PROPERTIES AND STRUCTURES OF SULFONATED SYNDIOTACTIC
POLYSTYRENE AEROGEL AND SYNDIOTACTIC POLYSTYRENE/SILICA
HYBRID AEROGEL

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Huan Zhang

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PROPERTIES AND STRUCTURES OF SULFONATED SYNDIOTACTIC POLYSTYRENE AEROGEL AND SYNDIOTACTIC POLYSTYRENE/SILICA HYBRID AEROGEL

Huan Zhang

Thesis

Approved: 

Advisor
Dr. Sadhan C. Jana

Accepted: 

Department Chair
Dr. Robert A. Weiss

Faculty Reader
Dr. Bryan Vogt

Dean of the College
Dr. Stephen Z.D. Cheng

Faculty Reader
Dr. Nicole Zacharia

Dean of the Graduate School
Dr. George R. Newkome

Date
ABSTRACT

This study focuses on hybrid aerogels of syndiotactic polystyrene (sPS) and silica where silica concentration is varied and silica condensation conditions are varied to produce various mesoporous materials. In addition, the study investigates hybrid materials obtained by coating sulfonated syndiotactic polystyrene on a cellulose filter paper.

In first part of this study, syndiotactic polystyrene is modified by sulfonation to enable further chemical modifications. Specifically, sulfonated syndiotactic polystyrene (ssPS) is coated on macroporous cellulose filter paper using a dip coating process, ssPS is turned into gel by thermoreversible gelation, and finally aniline is polymerized on ssPS strands to obtain a hybrid aerogel with electrical conductivity. The aerogels are recovered by removing the solvents under supercritical conditions. The ssPS aerogels are coated on cellulose filter materials to derive two benefits: first, to capitalize on the large surface area of ssPS aerogels and second, to exploit the mechanical strength of the cellulose filter.

In second part of this study, silane precursor is absorbed inside the macropores of sPS gels and silica gels are grown under both a two-step reaction and a one-step reaction. Type A silica aerogel is synthesized by acid-base catalyzed sol-gel method, while type B silica aerogel is prepared only by acid catalyzed sol-gel process. Type A silica gels exhibit pearl-necklace structure, while type B silica gels are composed of strand-like
silica particles. In the process, the mesoporous hydrophilic silica particles are combined with macro- and microporous hydrophobic sPS in single articles. This unique combination of organic and inorganic materials and their associated surface area and surface energy offer a number of attractive properties.

The sPS/silica hybrid aerogels are fabricated from different concentrations of sPS in solution and from different weight ratio of sPS to silica. The sPS/silica hybrid aerogels exhibit predominant pores located in the mesopore range (2~50 nm), and at higher silica content, silica particles undergo more aggregation as evident from larger fractions mesopore size (~15 nm). In contrast to native sPS aerogel, the compressive modulus of hybrid aerogel is increased up to 100%. In addition, the hybrid aerogels present specific surface area as high as 693 m²/g, high porosity, fast absorption and high absorption capacity of crude oil. Type A hybrid aerogels are composed of both fiber-like strands of sPS and pearl-necklace particles of silica. At low weight ratio of sPS to silica, the silica forms aggregates on sPS backbones as conformal coating. At higher weight ratio of sPS to silica, the silica particles not only coated on the polymer backbones, but also filled the macropores of sPS. Type B hybrid aerogels present fiber-like interpenetrating networks formed by sPS strands of 50-100 nm and silica strand of 200 nm.
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CHAPTER I

INTRODUCTION

Aerogels are highly porous, low density, solid state materials with three dimensional network structures. The network structures are produced first in the starting gels and aerogels are derived by removing the liquid component from gels under supercritical conditions. Aerogels attract significant academic and industrial interest owing to its extremely low density, high porosity, and high surface area. However, their applications are limited due to some of their inherent defects. For example, silica aerogels are fragile and friable materials. The structure of native silica aerogel can be easily crushed by a stress of 31 kPa \[1\]. Accordingly, many strategies emerged in last decades to tailor the network structures and to obtain reinforcement.

Aerogels have been made from polymers \[2–5\], transition metals \[6–9\], and montmorillonite clay/polymer composites \[10,11\]. Since first reported in the 1930s \[12\], silica aerogels have became most widely used and extensively studied due to versatile chemistry and remarkable properties, e.g., density \(\sim 3-350 \text{ mg/cm}^3\) \[13,14\], high porosity (>95%), large surface area (ca. 1000 m\(^2\)/g), low thermal conductivity (0.004-0.03 W/m \(\cdot\) K), low dielectric constant (1.1-2.2) \[15,16\], and low index of refraction (~1.05) \[17\]
Due to these interesting properties, silica aerogels found many potential applications in thermal insulation, energy media, molecular separation, high energy physics, to name a few [14],[18’22]. Two unfavorable properties limit the applications of silica aerogels – first, the hygroscopic nature and second, the inherent fragility of the silica networks. The network structures of silica aerogels are formed by the condensation reaction between "Si-OH" groups. However, not all Si-OH groups are fully condensed. Thus, silica aerogels can be easily destroyed by placing a small drop of water on its surface [23,24]. The hygroscopic silica particles absorb water into its pores. The capillary stress causes compressive stress and crushes the networks [25]. A native silica aerogel derived from tetramethoxysilane (TMOS) with a density of 0.12 g/mL can be completely shattered into dust under a small load of 31 kPa [1]. This is due to weak network structures formed by many "pearl necklaces" that are tied together by a limited number of "Si-O-Si" bonds at the necks of the secondary silica particles.

Many effective methods of reinforcement of silica aerogel have been developed. The most straightforward way is to increase the total number of connecting points between the secondary particles by increasing the density [26]. In addition, strengthening the neck region using multifunctional particles, and reinforcing the network with nanofibers showed large increases in mechanical strength [27-33]. It is reported [34,35] that silica aerogels can be effectively strengthened by a conformal coating of polymer on silica backbone. In this context, one can capitalize on the unique properties of silica aerogels if silica aerogels are efficiently packaged in another porous material and the carrier porous material provides mechanical integrity.
Since first reported by Daniel et al. in 2005 [36], syndiotactic polystyrene (sPS) aerogel has also attracted significant interest. sPS aerogel is a highly porous, high surface area and low density material obtained from physical sPS gel by replacing the liquid component with a gas by supercritical drying or freeze drying methods. The network structures of sPS aerogel are composed of three-dimensional polymeric strands, and the connectivity of network is obtained from the intermolecular physical bonding at the crystalline junctions [37]. sPS aerogels offer unique three-dimensional network structures, consisting of micro- (<2 nm) and macropores (>50 nm), formed by the intermolecular physical bonds at the crystalline junctions [36]. The micropores can trap volatile organic compounds, e.g., 1,2-dichloroethane in the crystalline nanocavities of sPS strands [37]. It is reported that \( \delta \)-form sPS aerogels are effective in adsorption of volatile organic compounds (VOC) [37, 38]. Hydrogen adsorption experiments indicated that the adsorption occurred in the ordered cavities of the nanoporous polymeric crystalline states [39,40] and the VOC diffusivity in \( \delta \)-form sPS aerogels with porosity of 98.5% is about 7 orders of magnitude faster than in \( \delta \)-form sPS films [37]. However, hydrophobicity of sPS chains, inferior compressive mechanical properties although much better than silica, and relative chemical inertness also limit the applications of sPS aerogels.

This thesis is divided as follows. Chapter II presents the review of associated literature. Chapter III discusses the properties of sulfonated syndiotactic polystyrene (ssPS) aerogels. Syndiotactic polystyrene was modified by introducing the sulfonic acid groups on the polymer main chain such that further chemical modification is later possible. The ssPS gel was then coated on cellulose filter to take advantage of its mechanical strength. A further modification was studied by polymerizing aniline on the ssPS-filter. It is reported
that highly conductive polyaniline/sulfonated polystyrene composites can be synthesized by in-situ polymerization of aniline within the sulfonated syndiotactic polystyrene matrices. The randomly distributed sulfonic acid groups were localized within the polyaniline backbones and formed the ionic domains which act as templates for protonation of aniline to form the aniline salt. Polymerization of aniline within these fixed ionic domains was initiated by allowing diffusion of an oxidant. In this study, the ssPS-filter was used as template for in-situ polymerization of aniline. The polyaniline domains formed on ssPS polymer strands. As a result, a conductive filter film was obtained, which can find application as a capacitor.

Chapter IV extends a novel type of hybrid aerogel reported by Wang and Jana. [25]. The sPS/silica aerogel was obtained by a two-step sol-gel process. sPS gel was first prepared and the silica precursor was absorbed into the sPS gel. Subsequently, the silanes were turned into gels. The silanes were converted into gels following two methods – first, a two-step acid-base catalyzed sol-gel process and second, a one-step acid catalyzed sol-gel process. The ratio of sPS to silica was varied to obtain several morphological forms, surface area, and compressive properties. Wang and Jana [25] used a fixed concentration of silane in this work. Also they followed a two-step sol-gel process to yield silica particles with pearl-necklace morphology. The sPS strands were prevented from buckling by the rigid silica pearl necklace particles grown inside the macropores. On the other hand, the sPS networks acted as cage for silica particles and prevented their brittle rupture.
CHAPTER II

REVIEW OF LITERATURE

2.1 What is an aerogel?

Aerogel is a highly porous, ultralight material derived from a gel where the liquid is replaced with a gas. The first aerogel was reported by Steven S. Kistler in 1931 [12]. Kistler dispersed colloidal silica particles in distilled water. The silica particles then connected with each other by chemical bonds during condensation of the silanol groups and formed a gel. The aerogel was obtained by using a supercritical drying process [12],[42] in which the liquid is removed above its critical point such that the distinct liquid and gas phases do not exist. A xerogel in comparison is obtained from a gel which is dried under ambient conditions. The absence of surface tension in supercritical drying preserves the perfect network structure of aerogel. Due to the presence of a large volume of gas, the aerogel has many outstanding properties, such as extremely low-density (3-150 mg/cm³) [14],[43], high porosity (>95%), large surface area (500-1200 m²/g), low dielectric constant (1.1-2.2) [14-16],[44,45], low thermal conductivity (ranging from 0.004 to 0.023 W/m·K), and low index of refraction (~1.05) [17]. In addition, they present different morphologies (monoliths or powders) and offer optical properties [46,47]. These remarkable properties promote a wide range of applications. Aerogels
found usage in high-energy particle physics [21],[48] to generate Cherenkov radiation by passing charged particles through the aerogel at speeds faster than the speed of light [49]. Recently, more academic and industrial attention is focused on the aerogels, and new applications have emerged in thermal and acoustic insulation [18],[20,21], catalysis [50], as storage media [51], and filtration media [37]. In addition, silica aerogels find applications in life sciences such as in dealing with biocatalysis [52-54], with a lipase enzyme, or in a process to detect a viral particle by immobilized bacteria [55-60].

2.2 Supercritical drying

An aerogel is obtained when the wet gel is dried under supercritical condition. The drying process is extremely important. During evaporation of the liquid within the pores of gel, the capillary stresses inevitably occur whenever gas-liquid menisci appear at the pore boundaries. Consequently, the aerogels tend to crack. Strategies to avoid cracking have been studied. There are three main techniques of drying of silica gels [61],[62] (shown in Figure 1.1):

1. Freeze-drying – this necessitates bypassing the triple point during drying.
2. Evaporation – this implies the crossing of the liquid-gas equilibrium curve during drying.
3. Supercritical drying – this necessitates bypassing the critical point.

In general, freeze-drying leads to cracked pieces or even powder-like products [63]. Evaporation without specific surface treatments and/or aging treatments [64] results in “dense” (e.g., $\rho > 0.25$ g/cm$^3$) [65] and even cracked materials called xerogel. Supercritical drying is considered a much better way of making aerogels, because it
eliminates capillary stresses. This also allows fabrication of aerogels with large dimensions. In supercritical drying, the solvent in the gel is removed above its critical point (shown in Figure 1), thus the distinction between the liquid and gas no longer exists. In principle, supercritical drying can be performed in different organic solvents in their supercritical state. The critical constants of the common drying fluids are listed in Table 1, where $T_c$ and $P_c$ are the critical temperature and pressure, respectively. Carbon dioxide is the most popular liquid used for supercritical drying, because of its very low critical temperature and pressure.

![Figure 1. Pressure-temperature phase diagrams. Supercritical drying (arrow 1) goes beyond the critical point of the working fluid. The arrow 2 shows ordinary drying, and the arrow 3 shows two phase changes in freeze-drying.](image)

**Table 1. Critical constant for some solvents [66].**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T_c$ (°C)</th>
<th>$P_c$ (MPa)</th>
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</thead>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1. Critical constant for some solvents (continued)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Constant</th>
<th>Value</th>
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<tbody>
<tr>
<td>Methanol</td>
<td></td>
<td>240</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td>243</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td>235</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td></td>
<td>374</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td></td>
<td>31</td>
</tr>
</tbody>
</table>

2.3 Silica aerogel

Silica aerogel are most widely used and extensively studied. The structure of silica aerogel strongly depends on the process of gelation. Two-step acid-base catalyzed sol-gel process is the most widely used synthesis method for silica aerogel.

2.3.1 Silica sol-gel chemistry

The sol-gel process is primarily used to produce a variety of inorganic networks from silica or metal alkoxide monomer precursors. This process usually involves hydrolysis and condensation of metal alkoxides, in which a colloidal suspension (sol) gradually evolves to form a network in a continuous liquid phase (gel) [67],[68]. The most widely used precursors for silica aerogel are alkoxyssilanes, such as tetraethxosilane (TEOS) and tetramethoxysilane (TMOS).

Hydrolysis occurs when a metal alkoxide (M-OR) reacts with water, forming a metal hydroxide (M-OH). It can proceed in either acidic or basic conditions. For acid-catalyzed reaction, the transition state is positively charged and the hydrolysis is strongly
accelerated [69] since the silicon atom is more susceptible to attack by water due to the protonated alkoxide, which reduces the electron density of connected silicon atom. The silicon is attacked by a water molecule from the opposite side of the protonated alkoxy group and the water molecule gains a positive charge because the alkoxy groups are more electron-donating than the hydroxyl groups. The mechanisms of hydrolysis reaction in acidic and basic conditions are shown in Figure 2.

Acid-catalyzed hydrolysis:

Base-catalyzed hydrolysis:
Figure 2. Hydrolysis mechanism of alkoxy silanes under acid/base catalyzed conditions

[67]

Two partially hydrolyzed molecules combine together in a condensation reaction to give a molecule of metal oxide species (M-O-M). The condensation reaction yields one water molecule. These reactions can proceed under either acidic or basic conditions. The condensation reaction occurs relatively slowly when catalyzed by acid. The rate of nucleophilic attack on a protonated silanol is slow because the nucleophiles tend to be inhibited in the presence of the acid. The base-catalyzed condensation reaction is widely used and its mechanism may involve penta- or hexa-coordinated silicon intermediates or transition states [70]. The schemes of condensation reaction under both acidic and basic conditions are shown in Figure 3.

**Acid-catalyzed condensation:**

![Acid-catalyzed condensation](image1)

**Base-catalyzed condensation:**

![Base-catalyzed condensation](image2)
2.3.2 Structure of silica aerogels

According to Iler, the process of basic sol-gel polymerization can be divided in three stages [69]. In the first stage, the monomers react to form particles. The second stage produces the growth of particles. In the third stage, the final gel is obtained, and the particles link together into chains to form the networks. In these three stages, many factors affect the structures of silica aerogel, such as pH, monomer concentration, water/monomer molar ratio, reaction time, etc. [67],[72]. For acid-catalyzed sol-gel process, the hydrolysis reaction is the fastest, and the condensation is slow. A silanol with more alkoxy groups produce more stable positively charged transition states since the alkoxy groups are more electron-donating than hydroxyl groups. Therefore, an open network structure is formed initially, which undergoes further hydrolysis and condensation reactions. Hence, the silica gels are formed by linear or randomly branched long chains. They ultimately present a bushy network as shown in Figure 4 (a). On the other hand, for base-catalyzed sol-gel process, the hydrolysis steps proceed rapidly and
the hydrolyzed specie undergo the faster condensation reactions. Thus, highly cross-linked sol particles are formed initially and link together to form a gel with large pores between the interconnected particles as shown in Figure 4 (b).

Figure 4. Gel network structure for acid and base catalyzed reactions [70] (Adapted from Ref 70).
2.4 Syndiotactic polystyrene aerogels

Since syndiotactic polystyrene (sPS) was synthesized by researchers at Idemitsu Kosan Central Research Laboratory in 1986 [73], it attracted strong interests in academia and industries because of its complex polymorphic behaviors under different conditions.

2.4.1 Syndiotactic polystyrene/solvent system

sPS/solvent system exhibit complicated behavior due to the complex polymorphic crystal shape of sPS. A lot of sPS/solvent systems have been well studied, such as the solution of sPS with toluene [74-75], benzene [76], chloroform [74],[77] chlorobenzene [78], 1,2-dichorobenzene, 1,2-dichloroethane [79], tetrahydrofuran [80], trans-decalin [81], cis-decalin [81], etc. The complex polymorphic behavior can be described in terms of the formation of different polymer-rich phases. The stable conformations in sPS crystalline forms are classified into two types. One is characterized by all-trans (T₄) planar zigzag chain conformation [82], and the other is characterized by the formation of polymer-solvent compound which adopt a trans-trans-gauche-gauche (T₂G₂) helix conformation [83]. The sPS can crystallize in four crystalline modifications. The crystalline in which the polymer chains adopt the T₄ conformation is called α-, β-modifications, and the γ-, and δ- modifications are characterized by the T₂G₂ helical conformation. As shown in Figure 5, the polymer-rich phase structure is determined by the result of the combined effect of thermodynamics and kinetics. In the case of good solvent, i.e., o-xylene, only the δ-phase (helical conformation) is formed at low polymer concentrations. At high polymer concentrations, the β-phase (planar zigzag conformation) is thermodynamically stable phase and the metastable δ-phase is observed when the
concentrated solutions are quenched first (Figure 5 (a)). In the case of poor solvent, the β-phase is the most stable phase over the whole concentration range, and quenching to room temperature results in the formation of δ-phase (Figure 5 (b)).
According to Roels et al. [78], the phase behavior of sPS in different solvent is strongly related to the solvent qualities. The different solvent can be listed in the following order with increasing solvent quality: decalin < 1, 2, 4-trichlorobenzene < o-xylene < 1, 2-dichlorobenzene < chlorobenzene < chloroform. The stability of the zigzag conformation phase which is considered as a “classical” crystalline phase increases with decreasing the quality of the solvent. This phase represents a stable phase in poor solvents, such as decalin. The helical phase shows an opposite solvent quality dependence, presenting stable phases in good solvent, such as chloroform. It is also reported [85] that the stability of the TTGG ordered conformation in both gel and crystalline phases are strongly dependent on the solvent-polymer interactions, including the kind of solvent and the gelation temperature.

Daniel et al. [86] studied the rheological behavior of sPS gels formed with 1-chlorotetradecane (CTD), a non-volatile bulky solvent. The gel presents a zigzag planar conformation. The rheological behavior was compared for s-PS/CTD gels with different crystalline phase. The rheological measurements have shown that the gels with the s(2/1) helical crystalline phase are generally more stable than trans-planar sPS gels. In fact, for equal polymer concentrations, the dynamic storage modulus $G'$ of the gel with helical crystalline phases is much higher than that of gels with trans-planar crystalline phases. This rheological behavior can be attributed to different morphologies. For the crystalline phase with planar zigzag conformation, the crystalline structure of the gel is observed as lamellar. For the crystalline phase with helical conformation, sPS gel shows fiber-like network structures.
2.4.2 Thermo-reversible gelation of sPS

Gel is a unique class of materials possessing network structures. According to the connection type, gels can be subdivided into two categories-chemical gels and physical gels. Like isotactic polystyrene (iPS) and atactic polystyrene (aPS), the sPS thermo-reversible gels can be obtained easily by heating sPS/solvent mixture till formation of a homogeneous solution, and cooling the solution down to room temperature. The solution then undergoes the sol-gel process, where the sPS polymer chains act as the framework and the liquid component is confined within the framework. The sol-gel transition can be reversed by cycling the temperature. According to Daniel et al. [87], the thermo-reversible gel can be defined as follows: (1) The gel is primarily a network which is considered as a large system of lines, tubes, etc. which are connected with each other. (2) The phase transition responsible for the creation of the gel junction must be first order. (3) The gels do not disaggregate when immersed in an excess of preparation solvent.

The process of thermo-reversible gelation of crystalline phases with helical conformation is investigated by small angle neutron scattering. It is found that the chains adopt a worm-like conformation in the gel state [88], indicating that the chains do not fold in the gel state as with the spherulitic structures. Since the structure of sPS differs significantly from that of isotactic polystyrene (iPS), a new model is offered for understanding the gelation phenomenon. This model considers that the helix stabilization and the unfolded polymer chains are attributed to the solvent molecules which are housed within the cavities formed by the adjacent phenyl groups of the helix. The only remaining possibility for the chains to organize is to form a fibrillar morphology as is expected for a gel.
2.4.3 Types of sPS aerogels

In the crystalline state, sPS polymer chains adopt two different conformations. One is all-trans planar zigzag (T4) conformation that can be separated into α- and β- crystalline forms. These can be obtained from melt or by annealing [8991]. Another one is s(2/1)2 helical conformation (T2G2) which is observed in the γ-, δ- and ε- crystalline forms of polymer[92]. The crystal structures of δ- and ε- forms with empty cavities are able to absorb low molecular weight guest molecules even from extremely diluted solutions.

The crystalline phase and the structures of sPS aerogels depend on the structure, e.g., cocrystalline or β form of the crystalline junctions formed at the start of gelation of sPS solutions [36]. The polymer-rich phase of sPS gels (type I gels) obtained with low-molecular-mass guest molecules [81] present a cocrystal phase. The sPS aerogel obtained from type I gels exhibit the nanoporous crystalline δ -form. For example, the sPS aerogel prepared from chloroform is δ-aerogel, where the polymer-rich crystalline phase is the δ-crystalline structure [36]. The crystalline structures of the aerogel derived from sPS/chloroform are inferred from X-ray diffraction pattern. The diffraction pattern displays strong reflections located at 2θ (CuKα) = 8.3, 13.5, 16.8, 20.7, and 23.5°, and a weak diffraction peak at 2θ≈10.6°, which represent the microporous δ-phase [36]. The crystalline phase of δ-aerogel possesses two identical cavities and eight styrene monomeric units per unit cell. The sPS β form aerogels showing a lamellar crystals structure are derived from β form gel, which is obtained with bulky solvent molecules [36] and shows pastelike solid state with low elasticity. The corresponding X-ray diffraction pattern displays strong reflections at 2θ=6.1, 12.3, 13.6, 18.5 and 20.2° [36].
The \( \varepsilon \) -aerogel is discovered recently by immersion of \( \gamma \) -aerogel (film or powder) in chloroform for 12 h followed by supercritical drying at a pressure of 20 MPa, temperature of 40°C for 2 h. [93]. The \( \gamma \) -aerogel is obtained from a sPS/1, 2-dichloroethane gel by supercritical carbon dioxide extraction of the solvent at 130°C. The X-ray diffraction pattern of \( \varepsilon \) -aerogel displays strong reflections at \( 2\theta = 6.9, 8.1, 13.7, 16.2, 20.5, 23.5 \) and 28.5° [2]. Unlike the \( \delta \)-aerogel with isolated cavities, the \( \varepsilon \) -aerogel presents channel-shaped cavities crossing the unit cells along the c-axis [2]. The SEM analysis shows that the obtained \( \varepsilon \) -aerogel exhibits open pore structures with macropore diameters in the range of 0.5-2 \( \mu \)m. The sPS aerogels are effective in adsorption of volatile organic compounds (VOC) from aqueous diluted solutions, only when a nanoporous crystalline phase (\( \delta \) or \( \varepsilon \)) is present and the guest uptake depends strongly on the guest molar volume. [93].
CHAPTER III

SULFONATED SYNDIOTACTIC POLYSTYRENE AEROGEL-COATED
MESOPOROUS SURFACES

3.1 Introduction

As presented in Chapter II, syndiotactic polystyrene (sPS) can easily form thermo-reversible gels formed with fiber-like strands. The network structure of sPS is composed of three-dimensional polymeric strands, where the connectivity of network is formed by the intermolecular physical bonding at crystalline junctions [37]. sPS aerogel is a highly porous, high surface area and low density material obtained from physical sPS gel by replacing the liquid component with a gas by supercritical drying or freeze drying methods. sPS aerogel has attracted significant academic and industrial interest not only for its outstanding properties, but also for its unique physically bonded network structures. However, the nature of high chemical inertness and lack of flexibility in planting functional groups limit applications of sPS aerogels.

Syndiotactic polystyrene can be functionalized by introducing the sulfonic acid groups in the polymer backbones. Hsu and coworkers [94] developed a sulfonation procedure of sPS. In their research, purified chloroform was used as the solvent and acetyl sulfate was used as the sulfonating reagent. The sulfonated syndiotactic polystyrene (ssPS) consists of non-polar polystyrene backbone and polar sulfonated acid groups which form a unique
microphase separated ionic-rich domains [95]. It was also reported [45] that highly conductive polyaniline/sulfonated polystyrene composites could be synthesized by in situ polymerization of aniline within the sulfonated syndiotactic polystyrene matrices. The randomly distributed sulfonic acid groups are localized within the polyaniline backbones and form the ionic domains which act as templates for protonation of aniline to form the aniline salt. The aniline within these fixed ionic domains is polymerized by allowing diffusion of an oxidant. The process is shown in schematically Figure 6.

![Figure 6. Schematic of polyaniline formation on sulfonated polystyrene.](image)

3.2 Experimental

In this part, the process of sulfonating sPS and process of making ssPS-coated filter gels were described, and several characterizations were used to analyze the properties of materials.
3.2.1 Materials

The syndiotactic polystyrene (sPS) used in these studies (molecular weight $M_w = 300,000$ g/mol, density $1.05$ g/cm$^3$) was purchased from Scientific Polymer Products, Inc. (Ontario, NY). The sPS in the form of pellets was grinded into powder for easy dissolution in solvents. Chloroform (>99% purity), sulfuric acid (96.2% purity), acetic anhydride (94%) were purchased from Fisher Scientific. Chloroform (400 mL) used as the solvent was washed with 300 mL of distilled water at least 4 times to remove the ethanol preservative. Figure 7 illustrates the chemical structure of sPS.

![Figure 7. Chemical structure of sPS](image)

Raw materials for synthesize polyaniline. Aniline (>99%) and ferric chloride were obtained from Fisher Scientific. Whatman, Grade 1 filters were used as the macroporous surfaces to support coating layers of ssPS.

3.2.2 Preparation of sulfonating agent

Chloroform (35 mL) was taken into a vial (50 mL) and acetic anhydride (0.108 mol) was added to it. The vial was put into ice bath. Sulfuric acid (0.036 mol) was slowly added into the solution under vigorous stirring for about 5 minutes. The solution was then diluted with chloroform in a 50 mL volumetric flask at room temperature. In this study,
the molar ratio of acetic anhydride and sulfuric acid was kept at 3:1. It was assumed that sulfuric acid reacted completely and produced acetyl sulfate as the active component of the sulfonating agent.

3.2.3 Process of sulfonating sPS

The sPS was sulfonated in a 1000 mL three-neck flask. The flask was immersed in the oil bath and equipped with a dropping funnel and condenser shown in Figure 8. Chloroform (400 mL) and sPS (6 g) were added into the flask. The mixture was heated at 180 °C under vigorous stirring by using a stir bar. When all the sPS was dissolved in chloroform, the solution was cooled to 70 °C. The sulfonating agent was added into solution slowly by using the dropping funnel. After the solution was stirred for 3 hours, the reaction was terminated by adding 10 mL methanol. The sulfonated sPS (ssPS) then was precipitated in deionized water and the precipitate was washed by deionized water several times until the pH of the mixture did not change any more. The ssPS was dried in the vacuum oven 2 days at 80 °C.
3.2.4 Measurement of the degree of sulfonation

In this study, the degree of sulfonation was analyzed by using the methods reported by Li and coworkers [96]. The degree of sulfonation was determined by titration process and is defined as the mole percentage of styrene units that was sulfonated, and was calculated using following equation:

\[
\text{Degree of sulfonation} \% = \frac{104nV}{m - 81nV} \times 100
\]  

In equation (1), \(n\) and \(V\) are the concentration and volume of sodium hydroxide used in titration, and \(m\) is the weight of ssPS sample. The numbers 104 and 81 are the molar mass of styrene unit and sulfonated acid group, respectively. ssPS with 10 mol\% sulfonation was used in the rest of the work.
3.2.5 Process of making ssPS-coated-filter gels

Sulfonated syndiotactic polystyrene was added to THF in a hermetically sealed vial. The mixture was heated to 100 °C in the oil bath under vigorous stirring. When all the ssPS was dissolved in THF, a yellow, homogenous solution was obtained. Then the boiling solution was cooled to 70 °C. By using a dip coater, the filter was immersed into the solution for one minute and taken out. In this manner, a coating layer of ssPS formed on the surface (shown in Figure 9). The thickness of ssPS coated on the surface of the filter was controlled by the speed of pulling of the filter and the viscosity of the solution. The filter was then transferred to ethanol in a sealed bottle for 24 hours where the gelation process occurred.

![Schematic view of dip coater.](image-url)
3.2.6 Polymerization of aniline on the ssPS-coated-filter aerogel

After the ssPS gelled completely on the surfaces of the filter, the solvent ethanol was exchanged with distilled water. Then, the ssPS-coated-filter was immersed in 0.35 mol/L aniline aqueous solution for 12 hours at room temperature so that the ssPS-coated-filter had adsorbed enough aniline monomer. The ssPS-coated-filter was washed by distilled water to remove excess aniline and immersed in 1.0 mol/L FeCl$_3$ aqueous solution. After 12 hours, the material was taken out and the dark-green PANI-coated-filter was obtained as shown in Figure 10. The filter was washed with 1.0 mol/L HCl aqueous solution and subjected to solvent exchange with ethanol.

![Figure 10](image.png)

Figure 10. The PANI-coated-filter is shown in graph (a). The cellulose filter shown in graph (b).

The PANI-coated-ssPS aerogels were obtained after supercritical drying. First, the solvent in the gels was exchanged with liquid CO$_2$ and the liquid CO$_2$ was removed after taking the system above its critical point. For this purpose, the gels were soaked in liquid CO$_2$ for 30 minutes, followed by drainage of the solvent, and refilling the specimen with fresh liquid CO$_2$ [97]. This process was repeated 4 times and the gels were heated to
50 °C and kept at 11.5 MPa pressure for 1 hour above the critical point of \( \text{CO}_2 \) (31 °C, 7.4 MPa) [98]. The aerogels were obtained after all \( \text{CO}_2 \) in the chamber were vented under the supercritical condition.

3.2.7 Characterization methods

3.2.7.1 Bulk density, skeletal density, and porosity

The bulk density of aerogels was obtained by measuring the mass and volume of the circular disc specimens. The radius and thickness of circular disc specimens were measured by a micrometer with a tolerance of 0.01 mm. The skeletal density was obtained by using an Accupyc 1340 Helium Pycnometer (Micrometrics Instrument Corp). The porosity was calculated by using the following equations:

\[
P = (1 - \frac{\rho_b}{\rho_s}) \times 100\%
\]

\[
\rho_b = \frac{4m}{\pi D^2 t}
\]

In equations (2) and (3), \( P \) is porosity, \( \rho_b \) and \( \rho_s \) are bulk density and skeletal density, respectively, \( m \) is the weight of the aerogel specimen, and \( R \) and \( t \) are the radius and thickness, respectively.

3.2.7.2 Morphology

The morphology of aerogels was characterized by scanning electron microscopy (SEM), JEOL JSM5310 with operating voltage 1 kV. The morphologies of surface and cross-section of the specimens were observed. The PANI-coated aerogels were fractured after dipping in liquid nitrogen for 10 minutes and the specimens were then mounted on an aluminum stub by using adhesive carbon tape. The fractured surface and cross-section
of the specimens were then sputter-coated with silver by using Sputter Coater, Model ISI 5400.

3.2.7.3 Surface properties

The surface area, average pore size, and pore size distribution were obtained from the analysis nitrogen adsorption-desorption isotherms using Micromeritics Tristar II 3020 Analyzer. The surface area of the specimen was calculated by using Brunauer-Emmet-Teller (BET) method and the pore size distribution was calculated by using Brunauer-Joyner-Halenda (BJH) method.

3.2.7.4 Thermal properties

The thermal stability of specimens was investigated using a thermogravimetric analysis (TGA) 2050 device (TA Instrument, New Castle, DE) under nitrogen atmosphere. The specimens were placed in a platinum pan and heated from room temperature to 800 °C at a heating rate of 20 °C/min. In a mass versus temperature plot, the temperature at the onset of thermal degradation or 5% mass loss was estimated.

3.2.7.5 Electrical resistivity

The resistivity of PANI-coated aerogels was measured by using a Keithley picoammeter (Keithley 487) and Model 8009 Resistivity Test Fixture. The volume resistivity ($\sigma_v$) was calculated from the following equation:

$$\sigma_v = \frac{32.86}{t} R_v; \text{Ohm-centimeter}$$  \hspace{1cm} (4)

In equation (4), $\sigma_v$ is the volume resistivity, $t$ is the thickness of the specimen in centimeters, and $R_v$ is the resistance measured by Keithley picoammeter.

The surface resistivity is given as:
\[ \sigma_s = 13.35 R_s, \text{ in Ohm} \]  \hspace{1cm} (5)

where \( \sigma_s \) is the surface resistivity of the sample, \( R_s \) is the resistance measured by Keithley picoammeter.

In equations (4) and (5), the numerical constants 22.9 and 53.4 are based on the physical dimensions of the electrodes of the Model 8009.

3.3 Results and discussion

3.3.1 Density

The physical dimensions, density, and porosity of cellulose filter and filter coated with ssPS aerogel are presented in Table 2. The thickness of the filter increased by 33.3 percent due to coating layer of ssPS aerogel, while the mass increased by 27.8 percent. This is supported by a reduction of bulk density – the bulk density decreased from 0.478 g/cm\(^3\) for the filter to 0.414 g/cm\(^3\) for ssPS-coated filter. In addition, the skeletal density decreased by 4.2 percent. In addition, the skeletal density of ssPS (1.138 g/cm\(^3\)) is lower than that of the cellulose filter (1.58 g/cm\(^3\)). It is apparent that the coating of ssPS aerogel caused a 4.3% increase in porosity of the ssPS-coated filter.

Table 2. Physical properties of cellulose filter and ssPS-coated-filter aerogel. The specimens of radius 24.52 mm were used in measurement.

<table>
<thead>
<tr>
<th></th>
<th>Cellulose filter</th>
<th>ssPS-coated-filter aerogel</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass</td>
<td>0.1627 g</td>
<td>0.1875 g ((\uparrow 15.2%))</td>
</tr>
<tr>
<td>radius</td>
<td>24.52 mm</td>
<td>24.52 mm</td>
</tr>
</tbody>
</table>
Table 2. Physical properties of cellulose filter and ssPS-coated-filter aerogel. The specimens of radius 24.52 mm were used in measurement (continued).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>0.18 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24 mm (↑33.3%)</td>
<td></td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.478 g/cm$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.414 g/cm$^3$ (↓ 13.4%)</td>
<td></td>
</tr>
<tr>
<td>Skeletal density</td>
<td>1.5807 ± 0.00189 g/cm$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5144 ± 0.0058 g/cm$^3$ (↓ 4.2%)</td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>69.7%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>72.7% (↑ 4.3%)</td>
<td></td>
</tr>
</tbody>
</table>

3.3.2 Morphology

The morphology of the cellulose filter, sPS-aerogel filter, sulfonated sPS-coated-filter aerogel, polyaniline-coated-filter aerogel was characterized by SEM. Representative images are shown in Figure 11, Figure 12, and Figure 13.
Figure 11. SEM images of the surfaces of cellulose filter (a), sPS-coated-filter aerogel (b), ssPS-coated-filter aerogel (c), and polyaniline-coated-filter aerogel (d).
Figure 12. SEM images of the cross-section of cellulose filter (a), ssPS-coated-filter aerogel (b). The internal space of the ssPS-coated-filter aerogel is shown in (c).
Figure 13. SEM images of the structure of sPS aerogel (a), ssPS aerogel (b), and polyaniline-coated aerogel (c).

It is observed in Figure 11 (a) that the surface of the filter is covered by interconnected cellulose fibers of typical diameter $\sim 20 \mu m$. Compared with sPS-aerogel as shown in Figure 13 (a), the surface of ssPS-aerogel appears much rougher (Figure 13 (b)). The polyaniline appears as small particles on the surfaces of ssPS aerogel as shown in Figure 11 (d). From Figure 12 (b) and (c), it is seen that the ssPS aerogel coated the surface of the filter, and some strands of ssPS also diffused inside the cellulose fiber networks. Figure 13 (a) and (b) show that the sPS aerogel and ssPS aerogel have similar fibrillar structure. However, a denser fibrillar structure is observed in the case of sPS. The less dense packing in the case of ssPS is attributed to the loss of crystallinity of sPS due to sulfonation. In Figure 13 (c), it is seen that polyaniline formed aggregates on the polymer strands and appeared as small particles.
3.3.3 Surface properties

The surface area and pore size distribution of the cellulose filter, ssPS-coated-filter aerogel, and polyaniline-coated-filter aerogel were characterized by the nitrogen adsorption–desorption isotherms as shown in Figure 14. According to IUPAC classification, the porosity is identified in a wide range of diameter including micropores (< 2 nm), mesopores (2-50 nm), and macropores (> 50 nm) [99]. For P/P₀ < 0.06, the rise in quantity adsorbed is due to adsorbing molecules which are interacting with the micropores. Note that the micropores are the most energetic regions of the solid surfaces. The contributions of micropores to the adsorption process ceases after the knee in the curves (point K in Figure 14). The multilayer adsorption on the surfaces of mesopores and macropores show a low slope region in the middle of the isotherm. The hysteresis loop at the end of the isotherm is due to capillary condensation of nitrogen in mesopores. The pore size distribution determined using the BJH method is shown in Figure 15. The BET surface area of cellulose filter, ssPS-coated-filter aerogel, and polyaniline-coated-filter aerogel are listed in Table 3. It is seen that the surface area of cellulose filter is extremely small (0.95 m²/g) compared to the aerogel specimens. However, the surface area increases by about 60 times when the mass of the filter only increases by 15.2% after ssPS aerogel is coated onto it. The surface area coated with polyaniline reduced to 12 m²/g which is still a factor 12 higher than the cellulose filter.
Figure 14. Nitrogen adsorption-desorption isotherms at 77 K of cellulose filter, ssPS-coated aerogel and polyaniline-coated-filter aerogel.

Figure 15. Pore size distribution of cellulose filter, ssPS-filter aerogel and polyaniline-ssPS-filter aerogel.
Table 3. Surface area and average pore size of different materials.

<table>
<thead>
<tr>
<th></th>
<th>Cellulose filter</th>
<th>ssPS-coated filter aerogel</th>
<th>Polyaniline-coated filter aerogel</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface area: m²/g</td>
<td>0.95</td>
<td>60</td>
<td>12</td>
</tr>
<tr>
<td>Average pore size:</td>
<td>12</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>nm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3.4 Thermal property

The thermal stability of sPS, ssPS with 10 mol% sulfonation, cellulose filter, ssPS-coated-filter aerogel, and polyaniline-coated-filter aerogel was investigated as reflected from the TGA traces in Figure 16 and Figure 17. It is observed in Figure 16 that in comparison to sPS, the onset temperature of the mass-loss process reduced slightly for ssPS. Figure 17 shows that the decomposition temperature of cellulose filter is higher than that of ssPS-coated filter aerogel and polyaniline-coated-filter aerogel due to lower decomposition temperature of ssPS and polyaniline.
Figure 16. TGA traces of sPS and ssPS.
3.3.5 Electrical resistivity

The aerogels specimens were trimmed to a rectangular shape for facilitating electrical conductivity measurement. Figure 18 shows the relationship between the voltage and current. It is apparent that the polyaniline-coated aerogel is a conductive material.

The surface and volume resistivity of the polyaniline-coated-filter aerogel was obtained from the following relationships:

\[
\sigma_s = 13.35R_s = 13.35 \times 75 \Omega = 1016k\Omega
\]  \hspace{1cm} (6)
\[
\sigma_v = \frac{32.86}{t} R_s (\text{ohm} - \text{centimeter}) = \frac{32.86}{0.033 \text{cm}} \times 0.23 \Omega = 229 \Omega \cdot \text{cm}
\]  \hspace{1cm} (7)

where, \( \sigma_s \) and \( \sigma_v \) are the surface resistivity and volume resistivity, respectively, and \( t \) is the thickness of the aerogel, \( R_s \) and \( R_v \) are the resistance value measured by Keithley picoammeter.
Figure 18. The relationship between the voltage and current. ssPS-coated aerogel is shown in graph (a), polyaniline-coated aerogel is shown in graph (b).
CHAPTER IV

TAILORING MORPHOLOGY AND STRUCTURE PROPERTIES OF
SYNDIOTACTIC POLYSTYRENE-SILICA HYBRID AEROGELS

4.1 Introduction

Aerogels are characterized by high porosity, low density, large pore surface area, fractal pores, and low thermal conductivity. However, the synthesis process and conversion of parent gel into an aerogel structure are often cumbersome. The pore networks and the pore volumes of the gel are sometimes compromised in the drying process if supercritical conditions are not used.

Silica aerogel have became most widely used and extensively studied due to versatile chemistry and remarkable properties. However, the hygroscopic nature and the inherent fragility of the silica networks strongly restrict the application of silica aerogel. The silica aerogel can be easily destroyed by placing a small drop of water on its surface due to the residual “Si-OH” bonds in the silica particles [23],[24]. The fragile property of native silica aerogel is due to weak network structures formed by many “pearl necklaces” that are tied together by a limited number of “Si-O-Si” bonds at the necks of the secondary silica particles. In past decades, many studies have been devoted to polymer reinforcement and surface modification of silica aerogels. In 1990s, the silica aerogel derived from tetraethoxysilane (TEOS) was first successfully reinforced by reacting with
hydroxyl-terminated polydimethylsiloxane (PDMS) [12]. The surface area of this aerogel was up to 1200 m$^2$/g and the strength of reinforced aerogel was better than that of corresponding silica aerogel. In 2000s, Leventis and coworkers [100],[101] reported that the silica aerogels could be reinforced by reacting the residual –OH groups on the surfaces with the isocyanates. By this method, the weak neck zone between the particles was coated by crosslinked polyurethane. In this research, two different methods were used to synthesize silica aerogel: one-step base catalyzed sol-gel process and two-step acid-base catalyzed sol-gel process. The reinforced silica aerogel required more than ~30 times breaking force than that of corresponding native aerogel with increasing density up to ~3 times. The silica aerogel reinforced by incorporating methyltrimethoxysilane (MTMS) and bis(trimethoxysilylpropyl)amine (BTMSPA) was studied by Nguyen et al. [29]. The dipropylamine spacer from BTMSPA worked as both a flexible linking group and a reactive site via its secondary amine to reacting with a tri-isocyanate. The compressive strength increased owing to the tri-isocyanate which provides an extra degree of branching. According to Wang and Jana [25], the compressive modulus of silica aerogel increased when the sPS gel grew in the silica gel.

In this chapter, the pores of sPS gel were used to grow silica aerogel. The organic-inorganic hybrid aerogels were synthesized by “growing gel in a gel”. Two types of silica aerogel networks were prepared. The work specifically focused on the effects of silica content on pore surface area, porosity, hydrocarbon liquid absorption capacity, and compressive properties of the hybrid aerogel.
4.2 Experimental

4.2.1 Materials

All solvents and reagents were used as received. Syndiotactic polystyrene pellets (molecular weight $M_n$ =300,000 g/mol, density 1.05 g/cm$^3$) were purchased from Scientific Polymer Products, Inc. (Ontario, NY). The sPS pellets were ground into powder for easy dissolution in solvents. Tetraethylorthosilicate (TEOS, reagent grade, 98%), ammonium hydroxide solution (28-30%, NH$_3$ basis), and nitric acid (purity 64-66%) were purchased from Sigma Aldrich. Reagent grade tetrahydrofuran (THF) and ethanol were obtained from Fisher Scientific. Figure 19 shows the chemical formula of TEOS.

\[
\begin{align*}
\text{H}_5\text{C}_2\text{O} & \quad \text{Si} \quad \text{OC}_2\text{H}_5 \\
\text{OC}_2\text{H}_5 & \\
\end{align*}
\]

Figure 19. Chemical formula of TEOS.

4.2.2 Preparation of sPS/Silica Hybrid Aerogels

As the gelation mechanisms of sPS and silica are quite different, it is hard to obtain a sPS/silica hybrid aerogel by simply mixing these two gel precursor materials together. In this work, first, sPS gel was prepared by thermoreversible gelation. Second, the silica gel precursor, TEOS was absorbed into the macropores of sPS gel and allowed to undergo hydrolysis and condensation reactions to produce silica particle networks. In this work, two types of silica aerogel were grown in sPS gel. In Type A, silica aerogel was
synthesized by acid-base catalyzed sol-gel process. In Type B, silica aerogel was prepared by acid catalyzed hydrolysis and condensation process. The hybrid aerogel specimens are denoted as “sPS-g/mL-TEOS-mol/L” in the rest of the work. For example, sPS-0.02-TEOS-0.25 aerogel represents the hybrid aerogel derived from 0.02 g/mL solution of sPS and 0.25 mol/L solution of TEOS. Eight different hybrid aerogel samples were prepared in this study including two different concentrations (0.02, 0.04 g/mL) of sPS and four different concentrations (0.1, 0.25, 0.5, 0.7 mol/L) of TEOS.

For synthesis of Type A hybrid aerogel, here we describe the process of a representative aerogel specimen, sPS-0.02-TEOS-0.25. sPS power (0.2 g) was dissolved in THF (10 mL) in a sealed vial and the mixture was heated to 160 °C in oil bath under vigorous stirring until the sPS power dissolved completely and a transparent, homogeneous solution was obtained. The solution was transferred to a cylindrical mold and allowed to stand for 24 hours at room temperature to obtain sPS gel. The gel was immersed in ethanol to remove THF from the gel.

Solution A containing TEOS (8.3332 g), ethanol (100 mL), and deionized water (2.16 mL) and solution B containing ethanol (46.04 mL) and deionized water (2.88 mL) were prepared separately. The sPS gel was immersed in solution A for 12 hours so that TEOS and deionized water could diffuse inside the gel. Subsequently, the pH of solution A was adjusted to a value of 2.0 by adding nitric acid. The gel was kept in this solution for 1.5 h to conduct hydrolysis of TEOS within the gel network. The sPS gel with hydrolyzed TEOS was transferred to solution B and the pH was adjusted to 9.0 using ammonium hydroxide so that silica sol could transform into silica gel by silane condensation. The gel was allowed to stand in solution B for 24 h for complete gelation of the silane. The
residual water and TEOS were removed by washing hybrid gel with ethanol five times. The hybrid gel was dried using supercritical carbon dioxide at 50 °C and 11.5 MPa pressure. The hybrid aerogel samples were kept in a vacuum oven overnight to remove residual solvent.

For Type B hybrid aerogel, the preparation process of specimen of sPS-0.02-TEOS-3 is presented. The sPS gel was first synthesized by thermoreversible gelation scheme described above. The solution of TEOS was prepared by dissolving TEOS (62.499 g) and deionized water (27 mL) in ethanol. The pH of solution of TEOS was then adjusted to a value of 1 by adding nitric acid. sPS/silica hybrid gel was formed after keeping the sPS gel in a solution of TEOS for 2 weeks. The hybrid aerogel was obtained by solvent exchange and supercritical drying.

4.2.3 Characterization

4.2.3.1 Bulk density, skeletal density, and porosity

The dimensional and structural changes induced by hybrid aerogel preparation methods are shown in Table 1. The bulk density $\rho_b$ of hybrid aerogels was obtained by measuring the mass and volume of the each cylindrical specimen. The skeletal density $\rho_s$ was obtained using an Accupyc 1340 Helium Pycnometer (Micrometrics Instrument Corp). The diameter shrinkage $\delta$ is defined as the change of diameter from hybrid gels to the diameter of corresponding aerogels samples. The porosity $P$ of hybrid aerogel and bulk density $\rho_b$ were calculated using the equation (2), (3) and the diameter shrinkage $\delta$ was calculated using the following equations:

$$\delta = 1 - \frac{D}{D_o}$$

(8)
In equations (8), $D$ is diameter of the hybrid aerogel specimen measured by a micrometer with a tolerance of 0.01 mm, and $D_0$ is the diameter of the hybrid gel.

4.2.3.2 Thermogravimetric analysis

The thermal stability of hybrid aerogels was studied by subjecting the specimens to thermal scans in thermogravimetric analyzer (TGA), model TGA 2050 device (TA Instrument, New Castle, DE) under nitrogen atmosphere. The temperature range was from room temperature to 800 °C at a heating rate of 20 °C/min.

4.2.3.3 Nitrogen adsorption-desorption measurement

The surface area and pore size distribution were obtained by analyzing nitrogen adsorption-desorption isotherms [10] using Micromeritics Tristar II 3020 Analyzer. The surface area was calculated using Brunauer-Emmet-Teller (BET) method and the pore size distribution was calculated using Brunauer-Joyner-Halenda (BJH) method.

4.2.3.4 Morphology

The morphology of hybrid aerogels was examined by scanning electron microscope (SEM), JEOL JSM5310 with operating voltage 5 kV. For this purpose, the hybrid aerogel specimens were fractured at room temperature and mounted on an aluminum stub using adhesive carbon tape. The fractured surface was then sputter-coated with silver under argon atmosphere by using Sputter Coater, Model ISI 5400.

4.2.3.5 Compressive test

The compressive modulus was obtained from stress-strain data using Instron 5567 (Canton, MA) tensile tester following ASTM D595 method. The crosshead speed for the measurement was chosen as 1.27 mm/min.
4.2.3.6 Contact angle measurement

The contact angles of hybrid aerogel were measured using a Rame Hart contact angle goniometer (model 500) under ambient conditions. The cylindrical aerogel specimens were compressed into discs at 3500 psi to eliminate the effect of pore structures. In static sessile drop method, a 6μL drop of water and a 4μL drop of hydrocarbon oil were placed on the surface of aerogel specimens. The values of contact angles of water and hydrocarbon oil were measured by using the ImageJ software. Five measurements were taken for each aerogel specimen.

4.3 Results and discussion

In this part, the properties of type A hybrid aerogels and type B hybrid aerogels were discussed, separately.

4.3.1 Type A hybrid aerogels

The physical properties, thermal stability, morphology property, pore size distribution, surface area, compressive properties, contact angles, oil and water absorption were discussed as following.

4.3.1.1 Density, shrinkage, and porosity

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Diameter shrinkage (%)</th>
<th>Bulk density (g/mL)</th>
<th>Skeletal density (g/mL)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-0.02</td>
<td>12.3</td>
<td>0.030</td>
<td>1.0678 ± 0.0040</td>
<td>97.2</td>
</tr>
</tbody>
</table>

Table 4. Composition and properties of sPS/silica hybrid aerogels
As shown in Table 4, the bulk density of the aerogels increased with an increase of concentration of TEOS. This is due to an increase in the amount of silica particles residing in the fixed volume of marcopores of sPS. The skeletal density of native silica
aerogel is larger than that of sPS aerogel. Thus, the value of skeletal density of hybrid aerogel samples shows the same trend as bulk density with an increase in the concentration of TEOS. All aerogel specimens exhibit high values of porosity as listed in the Table 4. However, a slight reduction of porosity is observed in the case of hybrid aerogels, corresponding to an increase of bulk density. The shrinkage of hybrid aerogel is much smaller compared to native sPS aerogel. For example, the value of shrinkage of sPS-0.02 aerogel is 12.3% which is about four times the shrinkage observed for sPS-0.02-TEOS-0.7 aerogel. This is attributed to rigid silica particles filling the pores of hybrid aerogel. This rigid networks prevent the weak networks of sPS from shrinkage.

4.3.2 Thermal stability

![Diagram showing thermal stability](image_url)
From left to right, the concentrations of TEOS decrease from 0.7 mol/L to zero.

The thermal stability of sPS aerogel and hybrid aerogels are inferred from the TGA traces as shown in Figure 20. It is observed that sPS aerogel began to decompose at around 400 °C, due to degradation of polystyrene backbone; complete decomposition occurred at around 450 °C. Silica aerogels also show small weight loss at around 100 °C
due to residual moisture and greater weight loss at around 300 °C due to decomposition of unreacted TEOS and methyl groups [102]. The residues from TGA analysis – all silica – yield information on the amount of silica present in hybrid aerogels. Two trends are observed from TGA traces in Figure 20 (a) and (b). First, the weight percent of silica in hybrid aerogel increased with the increase of concentration of TEOS in solution for a given concentration of sPS in THF solution. Second, the amount of silica in hybrid aerogel decreased with an increase of concentration of sPS in THF solution. For example, the weight percent of silica in sPS-0.02-TEOS-0.25 aerogel specimen is much higher than that of sPS-0.04-TEOS-0.25 aerogel specimen, or of sPS-0.04-TEOS-0.5 aerogel specimen. One can attribute such observation to a reduction of macropore volume defined by sPS concentration – the higher density of sPS strands at 0.04 g/mL polymer concentration left much less pores for absorption of TEOS [103].

Figure 21 shows the images of aerogels before and after heated to 800 °C in air. It is seen that the native sPS aerogel decomposed completely after the heat treatment, while the hybrid aerogels yielded continuous silica aerogel structure as residue. This proves that the hybrid aerogels possess a co-continuous network structure.

4.3.3 Morphology property
The morphology of aerogels of sPS, hybrid material, and native silica are compared in Figure 22. Figure 22(a) shows that sPS aerogel had fiber-like network structure formed by sPS strands of 50-100 nm in diameter. The macropores (>50 nm) of sPS aerogel are readily apparent in Figure 22(a). The native silica aerogel in Figure 22(f) shows aggregated particles of typical diameter 85-100 nm. It is obvious that the hybrid aerogels were composed of both fiber-like strands of sPS and pearl-necklace particles of silica. At low concentration of TEOS, the silica particles could not form gel networks. Instead, they formed aggregates on sPS backbones as conformal coating (Figure 22b-c). At higher concentration of TEOS, however, the silica particles not only coated on the polymer backbones, but also filled the macropores of sPS, as evident from Figure 22 (d-e).

4.3.4 Pore size distribution and surface area

The data on surface area and pore size distribution of native aerogel and hybrid aerogel obtained from nitrogen adsorption-desorption isotherms are presented in Table 5 and Figure 23 respectively.
Figure 23. Pore size distribution of two series of hybrid aerogels.

Table 5. Surface areas of native sPS aerogel and hybrid aerogel.

<table>
<thead>
<tr>
<th>TEOS-0</th>
<th>TEOS-0.1</th>
<th>TEOS-0.25</th>
<th>TEOS-0.5</th>
<th>TEOS-0.7</th>
</tr>
</thead>
</table>

52
Table 5. Surface areas of native sPS aerogel and hybrid aerogel (continued).

<table>
<thead>
<tr>
<th></th>
<th>398 m²/g</th>
<th>432 m²/g</th>
<th>610 m²/g</th>
<th>632 m²/g</th>
<th>693 m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sPS-0.04</td>
<td>368 m²/g</td>
<td>417 m²/g</td>
<td>538 m²/g</td>
<td>550 m²/g</td>
<td>618 m²/g</td>
</tr>
</tbody>
</table>

The higher surface area of hybrid aerogels compared to sPS is due to the contributions of mesopores of silica. The surface area increases with silica concentration. Figure 23 shows that native sPS aerogel has no predominant pores located in the mesopores range (2~50 nm). The pore size distributions of aerogel specimens sPS-0.02-TEOS-0.1 and sPS-0.02-TEOS-0.25 show a small peak in the mesopores zone. These mesopores are contributed by the silica aerogel containing a predominant pore size of around 9 nm [1]. At higher silica content, silica particles underwent more aggregation as evident from larger mesopores size (~15 nm), e.g., for the aerogel specimen sPS-0.02-TEOS-5. Mesopores are much more prominent in the case of aerogel specimen sPS-0.02-TEOS-7. The hybrid aerogels at higher sPS concentration show similar trends. However, in contrast to native silica aerogel, all hybrid aerogels show larger predominant mesopores. We attribute this to restricted growth of silica networks with the macropores of sPS, e.g., 30 nm predominant pore of sPS-0.04-TEOS-0.7 aerogel compared to ~20 nm for sPS-0.02-TEOS-0.7 aerogel.

4.3.5 Contact angle

The contact angles of water on compressed disc of aerogel specimens are shown in Table 6, and the contact angles of hydrocarbon oil are shown in Table 7.
Figure 24. Images of aerogels exposed to water. (a) 0.7 mol/L silica aerogel, sank to the bottom of water and collapsed under a tender touch. (b) sPS-0.04-TEOS-0.7 aerogel, floated on the surface of water, kept a strong structure after immersed in the water using an external force.

Table 6. Contact angles of water for sPS-0.02-TEOS aerogels.

<table>
<thead>
<tr>
<th>sample name</th>
<th>sPS-0.0</th>
<th>sPS-0.02-TEO</th>
<th>sPS-0.02-TEO</th>
<th>sPS-0.02-TEO</th>
<th>sPS-0.02-TEOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>contact angle °</td>
<td>102.3</td>
<td>100.5</td>
<td>95.7</td>
<td>82.5</td>
<td>75.2</td>
</tr>
</tbody>
</table>

Table 7. Contact angles of hydrocarbon oil for sPS-0.02-TEOS aerogels

<table>
<thead>
<tr>
<th>sample name</th>
<th>sPS-0.02</th>
<th>sPS-0.02-TEO</th>
<th>sPS-0.02-TEOS</th>
<th>sPS-0.02-TEOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>contact angle °</td>
<td>2.4</td>
<td>7.7</td>
<td>10.4</td>
<td>13.4</td>
</tr>
</tbody>
</table>

As shown in Figure 24 (a), when exposed to water, the native silica absorbed water and the whole body of silica aerogel collapsed under a tender touch because the “pearl necklace” structure was destroyed by the capillary force. The hybrid aerogels, on the other hand, show a different behavior. It is seen that sPS-0.04-TEOS-0.7 aerogel floated on water and could keep its structure intact after being immersed in the water using an
external force. The contact angles of water on compressed disc of aerogel specimens are shown in Table 6. It is seen that sPS aerogel is hydrophobic and the value of contact angle of hybrid aerogels decreased with an increase of the concentration of TEOS. The silica particles are the hydrophilic in nature. The contact angles of hydrocarbon oil are shown in Table 7. For native sPS aerogel, it shows strong lipophilicity due to the presence of hydrocarbon groups in sPS. Also higher values of contact angles of hydrocarbon oil are observed in the case of hybrid aerogels, especially of higher concentration of TEOS. This is due to the hydrophilic nature of silica aerogel.

4.3.6 Compressive properties

![Graph showing compressive modulus vs. concentration of TEOS](image-url)
Figure 25. (a) Compressive moduli of hybrid aerogels. (b) Compressive stress-strain curves of selected hybrid aerogel.

Typical compressive stress-strain curves of selected aerogel specimens are shown in Figure 25(a). At small compressive strain, both hybrid aerogel and native aerogel exhibit linear elastic response. The silica aerogels cracked under a very low compressive load at a strain of ~20%, while sPS aerogel can bear higher deformation without shattering. However, the sPS aerogel underwent buckling at low compressive stress and turned into dense solids at large load. The hybrid aerogel, however, show much better compressive stress-strain behavior – they did not shatter under large load. These results can be interpreted as follows. (1) Silica particles shattered at low strain due to a limited number of Si-O-Si bonds at the neck of the secondary silica particles and weak “pearl necklace” structures [104]. (2) The sPS aerogels experience buckling at low compressive load due to weak network structure and a large number of macropores. (3) In hybrid aerogels, the
sPS strands are prevented from buckling by rigid silica necklace particles grown inside the macropores. On the other hand, the sPS networks act as cage for silica particles and prevent their brittle rupture. The compressive moduli of hybrid aerogels in Figure 25 (b) show an increase with an increase of concentration of TEOS and sPS.

4.3.7 Oil and water absorption

Table 8. Crude oil absorption data for all specimens.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Weight increase percentage (%) at Equilibration time</th>
<th>Theoretical weight increase percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 s  15 s  30 s  1 min</td>
<td></td>
</tr>
<tr>
<td>sPS-0.02</td>
<td>720  731  746  755</td>
<td>2 min  2581</td>
</tr>
<tr>
<td>sPS-0.02-TEOS-0.1</td>
<td>617  665  679  697</td>
<td>1 min  1992</td>
</tr>
<tr>
<td></td>
<td>719  750  761  760</td>
<td>30s   1371</td>
</tr>
<tr>
<td>sPS-0.02-TEOS-0.5</td>
<td>739  796  798  797</td>
<td>30s   1128</td>
</tr>
<tr>
<td>sPS-0.02-TEOS-0.7</td>
<td>620  623  628  625</td>
<td>15s   760</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5 min  1 min  5 min  15min</td>
<td>Equilibration time</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Theoretical weight increase percentage (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 8. Crude oil absorption data for all specimens (continued).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>0.5 min</th>
<th>1 min</th>
<th>5 min</th>
<th>20 min</th>
<th>Equilibration time</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-0.04</td>
<td>125</td>
<td>180</td>
<td>230</td>
<td>248</td>
<td>1397</td>
</tr>
<tr>
<td>sPS-0.04-TEOS-0.1</td>
<td>90</td>
<td>128</td>
<td>211</td>
<td>223</td>
<td>20 min</td>
</tr>
<tr>
<td>sPS-0.04-TEOS-0.25</td>
<td>243</td>
<td>296</td>
<td>300</td>
<td>302</td>
<td>5 min</td>
</tr>
<tr>
<td>sPS-0.04-TEOS-0.5</td>
<td>186</td>
<td>250</td>
<td>308</td>
<td>310</td>
<td>5 min</td>
</tr>
<tr>
<td>sPS-0.04-TEOS-0.7</td>
<td>300</td>
<td>332</td>
<td>334</td>
<td>335</td>
<td>1 min</td>
</tr>
</tbody>
</table>

Table 9. Water absorption data for sPS-0.02-TEOS aerogel.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Weight increase percentage (%) at Equilibration time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 min</td>
</tr>
<tr>
<td>sPS-0.02</td>
<td>3</td>
</tr>
<tr>
<td>sPS-0.02-TEOS-0.1</td>
<td>8</td>
</tr>
<tr>
<td>sPS-0.02-TEOS-0.25</td>
<td>20</td>
</tr>
<tr>
<td>sPS-0.02-TEOS-0.5</td>
<td>24</td>
</tr>
<tr>
<td>sPS-0.02-TEOS-0.7</td>
<td>48</td>
</tr>
</tbody>
</table>
Figure 26. Images of sPS-0.04-TEOS-0.7 aerogel and sPS-0.04-TEOS-0.1 aerogel at different time during oil absorption test, sPS-0.04-TEOS-0.7 aerogel: (a): 1s, (b) 15s, (c) 30s; sPS-0.04-TEOS-0.1 aerogel: (d): 1s, (e) 15s, (f) 30s.

Figure 27. Image (a) and (b) show the hybrid aerogel and native sPS aerogel before and after oil absorption test. Image (c) and (d) show the hybrid aerogel before and after water absorption test.

In order to learn more synergistic effects of the hybrid aerogel, the oil and water absorption tests were performed by putting the specimens in hydrocarbon oil and weighing these aerogels at set intervals. For the series of sPS-0.02-TEOS-mol/L aerogels, as soon as the samples were placed on the crude oil, plenty of tiny air bubbles were evicted from the aerogels and showed a fast absorption rate due to the high surface area,
large capillary force, and the inherent fast absorption kinetics of sPS aerogel. The same phenomenon is seen for the sPS-0.04-TEOS-0.7 aerogel as shown in the Figure 26. It is observed from Table 8 that the equilibration time of absorption of crude oil decreased with the increase of concentration of TEOS. This situation is more obvious in the case of sPS-0.04-TEOS aerogel. For example, as shown in Figure 26, the sPS-0.04-TEOS-0.1 aerogel exhibits much slower absorption rate compared with sPS-0.04-TEOS-0.7 aerogel.

The theoretical weight increase percentage listed in Table 8 is calculated using following equation.

\[
\text{Theoretical weight increase percentage (\%) = } \frac{m_{\text{oil}}}{m_{\text{initial}}} \times 100\% = \frac{\rho_{\text{oil}} V_{\text{oil}}}{m_{\text{initial}}} \times 100\% = \frac{0.801 P V_{\text{aerogel}}}{m_{\text{initial}}} \times 100\%
\]  

\( (11) \)

In the equation (11), \( m_{\text{oil}} \) is the mass of crude oil absorbed by hybrid aerogel specimen when all pores are filled with crude oil, \( m_{\text{initial}} \) is the mass of specimen before exposure to the oil, \( \rho_{\text{oil}} \) is the density of crude oil which is equal to 0.801 g/mL. \( V_{\text{oil}} \) and \( V_{\text{aerogel}} \) are the volume of absorbed oil and specimen, respectively. \( P \) is the porosity of aerogel. It is seen that all aerogels show high absorption capacity attributed to high porosity and low bulk density. The theoretical weight increase percent of specimens decreased with the increase of concentration of TEOS due to a larger bulk density and smaller porosity. For sPS-0.02-TEOS-0.1 aerogel and sPS-0.04-TEOS-0.1 aerogel, the weight gain of specimen after absorbing oil (697\% and 223\%, respectively) are smaller than that of native sPS (755\% and 248\%, respectively). This corresponds to the trend of theoretical value of weight gain. However, an opposite trend is observed for aerogels at a higher concentration of TEOS, e.g., 697\% increase for sPS-0.02-TEOS-0.1 aerogel, 760\% increase for sPS-0.02-TEOS-0.25 aerogel, 797\% increase for sPS-0.02-TEOS-0.5 aerogel.
It can be attributed to the increasing amount of pores in the mesopore size. There is a sudden drop in weight increase for sPS-0.02-TEOS-0.7 aerogel due to the large increase of bulk density and reduction of porosity. It is also seen that in contrast to native sPS aerogel, the hybrid aerogel with high concentration of TEOS almost reaches the theoretical absorption level. The results of water absorption test are presented in Table 9. It is seen that the native sPS aerogels almost have no capacity of absorbing water due to its hydrophobic nature. The hybrid aerogels with a higher concentration of TEOS, on the other hand, exhibit a larger capacity of absorbing water attributed to the residual "Si-OH" groups on the silica aerogel. Figure 26 (a) and (b) show the aerogel specimens before and after absorbing oil, respectively. It is seen that large shrinkage of native sPS aerogel occurred after the test, because the weak sPS networks were destroyed by the capillary force when absorbing the crude oil. However, the shrinkage of hybrid aerogel was much smaller due to the support of silica rigid particles, and there is almost no shrinkage for sPS-0.02-TEOS-0.7 aerogel. On the other hand, the hybrid aerogel with high concentration of TEOS shows large shrinkage after water absorption due to the presence of hygroscopic silica aerogel.
4.3.8 Type B hybrid aerogel

Figure 28. (a) TGA curves of Type B hybrid aerogels, (b) The Type B hybrid aerogels before and after heated to 800 °C in air.

Thermal stability of Type B hybrid aerogels is analyzed from TGA traces as shown in Figure 28 (a). It is seen that the Type B hybrid aerogels present similar thermal decomposition trend. The hybrid aerogels show small weight loss at low temperature due
to residual moisture and due to decomposition of unreacted TEOS and methyl groups. They show much higher weight loss at the temperature between 300-450 °C due to degradation of polystyrene backbone. According to TGA analysis, there are about 55% residues which are due to silica present in hybrid aerogels. It is also seen that the Type B hybrid aerogels leave continuous, integral silica aerogel networks (Figure 28 (b)) after heated to 800 °C in air. Thus, one can infer that the Type B hybrid aerogels possess an interpenetrating polymer network structure within the sPS aerogel.

![Figure 29. SEM images of silica aerogel from acid hydrolysis and condensation (a) and Type B hybrid aerogel (b).](image)

The morphology of acid-derived silica aerogel and Type B hybrid aerogel are shown in Figure 29 (a) and (b), respectively. The sol-gel process of TEOS is much different under acidic condition. The hydrolysis reaction is greatly accelerated [69], while the condensation reaction proceeds relatively slowly. In this manner, the silica gels are formed by linear or randomly branched long chains and ultimately present a bushy network of short strands of silica, as shown in Figure 29 (a). Typical diameter of short strands is about 200 nm. The morphology of Type B hybrid aerogel (Figure 29 (b)) is
similar to that of native sPS aerogel. The network structure is a combination of silica aerogel in Figure 29(a) and sPS aerogel, forming interpenetrating networks. The bulk density of hybrid aerogel (0.0925 g/cm$^3$) is higher than that of native sPS aerogel (0.0303 g/cm$^3$) due to the presence of about 55 wt% of silica. The skeletal density of hybrid aerogel (1.5659 g/cm$^3$) is also higher than that of native sPS aerogel (1.0678 g/cm$^3$) owing to higher skeletal density of silica aerogel (1.7973 g/cm$^3$). The presence of solid silica particles in the macropores of sPS aerogel result a slightly lower porosity (94.1%) in hybrid aerogel compared to native sPS aerogel (97.2%).

Table 10. Surface area of native sPS aerogel, acid-derived silica aerogel and Type B hybrid aerogel.

<table>
<thead>
<tr>
<th></th>
<th>sPS-0.02</th>
<th>sPS-0.02-TEOS-3</th>
<th>acid-derived silica aerogel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m$^2$/g)</td>
<td>399</td>
<td>363</td>
<td>325</td>
</tr>
</tbody>
</table>

Figure 30. Pore size distribution of native sPS aerogel, acid-derived silica aerogel and type B hybrid aerogel.

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The surface area and pore size distribution of native sPS aerogel, acid-derived silica aerogel, and type B hybrid aerogel are shown in Table 10 and Figure 30, respectively. Compared to native sPS aerogel and acid-base derived silica aerogel, the acid-derived silica aerogel exhibit smaller surface area, and the surface area of hybrid aerogel is smaller than that of native sPS aerogel due to the presence of acid-derived silica aerogel in them. As discussed earlier, native sPS aerogel has no predominant pores located in the mesopores range (2-50 nm). In contrast, the pore size distributions of type B hybrid aerogel show a small peak in the mesopores zone due to the presence of the acid-derived silica aerogel which exhibits a predominant pore size of around 4 nm as shown in the Figure 30.

Table 11 Oil absorption and water absorption data for sPS-0.02-TEOS-3 acid-derived aerogel.

<table>
<thead>
<tr>
<th>Weight increase percentage (%) at Equilibration time (min)</th>
<th>Theoretical weight increase percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 s 15 s 30 s 60 s</td>
<td></td>
</tr>
<tr>
<td>Oil absorption</td>
<td></td>
</tr>
<tr>
<td>601 698 718 720</td>
<td>30 s 851</td>
</tr>
<tr>
<td>0.5 min 1 min 5 min 15 min</td>
<td></td>
</tr>
<tr>
<td>Water absorption</td>
<td></td>
</tr>
<tr>
<td>401 421 530 533</td>
<td>5 min 1062</td>
</tr>
</tbody>
</table>
Figure 31. Image (a) and (b) show Type B hybrid aerogel before and after oil absorption.

Image (c) and (d) show Type B hybrid aerogel before and after water absorption.

Type B hybrid aerogel specimens were used in oil and water absorption tests, as described in section 4.3.7. It is seen from the data in Table 11 that the Type B hybrid aerogels exhibit higher capacity of absorption of crude oil. The experimental absorption levels show weight increase almost close to the theoretical weight increase. In addition, the Type B hybrid aerogel present a high absorption rate. In this case, high porosity, large capillary force, and the inherent fast absorption kinetics of sPS aerogel are responsible.

Compared with native sPS aerogels and Type A hybrid aerogels made form low concentration of TEOS which exhibit large shrinkage after absorbing oil, the Type B hybrid aerogel showed no shrinkage after oil absorption test. It is interesting to observe that the Type B hybrid aerogel also show high capacity of absorbing water as seen from the data presented in Table 11. This can be explained as follows: Under acidic condition,
the rate of hydrolysis process of TEOS is much higher than that of condensation process. This results in many residual hydroxyls on the silica particles. Thus, silica aerogel produced from acid hydrolysis and condensation reaction should exhibit higher hygroscopic nature. The Type B hybrid aerogel also showed almost no shrinkage after absorbing water. In comparison, Type A hybrid aerogels showed much larger shrinkage, as shown in Figure 27 (c), (d). The strand-like silica networks in acid derived silica aerogel are apparently much stronger than the “pearl necklace” structures in acid-base derived silica aerogel.
CHAPTER V

SUMMARY

Chapter III established that macroporous cellulose filters can be easily coated with ssPS aerogel to obtain a porous material showing both mesoporous and macroporous surfaces. The ssPS aerogel was coated on the top surface of the cellulose filter. In addition, some ssPS chains diffused into the macropores of the cellulose filter to offer good bonding between the materials. The sulfonic acid groups facilitated polymerization of aniline monomer. The polyaniline formed aggregates on the polystyrene main chain and produced electrically conductive networks. The surface area of ssPS-coated filter was about 60 times higher than that of the cellulose filters. This is attributed to the mesopores of ssPS aerogels. The surface area reduced upon polymerization of aniline on ssPS, indicating filling of a large fraction of mesopores. The value of electrical conductivity shows that this material has the potential to be capacitors. A future study should investigate the capacitance, mechanical properties of the polyaniline-coated-filter aerogels study and evaluate the effect of degree of sulfonation of sPS on capacitance of aerogel.

Chapter IV established that novel sPS/silica hybrid aerogel can be fabricated by a simple two-step process, in which the sPS gel is prepared first and its macropores act as cage to contain the silica gel. The Type A hybrid aerogels exhibit much higher surface area than sPS aerogel due to the contributions of silica aerogel, and present mesopores distribution. A synergy in mechanical properties is found. The Type A hybrid aerogel also
present a fast absorption and high absorption capacity of crude oil. Compared with Type A hybrid aerogel, the Type B hybrid aerogel exhibit an IPN structure, and high absorption capacity of water in addition to high absorption capacity of crude oil.
REFERENCES


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