^{-1}\).\(^{100,132-135}\) It is seen that the peaks for ethoxy group (2,980, 2,935 and 2,905 cm\(^{-1}\)) are more intense than that for residual hydroxyl group (3,500 cm\(^{-1}\)) indicating that the residual hydroxyl groups on the surfaces of silica particles were converted to ethoxy groups by esterification.

Material properties of silica aerogels depended on the type of drying solvents used in the conventional methods. The data in Table 4 show that the solvent primarily affected the skeletal density, internal surface area, and hydrophobicity. For example, the skeletal density value of 2.159 g/cm\(^3\) obtained using EtOH as the drying liquid is substantially higher than 1.814 g/cm\(^3\) obtained for materials dried using supercritical CO\(_2\). The skeletal density of amorphous silicon dioxide is 2.2 g/cm\(^3\).\(^{127}\)

A reason can be invoked to explain higher skeletal density in materials obtained by the rapid production method. The soluble nature of silica in supercritical ethanol resulted in active eliminations of micropores and also replaced large majority of Si-OH groups with Si-OCH\(_2\)CH\(_3\) groups. It was reported in literature that elimination of micropores can cause an increase of skeletal density.\(^{96}\) The higher skeletal density also resulted in larger \(V_{\text{total}}\) and lower \(\rho_b\). The mesoporosity, as judged from the value of \(V_{\text{BJH}}\), shows reduction when the specimens were dried under supercritical ethanol.
The BET surface area of silica aerogels synthesized from conventional methods also show sensitivity to the nature of the drying solvent. For example, the use of ethanol as the supercritical fluid resulted in a value of $S_{\text{BET}} \sim 841 \, \text{m}^2/\text{g}$ for ethanol compared to $947 \, \text{m}^2/\text{g}$ for supercritical CO$_2$ because of the structural rearrangement caused by dissolution-redeposition reactions in ethanol system that rendered structural crevices and necks smooth and flat. Esterification reactions can also lower the value of $S_{\text{BET}}$.

It was observed from the values of water contact angle in Table 4 that drying under supercritical CO$_2$ produces hydrophilic surfaces as evident from the low values of contact angle, $\sim 27^\circ$. Hydroxyl groups attached on the silica surfaces were responsible for the hydrophilic surfaces. The peak at $3,500 \, \text{cm}^{-1}$ in FTIR spectra in Figure 21 provided evidence that the hydroxyl group content was significant in this material.

The data in Table 4 provide evidence of the effect of silylation that the surfaces of silica aerogels were modified in the silylation step. Recall that the silylation step was carried out for 3 days in the conventional process while only 5 hours was needed in the rapid process. Almost identical water contact angle values - $123^\circ$ and $121^\circ$- indicated that surface modification was effective in the rapid method. The presence of peaks at 1,316, 1,267, 1,215, 905, and 808 cm$^{-1}$, in these materials correspond to trifluoropropyl group (CF$_3$CH$_2$CH$_2$-) of SiF3. The silylation process increased the bulk density and reduced the total pore volume and $S_{\text{BET}}$ of the materials. The BET surface area of materials produced by conventional process using supercritical CO$_2$ reduced from $947 \, \text{m}^2/\text{g}$ with no silylation to $735 \, \text{m}^2/\text{g}$ after modification with SiF3. This was attributed to attachment of SiF3 on the surfaces of the pearl-necklace silica gel networks.
Figure 22. SEM images of silica aerogels for (a) IRP, (b) IRP/SiF3, (c) CON, (d) CON.CO2, and (e) CON.CO2/SiF3
However, no such dramatic drop was observed in the case of materials prepared by rapid method and dried under supercritical condition of ethanol, e.g. $S_{\text{BET}}$ was 859 and 863 m$^2$/g before and after silylation respectively, although the value of water contact angle increased from 100° to 121° due to silylation. Recall from the discussions associated with the IR spectra above that ethanol esterified the Si-OH groups effectively during the drying step. This also occurred in the system where the silylation reactions
were carried out inside the reactor before supercritical drying. However, CF$_3$ groups in SiF$_3$ molecules are more effective in converting the silica particle surface hydrophobic than the ethyl groups of ethanol. As a result, higher values of water contact angle resulted due to silylation.

Figure 22 presents SEM images of silica aerogels fabricated by conventional and rapid methods. In all cases, spherical particles of size tens of nanometer are observed. Recall that gel networks are formed with spherical particles when basic conditions are used for condensation of silica sols.$^{23}$ Figure 23 presents the image of a net shape cylindrical silica aerogel monolith with a central hole produced by the rapid method. The monolith had 25 mm outer diameter, 7 mm wall thickness, and 40 mm height.

4.4 Conclusions

A rapid method of fabrication of silica aerogel monoliths was studied whereby the processes of aging, washing, and supercritical drying were carried out sequentially in a reactor to shorten the total time of fabrication to about 13 hours from several days in conventional methods. The data presented in this study revealed several key steps. First, higher temperature is required in aging or silylation steps to expedite the chemical reactions in these processes. This was achieved by aging the gel at 70 °C and 1.4 MPa in an aging solution under nitrogen atmosphere. Second, ultrasonication or shear flow should be applied for expediting impurity removal in the washing step. In this work ultrasonication at 20 kHz produced good results. Third, the time-consuming solvent exchange step must be avoided and specimens must be dried under supercritical condition.
of the solvent that was used in the washing step. The aerogel materials produced by direct drying under supercritical condition of ethanol were crack free and provided higher hydrophobicity than those produced by drying under supercritical condition of CO$_2$. 
CHAPTER V

EFFECT OF PH ON SILICA AEROGEL MONOLITH PROPERTIES AND METHOD OF FABRICATION OF GRADIENT DENSITY AEROGELS

5.1 Introduction

Structure development in silica gels is a strong function of pH as revealed in earlier work using X-ray and rheological techniques. Linear structures are obtained under acidic conditions, especially at low concentration of water, while highly branched networks of spherical particles are obtained under basic condition or at high concentration of water. Silica gels condensed under basic conditions are mass fractals, while those condensed under acidic conditions show either no fractal structures or surface fractals. The amount of water in a sol also influences the structure. Silica gels condensed under acidic or basic conditions have similar structural growth when the alkoxy silane is hydrolyzed with small amounts of water, typically at water to alkoxy silane molar ratio of 4.0. Another study showed that high water to alkoxy silane molar ratio, e.g., 20 yields highly branched structure while water to alkoxy silane molar ratio ~1.0 produces linear structures. In all cases, the alkoxy silane was hydrolyzed under identical acidic condition. These results indicate that the catalytic conditions, such as acidic vs. basic, and the concentration of water are two key factors to influence the silica network structures.
Silica aerogels are commonly fabricated via a two-step process – first, wet gels are synthesized from sol-gel reactions and second, the liquid from the gels is removed via drying. A double-catalyzed sol-gel reaction scheme shortens the gelation time to a few minutes. A solution of alkoxy silane in water and alcohol mixture is hydrolyzed under acidic condition and then condensed under basic condition.\textsuperscript{78} A study reported that the gelation time bears a logarithmic relationship with pH maintained in the condensation reaction step.\textsuperscript{79}

Among the aerogel properties, porosity and bulk density are strong functions of drying conditions. Compressive stresses develop on silica networks due to surface tension force at the receding liquid meniscus and cause significant shrinkage and monolith fracture when the gels are dried under ambient conditions.\textsuperscript{23} In view of this, gels are commonly dried under supercritical conditions to obtain high porosity and low bulk density, although such conditions do not eliminate shrinkage completely. Prior work showed that shrinkage of silica gels dried under supercritical conditions is dependent on the value of pH used in the sol-gel reactions. The bulk density of gels synthesized under basic conditions, i.e., at pH>7.0, decreases with an increase of pH. Typical shrinkage is much less, e.g., 5\% compared to 25\% shrinkage observed for gels synthesized under basic conditions.\textsuperscript{96} The skeletal density also increases with an increase of pH due to elimination of the micropores.\textsuperscript{96}

The textural properties of pores, such as pore volume, pore size, and surface area are dependent on the drying condition as well.\textsuperscript{98} Lower bulk density and higher porosity also result from syneresis of the gel structures with thermal aging in the presence of water\textsuperscript{84} or silane precursor\textsuperscript{76} as a result of stronger silica networks and lower shrinkage.
Thus, one can infer that the silica aerogels produced at higher pH in condensation reactions should have higher pore volume and pore size. The internal surface area is a strong function of the solvent used in supercritical drying. For example, silica gels dried in an alcoholic solvent produce much lower internal surface area than gels dried in carbon dioxide due to enhanced structural rearrangement in the case of alcoholic solvents.99,100 These studies provide some guidance on how pH can be used as a tool to obtain silica gel structures of gradient density or gradient porosity in the same aerogel monolith.

Gradient density aerogels are attractive as they meet the requirements of a number of applications such as the interstellar grain collectors and acoustic impedance matching materials.109,110 A gradient density silica aerogel is obtained if a suitable precursor gradient density gel exists. Gradient density gels can be prepared by mixing sols of different solid concentration110 or from layer-by-layer gelation process of sols that vary in solid concentration across the specimen depth.10

In this work, first a correlation was established between the bulk density of monoliths and the pH of the sol in basic condensation reactions. This knowledge was then used in preparation of gradient density silica aerogels by varying the pH of the sol in the condensation step while maintaining the alkoxy silane concentration constant.

5.2 Materials and methods

Silica gels were produced via double catalyzed sol-gel reactions, aging, washing, and solvent extraction in supercritical drying process. The pH was varied in the condensation step to obtain different solid network morphology. The silane precursor was
hydrolyzed in water-alcohol solution under acidic condition. Solution I was prepared by mixing TEOS, a quantity of 200 proof ethanol (EtOH), and deionized water (DIW) in the molar ratio TEOS:EtOH:DIW = 1:7.65:3.1. Solution I was mixed with nitric acid and stirred for one hour at room temperature to obtain a silane solution due to hydrolysis of TEOS at a pH of 1.4. Solution II containing EtOH and ammonium hydroxide in molar ratio 3.82:1 was then mixed with solution I to obtain the sol with alkaline pH>7.0. The total molar ratio of TEOS/EtOH/DIW in the sol was 1:11.47:3.1. The amount of ammonium hydroxide in solution II was varied to obtain different pH values during the condensation step. Five different sols were prepared with a unique pH for each sol, as listed in Table 5.

Table 5. pH of the sol and corresponding gel time.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>pH of sol</th>
<th>Gel time t_{gel} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol-gel#1</td>
<td>7.4</td>
<td>24</td>
</tr>
<tr>
<td>Sol-gel#2</td>
<td>7.7</td>
<td>11</td>
</tr>
<tr>
<td>Sol-gel#3</td>
<td>8.1</td>
<td>6</td>
</tr>
<tr>
<td>Sol-gel#4</td>
<td>8.4</td>
<td>3</td>
</tr>
<tr>
<td>Sol-gel#5</td>
<td>8.5</td>
<td>3</td>
</tr>
</tbody>
</table>
5.2.1 Preparation of monolith

The sols were injected into polyethylene molds by a syringe and the molds were sealed. The silane molecules underwent condensation reactions in the mold and produced the gel. The gel times are presented in Table 5. The gel times were measured with the time taken for sols turning hard without flowing inside a mold. The sols were checked every 30 sec so that $t_{gel}$ had an accuracy of the 30 sec. The gel was allowed to age in the mold for 24 hours. The gels were then washed in EtOH for 3 days to obtain alcogels. The alcogels were placed in an autoclave for solvent exchange and supercritical drying in carbon dioxide. The alcogels were rinsed at least six times in liquid carbon dioxide. The autoclave was then pressurized to 6.2 MPa initially by introducing carbon dioxide. The autoclave was heated to 50 °C and its pressure was raised to 10.3 MPa. The autoclave was kept at this temperature and pressure for one hour and then depressurized slowly to atmospheric pressure under isothermal condition.

5.2.2 Preparation of gradient density monolith

The gradient density aerogels were prepared by sequential injection of the sols listed in Table 5. First, a sol, say Sol-gel#1 was injected into the mold with a desired volume and allowed to stand. A second sol, say Sol-gel#2 was injected before the previously injected sol turned into gel completely. The elapsed time between two successive injection steps was scaled with the gel time. The sequence was repeated until all sol intended for the gel formulation were introduced. Figure 24 shows schematic of the sequentially injected sols in a mold to produce a depth-wise gradient density gel. The
gels were aged, washed, and supercritically dried following the method as described in Chapter III for fabrication of aerogel monoliths of single density.

Figure 24. Preparation of a gradient density gel via sequential injections of sols of different pH.

The pH of sol was measured using PH220A pH meter provided by EXTECH (Nashua, NH). The pH meter was calibrated in a standard solution of pH 7.0 before it was used. Bulk density ($\rho_b$) was measured from the weight-to-volume ratio and the skeletal density ($\rho_s$) was measured at room temperature by using helium pycnometer (Accupyc II 1340, Micromeritics, Norcross, GA) as described in Chapter III.
Internal surface area ($S_{BET}$), nitrogen absorption pore volume ($V_{BJH}$), and average pore size ($D_{BJH}$) were obtained from nitrogen sorption isotherms as described in Chapter III. $S_{BET}$ was obtained using Brunauer-Emmett-Teller (BET) method with 10 adsorption points for partial pressure ($p$) in the range $0.05<p/p_0<0.3$, where $P$ and $P_0$ are equilibrium and saturation pressure respectively. The values of $V_{BJH}$ and $D_{BJH}$ were obtained by Barrett-Joyner-Halenda (BJH) method. The adsorption branch of adsorption-desorption isotherms was used as it is more related to the cavity shaped pores. Also, the possible elastic or plastic deformation of the pores during sorption may influence the desorption branch.

Small angle x-ray scattering (SAXS) was used for the structural study. The size of condensed particles was obtained from Guinier’s limiting law which is valid for $qR_g << 1$ where $q$ is the scattering vector and $R_g$ is the radius of gyration. The fractal dimension, $\sigma$ was obtained at the angle satisfying $qR_g > 1$ by the power law. For SAXS, Rigaku MicroMax-002+ X-ray generator (Rigaku, Tokyo, Japan) with wavelength 1.54Å from Cu source was used. More information about SAXS can be found in Chapter III.

For gradient density aerogels, additional X-ray analysis was carried out. The source of X-ray beam was aligned directly onto a detector, so that the angle was zero. In this configuration, the intensity of the X-ray flux through an aerogel sample is inversely proportional to the density of the sample. To measure the density change in a monolith of the gradient density aerogel using this technique, the X-ray source was moved to the direction of the gradient in density and the X-ray flux through the specimen was counted. Figure 25 presents a schematic of how X-ray beam was used to detect gradient of density in monolithic aerogels.
5.3 Results and discussion

Table 6 lists the properties of aerogel monoliths produced from different sols as presented in Table 5. It is seen that gel time, bulk density, average radius of silica particles, and fractal length scale all reduced with an increase of pH of the sol. However, the values of skeletal density, internal surface area, volume of pores, and the size of pores all increased with an increase of pH of the sol.

A phenomenological equation can be used to study gel time in condensation reactions, as presented in equation (37). Similar equation was used to study gelation in reactions of multi-functional monomers, such as in the curing of multi-functional epoxy resins.\(^\text{138}\)

\[
\frac{df}{dt} = k_c(1 - \xi)^n \zeta^m
\]  

(37)

In equation (37), \(\xi\) is the conversion of silanes, \(k_c\) is the overall reaction rate constant, \(\zeta\) is the relative concentration of the catalyst to the initial concentration of the alkoxy silane, and \(m\) and \(n\) are the order of reactions with respect to silane and hydroxyl groups.
Table 6. Bulk density ($\rho_b$), skeletal density ($\rho_s$), internal surface area ($S_{BET}$), nitrogen absorption pore volume ($V_{BJH}$), computed total pore volume ($V_{total}$), average pore size ($D_{BJH}$), average radius of the condensed particles ($R_0$), and fractals ($\sigma$) of silica aerogels produced with different pH.

<table>
<thead>
<tr>
<th>Property</th>
<th>Sol-gel#1</th>
<th>Sol-gel#2</th>
<th>Sol-gel#3</th>
<th>Sol-gel#4</th>
<th>Sol-gel#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.4</td>
<td>7.7</td>
<td>8.1</td>
<td>8.4</td>
<td>8.5</td>
</tr>
<tr>
<td>$\rho_b$ ($g/cm^3$)</td>
<td>0.229±0.002</td>
<td>0.190±0.003</td>
<td>0.176±0.007</td>
<td>0.149±0.008</td>
<td>0.138±0.006</td>
</tr>
<tr>
<td>$\rho_s$ ($g/cm^3$)</td>
<td>1.623±0.007</td>
<td>1.733±0.011</td>
<td>1.747±0.025</td>
<td>1.785±0.015</td>
<td>1.791±0.006</td>
</tr>
<tr>
<td>$S_{BET}$ ($m^2/g$)</td>
<td>868</td>
<td>911</td>
<td>936</td>
<td>958</td>
<td>963</td>
</tr>
<tr>
<td>$V_{BJH}$ ($cm^3/g$)</td>
<td>1.33</td>
<td>1.46</td>
<td>1.63</td>
<td>1.71</td>
<td>1.73</td>
</tr>
<tr>
<td>$V_{total}$ ($cm^3/g$)</td>
<td>3.74</td>
<td>4.68</td>
<td>5.09</td>
<td>6.12</td>
<td>6.71</td>
</tr>
<tr>
<td>$D_{BJH}$ (nm)</td>
<td>8.0</td>
<td>7.9</td>
<td>8.4</td>
<td>8.4</td>
<td>8.5</td>
</tr>
<tr>
<td>$R_0$ (nm)</td>
<td>16.5</td>
<td>16.4</td>
<td>16.1</td>
<td>16.0</td>
<td>15.8</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>2.7</td>
<td>2.7</td>
<td>2.6</td>
<td>2.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Recall that condensation reactions took place under basic conditions. Therefore, ζ is the relative concentration of OH\(^-\). If it is assumed that gelation occurred in each case at the same conversion of silanes, the gel time \((t_{gel})\) can be expressed in the form as in equation (38).

\[
\ln t_{gel} = p - q \cdot pH
\]  \hspace{1cm} (38)

In equation (38), p and q are constants. As presented in equation (38), \(t_{gel}\) has an exponential relationships with pH.

![Graph](image)

Figure 26. Gel time of silica sol as a function of pH in the condensation reaction step.
Figure 26 shows a plot of experimental gel time (Table 5) as a function of pH in the condensation reaction step. The exponential relationship between gel time and pH shows an $R^2$ value 0.987 and the corresponding values of $p$ and $q$ in equation (38) are 17.2 and 1.9 respectively. Similar trend was observed for gel time in the case of silica gel condensation under acidic condition. A recent study showed that the gel time for condensation of polyethoxydisiloxane also exponentially decreased with an increase of ammonium hydroxide concentration.

Figure 27. Bulk density of silica aerogels as a function of pH in the condensation step.
The bulk density of silica aerogels reduced with an increase of pH in the condensation reaction step, as shown in Figure 27. Note that the silane content of all silica sols in Table 5 was the same. Nevertheless, the reduction of bulk density is significant, e.g., from 0.229 g/cm$^3$ for Sol-gel#1 to 0.138 g/cm$^3$ for Sol-gel#5 with an increase of pH from 7.4 to 8.5. It was interpreted that the apparent dependence of bulk density on pH follows the trend of skeletal density. The skeletal density of silica gels is determined by the pH, e.g., the skeletal density increased from 1.623 g/cm$^3$ to 1.791 g/cm$^3$ with an increase of pH from 7.4 to 8.5. It was apparent that silica structures of higher skeletal density resisted shrinkage in the drying step and produced lower bulk density.

![SAXS patterns for silica aerogels. The specimen designation Sol-gel#1, Sol-gel#2, Sol-gel#3, Sol-gel#4, and Sol-gel#5 follow the direction of the arrow.](image-url)

Figure 28. SAXS patterns for silica aerogels. The specimen designation Sol-gel#1, Sol-gel#2, Sol-gel#3, Sol-gel#4, and Sol-gel#5 follow the direction of the arrow.
Figure 29. SEM images of silica aerogels obtained from sols (a) Sol-gel#1, (b) Sol-gel#2, (c) Sol-gel#3, (d) Sol-gel#4, and (e) Sol-gel#5.
The similarity of SAXS patterns in Figure 28 indicates that the silica microstructures, i.e., the patterns of aggregation of individual silica particles, in the aerogel monoliths were almost identical. The trend in Figure 28 indicates that the microstructures consisted of spheres with broad distribution of sizes. SEM images presented in Figure 29 also show that the condensed particles were all spherical and that the pH of condensation reactions did not have appreciable influence on the microstructures. The SEM images reveal that the size of condensed particles was several tens of nanometer.

![Graph](image)

Figure 30. Average radius of condensed particles as function of pH in the condensation reaction step.
The SAXS plots presented in Figure 28 were converted into Guinier plots and the average radii of condensed particles, $R_0$ were computed as presented in Table 6 and Figure 30. The data in Figure 30 show that $R_0$ decreased with an increase of pH. This was attributed to faster nucleation of silica particles at higher pH resulting in smaller particles. The SAXS plots were also converted to Porod plots and fractal dimensions were obtained from the Porod exponent. Figure 31 presented fractal length scale as a function of pH in the condensation reaction step.

![Figure 31. Fractal length scale of silica aerogels as function of pH in the condensation reaction step.](image)

96
The fractal length scale was almost invariant to pH changes as seen in Figure 31. These fractals were mass fractals and are reported for silica gels produced by condensing the silanes under basic condition.²³ Mass fractals are generally obtained from microstructures of branched bodies or networks, and are related to the density of the structures.

Figure 32 shows nitrogen sorption data of the monoliths produced at different pH. The sorption data are of classical type IV isotherms with hysteresis. The hysteresis resulted from capillary condensation of nitrogen gas in the pores of silica aerogels.¹⁰⁴ The volume and size of pores and the internal surface area obtained from nitrogen sorption isotherms are listed in Table 6. The values of $V_{\text{BJH}}$ and $V_{\text{total}}$ increased respectively from 1.33 to 1.73 cm$^3$/g, and 3.74 to 6.71 cm$^3$/g with an increase of pH from 7.4 to 8.5. The value of $D_{\text{BJH}}$ also increased from 8.0 to 8.5 nm. As was discussed in conjunction with the skeletal density, the gel networks were produced with denser solid skeletal structures at high pH in the condensation reaction step resulting in less shrinkage in the drying step and large volume and size of pores. The smaller size of condensed silica particles obtained at higher pH explains why the surface area increased substantially from 868 m$^2$/g for Sol-gel#1 to 963 m$^2$/g for Sol-gel#5.

The trend of bulk density vs. pH data in Table 6 and Figure 27 establishes that the method of preparation of gradient density aerogels that was followed in this work would indeed work. The first set of gradient density gels with the density varying in depth-direction was obtained by sequential injection of silica sol Sol-gel#4, Sol-gel#3, and Sol-gel#2 into the mold. The time of injection was adjusted according to the gel time reported in Table 5.
Figure 32. Nitrogen sorption isotherms of silica aerogels of (a) Sol-gel#1, (b) Sol-gel#2, (c) Sol-gel#3, (d) Sol-gel#4, and (e) Sol-gel#5.
Each sol was injected into a mold at the time of about one min before the gel time of the previously injected sol. For example, the injection of Sol-gel#3 was made at about 2 min after the injection of Sol-gel#4.

Figure 33 shows how X-ray flux varied with specimen depth for gradient density silica aerogel and single density silica aerogels of bulk density (b) 0.138 g/cm$^3$ and (c) 0.108 g/cm$^3$.

Figure 33 shows how X-ray flux varied with specimen depth for gradient density silica aerogel and single density silica aerogel monoliths of two bulk densities. Note that X-ray source was moved to the direction of the specimen depth to see the variation of X-
ray flux. Recall that the X-ray flux is inversely proportional to the density of the specimen. The data indicate that the X-ray flux in the case of gradient density aerogel varied monotonically with the specimen depth, while that of two single density aerogels remained insensitive to the specimen depth. It is inferred from the X-ray data in Figure 33, curve (a) that the density varied by almost 30% over 12 mm specimen depth. Similar trend was obtained in a study\textsuperscript{10} where the solid concentration of the sol was varied to obtain gradient density. The data in curve (a), Figure 33 indicate that density gradient, i.e., the slope is constant due to diffusion of ammonium hydroxide between different sol layers creating a constant gradient of pH across the injected sol layers. Thus, the sequential injection method considered in this work is much simpler and more practical than the methods reported elsewhere.\textsuperscript{10,110}

5.4 Conclusions

This work first yielded information that silica aerogel bulk density can be varied appreciably by varying the pH in the condensation reaction step in a small range, e.g., 7.4-8.5. The bulk density variation with pH is a direct consequence of denser solid networks as quantified by higher skeletal density at higher pH leading to less shrinkage. The characteristic silica particle size also reduced with an increase of pH resulting in higher surface area. The gradient density aerogels produced by sequential injection of silica sols of different pH showed approximately 30% change in the density across the monolith depth of 12 mm. The data presented validate the method of production of gradient density aerogels described in this work.
CHAPTER VI

MACROPOROUS POLYMER AEROGELS FOR EFFICIENT REMOVAL OF AIRBORNE NANOPARTICLES

6.1. Introduction

It is widely known that exposures to airborne particles can cause severe health hazards to human being including nausea, breathing difficulties, bronchitis, birth defects, serious developmental delays, weakened immune systems, and even cancers.\(^1\,2\) The significance of the hazards is a function of the size of the airborne particles. For example, smaller particles can easily penetrate into the human body and reach the pulmonary alveoli.\(^4\) Fine particles of size 0.1 \(\mu\)m-1 \(\mu\)m and ultrafine particles of size < 0.1 \(\mu\)m are more detrimental to human health than the coarse grain particles of size > 1 \(\mu\)m. The health hazards are compounded by the presence of pathogens of size 20-2,000 nm residing in these particles.\(^5\) Removal of small particles and pathogens by filtration can significantly improve the quality of air and reduce the health hazards. The use of high efficiency particulate absorption (HEPA) filters fabricated from fiber mats are widely used for the purpose. The filtration efficiencies of HEPA filters are high at 99.95\% for removing around 0.3 \(\mu\)m particles as per EN 1822-1:2009 classification at comparably low pressure drops. However, published literature on evaluation of HEPA filters for removal of airborne nanoparticles of sizes 100 nm and smaller are scarce.
A wide range of industrial applications use porous media for filtration due to their large surface area and pore volume. In this context, monolithic aerogels fabricated from inorganic or organic sources present several attributes as filter media. The aerogel monoliths have low solid contents, high porosity with various pore sizes, and large surface areas. For example, silica aerogels derived from alkoxy silanes offer large surface areas, up to 1,000 m$^2$/g, significant mesopore fractions, and porosities over 90%. The δ-form syndiotactic polystyrene (sPS) aerogels also offer macropores and porosities up to 97%; the nanocavities of crystalline strands of sPS selectively absorb small organic molecules. Despite offering several attractive characteristics, research on filtration of nanometric airborne particles by monolithic aerogels is scarce. A handful of studies used aerogel granules or microspheres in packed beds. Some literature reports are available on the use of aerogels impregnated into HEPA filters for airborne particle filtration, colonization of bioluminescent organisms inside a monolithic silica aerogel to detect viral particles, and applications of heterogeneous catalyst for removal of pollutants, such as removal of cyanides or combustion gases by monolithic silica aerogel composites containing metal oxides. Literature on direct investigations of filtration of airborne nanoparticles by monolithic aerogels is scarce.

This chapter investigated the utility of monolithic δ-form sPS aerogels for nanometric airborne particle filtration. The values of permeability and filtration efficiency were two key measured properties needed to quantify the performance of the aerogels for use as filtration media. In this context, monolithic sPS aerogels of single density and gradient density were examined.
6.2 Materials and methods

sPS aerogel monoliths were fabricated using a two-step process involving thermoreversible gelation and supercritical drying as described in Chapter III. The solutions of sPS in THF was turned into δ-form sPS gel via natural cooling. The concentration of sPS in the solution was varied to obtain different values of porosity. sPS solutions with concentrations 0.010, 0.015, 0.020, 0.025, 0.030, 0.040, and 0.050 g/mL were prepared by dissolving sPS powder in THF in sealed glass containers kept in oil bath at 120 °C. The solution was poured in a disc shaped mold of 30 mm diameter and allowed to gel as the solution gradually cooled to room temperature. The thickness of the disc shaped gels was maintained at around 3.5-4.0 mm. The gels were aged in the mold for a day and washed and solvent exchanged with 200-proof ethanol for at least 3 days. sPS aerogels were obtained by supercritical drying in carbon dioxide. For this purpose, ethanol in sPS gel was exchanged with liquid carbon dioxide before the supercritical drying step.

Monolithic gradient density aerogels were produced by a sequential injection method as described in Chapter III. One gradient density aerogel was obtained by first injecting a solution of 0.05 g/mL sPS into the mold followed by injection of 0.03 and 0.01 g/mL solutions. The time interval of each injection was varied based on the gelation time of each solution. The gelation time of the solution containing 0.05 g/mL sPS was about 4.5 min. Thus, the 0.03 g/mL solution was injected before the 4.5 min mark or shortly afterwards. In this work, two types of gradient density aerogels were produced respectively by injecting solutions before and after gelation of the previously injected solutions.
The value of bulk density, $\rho_b$, was obtained from the weight-to-volume ratio of the specimens. The air permeability was obtained by Frazier air permeability tester (Frazier Precision Instrument, Hagerstown, MD) as described in Chapter III. The sample holder that covers the lateral face of the aerogel and prevents lateral flow of air was used. The gaps between the specimen and the sample holder were eliminated using vacuum grease. Eight points of pressure drop, $\Delta P$ and volumetric flow rate, $Q$ were obtained by controlling the power of the vacuum pump in Frazier tester, and the slop $Q/\Delta P$ was used in evaluation of air permeability, $k$. Pressure drop per unit thickness, $\Delta P/L$, was calculated from permeability and air flow rate.

Filtration efficiency ($E$) was measured using TSI-8130 filter tester (TSI Inc., Shoreview, MN) as described in Chapter III. The face velocity ($U_f$) of air flow was varied between 25, 40, and 50 cm/sec. TSI-8130 filter tester (TSI Inc., Shoreview, MN) generated polydisperse sodium chloride nanoparticles. The diameter of generated particles ranged from 25-150 nm with an average diameter of 75 nm. The filter tester was able to measure the filtration efficiency with an accuracy up to 99.999%.

The absorption capacity of the particles is an important attribute as it relates to the life-time of a filter. The absorption capacity was estimated by the value of porosity ($\Pi$) as described in Chapter III.

The internal structures of the sPS aerogel specimen were examined by scanning electron microscope (JEOL JSM5310) to visually identify how the trapped nanometric NaCl particles were retained. For this purpose, the aerogel specimens were recovered after filtration and frozen in liquid nitrogen. The frozen specimens were cut into pieces
and a representative piece was mounted on an aluminum stub using carbon tape. The samples were sputter coated by silver (ISI-5400 Sputter Coater, Polaron), and images were taken at accelerating voltage of 5.0 kV.

Transmitted light microscopy (Olympus SZ-PT, Tokyo, Japan) was used to investigate the filtration mode in monolithic sPS aerogels as described in Chapter III. For this purpose, images of cross-sectional planes of aerogel specimens after subjecting them to filtration for 100 times of particle passage were obtained. The focus was adjusted to obtain images at different depths.

6.3 Results and discussion

The values of bulk density, porosity, permeability, and filtration efficiency of the monolithic δ-form sPS aerogels are presented in Table 7. The number in specimen designation in Table 7, e.g., 0.010 in “sPS-0.010” indicates polymer concentration in g/mL in original solution. The averaged values and standard deviation are reported where at least four multiple measurements were made.

The permeability data reported in Table 7 followed a power-law relationship with the bulk density, as presented in equation (39).

\[ k = c \rho_b^{-d} \]  

(39)

In equation (39), \( c \) and \( d \) are constants with values 0.0013 and -2.087 respectively determined from the relationship presented graphically in Figure 34 in a unit of \( 10^{-10} \text{ m}^2 \).
Table 7. Bulk density ($\rho_b$), porosity ($\Pi$), permeability ($k$), filtration efficiency ($E$), and pressure drop per a unit thickness ($\Delta P/L$) of monolithic $\delta$-form sPS aerogels.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$\rho_b$ (g/cm$^3$)</th>
<th>$\Pi$ (%)</th>
<th>$k$ ($\times 10^{-10}$ m$^2$)</th>
<th>$E$ (%)</th>
<th>$\Delta P/L$ (mmH$_2$O/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-0.010</td>
<td>0.020±0.001</td>
<td>98.11</td>
<td>4.00±0.78</td>
<td>93.468±0.444</td>
<td>23.7</td>
</tr>
<tr>
<td>sPS-0.015</td>
<td>0.025±0.003</td>
<td>97.63</td>
<td>3.35±0.41</td>
<td>95.860±0.609</td>
<td>28.3</td>
</tr>
<tr>
<td>sPS-0.020</td>
<td>0.030±0.001</td>
<td>97.16</td>
<td>2.23±0.36</td>
<td>98.889±0.998</td>
<td>42.5</td>
</tr>
<tr>
<td>sPS-0.025</td>
<td>0.034±0.003</td>
<td>96.78</td>
<td>1.45±0.31</td>
<td>99.734±0.117</td>
<td>65.4</td>
</tr>
<tr>
<td>sPS-0.030</td>
<td>0.042±0.002</td>
<td>96.02</td>
<td>0.99±0.30</td>
<td>99.998±0.001</td>
<td>95.8</td>
</tr>
<tr>
<td>sPS-0.040</td>
<td>0.055±0.006</td>
<td>94.79</td>
<td>0.56±0.11</td>
<td>&gt; 99.999</td>
<td>169.4</td>
</tr>
<tr>
<td>sPS-0.050</td>
<td>0.061±0.002</td>
<td>94.22</td>
<td>0.44±0.15</td>
<td>&gt; 99.999</td>
<td>215.7</td>
</tr>
</tbody>
</table>
Figure 34. Plot of air permeability as a function of the bulk density of monolithic δ-form sPS aerogels.

A similar trend of the power law relationships between permeability and bulk density was reported for mesoporous carbon aerogels, although the permeability of carbon aerogels was much lower, $10^{-16}-10^{-14}$ m$^2$.\textsuperscript{114} It is apparent from the data presented in Figure 34 that macroporous sPS aerogels offered much higher permeability, in the orders of $10^{-10}-10^{-11}$ m$^2$, due to high values of porosity, 90-98\% (Table 7). The permeability of sPS aerogels reported in Figure 34 are within the range appropriate for practical filtration applications.
Figure 35. Filtration efficiency for nanometric NaCl particles as a function of the bulk density of monolithic δ-form sPS aerogels measured at $U_f \approx 50$ cm/s.

The filtration efficiency ($E$) also follows a power-law relationship with the bulk density for $E<1$, as seen in Figure 35. Such power-law behavior can be expressed as in equation (40):

$$E = [p(\rho_b - q)]^{1/r} \quad \text{for } E < 1 \quad (40)$$

In equation (40), $p$, $q$, and $r$ are constants with values 50, 0.015, and 19 respectively obtained from fitting the permeability data presented in Table 7. The data in Figure 35 revealed that high efficiency of nanoparticle filtration can be achieved using monolithic
δ-form sPS aerogels of bulk densities of 0.042 g/cm$^3$ or higher. The permeability values corresponding to such high efficiency were found to be of the orders of $10^{-10}$ - $10^{-11}$ m$^2$, which are the similar to the order of magnitude of the reported value for packed beds.$^{34}$

It is important to determine the organization of airborne nanoparticles that were retained inside the pores of aerogel monoliths during filtration test. Figure 36 presents SEM images of sPS aerogel before and after the filtration test. The open pore structures of sPS aerogel monoliths are apparent in Figure 36(a). It is seen in Figure 36(b) that the open pores seen in Figure 36(a) are now filled with sodium chloride particles indicating that the nanoparticles penetrated into the aerogel materials during filtration. However, the pore structures in Figure 36(b) appear condensed in comparison with the materials before filtration test, as in Figure 36(a). This condensed structure originated from the manner of the specimen preparation for SEM. Recall that the aerogel specimens recovered after filtration were placed in liquid nitrogen and then fractured to reveal the cross-sectional plane. In the process, the aerogel specimen experienced substantial visible shrinkage, which helped retain the NaCl nanoparticles within the pores. The image in Figure 36(b) raises an interesting question about the filtration mechanism, e.g., if filtration occurred by cake filtration, depth filtration, or a combination of the two. The filtration efficiency data obtained for all aerogel specimens considered in this study revealed that filtration efficiency remained unchanged with the number of passes up to 10 passes that was exercised in this work. This indicates the absence of surface cake formation up to 10 passes.
Figure 36. SEM images of the sPS aerogel before filtration (a) and sPS aerogel with captured nanometric NaCl particles after filtration (b).
Figure 37. Optical microscopy image of sPS aerogels after 100 times of nanoparticle passages.

The SEM image indicates that filtration occurred primarily by depth filtration mechanism. It is quite possible that some degree of cake filtration occurred due to trapping of larger NaCl particles inside the macropores, but its effect on overall filtration efficiency was not apparent as filtration experiments were conducted for only 10 passes. To answer the question and clarify the mode of filtration, NaCl nanoparticles were allowed to pass through a representative monolith 100 times and the images of the recovered monolith were examined by optical microscopy. The optical microscope image in Figure 37 shows fractal NaCl particle networks grown inside of the monolith. This image, taken at some unknown depth inside the monolith, confirms that depth filtration in conjunction with cake formation was the primary mode of filtration in this case. Surface
filtration with cake formations was also observed on the surface of the monolith at another location of the specimen, but the extent of surface filtration was small.

The filtration efficiency and permeability data of gradient density aerogel materials were examined. Previously, gradient density aerogels were investigated in the context of interstellar grains collectors and acoustic impedance matching materials.\textsuperscript{109,110} One anticipates that gradient density aerogels can also be used in filtration due to its unique feature in the form of gradients in porosity. For this purpose, sPS aerogels fabricated with variation of bulk densities across the specimen thickness were prepared by sequential injection of solutions differing in sPS concentration e.g., 0.05, 0.03, and 0.01 g/mL in the order. The performances of these materials were compared with that of a single density material (sPS-0.040) with bulk density 0.055 g/cm\(^3\) and the same thickness. The specimen sPS-0.040 provided > 99.999 \% filtration efficiency as presented in Table 7 and Figure 35.

It is not intuitive if the gradient density sPS aerogel synthesized from one discrete layer of bulk density 0.055 g/cm\(^3\) or higher and the other layer from lower bulk density materials, such as 0.02 g/cm\(^3\) can also provide a filtration efficiency of > 99.999 \%. To answer this question, one can invoke composite layered structures of successively larger pores or higher porosity. Such composite layered structures are more attractive as they provide higher porosity to potentially have greater volume for collection of the particles, and thus to offer higher retention capacity. Two kinds of gradient density sPS aerogels were produced in this work. Specimen sPS-g1 was produced by sequential injection of sPS solutions of 0.010, 0.030, and 0.050 g/mL concentration. Each solution was injected after the previously injected solution formed a gel and the monolith had a clear boundary.
- a skin of each injected gel - between the layers. The skin or the skin layer was denser than the inner body of the structure of the gels. The gel specimen sPS-g2 was also a gradient density material obtained from the same solutions as sPS-g1 except that the sequential injections were performed before the previously injected solutions had time to gel. In this case, no clear boundaries were observed in the specimens. Table 8 summarizes the values of bulk density, porosity, permeability, and filtration efficiency obtained for aerogel specimens sPS-g1 and sPS-g2.

It is evident from the comparison of the data presented in Tables 7 and 8 that gradient density aerogels sPS-g1 and sPS-g2 come very close to single density aerogel sPS-0.030 in terms of bulk density and porosity. The air permeability of the gradient density aerogels is, however, lower. The values of permeability of sPS-g1 and sPS-g2 could not be obtained because permeability of the gradient density aerogels was lower than the limit of measurement with the air permeability tester. However, it was evident that permeability of the gradient density aerogels fell below the single density aerogels of the same bulk density. The above reduction in permeability in the case of sPS-g1 and sPS-g2 specimens could be caused from additional skin layers that formed in the composite structures due to the sequential injection process. Recall that sequential injection took place in sPS-g1 after a previously injected solution gelled. Even in the case where sequential injections were made before the gelation of a previously injected solution, e.g., in the case of sPS-g2 aerogel specimen, the presence of additional skin layers could not be completely ruled out due to the time gap between the injections. This accounts for lower permeability of sPS-g2 compared to the single density aerogels.
Table 8. Bulk density ($\rho_b$), porosity ($\Pi$), permeability ($k$), and filtration efficiency ($E$) of gradient density aerogels.

<table>
<thead>
<tr>
<th>Property</th>
<th>sPS-g1</th>
<th>sPS-g2</th>
<th>sPS-g3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_b$ (g/cm$^3$)</td>
<td>0.041±0.003</td>
<td>0.043±0.002</td>
<td>0.022±0.002</td>
</tr>
<tr>
<td>$\Pi$ (%)</td>
<td>96.12</td>
<td>95.93</td>
<td>97.92</td>
</tr>
<tr>
<td>$k$ ($\times 10^{-10}$ m$^2$)</td>
<td>N/A</td>
<td>N/A</td>
<td>0.97±0.29</td>
</tr>
<tr>
<td>$E$ (%) @ $U_f$≈50 cm/s</td>
<td>&gt; 99.999</td>
<td>&gt; 99.999</td>
<td>&gt; 99.999</td>
</tr>
<tr>
<td>$E$ (%) @ $U_f$≈40 cm/s</td>
<td></td>
<td></td>
<td>&gt; 99.999</td>
</tr>
<tr>
<td>$E$ (%) @ $U_f$≈25 cm/s</td>
<td></td>
<td></td>
<td>99.981±0.009</td>
</tr>
</tbody>
</table>

The filtration efficiency of aerogel specimens sPS-g1 and sPS-g2 was > 99.999 % (Table 8). The > 99.999 % efficiency mark was reached for aerogels of single density when the bulk density was 0.055 g/cm$^3$ or higher (Table 7). However, a lower overall bulk density of 0.041 g/cm$^3$ was enough in the case of gradient density aerogels to reach the maximum efficiency value. The skin layers that formed due to the sequential injections contributed to the improvement.
The effect of skin layer was further elaborated by expanding the discussion to another gradient density aerogel (sPS-g3) prepared by sequential injection of only two solutions. The solution with 0.02 g/mL sPS was injected first into the mold followed by injection of 0.01 g/mL solution without giving much time for gelation of the former solution. The data in Table 8 showed that sPS-g3 offered filtration efficiency 99.98 % at the face velocity of 25 cm/s and > 99.999 % efficiency at face velocities of 40 and 50 cm/s. It is known in literature that lower face velocity results in an increase of filtration efficiency of nanoparticles due to an increase of contribution of the diffusional deposition mechanism. However, the data obtained in this study is counterintuitive, as is evident from the data reported in Table 8. This interesting observation is needed to be further explored.

The trend observed in Figure 38 revealed another interesting information. The sPS-g3 gradient density aerogel with bulk density of 0.022 g/cm³ provided the same filtration efficiency (> 99.999 %) as sPS-g1 and sPS-g2 at face velocity of 50 cm/s. However, the data in Table 8 show that this aerogel had much lower bulk density than the other two gradient density aerogels mentioned above. This indicates that the skin layers generated by the sequential injections even in a two-layer material helped increase the filtration efficiency with air permeability of $0.97 \times 10^{-10} \text{ m}^2$. A complete investigation of the expanse of the skin layer and its influence on air permeability is discussed in Chapter VII.
Figure 38. Filtration efficiency of the gradient density aerogels of δ-form sPS aerogel measured at $U_f \approx 50$ cm/s.

6.4 Conclusions

This chapter established the applicability of monolithic sPS aerogels in nanometric particle filtration and presented several strategies for achieving high filtration efficiency while keeping high values of air permeability. The data presented in this chapter established that both permeability and filtration efficiency of single density sPS aerogels have power-law relationships with bulk density. It was also revealed that monolithic sPS aerogels with bulk density 0.042 g/cm$^3$ or higher are needed to obtain high efficiency (> 99.95 %) while permeability values are at an acceptable levels of 10$^{-10}$-
The internal porous structures of aerogels were able to retain the nanometric NaCl particles. Depth filtration in conjunction with cake formation was the primary mode of filtration in the monolithic aerogels. This chapter also showed that design of gradient density in aerogels by sequential injection of polymer solutions can be an effective method to obtain higher porosity for retention of particles, lower bulk density, and > 99.999% efficiency in comparison to single density aerogels. Skin layers formed during sequential solution injection were found responsible for higher efficiency.
CHAPTER VII

THE EFFECT OF SKIN LAYERS ON PERMEABILITY OF POLYMER AEROGELS

7.1 Introduction

Many types of aerogels have been fabricated from inorganic or organic sources, and they have unique characteristics of open pore structures with high porosity, large surface area, and various pore sizes.\(^7-31\) For example, silica aerogels derived from inorganic sources of alkoxy silanes have porosity over 90\%, extremely large surface area up to 1,000 m\(^2\)/g, and broad distribution of pore sizes, including a significant fraction of mesopores (diameter: 2-50 nm).\(^11-23\) Of these, the \(\delta\)-form syndiotactic polystyrene (sPS) aerogels provide porosity up to 97\% with significantly developed macropores of diameter > 50 nm.\(^24-31\)

An attractive attribute of aerogels is high porosity that should also produce high values of air permeability. Several studies reported permeability of aerogels, for example, monolithic silica aerogel show air permeability of \(10^{-15}\) m\(^2\).\(^112\) Another study reported silica aerogel permeability of \(10^{-12}\) m\(^2\) \(^39\) and observed further reduction due to incorporation of titanium oxide. Permeability of carbon aerogels was also studied and permeability in the range of \(10^{-16}-10^{-14}\) m\(^2\) reported for materials with bulk density of 0.05-0.44 g/cm\(^3\).\(^114\) This study showed that permeability followed a power-law relationship with bulk density. Silica aerogel spheres arranged in packed bed showed
higher permeability of $2.2 \times 10^{11}$ m$^2$ than monolithic silica aerogels.\textsuperscript{34} The porosity and pore size were identified as major factors that decide permeability of aerogel materials.

Prior work, however, did not take into consideration the effects of skin layers that are ubiquitous in aerogel materials. The skin layers form at the outer surfaces on aerogel monoliths and are denser than the inner body.\textsuperscript{89} The mechanism of skin layer formation has not been unequivocally established yet, but faster gelation at the surfaces of the gels and rapid evaporation of the mother liquid from the surfaces are two possible factors that allow formation of skin layers. It is hypothesized that the skin layers with much different bulk density than the bulk should affect permeability. This chapter is devoted on characterization of skin layers formed on the surfaces of $\delta$-form sPS aerogel monoliths and the effect of such skin layers on air permeability of monolithic aerogels.

### 7.2 Materials and methods

sPS aerogel monoliths were fabricated using the same method described in Chapter III: the two-step process involving thermoreversible gelation and supercritical drying.\textsuperscript{24-31}

The concentration of sPS in the solution was varied to obtain different values of porosity. sPS solutions with concentration 0.01, and 0.03 g/mL were prepared by dissolving sPS powder in THF in sealed glass containers kept in an oil bath at 120 °C. The solution was poured in a disc shaped mold of 30 mm diameter and allowed to gel as the solution gradually cooled to room temperature. The thickness of the gel was varied between 1 to 4 mm by pouring different amounts of polymer solution. The gels were aged
in the mold for a day and washed and solvent exchanged with 200-proof ethanol for at least 3 days. The sPS alcogels are then placed in a supercritical drying chamber for solvent exchange with liquid carbon dioxide and supercritical drying. The chamber was heated and pressurized to reach the supercritical condition of carbon dioxide. In this work, the chamber was heated to 50 °C, and the pressure was 10.3 MPa. The specimens were kept in the chamber under supercritical conditions for one hour to stabilize after which the chamber was depressurized slowly to atmospheric pressure under isothermal condition and sPS aerogels were retrieved. sPS pellets with 98% syndiotacticity and molecular weight of 300,000 g/mol was provided by Scientific Polymer Products Inc. (New York, NY). The sPS pellets were converted into powders for easy dissolution in a solvent. Reagent grade tetrahydrofuran (THF) purchased from Fisher Scientific was used as the solvent.

The value of bulk density, $\rho_b$ was obtained from the weight-to-volume ratio of the specimens. The air permeability was obtained using Frazier air permeability tester (Frazier Precision Instrument, Hagerstown, MD) as described in Chapter III. A sample holder that covers the lateral face of the aerogel and prevents the lateral flow of air was used. The gaps between the specimen and the sample holder were eliminated using vacuum grease. Eight data points of pressure drop, $\Delta P$ vs. volumetric flow rate, $Q$ were obtained by controlling the power of the vacuum pump in Frazier tester, and the slope of $Q$ vs. $\Delta P$ curve was used for evaluation of air permeability, $k$.

Optical microscopy (Olympus SZ-PT, Tokyo, Japan) was used in verifying the skin layers. sPS aerogel specimens were cut in half using sharp razor blades and the cross-section was imaged by the optical microscope.
7.3 Theoretical

The permeability of a composite material made up of multiple layers of different permeability can be derived from Darcy’s law, as in equation (41).

\[ k_t = \frac{L}{\sum_j \frac{L_j}{k_j}} \]  

(41)

In equation (41), \( k_t \) is the permeability of the composite with total thickness \( L \), \( k_j \) is the permeability of each component layer of thickness \( L_j \), with \( i=1,2,3,..n \). Equation (41) is derived with the following assumptions – (i) the layers have the same cross-sectional area \( A \) and (ii) the flow is unidirectional and normal to the faces of the layers. For a two-layer material, such as the ones being considered in this work consisting of a skin layer and the bulk layer, a simplified form of equation (41) is presented in equation (42).

\[ k_t = \frac{L}{\left(\frac{L_o}{k_o} + \frac{L_i}{k_i}\right)} \]  

(42)

In equation (42), the subscripts \( o \) and \( i \) represent respectively the skin layer and the inner body of the aerogel monolith and the composite thickness \( L=L_o+L_i \). Equation (42) can be rearranged as follows:

\[ \frac{1}{k_t} = L_o \left(\frac{1}{k_o} - \frac{1}{k_i}\right) \frac{1}{L} + \frac{1}{k_i} \]  

(43)

Equation (43) indicates that the intercept of the plots of \( 1/k_t \) vs. \( 1/L \) is \( 1/k_i \). In this manner, the permeability of the inner body can be obtained from the intercept. For this purpose, permeability measurements must be carried out using aerogel monoliths of at least two different thicknesses. The two unknowns, \( k_o \) and \( L_o \), in equation (43) can be obtained
from the value of slope, \( L_0 \left( \frac{1}{k_o} - \frac{1}{k_i} \right) \) in equation (43) and by using experimental value of \( k_i \) in the limit \( L \rightarrow L_o \); in this case, the entire aerogel monolith is composed of skin layer and there is no inner body.

7.4 Results and discussion

Table 9 lists the values of permeability of sPS aerogels as function of specimen thickness. Also shown are standard deviation of measurements using at least four specimens of the same composition. The specimen were designed as “sPS-x,” with \( x = 0.01, 0.02, 0.03, \) and \( 0.05 \) g/mL of sPS in original solution. The thickness-dependent permeability shown in Table 9 indicated that the monolithic aerogels were made up of different permeable parts, which we believe are skin layers and the inner body. However, it is not known, if the skin layer thickness differed from specimen to specimen or remained almost constant considering that the details of aerogel preparation method was the identical in all cases.

The experimental data were plotted as \( 1/k \) vs. \( 1/L \) (Figure 39) and the intercept of the linear trend line yielded the value of \( k_i \). The linear fit of the experimental data are presented in equation (44), (45) and (46).

\[
\frac{1}{k} = 0.29 \left( \frac{1}{L} \right) + 0.19 \quad \text{(for sPS-0.01)} \quad (44)
\]

\[
\frac{1}{k} = 0.50 \left( \frac{1}{L} \right) + 0.32 \quad \text{(for sPS-0.02)} \quad (45)
\]

\[
\frac{1}{k} = 0.95 \left( \frac{1}{L} \right) + 0.77 \quad \text{(for sPS-0.03)} \quad (46)
\]
The slope gives the value of $L_0 \left( \frac{1}{k_o} - \frac{1}{k_i} \right)$. A plot of the values of this slope vs. $1/k_i$ yields another slope, and the slope corresponds to the value of $L_0$.

Table 9. Permeability ($k$) of monolithic $\delta$-form sPS aerogels with different thicknesses of about 1 – 4 mm.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Specimen thickness (mm)</th>
<th>$k$ ($\times 10^{-10}$ m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-0.01-1</td>
<td>1.12±0.08</td>
<td>2.21±0.45</td>
</tr>
<tr>
<td>sPS-0.01-2</td>
<td>2.78±0.05</td>
<td>3.29±0.31</td>
</tr>
<tr>
<td>sPS-0.01-3</td>
<td>3.78±0.12</td>
<td>3.62±0.70</td>
</tr>
<tr>
<td>sPS-0.01-4</td>
<td>4.25±0.08</td>
<td>4.00±0.78</td>
</tr>
<tr>
<td>sPS-0.02-1</td>
<td>1.14±0.07</td>
<td>1.31±0.38</td>
</tr>
<tr>
<td>sPS-0.02-2</td>
<td>1.91±0.07</td>
<td>1.63±0.24</td>
</tr>
<tr>
<td>sPS-0.02-3</td>
<td>2.45±0.11</td>
<td>1.85±0.34</td>
</tr>
<tr>
<td>sPS-0.02-4</td>
<td>3.79±0.09</td>
<td>2.23±0.55</td>
</tr>
<tr>
<td>sPS-0.03-1</td>
<td>1.27±0.11</td>
<td>0.65±0.20</td>
</tr>
<tr>
<td>sPS-0.03-2</td>
<td>1.82±0.06</td>
<td>0.79±0.15</td>
</tr>
<tr>
<td>sPS-0.03-3</td>
<td>3.05±0.07</td>
<td>0.88±0.29</td>
</tr>
<tr>
<td>sPS-0.03-4</td>
<td>3.55±0.09</td>
<td>0.99±0.30</td>
</tr>
</tbody>
</table>
Figure 39. Plot of $1/k$ vs. $1/L$ for monolithic $\delta$-form sPS aerogels.

Table 10 lists the obtained values of permeability of the skin layer and inner body, and the thicknesses of skin layers. In Table 10, the values of $k_i$ are seen to be higher than $k_0$ by a factor of 2.4, 2.6, and 2.5 for specimens sPS-0.01, sPS-0.02, and sPS-0.03 respectively. This indicates that the skin layers were denser than the inner body and that these were responsible for rendering the permeability data dependent on thickness. It is also seen in Table 10 that the skin layer thickness was 0.55 mm.

The optical image in Figure 40 clearly showed a skin layer at the top surface of the specimen. The skin layer appears darker and is of approximately 500 $\mu$m thickness, which corresponds to the data reported in Table 10.
Table 10. Permeability of the inner bodies ($k_i$) and skin layers ($k_0$), and the thicknesses of skin layers ($L_0$) of monolithic $\delta$-form sPS aerogels.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$k_i$ ($\times 10^{-10}$ m$^2$)</th>
<th>$k_0$ ($\times 10^{-10}$ m$^2$)</th>
<th>$L_0$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-0.01</td>
<td>5.26</td>
<td>2.15</td>
<td>0.55</td>
</tr>
<tr>
<td>sPS-0.02</td>
<td>3.13</td>
<td>1.21</td>
<td>0.55</td>
</tr>
<tr>
<td>sPS-0.03</td>
<td>1.30</td>
<td>0.53</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Figure 40. The optical image of the skin layer in $\delta$-form sPS aerogel monolith. The observed thickness of the skin layer is 500 μm.
In view of the data in Table 10 and the optical image in Figure 40, one can infer that a specimen of about 1.1 mm thickness should have nothing but the skin layers. To verify this, a set of very thin sPS aerogel monoliths of 0.4 mm thickness were fabricated corresponding to sSP-0.01, sPS-0.03 and sPS-0.05 and their bulk density values measured. A representative thin semi-transparent aerogel specimen is shown in Figure 41.

![Figure 41. The monolithic δ-form sPS aerogel with a thickness of about 0.4 mm](image)

Table 11 lists the values of bulk density of the monolithic sPS aerogels of two different thicknesses. One is for the thickness of 0.4 mm ($\rho_{0.4}$) and the other is for 4 mm ($\rho_4$). The bulk density $\rho_{0.4}$ can be assumed to be the bulk density of the skin layer as the specimen thickness of 0.4 mm was lower than the skin layer thickness.
Table 11. Bulk density of monolithic δ-form sPS aerogels with thicknesses of 0.4 mm ($\rho_{0.4}$), 4 mm ($\rho_4$), and computed bulk density of the inner body ($\rho_i$).

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$\rho_{0.4}$ (g/cm$^3$)</th>
<th>$\rho_4$ (g/cm$^3$)</th>
<th>$\rho_i$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-0.01</td>
<td>0.029±0.0009</td>
<td>0.020±0.0012</td>
<td>0.017</td>
</tr>
<tr>
<td>sPS-0.03</td>
<td>0.073±0.0016</td>
<td>0.042±0.0018</td>
<td>0.031</td>
</tr>
<tr>
<td>sPS-0.05</td>
<td>0.130±0.0012</td>
<td>0.061±0.0018</td>
<td>0.037</td>
</tr>
</tbody>
</table>

As expected, the bulk density of 0.4 mm thick specimen is higher than the 4 mm thick specimen. The composite bulk density of a monolithic aerogel made up of the skin layer and the inner body is obtained from equation (47):

$$\rho_b = \frac{\rho_o L_0 + \rho_i (L-L_0)}{L}$$  \hspace{1cm} (47)

In equation (47), $\rho_o$ and $\rho_i$ are bulk density of the skin layer and inner body respectively. From equation (47), $\rho_i$ can be obtained from the values of $\rho_b$ and corresponding specimen thickness, L. The bulk density of the inner bodies thus obtained is listed in Table 11.
Figure 42. Comparison of computed permeability with experimental data of 4 mm thick monolithic $\delta$-form sPS aerogel as a function of sPS concentrations.

The permeability of monolithic sPS aerogels of 4 mm thickness fabricated from different sPS concentrations was computed from the values of $k_i$, $k_0$, and $L_0$ and compared with experimental data as presented in Figure 42. To compute permeability, $k_i$ and $k_0$ were regressed first by a logarithmic function using the data in Table 10 as presented in equations (48) and (49).

$$k_i = -3.547 \ln \psi - 10.987 \quad (48)$$

$$k_0 = -1.462 \ln \psi - 4.562 \quad (49)$$
where $\psi$ is sPS concentration in g/mL of solution. With the assumption of 0.5 mm thickness for the skin layers, the permeability value was computed using equation (42). As is evident from Figure 42, the computed values correspond well with the experimental data.

7.5 Conclusions

The dependence of permeability data on aerogel specimen thicknesses indicated that the aerogel monoliths were composed of a skin layer and an inner body. A simple model of permeability for a multi-layered body fit the experimental data well and yielded such information as thickness of the skin layers and permeability of the inner bodies. The permeability of the skin layers was about a factor of 2.5 lower than the inner bodies due to higher bulk density for the skin layers. Higher bulk density corresponds to lower porosity. The permeability model produced that the skin layer thickness of 0.55 mm was independent on sPS concentration of the original solutions.
CHAPTER VIII

THE ROLE OF MESOPORES IN ACHIEVING HIGH EFFICIENCY AIRBORNE NANOPARTICLE FILTRATION USING AEROGEL MONOLITHS

8.1 Introduction

Small airborne particles, e.g., the fines with size 0.1 μm-1 μm and ultrafines with size < 0.1 μm, are detrimental to human health as they can penetrate the human body and reach pulmonary alveoli. These hazards become more alarming when the viral particles of size 20-2,000 nm attach to the surfaces of airborne particles and enter the human body. Nausea, breathing difficulties, bronchitis, birth defects, serious developmental delays, weakened immune systems, and even cancer are some of the aftermaths of exposure to and inhalation of these airborne particles. In this context, air purification by filtration to remove the airborne nanoparticles is a logical measure for protection of human health.

The high efficiency particulate absorption (HEPA) filters improve air quality by filtering airborne particles at efficiency over 99.95% as per EN 1822-1:2009 classification. However, removal of airborne nanoparticles of sizes 100 nm and smaller using fiber mat-based HEPA filters still remains a challenge. In this context, aerogel monoliths offer several attractive features as filter media. They are composed of solid networks with open pore structures, high porosity, large surface area, and cascading
pores. Silica aerogels, the most studied aerogels to date, are mesoporous with pores 2-50 nm in diameter and offer surface area up to 1,000 m$^2$/g and porosity over 90 %. The $\delta$-form syndiotactic polystyrene (sPS) aerogels have porosity > 97 %, contain a small fraction of pores in the micropore (< 2 nm) range inside the nanocavities of crystalline strands, and a major fraction of pores as macropores.

Monolithic aerogels have the potential to serve as standalone filter media. However, only a few studies exploited the aerogel granules and microspheres in removal of airborne particles by arranging them in packed beds. Several studies focused on viral particle detection by bioluminescent organisms colonized in silica aerogels, and removal of pollutants, such as cyanides or combustion gases by using monolithic silica aerogel composites as the medium for heterogeneous catalysts. Prior work on direct usage of monolithic aerogels for filtration of airborne nanoparticles is scarce. In Chapter VI, it was shown that the removal of airborne nanoparticles of size 25-150 nm (mean size 75 nm), with high efficiency (> 99.95 %) and air permeability of the order of $10^{-10}$ - $10^{-11}$ m$^2$ was carried out using macroporous monolithic $\delta$-form sPS aerogels. No detailed work exists on evaluation of airborne nanoparticle filtration potential of aerogel monoliths with only the mesopores or with pore structures consisting of both the meso- and macropores.

The mesopores with pore dimensions 2-50 nm present interesting scenarios for fluid flow and thermal transport. These can be interpreted in terms of Knudsen number ($Kn$). A purely viscous fluid flow regime is obtained when $Kn << 1$ for monolith pore size much larger than the mean free path of the gas molecules. Note that for this regime, the viscous flow is driven by the pressure gradient and the viscosity of the fluid as per Darcy’s law. The fluid flow becomes diffusional in nature when $Kn >> 1$ for the
mean free path much larger than the pore dimension. The diffusional flow is driven by the concentration gradient as per Fick’s law. At an intermediate range, $Kn \approx 1$, the pore dimensions are similar to the mean free path of the gas molecules. In this case, the fluid flow is governed by both the viscous and the diffusional components. The mean free path of air is approximately 20 nm at a pressure of 370 kPa and temperature of 296 K, which corresponds to the size of mesopores. It was reported that fluid flow through mesoporous silica aerogels at room temperature and pressure 6-200 kPa was in the intermediate regime. The diffusional flow in the mesopores promote the capture of airborne nanoparticles of size less than 100 nm which experience Brownian motion and come in contact with the filter media. However, mesopores are not conducive to high air permeability due to their small sizes. An aerogel monolith with appropriate proportion of meso- and macropores has the potential to offer both superior particle capture efficiency of mesopores and high air permeability of macropores.

A set of organic-inorganic hybrid macro- and mesoporous aerogel monoliths were produced and their effectiveness in nanoparticle filtration was evaluated in this chapter. The hybrid monoliths were produced by growing discontinuous silica aerogel particles inside the macropores of δ-form sPS following a method published earlier. This chapter answered the following questions. First, how sensitive is the air permeability data of the hybrid aerogel monoliths to mesoporous silica content? Second, how sensitive is the filtration efficiency data to mesoporous material content? In view of Chapter VI, macroporous sPS aerogel monoliths with porosity 96 % or lower are effective as high efficiency filtration media for removal of airborne nanoparticles. In this context, can one achieve even higher efficiency without dramatically decreasing the solid porosity, for
example, by incorporating appropriate quantities of mesoporous silica in a hybrid material with sPS? The answer to this question is not straightforward as introduction of mesopores may result in a reduction of air permeability and it is not known at the outset what fraction of mesoporous materials is appropriate. Third, considering the brittle nature of silica networks, do these monolithic filter media experience mechanical failure? Wang and Jana\textsuperscript{30} observed synergy of compressive modulus in hybrid sPS-silica aerogel systems and reported an increase of compressive modulus by 250\% over sPS aerogel monoliths.

8.2 Materials and methods

The monolithic $\delta$-form sPS aerogels were considered a baseline material. In conjunction, monolithic sPS-silica hybrid aerogel materials were developed to assess how mesopore content affects air permeability and filtration efficiency. sPS aerogel monoliths were fabricated using the same method as described in Chapter III: a two-step process consisting of thermo-reversible gelation and supercritical drying. The hybrid aerogel monoliths were fabricated by growing mesoporous silica particle networks inside the sPS macropores following a procedure reported by Wang and Jana.\textsuperscript{30} For this purpose, silica networks were grown inside the preformed sPS gels by double catalyzed acid-base sol-gel reactions and the hybrid materials were dried under supercritical condition.\textsuperscript{30,31}

sPS solutions with solids concentration 0.020, and 0.025 g/mL were prepared by dissolving sPS powder in THF in sealed glass containers kept in oil bath at 120 $^\circ$C. The porosity of sPS aerogel monoliths varied with the solid content. The solutions were
poured in a disc-shaped mold of 30 mm internal diameter and allowed to cool down to room temperature to form δ-form sPS gels. The thickness of the disc shaped gels was maintained at around 4.0 mm. The gels were aged in the mold for a day and washed and solvent exchanged with ethanol for at least 3 days. Ethanol in sPS gel was exchanged with liquid carbon dioxide and the materials were subjected to supercritical drying.

In the case of hybrid gels, disc-shaped sPS gels filled with ethanol were produced as above from sPS solutions of concentration 0.020 and 0.025 g/mL. TEOS solutions were prepared in a mixture of ethanol and deionized water (DIW) in the molar ratio TEOS:ethanol(EtOH):DIW = 1:x:5 with x = 37, 46, and 64. TEOS was hydrolyzed to form hydroxysilanes under stirring for one hour at room temperature after the pH of these solutions was adjusted to 2.0 by adding nitric acid. The sPS gel specimens were soaked in hydroxysilane solution for one day and transferred to another container where a solution of ammonium hydroxide and DIW in 1:1 volume ratio was poured over the gel specimen drop by drop using a pipette so as to increase the pH to around 9.0 and to promote condensation of hydroxysilanes into silica particle networks. The hybrid gels were aged for a day, washed and solvent exchanged with ethanol for 3 days, and finally solvent exchanged with liquid carbon dioxide before drying under supercritical condition. Table 12 lists the concentration of solutions used in synthesis of hybrid aerogels. sPS aerogel monoliths are represented by sPS20 and sPS25 while the hybrid aerogels are represented by Hx-y where x represents sPS concentration in g/L and y represents moles of ethanol per mole of TEOS in the solution.
Table 12. Specific concentration of sPS and TEOS used in synthesis of hybrid aerogels.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>sPS conc. (g / THF mL)</th>
<th>TEOS conc. (mol / L) [TEOS:EtOH molar ratio]</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS20</td>
<td>0.020</td>
<td>-</td>
</tr>
<tr>
<td>sPS25</td>
<td>0.025</td>
<td>-</td>
</tr>
<tr>
<td>H20-64</td>
<td>0.020</td>
<td>0.25 [1:64]</td>
</tr>
<tr>
<td>H20-46</td>
<td>0.020</td>
<td>0.33 [1:46]</td>
</tr>
<tr>
<td>H20-37</td>
<td>0.020</td>
<td>0.40 [1:37]</td>
</tr>
<tr>
<td>H25-64</td>
<td>0.025</td>
<td>0.25 [1:64]</td>
</tr>
<tr>
<td>H25-46</td>
<td>0.025</td>
<td>0.33 [1:46]</td>
</tr>
<tr>
<td>H25-37</td>
<td>0.025</td>
<td>0.40 [1:37]</td>
</tr>
</tbody>
</table>

The permeability of air was obtained by Frazier air permeability tester (Frazier Precision Instrument, Hagerstown, MD) as described in Chapter III. Pressure drop per unit thickness, ΔP/L, was calculated from permeability and air flow rate. Filtration efficiency (E) was measured using TSI-8130 filter tester (TSI Inc., Shoreview, MN) as described in Chapter III. The face velocity (Uf) of air during filtration test was 50 cm/sec.

The value of bulk density, ρb was obtained from the weight-to-volume ratio of the specimens. Skeletal density, ρs was obtained by using Helium pycnometry (Accupyc II
1340, Micromeritics, Norcross, GA) at room temperature. For this purpose, the aerogel specimens were completely dried in a vacuum oven to remove moisture. More information about helium pycnometry can be found in Chapter III.

Internal surface area, $S_{\text{BET}}$ was obtained from nitrogen sorption isotherms (TriStar II, Micromeritics, Norcross, GA) at temperature of 77 K using Brunauer–Emmett–Teller (BET) method.$^{128}$ Ten (10) adsorption points on the partial pressure ($p$) in the range $0.05 < p/p_0 < 0.35$ were used for evaluating $S_{\text{BET}}$, where $p_0$ is the total pressure. Pore size distribution was obtained from nitrogen sorption isotherms using Barrett-Joyner-Halenda (BJH) method.$^{129}$ More information about these techniques can be found in Chapter III.

The absorption capacity of the particles is an important attribute as it relates to the life-time of a filter. The absorption capacity was determined from the value of porosity ($\Pi$) as described in Chapter III.

The macropore volume fraction, $\phi_M$, was computed from the difference of total pore volume and the sum of volumes of micro- and mesopores as described in Chapter III. The micropore volume fraction of $\delta$-form sPS aerogels was inferred to be much less than 1 % from the data reported elsewhere.$^{24}$ It was confirmed using carbon dioxide sorption isotherms that sPS aerogels in this work contained micropore volume fraction of ~0.2 %. In view of this, the contributions of micropores to total pore volume was ignored.

The mechanical property of compressive stress-strain relationships were obtained via ASTM D595 method using Instron 5567 (Canton, MA) machine. For this purpose, cylindrical specimens of aerogels with diameter around 11 mm and height-to-diameter
ratio 1:1 were prepared. A 100 N load cell was used and the crosshead speed was 2 mm/min.

8.3 Results and discussion

A key determinant of the performance of the hybrid materials is the mesopore content. It is noted that sPS aerogels do not exhibit appreciable mesoporosity. Wang and Jana\textsuperscript{30} reported significant mesoporosity in sPS-silica hybrid aerogel by synthesizing silica gel networks within the macropores of sPS gels using high concentration of TEOS. The silica to sPS mass ratio in their work varied from 0.97 to 4.2. In this work, however, TEOS was used at much lower concentration than was used by Wang and Jana.\textsuperscript{30} It was not known a priori if the silica phase was present in the hybrid materials as single particles, as particle networks, or as a co-continuous aerogel networks as reported by Wang and Jana.\textsuperscript{30}

Figure 43 shows SEM images of sPS aerogel and its corresponding hybrid with silica. As seen in Figure 43(a), sPS aerogel (sPS20) had an open macropore structure formed by the polymer strands with diameter tens of nanometers. In the case of sPS-silica hybrid aerogels, discontinuous silica particles are seen adhered to sPS strands (Figure 43(b)). Table 13 lists the data of skeletal density of sPS and hybrid materials. In view of skeletal density of 1.801 g/cm\textsuperscript{3} for silica,\textsuperscript{30} the mass ratio of silica to sPS was calculated based on the skeletal density values. It is apparent that silica to sPS mass ratio in the hybrid materials varied between 0.74 and 1.44. The lower values of the mass ratio of
silica to sPS in this work resulted in the formation of discontinuous silica aerogels particles different from the co-continuous aerogel networks.

Figure 43(c) shows a representative image of the powder residue due to silica particles recovered after burning off the sPS chains from a hybrid aerogel monolith. The large particle aggregates observed in Figure 43(c) are due to sintering of silica particles. The images in Figure 43(b) and 44(c) establish that silica formed small particle aggregates and not a co-continuous silica gel inside the macropores of sPS gel. A co-continuous silica gel network was observed by Wang and Jana30 albeit at much higher TEOS concentrations. As will be seen later, the hybrid aerogels developed cracks at high concentrations of TEOS.

The mesoporosity of hybrid materials was confirmed by nitrogen sorption isotherms. The pore size distributions shown in Figure 44 verify that pores with size 20-30 nm were more abundant in sPS-silica hybrid materials. Note that the baseline materials sPS20 and sPS25 also had some mesopores, although the fractions of the mesopores are around 1 and 1.7 % by volume respectively for sPS20 and sPS25 (Table 13) and a large majority (over 98 %) of the pores are macropores. The silica particles increased the fraction of mesopores and reduced the fraction of macropores in hybrid aerogel monoliths. The data in Table 13 show that the macropore volume fraction reduced from 99 % for sPS20 specimen to 96.5 % for H20-37 hybrid aerogel.
Figure 43. Representative SEM images of (a) sPS aerogel (sPS20), (b) sPS-silica hybrid aerogels (H20-37), and (c) the sintered powder residue due to silica particles recovered after burning off the sPS chains in H20-37.
Table 13. Bulk density ($\rho_b$), skeletal density ($\rho_s$), porosity ($\Pi$), macropore fraction of total porosity ($\Phi_M$) of monolithic sPS and sPS-Silica hybrid aerogels.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$\rho_b$ (g/cm$^3$)</th>
<th>$\rho_s$ (g/cm$^3$)</th>
<th>$\Pi$ (%)</th>
<th>$\Phi_M$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS20</td>
<td>0.030±0.001</td>
<td>1.056</td>
<td>97.16</td>
<td>99.0</td>
</tr>
<tr>
<td>sPS25</td>
<td>0.034±0.003</td>
<td>1.056</td>
<td>96.78</td>
<td>98.3</td>
</tr>
<tr>
<td>H20-64</td>
<td>0.044±0.001</td>
<td>1.282±0.058</td>
<td>96.57</td>
<td>98.2</td>
</tr>
<tr>
<td>H20-46</td>
<td>0.052±0.003</td>
<td>1.344±0.056</td>
<td>96.13</td>
<td>96.7</td>
</tr>
<tr>
<td>H20-37</td>
<td>0.059±0.003</td>
<td>1.398±0.029</td>
<td>95.77</td>
<td>96.5</td>
</tr>
<tr>
<td>H25-64</td>
<td>0.054±0.001</td>
<td>1.270±0.061</td>
<td>95.74</td>
<td>97.1</td>
</tr>
<tr>
<td>H25-46</td>
<td>0.057±0.003</td>
<td>1.302±0.037</td>
<td>95.55</td>
<td>96.9</td>
</tr>
<tr>
<td>H25-37</td>
<td>0.061±0.001</td>
<td>1.315±0.036</td>
<td>95.35</td>
<td>96.1</td>
</tr>
</tbody>
</table>
Table 14. Permeability ($k$), filtration efficiency ($E$), internal surface area ($S_{\text{BET}}$), and pressure drop ($\Delta P/L$) of monolithic sPS and sPS-Silica hybrid aerogels.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$k$ ($\times 10^{-10}$ m$^2$)</th>
<th>$E$ (%)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$\Delta P/L$ (mmH$_2$O/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS20</td>
<td>2.23±0.36</td>
<td>98.889±0.998</td>
<td>379</td>
<td>42.6</td>
</tr>
<tr>
<td>sPS25</td>
<td>1.45±0.31</td>
<td>99.734±0.117</td>
<td>377</td>
<td>65.5</td>
</tr>
<tr>
<td>H20-64</td>
<td>2.18±0.55</td>
<td>99.011±0.425</td>
<td>383</td>
<td>43.5</td>
</tr>
<tr>
<td>H20-46</td>
<td>1.12±0.61</td>
<td>99.354±0.105</td>
<td>476</td>
<td>84.5</td>
</tr>
<tr>
<td>H20-37</td>
<td>1.22±0.79</td>
<td>99.963±0.047</td>
<td>490</td>
<td>77.5</td>
</tr>
<tr>
<td>H25-64</td>
<td>2.00±0.60</td>
<td>99.844±0.276</td>
<td>443</td>
<td>47.3</td>
</tr>
<tr>
<td>H25-46</td>
<td>0.97±0.39</td>
<td>99.989±0.016</td>
<td>426</td>
<td>97.8</td>
</tr>
<tr>
<td>H25-37</td>
<td>0.91±0.41</td>
<td>&gt;99.999</td>
<td>458</td>
<td>104.3</td>
</tr>
</tbody>
</table>
Figure 44. Pore size distribution from nitrogen sorption isotherms. (a) sPS concentration 0.020 g/mL, (b) sPS concentration 0.025 g/mL.
The values of bulk and skeletal density, porosity, and BET surface area are also listed in Table 13 and 14. It is apparent that inclusion of silica particles in the hybrid materials did not change the porosity values much, e.g., 97% porosity of sPS compared to 95% for hybrid materials. The surface area, however, increased substantially, e.g., from 379 m²/g for sPS20 specimen to ~490 m²/g for H20-37. The pearl-necklace skeletal structure of silica with about 5-30 nm secondary particles accounts for such an increase of the surface area. The values of permeability, filtration efficiency, and pressure drop of the monolithic sPS and sPS-silica hybrid aerogels are also presented in Table 14.

![Figure 45. Permeability of sPS and sPS-silica hybrid aerogels as a function of TEOS concentrations.](image)
Figure 45 shows the plots of permeability as a function of TEOS concentrations. Permeability values of sPS and sPS-silica hybrid aerogels are close to $10^{-10}$ m$^2$. It is noted that the permeability value did not change much after the incorporation of silica particles. Several reasons can be invoked to interpret the apparent independence of permeability to silica content. First, the porosity of the hybrid materials (~95%) remained close to that of sPS monoliths (97%). Second, the silica particle structures did not change the macropore volume much. Note that most of the air flow should be handled by the macropores in sPS aerogels.

Figure 46. Permeability as a function of macropore fraction of entire volume of an aerogel monolith.
Figure 46 presents a plot of air permeability vs. macropore fraction of entire volume of an aerogel monolith obtained from the product $\Pi \times \Phi_M$. The permeability data show correlation with the macropore fraction, i.e., the permeability increased from about $1 \times 10^{-10}$ m$^2$ to $2.25 \times 10^{-10}$ m$^2$ as the macropore fraction increased from 0.917 to 0.96.

![Figure 47. Filtration efficiency as function of TEOS concentrations.](image)

The effect of mesoporosity on nanoparticle filtration was examined by comparing the filtration efficiency of sPS aerogels and sPS-silica hybrid aerogels. Figure 47 presents the data on filtration efficiency of sPS and sPS-silica hybrid aerogels as a function of
TEOS concentrations. It is seen that filtration efficiency increased with an increase of TEOS concentrations. High filtration efficiency (> 99.95 %) was achieved with monolithic specimens H25-46 and H20-37 synthesized respectively from TEOS concentrations of 0.33 and 0.40 mol/L and sPS concentration of 0.025 and 0.020 g/mL. In filtration industry, the filtration efficiency values of 99%, 99.9% and 99.99% represent different categories of filtration as per EN 1822-1:2009 classification. In this context, achieving high efficiency (> 99.95 %) is considered important. These results indicate that the mesopores introduced in the materials increased the contribution of the diffusional deposition mechanism and increased filtration efficiency. Recall that a combination of viscous and diffusional flows operate in mesopores.112 The higher internal surface area in the hybrid aerogels may also have contributed to higher efficiency.

sPS-silica hybrid aerogels at even higher TEOS concentration, e.g., at 0.40 mol/L or higher were investigated. For this purpose, sPS gel with sPS concentration 0.020 g/mL was used. Figure 48 shows filtration efficiency as function of TEOS concentrations. Interestingly, the hybrid aerogels with TEOS concentrations over 0.6 mol/L showed large drop in filtration efficiency. Such drop of filtration efficiency is counter-intuitive as higher contents of silica should contribute to higher degree of diffusional deposition due to higher fractions of mesopores. The reduction of filtration efficiency in Figure 48 was caused from the cracks that developed in the monoliths during filtration tests due to brittle nature of the silica networks especially at TEOS concentrations over 0.6 mol/L were used. The inset of Figure 48 shows a representative image of cracked monolith recovered after filtration tests.
Figure 48. Filtration efficiency measured for sPS-silica hybrid aerogels at high TEOS concentration. The inset presents an image of a cracked monolith with 0.99 mol/L TEOS concentration recovered after filtration test.

The compressive property of sPS-silica hybrid aerogels was inferred from compressive stress-strain cures shown in Figure 49. The sPS-silica hybrid aerogel with TEOS concentration 0.33 mol/L (H20-46) showed compressive modulus 1.9 MPa, large plastic deformation (plateau), and a dramatic increase of stress at high strain due to compressive resistance. Similar observations were reported for mechanical property of aerogels. The sPS-silica hybrid aerogels with high TEOS concentration of 0.99 mol/L also showed similar stress-strain relationships with increased compressive modulus 4.8
MPa. However, in the hybrid aerogel developed with 0.99 mol/L TEOS, several points of failure were observed in the stress-strain curve. These points originated from silica network collapse. The collapse began at very early stage of strain around 1.5%. The crack generation in sPS-silica hybrid aerogels during filtration tests are related to this silica network collapse. TEOS concentrations beyond a certain value, such as 0.6 mol/L, rendered the hybrid aerogels brittle.

Figure 49. Compressive stress-strain curves for sPS-silica hybrid aerogels with TEOS concentrations of 0.33 and 0.99 mol/L. The inset presents the stress-strain curves at low strains. The circles indicate the break points in stress-strain curves.
8.4 Conclusions

The δ-form sPS aerogel monoliths and their hybrids with silica particles provided useful trends on air permeability and filtration efficiency of airborne NaCl nanoparticles. The data presented in this chapter established that silica aerogel particles formed discontinuous networks inside the macropores of δ-form sPS due to low concentrations of TEOS used in this work. The data also established clearly that even small fractions of mesopores from silica particles can significantly improve the filtration efficiency to values greater than 99.95% due to increased contribution from the diffusional deposition mechanism. The macropores with 96-98% of the total pore volume handled bulk of the air flow through the monolith thus guaranteeing high air permeability values of $10^{11} - 10^{10} \text{m}^2$. 
CHAPTER IX

ELECTROSTATICALLY ACTIVE POLYMER HYBRID AEROGELS AND AIRBONE NANOPARTICLE FILTRATION

9.1 Introduction

A number of health hazards are tied to exposure to air pollution, such as nausea, breathing difficulties, bronchitis, birth defects, serious developmental delays, weakened immune systems, and even cancers.\textsuperscript{1,2} According to a recent report published by World Health Organization (WHO), the death of approximately 7 million people in 2012 is attributed to exposure to air pollution.\textsuperscript{3} The buoyant particulate matters in air generated from natural activities or anthropogenic emissions are responsible for air pollution.\textsuperscript{40} The small buoyant particles can easily penetrate into human body and reach the pulmonary alveoli. Accordingly, small airborne particles are classified as fine and ultrafine particles with diameter respectively 0.1 $\mu$m-1 $\mu$m and < 0.1 $\mu$m.\textsuperscript{4} The pathogens residing on the surfaces of the particles compound the situation by causing more serious and complex hazardous effects.\textsuperscript{5}

The above health hazards can be significantly mitigated if airborne particles are removed from air streams using filter media. The filter media are generally fabricated from fiber mats. The high efficiency particulate absorption (HEPA) filters are a class of
widely used filter media for high efficiency air purification. The filtration efficiencies of HEPA filters are over 99.95% for removing around 0.3 μm size particles as per EN 1822-1:2009 classification. However, efficient means of removal of airborne nanoparticles with size 25-150 nm is scarce, although as discussed above particles of this size range are more detrimental to human health.

Aerogels present a class of materials with strong potential to serve as efficient filter media for removing airborne nanoparticles of size 10-300 nm. The aerogels offer open, tortuous pores with high porosity (80-95%) and large surface area (300-1000 m²/g). For example, silica aerogel provides surface area up to 1,000 m²/g, and 90 % porosity with significantly developed mesopores (diameter, 2-50 nm). The δ-form syndiotactic polystyrene (sPS) aerogel provides porosity up to 97% with significant fraction of pores as macropores (diameter > 50 nm). Despite strong promise, airborne nanoparticles filtration using aerogels has not been studied much.

Only few studies used aerogel granules or microspheres in packed beds for the purpose of removal of particles. Several studies focused on viral particle detection by bioluminescent organisms colonized in silica aerogels, and removal of pollutants, such as cyanides or combustion gases by using monolithic silica aerogel composites as the medium for heterogeneous catalysts. The removal of airborne nanoparticles of size 25-150 nm (mean size 75 nm), with high efficiency (> 99.95 %) and air permeability of the order of 10⁻¹¹ - 10⁻¹⁰ m² using macroporous monolithic sPS aerogels was shown in Chapter VI. Also, the function of mesoporous silica particle networks grown inside the macropores of sPS in an organic-inorganic hybrid aerogel system on airborne nanoparticle filtration was investigated in Chapter VIII. It was found that the mesoporous
silica particle networks increased the particle capture efficiency significantly without affecting the value of air permeability.

The filtration of airborne individual particles is governed by one or more of the five recognized mechanisms. Direct interception is the primary contributor of filtration of large particles by direct contact of the particles with the filter medium. In inertial impaction particles deviate from the streamlines due to inertia and are captured when they come in contact with the filter medium. Diffusional deposition is effective for particles of sizes 0.1 μm and smaller whereby Brownian motion induces the small particles to make contact with the filter medium. In conjunction, gravitational settling accounts for particle capture by the gravitational force. This mechanism is rare for airborne nanoparticle filtration due to small particle size and insignificant particle settling velocity. Electrostatic force is especially important for small size particles whereby particles are captured by the electrostatic attraction that originate as the particles pass through a filter medium. A few studies used fiber mats fabricated from electret or electrostatic fibers to investigate the effect of the electrostatic attraction on particle filtration. High capture efficiencies were maintained while using larger pore openings due to the use of electret fibers. However, the use of electrostatic force has not been comprehensively studied in reference to nanoparticle filtration.

Polyvinylidene fluoride (PVDF) chains with the repeat unit CH₂-CF₂ generate strong molecular dipole moment perpendicular to the axis of the molecular chains due to stronger electronegativity of fluorine atom than hydrogen atom. Five different crystalline polymorphs are known for PVDF, e.g., α, β, γ, δ and ε with unique electrical properties. The polymer chains in β, γ, and δ crystalline forms are packed to form
parallel dipoles and, therefore, are able to have a net spontaneous dipole moment. PVDF with these crystalline phases also possess piezo-, pyro- and ferroelectricity. Of these, the β-phase show the strongest spontaneous polarization. The α-phase is the most stable phase with no-polarity but show para-electricity due to the symmetry of the crystalline unit cell. The contribution of the electrostatic force on capturing airborne particles increases with reduction of the particle size and is especially suitable for nanoparticles. This chapter investigates the role of electrostatically active aerogels on nanometric particle filtration by developing a filter media based on a hybrid of sPS and PVDF.

9.2 Materials and methods

Two types of aerogels were fabricated in this work. The monolithic δ-form sPS aerogels were fabricated as a baseline material. In conjunction, a hybrid aerogel material of PVDF and sPS was developed to exploit the electrostatic force contributions of PVDF. sPS aerogel monoliths were fabricated by a two-step process involving thermos-reversible gelation and supercritical drying as described in Chapter III.24-31 The sPS-PVDF hybrid aerogel monoliths were fabricated by thermos-reversible gelation of sPS from a binary polymer solution of sPS and PVDF followed by supercritical drying of the gels in carbon dioxide.

The sPS aerogel monoliths were synthesized from sPS solution with the solid concentration 0.020 g/mL. The polymer solution was prepared by dissolving sPS powder in THF in a sealed glass container kept in oil bath at 120 °C. The solution was then poured in a disc shaped mold of 30 mm diameter and allowed to cool down at room
temperature. The solution produced δ-form sPS gel by natural cooling to room temperature. The thickness of the disc shaped gels was maintained at around 3.5-4.0 mm. The gels were aged in the molds for a day and then placed in a supercritical drying chamber for solvent exchange and supercritical drying in carbon dioxide. After the solvent exchange step, the chamber was heated and pressurized to reach the supercritical condition of carbon dioxide, e.g., 50 °C and 10.3 MPa pressure. The materials were kept in the supercritical dryer at the above pressure and temperature for one hour and the chamber was depressurized slowly under isothermal condition to atmospheric pressure to recover the aerogels.

The sPS-PVDF hybrid aerogels were produced following the same process as described above. The polymer solutions, in this case, were prepared by dissolving sPS and PVDF in THF at 120 °C. The total volume of the solids in solution in THF was kept the same as that of the sPS gel, e.g., 0.019 mL/mL, but the ratio of sPS and PVDF in the solutions was varied per the recipe presented in Table 15.

The value of bulk density, \( \rho_b \) was obtained from the weight-to-volume ratio of the specimens. The permeability of air was obtained by Frazier air permeability tester (Frazier Precision Instrument, Hagerstown, MD) as described in Chapter III. Pressure drop per unit thickness, ΔP/L, was calculated from permeability and air flow rate. Filtration efficiency (E) was measured using TSI-8130 filter tester (TSI Inc., Shoreview, MN) as described in Chapter III. The face velocity (U\(_f\)) of air during filtration test was 50 cm/sec. TSI-8130 filter tester (TSI Inc., Shoreview, MN) generated polydisperse sodium chloride nanoparticles. The diameter of generated particles ranged from 25-150 nm with
an average diameter of 75 nm. The filter tester was able to measure the filtration efficiency with an accuracy up to 99.999%.

Table 15. Concentrations of sPS and PVDF used in synthesis of sPS and sPS-PVDF hybrid aerogels.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Solid volume ratio (sPS:PVDF)</th>
<th>sPS concentration (g/mL)</th>
<th>PVDF concentration (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS20</td>
<td>10:0</td>
<td>0.020</td>
<td>0</td>
</tr>
<tr>
<td>sPS_PVDF-1</td>
<td>9:1</td>
<td>0.018</td>
<td>0.003</td>
</tr>
<tr>
<td>sPS_PVDF-2</td>
<td>7:3</td>
<td>0.014</td>
<td>0.010</td>
</tr>
<tr>
<td>sPS_PVDF-3</td>
<td>5:5</td>
<td>0.010</td>
<td>0.017</td>
</tr>
</tbody>
</table>

The absorption capacity of the particles is an important attribute as it relates to the life-time of a filter. The absorption capacity was estimated by the value of porosity (Π) as described in Chapter III.

The internal structures of sPS and sPS-PVDF hybrid aerogels were examined by scanning electron microscope (JEOL JSM5310) and transmission electron microscope (JEOL JSM1230) to visually identify the structures. For SEM, aerogel specimens were cut into pieces and a representative piece was mounted on an aluminum stub using carbon tape. The samples were then sputter coated by silver (ISI-5400 Sputter Coater, Polaron)
and images were taken at accelerating voltage of 5.0 kV. For TEM, the sPS/THF and sPS/PVDF/THF solutions were dropped on Cu grids, and the solutions were allowed to be dried at ambient condition. The dried specimens were observed by TEM with an accelerating voltage of 120 kV.

Skeletal density, $\rho_s$, was obtained by helium pycnometery (Accupyc II 1340, Micromeritics, Norcross, GA) at room temperature. More information about helium pycnometery can be found in Chapter III. The aerogel samples were completely dried in a vacuum oven to remove moisture which may affect the measured pressure. 25 times flushing in the pycnometer chamber by the measuring gas was carried out before the measurements.

A differential scanning calorimeter (DSC, TA Instrument DSC Q200) was used to investigate the thermal properties of sPS and sPS-PVDF hybrid aerogels. The thermal history of the aerogels was eliminated by the first heating cycle with heating rate of 20 °C/min from room temperature to 300 °C. The data obtained from the second heating cycle were used.

Fourier transform infrared spectroscopy (FTIR) was used to analyze chemical compositions and crystalline structures of sPS and sPS-PVDF hybrid aerogels as described in Chapter III.

Static surface charges of the aerogels were measured to identify the electrostatic activity of the aerogels as described in Chapter III. An electrostatic field meter (Simco FMX-003, Hatfield, PA) which can measure the static voltage values in the range of ±20 kV was used for this purpose. The electrostatic field meter was set to zero in ambient
air first, and then ten reading from different areas of surfaces of the specimen were taken. An average value was obtained for each specimen.

The macropore volume fraction, $\Phi_M$, is computed from the difference of total pore volume and the sum of volumes of micro- and mesopores as described in Chapter III. The micropore volume fraction can be obtained by carbon dioxide sorption isotherms. In the case of $\delta$-form sPS aerogels, however, the micropore volume fraction was inferred to be much less than 1 % from the data reported elsewhere.\textsuperscript{24} It was confirmed using carbon dioxide sorption isotherms that sPS aerogels in this work contained micropore volume fraction of $\sim$0.2 %. In view of this, the contributions of micropores to total pore volume was ignored and nitrogen sorption isotherms was used to determine the value of $\Phi_M$.

9.3 Results and discussion

![Figure 50. DSC traces of sPS aerogel (a), sPS_PVDF-1 (b), sPS_PVDF-2 (c), and sPS_PVDF-3 (d) at a scan rate of 20 °C/min under nitrogen.](image)
The thermal properties of sPS and sPS-PVDF aerogels were investigated using DSC. Figure 50 shows the DSC scans of the aerogels. The melting peak of sPS crystals was clearly visible in Figure 50 at around 273°C in all aerogels. However, the enthalpy of melting gradually reduced in sPS-PVDF hybrid materials due to an increase of the amount of PVDF. Recall that the hybrid aerogels were fabricated with the volume of the solids fixed at 0.019 mL per mL of THF. The sPS-PVDF hybrid aerogels show melting peaks at around 165°C due to the crystals of PVDF. The enthalpy of these peaks gradually increased with an increase of the volume ratio of PVDF.

The FTIR spectroscopy data shown in Figure 51 were used to identify the crystalline structures of sPS and PVDF chains in hybrid aerogels. The peaks at 1320 and 935 cm\(^{-1}\) are due to sPS crystalline structure with helical conformation.\(^{66}\) The peaks are also seen for hybrid aerogels. The peaks at 615, 765, and 795 cm\(^{-1}\) refer to the crystalline \(\alpha\)-phase of PVDF\(^{122,123,143}\) in sPS-PVDF hybrid aerogels. The peaks intensified with an increase of the volume ratio of PVDF. The peak at 430 cm\(^{-1}\) corresponding to the crystalline \(\gamma\)-phase of PVDF is seen in the all hybrid aerogels. The peak at 778 cm\(^{-1}\) corresponding to the same crystalline phase appeared for hybrid aerogel specimens sPS_PVDF-1 and sPS_PVDF-2, and the peak at 1234 cm\(^{-1}\) that also refers the same phase appeared for the specimen sPS_PVDF-3. The FTIR spectra confirm the presence of \(\delta\)-form clathrate crystalline phase of sPS, the prevailing \(\alpha\)-phase, and co-existing \(\gamma\) phase of PVDF in the hybrid aerogels sPS-PVDF. The crystalline \(\gamma\) phase of PVDF contributes the spontaneous polarity and, therefore, this phase is responsible for developing static charges on the surfaces of sPS-PVDF hybrid aerogels. The use of THF as the solvent in this study may have promoted the conversion of PVDF chains into polar crystalline phase
in the hybrid aerogel. The formation of polar crystalline phases in a PVDF film was reported earlier when a polar solvent was used.\textsuperscript{124,125}

![FTIR spectra of sPS aerogel (a) and hybrid aerogels (b-d). (b) sPS_PVDF-1, (c) sPS_PVDF-2, and (d) sPS_PVDF-3.](image)

Figure 51. FTIR spectra of sPS aerogel (a) and hybrid aerogels (b-d). (b) sPS_PVDF-1, (c) sPS_PVDF-2, and (d) sPS_PVDF-3.
Figure 52. SEM images of (a) sPS aerogel and hybrid aerogels (b) sPS_PVDF-1, (c) sPS_PVDF-2, and (d) sPS_PVDF-3.

The morphology of sPS and sPS-PVDF aerogels are shown in SEM (Figure 52) and TEM images (Figure 52). In SEM images, it was evident that both sPS and sPS-PVDF aerogels are made up of polymer strands with diameter tens of nanometer. No significant morphological difference among the aerogels was evident from the SEM images. We note that PVDF and polystyrene are immiscible polymers and should have formed separate domains.\textsuperscript{144,145} However, a closer examination of the SEM images
presented in Figure 52 and those taken at higher magnification reveals no distinguishable phase-separated domains of sPS and PVDF.

Figure 53. TEM images of strands of sPS with (a) low and (b) high magnifications, and strands of sPS-PVDF with (c) low and (d) high magnifications.
In TEM images, no significant morphological differences were also evident. However, in case of the sPS-PVDF mixture, some thick clusters and particle-like matters attached on polymer strands were observed as presented in Figure 53 (c) and (d). This indicated that PVDF chains probably coated or formed thick clusters on the sPS strands in the hybrid aerogels.

The effect of electrostatic property of PVDF in sPS-PVDF hybrid aerogels was visually inferred by exposing a piece of the aerogel specimens to a piece of glass which was earlier electrostatically charged by friction. All sPS-PVDF hybrid aerogels quickly responded to the electrostatic force and were found attracted to each other. The sPS aerogel monolith did not exhibit this behavior. Figure 54 shows that hybrid aerogel specimen sPS_PVDF-2 was attracted easily to the piece of glass. This was attributed to spontaneous polarity of the crystalline γ phase PVDF that developed the static surface charges. As will be seen later, this electrostatic property had an effect on nanometric particle filtration.

The values of bulk density, skeletal density, theoretical skeletal density, PVDF mass ratio, porosity, macropore fraction, permeability, pressure drop per a unit thickness, static surface charge, and filtration efficiency of monolithic sPS aerogel and sPS-PVDF hybrid aerogels are listed in Table 16.

The measured values of skeletal density of sPS-PVDF hybrid aerogels were found to be ~4% lower than the theoretical values obtained from the amounts of sPS and PVDF added into the solutions. This was attributed to some portions of PVDF that did not precipitate when THF was exchanged with liquid carbon dioxide. It was reported that
PVDF is not soluble in supercritical CO$_2$ until the temperature and pressure reach to 130° C and 160 MPa$^{146}$ while 50 °C and 10.3 MPa was the conditions for the supercritical drying in this work. Supercritical drying was not related to the lowered values of skeletal density.

Figure 54. Images captured from video showing no response from sPS aerogel and spontaneous attraction of sPS-PVDF hybrid aerogel to charged glass.

The mass ratio of PVDF and sPS in the hybrid aerogels can be computed the skeletal density data reported in Table 16 and the skeletal density data of PVDF ($\rho_s$: 1.78 g/cm$^3$). The PVDF mass ratio data are also listed in Table 16.
Table 16. Bulk density ($\rho_b$), skeletal density ($\rho_s$), theoretical skeletal density ($\rho_{st}$), PVDF mass ratio, porosity ($\Pi$), macropore fraction of total porosity ($\Phi_M$), permeability ($k$), pressure drop per a unit thickness ($\Delta P/L$), static surface charge ($V_e$), and filtration efficiency ($E$) of monolithic sPS aerogel and sPS-PVDF hybrid aerogels.

<table>
<thead>
<tr>
<th>Property</th>
<th>sPS20</th>
<th>sPS_PVDF-1</th>
<th>sPS_PVDF-2</th>
<th>sPS_PVDF-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_b$ (g/cm$^3$)</td>
<td>0.030</td>
<td>0.031±0.001</td>
<td>0.034±0.001</td>
<td>0.037±0.001</td>
</tr>
<tr>
<td>$\rho_s$ (g/cm$^3$)</td>
<td>1.056</td>
<td>1.085±0.009</td>
<td>1.223±0.007</td>
<td>1.349±0.010</td>
</tr>
<tr>
<td>$\rho_{st}$ (g/cm$^3$)</td>
<td></td>
<td>1.128</td>
<td>1.273</td>
<td>1.418</td>
</tr>
<tr>
<td>PVDF mass ratio</td>
<td>0</td>
<td>0.07</td>
<td>0.50</td>
<td>1.15</td>
</tr>
<tr>
<td>$\Pi$ (%)</td>
<td>97.16</td>
<td>97.14</td>
<td>97.22</td>
<td>97.26</td>
</tr>
<tr>
<td>$\Phi_M$ (%)</td>
<td>99.0</td>
<td>98.8</td>
<td>99.6</td>
<td>99.6</td>
</tr>
<tr>
<td>$k$ ($10^{-10}$ m$^2$)</td>
<td>2.23±0.36</td>
<td>1.50±0.59</td>
<td>2.41±0.71</td>
<td>2.54±0.65</td>
</tr>
<tr>
<td>$\Delta P/L$ (mmH$_2$O/cm)</td>
<td>42.5</td>
<td>63.2</td>
<td>39.3</td>
<td>37.3</td>
</tr>
<tr>
<td>$V_e$ (kV)</td>
<td>0.02±0.01</td>
<td>0.70±0.11</td>
<td>1.00±0.14</td>
<td>1.40±0.16</td>
</tr>
<tr>
<td>$E$ (%)</td>
<td>98.889</td>
<td>99.719±0.180</td>
<td>&gt; 99.999</td>
<td>&gt; 99.999</td>
</tr>
</tbody>
</table>
The data in Table 16 showed that the porosity of all aerogel specimens was greater than 97%. Accordingly, the air permeability fell in the range of $10^{-10}$ m$^2$. Figure 55 shows that the permeability values do not change with the mass ratio of PVDF to sPS indicating that high porosity (~97%) and large fractions of macropores were responsible for giving high air permeability in this case. The values of permeability are within the range appropriate for practical filtration applications and are around one order higher than the values reported for packed beds.$^{34}$

![Figure 55. Permeability of sPS and sPS-PVDF hybrid aerogels as function of PVDF to sPS mass ratio](image)
Figure 56 presents a plot of air permeability vs. macropore fraction of entire volume of an aerogel monolith obtained from the product $\Pi \times \Phi_M$. The permeability data show good correlation with the macropore fraction with R square value of 0.8228. Most of the air flow is handled by the macropores in aerogels.

![Permeability vs. Macropore Fraction](image)

Figure 56. Permeability as a function of macropore fraction of entire volume of an aerogel monolith.

sPS-PVDF hybrid aerogels were electrostatically active as the surface charges were significantly developed; the surface charge of sPS_PVDF-2 was -1.0 kV, while that of sPS aerogel was -0.02 kV (Table 16). A PVDF solid sheet with thickness of 0.5 mm
prepared by hot pressing showed much higher surface charge of -7 kV, and the values of the surface charges of the hybrid aerogels are much smaller than that of the hybrid aerogels used in this work. Recall that the solid volume in the hybrid aerogels was less than 3%, while it was 100% for a sheet of PVDF. Thus, the net surface charges measured on the surfaces of the aerogels should be lower than that of solid PVDF.

Figure 57. Filtration efficiency of nanometric NaCl particles at $U_r \approx 50$ cm/s and static surface charges as a function of PVDF to sPS mass ratio.
Figure 57 shows filtration efficiency and static surface charge of hybrid aerogels as function of PVDF to sPS mass ratio. It is seen that the value of filtration efficiency increased with an increase of PVDF weight ratio. Almost perfect filtration with efficiency $\geq 99.999\%$ was achieved in the presence of PVDF at mass ratio 0.5 and higher. In filtration industry, a filtration efficiencies of 99%, 99.9% and 99.99% are all in different categories as per EN 1822-1:2009, and achieving high efficiency ($> 99.95\%$) is considered important. The increased filtration efficiency with an increase of static surface charges indicates that the electrostatic force mechanism significantly contributes to nanometric particle filtration. The sPS-PVDF hybrid aerogels offer improved performances in nanometric particle filtration with the developed electrostatic property.

9.4 Conclusions

Monolithic sPS and sPS/PVDF hybrid aerogels were prepared by thermoreversible gelation and supercritical drying in carbon dioxide. sPS $\delta$-form clathrate crystalline phase, and PVDF $\alpha$ and $\gamma$ crystalline phases coexisted in the semi-crystalline polymer strand networks of the hybrid aerogels. sPS/PVDF hybrid aerogels were electrostatically active from spontaneous polarity of the $\gamma$ crystalline phase in PVDF. The sPS/PVDF hybrid aerogels were quickly responded and attached to a piece of charged glass, but sPS aerogels were not. Also, measured static surface charges of sPS/PVDF hybrid aerogels were significantly larger than that of sPS aerogel. Permeability of sPS and sPS-PVDF hybrid aerogels was invariant with the values of $10^{-10}$ m$^2$ because the porosity of the aerogels was kept in the same level of 97%. Different from the invariant permeability, filtration efficiency of nanometric NaCl particles increased and reached to
the maximum (≥ 99.999%) by the PVDF hybridizations with the mass ratio of 0.5 and higher. The electrostatic force significantly contributes to the captures of nanometric particles.
CHAPTER X

OVERALL SUMMARY AND RECOMMENDATIONS FOR FURTHER STUDY

Aerogels had long been thought of as materials with tremendous potential for fabrication of effective filter media due to their open pore structures with high porosity, various sizes of pores, and large surface area. However, only a few studies to date investigated removal of pollutants using aerogel spheres or granules. No direct investigation exists in current literature on airborne nanoparticle filtration using monolithic aerogels. This motivated the present work.

Nanometric particles were selected in this work as the target substance for removal as they are more detrimental to human health than the micrometer size particles. As a representative aerogel material, the macroporous δ-form syndiotactic polystyrene (sPS) aerogels were used as the baseline material. In conjunction, gradient density aerogels of δ-form sPS, organic-inorganic hybrid aerogels with mesoporous silica aerogel particles, electrostatically active sPS-polyvinylidene fluoride (PVDF) hybrid aerogels were synthesized and used.

This thesis work first explored if there were avenues to shorten the time-scale of fabrication of aerogel monoliths that followed sol-gel chemical reactions and involved the steps of aging, washing, and supercritical drying. A rapid method of fabrication of aerogel monoliths was developed based on sol-gel reactions of silanes to obtain silica
aerogels that took a total time of fabrication of about 13 hours compared to several days in conventional methods. The data presented in this study revealed several key steps. First, higher temperature is required in aging or silylation steps to expedite the chemical reactions in these processes. This was achieved by aging the gel at 70 °C and 1.4 MPa in an aging solution under nitrogen atmosphere. Second, ultrasonication or shear flow should be applied for expediting impurity removal in the washing step. In this work ultrasonication at 20 kHz produced good results. Third, the time-consuming solvent exchange step must be avoided and specimens must be dried under supercritical condition of the solvent that was used in the washing step. The aerogel materials produced by direct drying under supercritical condition of ethanol were crack free and provided higher hydrophobicity than those produced by drying under supercritical condition of CO₂.

It was recognized at the outset that monolithic aerogels with gradient density would be useful in a number of applications including nanoparticle filtration. In this thesis, a method was developed to obtain gradient density silica aerogels. First, it was established that silica aerogel bulk density could be varied appreciably by varying the pH in the condensation reaction step in a small range, e.g., between 7.4 and 8.5. The higher skeletal density of silica networks at higher pH led to less shrinkage and produced aerogel monoliths with more open pores and lower bulk density. The characteristic silica particle size also reduced with an increase of pH resulting in higher surface area. The gradient density aerogels produced by sequential injection of silica sols of different pH showed approximately 30% change in the density across the monolith depth of 12 mm.

This work then established the applicability of monolithic sPS aerogels in nanometric particle filtration and presented several strategies for achieving high filtration
efficiency while keeping high values of air permeability. The data established that both permeability and filtration efficiency of single density sPS aerogels had power-law relationships with the bulk density. It was also revealed that monolithic sPS aerogels with bulk density 0.042 g/cm$^3$ or higher would be needed to obtain high efficiency (> 99.95 %) while permeability values were at an acceptable levels of $10^{-10}$-$10^{-11}$ m$^2$. The internal porous structures of aerogels were able to retain the nanometric NaCl particles in a regime of depth filtration in conjunction with cake formation inside the monolith. This work also showed that design of gradient density in aerogels by sequential injection of polymer solutions could be an effective method to obtain higher porosity for retention of particles, lower bulk density, and > 99.999 % efficiency in comparison to single density aerogels. Skin layers formed during sequential solution injection were found responsible for higher efficiency.

The dependence of permeability data on specimen thicknesses indicated that the specimens were composed of a skin layer and an inner body. A simple model of permeability for a multi-layered body fit the experimental data well and yielded such information as the thickness of skin layers and its corresponding bulk density. The permeability of the skin layer was about a factor of 2.5 lower than the inner body due to almost twice as much bulk density than the bulk materials. The permeability model produced that the skin layer thickness of 0.57 mm was independent of sPS concentration.

The δ-form sPS aerogel monoliths and their hybrids with silica particles also produced useful trends on air permeability and filtration efficiency of airborne NaCl nanoparticles. The data established clearly that even small fractions of mesopores could significantly improve the capture efficiency of airborne nanoparticles to greater than
99.95% while almost no effect was observed on air permeability values in the range $10^{-11}$-$10^{-10}$ m$^2$.

The study also investigated the role of electrostatic force on nanoparticle filtration. Monolithic sPS and sPS-PVDF hybrid aerogels were prepared by thermoreversible gelation and supercritical drying in carbon dioxide. sPS δ-form clathrate crystalline phase, and PVDF α and γ crystalline phases coexisted in the semi-crystalline polymer strand networks of the hybrid aerogels. sPS/PVDF hybrid aerogels were electrostatically active from spontaneous polarity of the γ crystalline phase in PVDF. The sPS-PVDF hybrid aerogels were quickly responded and attached to a piece of charged glass, but sPS aerogels were not. Also, measured static surface charges of sPS-PVDF hybrid aerogels were significantly larger than that of sPS aerogel. Permeability of sPS and sPS-PVDF hybrid aerogels was invariant with the values of $10^{-10}$ m$^2$ because the porosity of the aerogels was kept in the same level of 97%. The filtration efficiency of nanometric NaCl particles increased and reached the maximum value of $\geq 99.999\%$.

Several recommendations are in order for further work on this topic. The present study primarily focused on air permeability and filtration efficiency and identified that significant macropores are essential for handling air flow while significant mesopores are better for achieving higher filtration efficiency. In this context, the following outstanding issues need to be looked at in a future work:

(1) Macropores are all larger than 50 nm. However, the present study did not evaluate if there is an optimum range of diameter of macropores for high air permeability and high filtration efficiency.
(2) Filtration industry requires that the filter media be regenerated after usage. This aspect should be evaluated in a future study.

(3) The data presented in this thesis indicated that the aerogel monoliths promoted depth filtration with cake formation inside the monoliths. One set of data revealed that cake formation occurred by dendritic deposition of NaCl particles. A future study should relate this dendritic growth to the fractal nature of the internal pore structures and evaluate if a random deposition or dendritic deposition will prolong the lifetime of the monolithic aerogel filters.

(4) The use of PVDF improved the filtration efficiency due to development of significant electrostatic force. A future study should look into mesoporous silica networks derived from fluorinated alkoxysilanes for potential electrostatic charge development and the effects of such charges on filtration efficiency.

(5) The present thesis did not focus much on mechanical characterization of the monoliths before and after filtration tests. Such information will be very useful to assess if the monoliths can survive long hours of filtration.
REFERENCES


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APPENDICES
APPENDIX A

GEL TIME AS A FUNCTION OF PH

A kinetic balance equation for gelation time of silanes in a condensation reaction was defined, as in equation (A.1).

\[
\frac{d\xi}{dt} = k_c (1 - \xi)^n \zeta^m \tag{A.1}
\]

In equation (A.1), \( \xi \) is the conversion of silanes, \( k_c \) is the overall reaction rate constant, \( \zeta \) is the relative concentration of the catalyst to the initial concentration of silane, and \( m \) and \( n \) are the order of reactions with respect to silane and hydroxyl groups. Recall that condensation reactions took place under basic conditions in this thesis research. Therefore, \( \zeta \) is the relative concentration of \( \text{OH}^- \), as described in equation (A.2)

\[
\zeta = \frac{[\text{OH}^-]}{[S_0]} \tag{A.2}
\]

where \( [S_0] \) is the initial concentration of silanes. Equation (A.1) can be rearranged as follows:

\[
\frac{d\xi}{(1-\xi)^n} = k_c \zeta^m dt \tag{A.3}
\]

Integration of equation (A.3) with the initial condition of \( \xi=0 \) at \( t=0 \) yields equation (A.4)

\[
(1 - \xi)^{1-n} = (n - 1)k_c \zeta^m t + 1 \tag{A.4}
\]
If it is assumed that gelation occurred at the same conversion of silanes at $\xi = \xi_{gel}$, the gelation time, $t_{gel}$ becomes:

$$t_{gel} = \frac{1-(1-\xi_{gel})^{1-n}}{(1-n)k_c} \zeta^{-m}$$  \hspace{1cm} (A.5)

In equation (A.5), the term $\frac{1-(1-\xi_{gel})^{1-n}}{(1-n)k_c}$ is a constant so $t_{gel}$ is a function of $\zeta^{-m}$. Equation (A.6) is obtained from equation (A.5) by substitution of terms using equation (A.2).

$$t_{gel} = \Omega \frac{[s_0]^m}{[OH^-]^m}$$  \hspace{1cm} (A.6)

where $\Omega$ is a constant. With the definitions of $pOH = -\log [OH^-]$ and $pH+pOH=14$, $t_{gel}$ is derived as in equation (A.7).

$$\log t_{gel} = p - m \cdot pH$$  \hspace{1cm} (A.7)

In equation (A.7), $p$ is a constant.
APPENDIX B

A BASIC FORMULA FOR FILTRATION EFFICIENCY

The filtration efficiency in depth filtration is defined by equation (B.1).

\[ E = 1 - \exp(-E_s S) \]  \hspace{1cm} (B.1)

where \( E_s \) is single-fiber efficiency, and \( S \) is the fiber projected area describing physical characteristics of a filter medium. Equation (B.1) has the exponential term. The formula for filtration efficiency in depth filtration can be derived by the definition as follows - the variation of the particle number, \( dN \), after passing through a filter layer with an infinitesimal thickness, \( dl \), is proportional to the number of the particles, \( N \), and the thickness, \( dl \). This definition corresponds to equation (B.2).

\[ dN = -\alpha NdI \]  \hspace{1cm} (B.2)

where \( \alpha \) is a constant. Integration of equation (B.2) with the initial particle number, \( N_0 \), and the entire thickness of the filter, \( L \), as described in equation (B.3) yields equation (B.4).

\[ \int_{N_0}^{N} \frac{dN}{N} = -\int_{0}^{L} \alpha dl \]  \hspace{1cm} (B.3)

\[ N = N_0 e^{-\alpha L} \]  \hspace{1cm} (B.4)

Finally, equation (B.5) is obtained with the definition of filtration efficiency, \( E \).
\[ E = \frac{N_0 - N}{N_0} = \frac{N_0 - N_0 e^{-\alpha L}}{N_0} = 1 - \exp(-\alpha L) \] (B.5)

Equation (B.5) is the basic form for defining filtration efficiency in depth filtration. The constant \( \alpha \) is related to parameters, such as single fiber efficiency, filter packing density, and fiber diameter, etc.