**The Role Of Mesopores In Achieving High Efficiency
Airborne Nanoparticle Filtration Using Aerogel Monoliths**

Sung Jun Kim¹, George Chase², and Sadhan C. Jana^{1*}

¹Department of Polymer Engineering

²Department of Chemical and Biomolecular Engineering

The University of Akron, Akron, OH 44325-0301, United States

(Corresponding author e-mail: janas@uakron.edu)

ABSTRACT

This study evaluates the role of small mesopore volume fraction in aerogel monoliths in achieving high efficiency airborne nanoparticle filtration. The diffusional flow in mesopores (diameter 2-50 nm) is more effective in nanoparticle capture than the viscous flow regime encountered in macropores (diameter > 50 nm). Substantial macropore fraction, however, is essential for achieving high air permeability. This idea is tested by evaluating the filtration efficiency of 25-150 nm diameter airborne sodium chloride nanoparticles and the permeability of air through hybrid aerogel monoliths with about 2-4 % by volume mesopore content. The hybrid aerogels are prepared by growing discontinuous silica aerogel particles in the macropores of δ -form syndiotactic polystyrene (sPS). The results show that air permeability is not much affected by the silica content although the particle capture efficiency is increased to greater than 99.95 % due to the contribution of diffusional deposition aided by the mesopores. The aerogels develop cracks and reduce filtration efficiency at high silica content due to brittle nature of silica particle networks.

INTRODUCTION

Small airborne particles, e.g., the fines with size $0.1\text{ }\mu\text{m}$ - $1\text{ }\mu\text{m}$ and ultrafines with size $< 0.1\text{ }\mu\text{m}$, are detrimental to human health as they can penetrate the human body and reach pulmonary alveoli.¹ 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.² 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.^{3,4} 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 for capturing airborne nanoparticles. They are composed of solid networks with open pore structures, high porosity, large surface area, and cascading pore sizes.⁵⁻²⁹ Pores are defined as micropores (pore diameter $d < 2\text{ nm}$), mesopore ($2 \leq d \leq 50\text{ nm}$), and macropores ($d > 50\text{ nm}$) as per IUPAC classification. Silica aerogels, the most studied aerogels to date, are mesoporous and offer surface area up to $1,000\text{ m}^2/\text{g}$ and porosity over 90 %.⁹⁻²¹ The δ -form syndiotactic polystyrene (sPS) aerogels have porosity $> 97\%$, contain a small fraction of pores in the micropore range inside the nanocavities of crystalline strands, and a major fraction of pores as macropores.²²⁻²⁹

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.³⁰⁻³³ Several studies focused on viral particle detection by bioluminescent organisms colonized in silica aerogels,³⁴ and removal of pollutants, such as cyanides or combustion gases by using monolithic silica aerogel composites as the medium for heterogeneous catalysts.^{7,35,36} Prior work on direct usage of monolithic aerogels for filtration of airborne nanoparticles is scarce. Recently, we reported

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} m² using macroporous monolithic sPS aerogels.³⁷ No detailed work exists on evaluation of airborne nanoparticle filtration potential of aerogel monoliths with 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) as defined in equation (1).^{38,39}

$$Kn = \lambda/d \quad (1)$$

In equation (1), λ is the mean free path of gas molecules and d is the mean diameter of the pores. A purely viscous fluid flow regime is obtained when $Kn \ll 1$ 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 $Kn \gg 1$ 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.³⁹ It was reported that fluid flow through mesoporous silica aerogels at room temperature and pressure 6-200 kPa was in the intermediate regime.³⁸ 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, therefore, has the potential to offer both superior particle capture efficiency of mesopores and high air permeability of macropores.

In this work, a set of organic-inorganic hybrid macro- and mesoporous aerogel monoliths were produced and their effectiveness in nanoparticle filtration was evaluated. The hybrid monoliths were produced by growing discontinuous silica aerogel **networks** inside the macropores of δ -form sPS following a method published earlier.²⁸ This study 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 Kim, Chase, and Jana³⁷, 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 straight forward 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 Jana²⁸ observed synergy of compressive modulus in hybrid sPS-silica aerogel systems and reported an increase of compressive modulus by 250% over sPS aerogel monoliths.

MATERIALS AND METHODS

The monolithic δ -form sPS aerogels were considered a baseline material in this work. 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 a two-step process consisting of thermo-reversible gelation and supercritical drying.²²⁻²⁹ The hybrid aerogel monoliths were fabricated by growing mesoporous silica particle networks inside the sPS macropores following a procedure reported by Wang and Jana.²⁸ 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.^{28,29} For materials, solid sPS pellets with 98% syndiotacticity and

molecular weight 300,000 g/mol were purchased from Scientific Polymer Products Inc. (New York, NY) and converted into powder form for easy dissolution in reagent grade tetrahydrofuran (THF) purchased from Fisher Scientific. 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.

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 °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.²⁶⁻²⁹ 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 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: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 1 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 H x - y where x represents sPS concentration in g/mL and y represents moles of ethanol per mole of TEOS in the solution.

Table 1. Specific concentration of sPS and TEOS used in synthesis of hybrid aerogels.

Specimen	sPS conc. (g / THF mL)	TEOS conc. (mol / L) [TEOS:ethanol molar ratio]
sPS20	0.020	-
sPS25	0.025	-
H20-64	0.020	0.25 [1:64]
H20-46	0.020	0.33 [1:46]
H20-37	0.020	0.40 [1:37]
H25-64	0.025	0.25 [1:64]
H25-46	0.025	0.33 [1:46]
H25-37	0.025	0.40 [1:37]

The permeability of air was obtained by Frazier air permeability tester (Frazier Precision Instrument, Hagerstown, MD). The disc shaped aerogel specimen of thickness 3.5-4.0 mm was placed in a sample holder that covers the lateral face of the aerogel and prevents lateral flow of air.³⁷ Vacuum grease was applied to seal the interface between the sample holder and the specimen. Filtration efficiency (E) was measured using TSI-8130 filter tester (TSI Inc., Shoreview, MN) and represents the fraction of NaCl particles captured after the incident particles pass through the filter once. The diameter of NaCl particles generated in situ in the TSI tester ranged from 25-150 nm with an average diameter of 75 nm. The TSI-8130 filter tester was able to measure the filtration efficiency with an accuracy up to 99.999%. The face velocity (V_f) of air during filtration test was 50 cm/sec.

Transmitted light microscopy (Olympus SZ-PT, Tokyo, Japan) was used to obtain images of cross-sectional planes of aerogel specimens after subjecting them to filtration for 100 passes of particle passage. The focus was adjusted to obtain images at different depths. The internal structures of the sPS and sPS-silica hybrid aerogels were examined by scanning electron microscope (JEOL JSM5310). 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.

The value of bulk density, ρ_b was obtained from the weight-to-volume ratio of the specimens. Skeletal density, ρ_s 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.

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.⁴⁰ 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. Pore size distribution was obtained from nitrogen sorption isotherms using Barrett-Joyner-Halenda (BJH) method.⁴¹

The absorption capacity of the particles is an important attribute as it relates to the life-time of a filter. In this work, the absorption capacity was determined from the value of porosity (Π) as in equation (2).

$$\Pi = 1 - \frac{\rho_b}{\rho_s} \quad (2)$$

The macropore volume fraction, Φ_M , was computed from the difference of total pore volume and the sum of volumes of micro- and mesopores. The micropore volume fraction of $\square$ -form sPS aerogels was inferred to be much less than 1 % from the data reported elsewhere.²² 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 and we resorted to using nitrogen sorption isotherms to determine the value of Φ_M as per equation (3).

$$\Phi_M = \frac{(1/\rho_b - 1/\rho_s) - V_{BJH}}{(1/\rho_b - 1/\rho_s)} \quad (3)$$

In equation (3), V_{BJH} is the specific volume of pores with size less than 50 nm as measured by nitrogen sorption isotherms.

The compressive stress-strain relationships were obtained via ASTM D595 method using Instron 5567 (Canton, MA) machine to evaluate the mechanical property change of the hybrid aerogels with change of TEOS concentration. 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.

RESULTS AND DISCUSSION

1. Mesoporosity in hybrid aerogels.

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 Jana²⁸ 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. 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.²⁸ Figure 1 shows SEM images of sPS aerogel and its corresponding hybrid with silica. As seen in Figure 1(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 1b). Table 2 lists the data of skeletal density of sPS and hybrid materials. In view of skeletal density of 1.801 g/cm³ for silica,²⁸ 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 1(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 1(c) are due to sintering of silica particles. The images in Figure 1(b) and 1(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 at much higher TEOS concentration.²⁸ As will be seen later, the hybrid aerogels developed cracks at high concentration of TEOS.

The mesoporosity of hybrid materials was confirmed by nitrogen sorption isotherms. The pore size distributions shown in Figure 2 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 2) 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 2 show that the macropore volume fraction reduced from 99 % for sPS20 specimen to 96.5 % for H20-37 hybrid aerogel.

The values of bulk and skeletal density, porosity, and BET surface area are also listed in Table 2. 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 5-30 nm secondary particles^{5,42} accounts for such an increase of the surface area.

Figure 1. Representative SEM images of (a) sPS aerogel synthesized from sPS concentration 0.020 g/mL (sPS20), (b) sPS-silica hybrid aerogels synthesized from sPS concentration 0.020 g/mL with TEOS to ethanol molar ratio 1:37 (H20-37), and (c) the sintered powder residue due to silica particles recovered after burning off the sPS chains in H20-37.

Figure 2. Pore size distribution from nitrogen sorption isotherms. (a) sPS concentration 0.020 g/mL, (b) sPS concentration 0.025 g/mL. The legends are defined in Table 1. The y-axis values represent the derivative of the pore volume per unit weight (V) of the specimen with respect to pore diameter (d).

Table 2. Bulk density (ρ_b), skeletal density (ρ_s), porosity (Π), macropore fraction of total porosity (Φ_M), permeability (k), filtration efficiency (E), internal surface area (S_{BET}), and pressure drop per unit thickness ($\Delta P/L$) of monolithic sPS and sPS-Silica hybrid aerogels.

Specimen	ρ_b (g/cm ³)	ρ_s (g/cm ³)	Π (%)	Φ_M (%)	k ($\times 10^{-10}$ m ²)	E (%) @ $V_f \approx 50$ cm/s	S_{BET} [m ² /g]	$\Delta P/L^a$ (mmH ₂ O/cm) @ $V_f \approx 50$ cm/s
sPS20	0.030 $\pm$ 0.001*	1.056*	97.16*	99.0	2.23 $\pm$ 0.36	98.889 $\pm$ 0.998*	379	42.6
sPS25	0.034 $\pm$ 0.003*	1.056*	96.78*	98.3	1.45 $\pm$ 0.31	99.734 $\pm$ 0.117*	377	65.5
H20-64	0.044 $\pm$ 0.001	1.282 $\pm$ 0.058	96.57	98.2	2.18 $\pm$ 0.55	99.011 $\pm$ 0.425	383	43.5
H20-46	0.052 $\pm$ 0.003	1.344 $\pm$ 0.056	96.13	96.7	1.12 $\pm$ 0.61	99.354 $\pm$ 0.105	476	84.5
H20-37	0.059 $\pm$ 0.003	1.398 $\pm$ 0.029	95.77	96.5	1.22 $\pm$ 0.79	99.963 $\pm$ 0.047	490	77.5
H25-64	0.054 $\pm$ 0.001	1.270 $\pm$ 0.061	95.74	97.1	2.00 $\pm$ 0.60	99.844 $\pm$ 0.276	443	47.3
H25-46	0.057 $\pm$ 0.003	1.302 $\pm$ 0.037	95.55	96.9	0.97 $\pm$ 0.39	99.989 $\pm$ 0.016	426	97.8
H25-37	0.061 $\pm$ 0.001	1.315 $\pm$ 0.036	95.35	96.1	0.91 $\pm$ 0.41	99.999 $\pm$ 0.00	458	104.3

* Originally reported in Ref. [37].

^a Pressure drop per unit thickness $\Delta P/L$ was calculated from permeability and air flow rate.

2. Filtration performance characteristics.

The values of permeability, filtration efficiency, and pressure drop of the monolithic sPS and sPS-silica hybrid aerogels are presented in Table 2. Pressure drop per unit length at a given face velocity $V_f \approx 50$ cm/sec was calculated from the value of permeability.

Figure 3 shows the plots of permeability as a function of TEOS concentration. Permeability values of sPS and sPS-silica hybrid aerogels are close to 10^{-10} m². 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 of sPS aerogels. Figure 4 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 $1 \times 10^{-10} \text{ m}^2$ to $2.25 \times 10^{-10} \text{ m}^2$ as the macropore fraction increased from about 0.92 to 0.96.

Figure 3. Permeability of sPS and sPS-silica hybrid aerogels as a function of TEOS concentration.

Figure 4. Permeability as a function of macropore fraction of entire volume of an aerogel monolith.

The effect of mesoporosity on nanoparticle filtration was examined by comparing the filtration efficiency of sPS aerogels and sPS-silica hybrid aerogels. Figure 5 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 concentration. 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 operates in mesopores.³⁸ The higher internal surface area in the hybrid aerogels may also have contributed to the higher efficiency.

Figure 5. Filtration efficiency as function of TEOS concentration.

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 6 shows filtration efficiency as function of TEOS concentration. 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. We attribute the reduction of filtration efficiency in Figure 6 to 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 6 shows a representative image of cracked monolith recovered after filtration tests.

Figure 6. Filtration efficiency measured at $V_f \approx 50$ cm/sec 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.

3. Mechanical properties

The compressive property of sPS-silica hybrid aerogels was inferred from compressive stress-strain curves shown in Figure 7. The sPS-silica hybrid aerogel with TEOS concentration 0.33 mol/L (H2O-

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.²⁸ 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 7. 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.

4. Mode of filtration

To verify the filtration mode, NaCl nanoparticles were allowed to pass through a representative sPS aerogel monolith 100 times and the images of the recovered monolith were examined by SEM and transmission optical microscopy. The optical microscope image in Figure 8(a) shows fractals of 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 SEM images of the cross-section of the monolith also verified that depth filtration occurred. The aerogel structure seen in image Figure 8(b) looks condensed as the specimen after filtration was immersed in liquid nitrogen to freeze the captured nanoparticles. In the process, the aerogel specimen experienced shrinkage, although NaCl particles captured in the pores are clearly visible in Figure 8(b).

Figure 8. Optical microscopy (a) and SEM (b) images of sPS aerogels after filtration.

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 paper 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} m². Visual inspection of the monoliths recovered after filtration confirmed that depth filtration in conjunction with cake formation was the primary filtration mode inside the aerogel monoliths, and that the role of surface filtration was insignificant.

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Figure 1. Representative SEM images of (a) sPS aerogel synthesized from sPS concentration 0.020 g/mL (sPS20), (b) sPS-silica hybrid aerogels synthesized from sPS concentration 0.020 g/mL with TEOS to ethanol molar ratio 1:37 (H20-37), and (c) the sintered powder residue due to silica particles recovered after burning off the sPS chains in H20-37.

Figure 2. Pore size distribution from nitrogen sorption isotherms. (a) sPS concentration 0.020 g/mL, (b) sPS concentration 0.025 g/mL. The legends are defined in Table 1. The y-axis values represent the derivative of the pore volume per unit weight (V) of the specimen with respect to pore diameter (d).

Figure 3. Permeability of sPS and sPS-silica hybrid aerogels as a function of TEOS concentration.

Figure 4. Permeability as a function of macropore fraction of entire volume of an anerogel monolith.

Figure 5. Filtration efficiency as function of TEOS concentration.

Figure 6. Filtration efficiency measured at $V_f \approx 50$ cm/sec 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.

Figure 7. 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.

Figure 8. Optical microscopy (a) and SEM (b) images of sPS aerogels after filtration.

List of potential reviewers

Prof. Gaetano Guerra, Department of Chemistry and Biology and INSTM Research Units,
Università degli Studi di Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, Italy e-mail:
gguerra@unisa.it

Prof. Yuris Dzenis, Department of Engineering Mechanics, University of Nebraska, Lincoln, NE
68588-0526, E-mail: **ydzenis@unl.edu**

Prof. Wallace Leung, Chair Professor of Dept. of Mechanical Engineering, The Hong Kong
Polytechnic University, Hung Hom, Kowloon, Hong Kong, Email: **mmwleung@polyu.edu.hk**

Prof. Seeram Ramkrishna, National University of Singapore, Email: **seeram@nus.edu.sg**

Prof. Peter Tsai, University of Tennessee, **ptsai@utk.edu**

Prof Da-Ren Chen, Virginia Commonwealth University, **dchen3@vcu.edu**

Prof. David Schiraldi, Case Western Reserve University, **das44@case.edu**

The Role Of Mesopores In Achieving High Efficiency Airborne Nanoparticle Filtration
Using Aerogel Monoliths

Sung Jun Kim, George Chase, Sadhan C. Jana*

Mesopores and macropores in hybrid monoliths govern respectively high efficiency and high air permeability.