<table>
<thead>
<tr>
<th>Title</th>
<th>Thermal conductivity variations with composition of gelatin-silica aerogel-sodium dodecyl sulfate with functionalized multi-walled carbon nanotube doping in their composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Mahesh, Sachithanadam; Joshi, Sunil Chandrakant</td>
</tr>
<tr>
<td>Date</td>
<td>2015-08</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10220/38853">http://hdl.handle.net/10220/38853</a></td>
</tr>
<tr>
<td>Rights</td>
<td>© 2015 Elsevier. This is the author created version of a work that has been peer reviewed and accepted for publication by International Journal of Heat and Mass Transfer, Elsevier. It incorporates referee’s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<a href="http://dx.doi.org/10.1016/j.ijheatmasstransfer.2015.04.046">http://dx.doi.org/10.1016/j.ijheatmasstransfer.2015.04.046</a>].</td>
</tr>
</tbody>
</table>
Thermal Conductivity Variations with Composition of Gelatin-Silica Aerogel - Sodium Dodecyl Sulfate with Functionalized Multi-Walled Carbon Nanotube doping in Their Composites

Mahesh Sachithanadam* and Sunil C. Joshi
School of Mechanical and Aerospace Engineering,
50 Nanyang Avenue, Nanyang Technological University,
Singapore – 639798.

Abstract
Silica aerogels are very light, highly porous nanomaterial with large internal surface area possessing excellent thermal insulation that may get affected when the binders and additives used in aggregation. This paper discusses the variations in thermal conductivity of a binder-treated gelatin silica aerogel-sodium dodecyl sulfate (GSA-SDS) composite blocks doped with COOH group functionalized multi-walled carbon nanotubes (FMWNT) prepared via freeze drying and frothing methods. The thermal conductivity of GSA-SDS and GSA-SDS/FMWNT composites was evaluated with several mass ratios of the composite mix for 1-D steady-state heat transfer at mean temperature, $T_m$ (300-370K), using Lee’s Disc method. The effects of silica aerogel granule size and mass ratio of FMWNT on the thermal conductivity were investigated. The lowest thermal conductivity achieved for the composite block was 0.016 W/m-K when 0.042 wt% FMWNT was added to gelatin aerogel mass ratio of 0.1:0.9 without SDS. Thermal conductivity predictive models were developed based on the numerous experiments carried out as a function of the aerogel granule size and the mass ratio of constituent materials. The predictive models for composites with FMWNT were validated to approximately 94.3 ± 2.4% accuracy with reduction of 7% in the thermal conductivity when compared with of the GSA composites.

Keywords:
A: Carbon Nanotubes, Silica Aerogels; B: Thermal Conductivity; C: Statistics; E: Freeze Drying

* Corresponding author: mahesh2@e.ntu.edu.sg (Mahesh Sachithanadam)
1. Introduction

Silica aerogels are translucent solids with a porosity of up to 99% [1] with extremely low thermal conductivity [2, 3]. Silica aerogels are available in various forms from monolithic to granules of regular and irregular shapes and also in powder form [1, 4-6] synthesized via sol-gel techniques followed by supercritical or ambient pressure drying [5, 7-13] to obtain the desired properties. The current commercial synthesis of silica aero-gels is achieved using inexpensive material such as water-glass (sodium silicate) in solution [4] added with a silylating agent followed by ambient pressure drying [4], to produce hydrophobic aerogels [9]. Silica aerogels have diversified applications in various fields such as electronic sensors, kinetic energy absorbers, fillers in paints and varnishes as well as agricultural and pharmaceutical [3] and these fascinating properties led to extensive research over the past four decades to improve the mechanical, thermal and acoustic properties [3, 14] of these materials. The most significant of all the properties would be the extremely low thermal conductivity, reportedly to be in the range 0.017 to 0.024 W/(m·K) as highlighted by Schmidt and Schwertfeger [3]. Reim et al. studied the use of silica aerogel granules as an embedded material in a glazing element for optical and thermal properties [15] achieving heat transfer coefficient of less than 0.4W/(m²·K) and total solar energy transmittance of 35%. The fascinating properties of silica aerogels cannot be translated into a commercial success because in granulate form they are highly brittle, and have low strength and modulus [16].

Commercially manufactured silica aerogels from Cabot Corp come in irregularly shaped granular form. The various sizes and irregular shapes of the silica aerogel granules result in a heterogeneous distribution in a given sample. As a result, material properties such as density, strength, thermal conductivity and acoustic absorptivity vary from one sample lot to another, thereby affecting experimental results. It is, therefore, necessary to evaluate the distribution of the granule sizes and its corresponding effects on the basic material properties and when used as a constituent material in a composite with other materials. In our previous work, we have successfully developed a composite block binding gelatin/SDS mixture to the silica aerogels [17]. The extensive studies carried out on the GSA-SDS composites showed improved mechanical properties over silica aerogel granules and more essentially it showed an unusual phenomenon of high strain recovery after compression exhibiting ductile behavior similar to
elastomeric foams such as polyethylene without compromising its overall density. The optimal results were achieved with 0.56% SDS is added to the aqueous gelatin solution.

Discovered in 1991 by Iijima, Multi-Walled CNT (MWNT) have remarkable mechanical properties, high thermal and chemical stability and excellent heat conduction with hardness of diamond and conductivity of graphite [18]. The structure of MWNT can be seen as a group of coaxial Single-Walled CNT (SWNT) forming a hollow cylinder of graphite sheets structured into different conformations for specific applications or design [19, 20]. Their strong $\pi - \pi$ interactions between them resulting in the formation of aggregates thus preventing homogeneous dispersion when blend into a matrix material to form a composite [21] resulting in underperformance of the composite and underpin the final properties. Modification to the structure of the CNT was achieved via chemical surface functionalization, a technique that allows functional groups to be attached to the CNT to provide better covalent bonding, adhesion and improvement in the dispersion of the CNT in the matrix material [22, 23]. CNT are very good thermal conductors and their conductivity have been measured as high as 3500 W/m-K [24, 25]. Sinha et.al [26] investigated the room-temperature thermal conductivity for SWNT and MWNT in the radial direction and found to be about 1.6 W/m-K and 1.52 W/m-K respectively which is as thermally conductive as soil. The wide variations in the CNT’s thermal conductivity due to its structure and the thermal path undertaken (radial or longitudinal axis) is the motivation behind the idea of doping the GSA composites with CNT; that is, to study the influence of its concentration in the GSA-SDS composites on thermal conductivity.

Various techniques to measure the thermal conductivity of a material are adopted by researchers depending on the resources and facilities available. Some of which are sandwiched panel design between two conductive plates [2], guarded hot plate method [27], vibrational thermal relaxation technique developed by Bernasconi et al. [28] and modified Tsao’s model predictive theoretical technique [29]. In this paper, effects of FMWNT-COOH and the distribution of silica aerogel granules on the thermal conductivity of GSA-SDS composites were investigated using the Lee’s Disc method. The GSA-SDS and GSA-SDS/FMWNT composites fabricated via the frothing and freeze drying (FD) methods are presented. Herein, FMWNT-COOH will be referred as FMWNT for simplicity.
2. Materials and Experimental Method

2.1 Materials

Hydrophobic translucent silica aerogel granules, Lumira LA1000, with bulk density of 0.065-0.08 g/cm$^3$, porosity of >90%, pore diameter ~ 20nm, surface area of 600-800 m$^2$/g were purchased from Cabot Corp® (USA). High Strength Gelatin from porcine skin (bloom strength 240-270; density ~1.043 g/cm$^3$) and SDS (density = 0.37 g/cm$^3$) were purchased from Sigma Aldrich. Functional MWNT-COOH (density = 2.1 g/cm$^3$, wall thickness – 5 to 10 nm, length 50 μm) were purchased from Nanostructured & Amorphous Materials, Inc.

2.2 Equipment

The aerogel particles distribution analyses were carried out using mechanical shaker. Sonication of gelatin solution was carried out using Fisher Scientific FB15051. Freeze drying of specimens was carried out on Martin Christ Free Dryer Alpha 1-2LD. The gelatin and the composite blocks were weighed on a high precision balance, Mettler Toledo AB-265S/Fact High Precision Balance. Thermal conductivity experiments were carried out via the Lee’s Disc method in an enclosed chamber, Thermotron Model SE-300.

2.3 Fabrication of gelatin-silica aerogel composites

2.3.1 Freeze Drying Method

A total of 34 samples of GSA and GSA-SDS composites were fabricated via frothing method from the established procedures in our previous works [17], comprising various mixtures of 3.0 to 50.0 wt% gelatin, 0.0 to 0.66wt% SDS and 50.0 to 97.0 wt% silica aerogels. In addition, 24 samples of GSA-SDS composite doped with 0.042 wt% and 0.084 wt% FMWNT were fabricated from the above procedures.

The FD method is similar to frothing method except that the curing of the specimens was carried out under vacuum at sub-zero temperature. The aqueous solution of gelatin is obtained via sonication as described in the previous section. The aerogels are mixed in the solution for about 10 minutes till a tacky mixture is obtained. Thereafter, the mixture is casted onto a petri dish of 100mm diameter or in a mold of 75 X 50 X 25mm on a metal dish laid with a porous sheet. The composite mold is covered with a transparent vacuum wrap or foil with holes and
secured with tape to allow for subsequent sublimation of water to take place when placed under vacuum and below the triple point of water. The composite is then cooled to 4°C in a refrigerator for 4 hours. This will allow for the gelatin solution to lyophilize. The composite is further cooled to -25°C in a freezer for another 3 hours. The fully frozen sample is sublimated at -35°C under vacuum for 24 hours. Full sublimation is achieved when the chamber temperature drops to -45°C. Thereafter, the temperature is raised to ambient temperature at 2°C min⁻¹. The pressure is increased by slight opening of the vent valve on the chamber for 4 hours. The simultaneous action of vacuum and temperature has two-fold effect on the composites. First, the vacuum facilitates a tight packing order of the aerogels thus minimizing void and pores of the gelatin mixture. Second, the double action of temperature and vacuum sublimes the water content in the gelatine solution thus leaving the gelatin to be networked around the aerogel granules. Thus binding is achieved physically. Frydrych et al. [30] developed gelatin/sepiolite nano-composites using the above principle albeit under different conditions. A total of 13 samples of GSA-SDS composites were fabrication via the FD method - a) five samples comprising of 10 to 50.0 wt% gelatin, 0.56wt% SDS and 50.0 to 90.0 wt% silica aerogels; b) eight samples comprising of 20 and 40.0 wt% gelatin, 0.56wt% SDS, 60 and 80 wt% silica aerogels comprising of 4 different granules sizes. In addition, another 12 samples of composition in b) were fabricated with various quantities of 0.017 wt%, 0.033 wt% and 0.050 wt% FMWNT doped in the GSA-SDS (20/80/0.56) composite. Similarly, 5 samples of Porous Gelatin (PG) were fabricated using the FD method.

2.4 Experimental Techniques

2.4.1 Aerogel Granule Size Distribution

The aerogels granules were placed in a mechanical sieve shaker consisting of 7 sieve sizes and a pan. The granules were sorted according to their particle distribution from 10 sample sets. Table 1 shows the distribution of the various sizes from 10 sets of these granules. The distribution shows that the bulk of the sizes range from 1.4 to 1.99mm accounting for more than 60% in all the 10 sets. As observed, most of the granule sizes are in the range of 1.00 to 2.8mm accounting for 95% of the distribution.
Table 1– Granule size distribution

<table>
<thead>
<tr>
<th>Granule Size (mm)</th>
<th>1st Set</th>
<th>2nd Set</th>
<th>3rd Set</th>
<th>4th Set</th>
<th>5th Set</th>
<th>Average</th>
<th>Max aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.35 ≤ x &lt; 3.75</td>
<td>0.28%</td>
<td>0.00%</td>
<td>0.45%</td>
<td>1.11%</td>
<td>0.14%</td>
<td>0.40%</td>
<td>1.12</td>
</tr>
<tr>
<td>2.8 ≤ x &lt; 3.35</td>
<td>0.57%</td>
<td>0.84%</td>
<td>0.89%</td>
<td>1.59%</td>
<td>1.88%</td>
<td>1.15%</td>
<td>1.19</td>
</tr>
<tr>
<td>2.36 ≤ x &lt; 2.8</td>
<td>5.67%</td>
<td>5.25%</td>
<td>7.61%</td>
<td>6.52%</td>
<td>6.50%</td>
<td>6.31%</td>
<td>1.18</td>
</tr>
<tr>
<td>2.00 ≤ x &lt; 2.36</td>
<td>14.45%</td>
<td>22.69%</td>
<td>23.27%</td>
<td>26.39%</td>
<td>23.99%</td>
<td>22.16%</td>
<td>1.18</td>
</tr>
<tr>
<td>1.40 ≤ x &lt; 2.00</td>
<td>73.37%</td>
<td>65.34%</td>
<td>60.63%</td>
<td>58.51%</td>
<td>57.51%</td>
<td>63.07%</td>
<td>1.42</td>
</tr>
<tr>
<td>1.00 ≤ x &lt; 1.40</td>
<td>3.40%</td>
<td>5.46%</td>
<td>6.26%</td>
<td>3.50%</td>
<td>6.79%</td>
<td>5.08%</td>
<td>1.39</td>
</tr>
<tr>
<td>0.50 ≤ x &lt; 1.00</td>
<td>2.27%</td>
<td>0.42%</td>
<td>0.89%</td>
<td>1.27%</td>
<td>2.02%</td>
<td>1.38%</td>
<td>1.98</td>
</tr>
<tr>
<td>x &lt; 0.5</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>1.11%</td>
<td>1.16%</td>
<td>0.45%</td>
<td>-</td>
</tr>
</tbody>
</table>

2.4.2 Experimental Thermal Conductivity Measurement

The experiment set up using Lee’s Disc method is shown in Fig. 1. It consists of 3 copper plates (CP) with the dimensions of 75 X 45 X 3mm and a heater measuring 75 X 45 X 1mm. The heater is connected to the constant power source at 5 levels of input: 1.18W, 1.92W, 3.16W, 4.75W and 6.84W. Thermal probes are placed on top of the 1st CP, at the side of the 2nd CP, at the side of the composite block and at the bottom of the 3rd CP. The composite is sandwiched between the CPs and placed in an enclosed chamber at ambient pressure and temperature for 1 to 2 hours until the thermal probe temperatures reached steady state and recorded during this period. Typical temperature profile of silica aerogel under the 5 level of power input is shown in Fig. 2. The profiles of the composites are similar to the one in Fig. 2.

The Thermal Conductivity of any substance is given by the Eq.1, where \( \dot{Q} \) is the quantity of heat flowing in Watts; \( \lambda \) is the thermal conductivity in W/K-m; \( \frac{dT}{dx} \) is the temperature gradient in K/m, across a sample of the material of uniform cross-section area \( A_y \) m².
\[
Q = (\lambda A_y)_{com} \frac{(T_2 - T_3)}{t_{com}}
\]

(1)

Fig. 1

Lee’s Disc Method to measure thermal conductivity

Fig. 2

Experimental temperature profile of silica aerogel granules under various power loading
When the electrical heater is turned on, heat will flow from the heater into CPs 1 and 2 and from CP2 across the composite block to CP3. The heat will be lost to the environment by emission and convection from the surface areas of CP1 and CP3 and from the rim of CP2, the rim of the heater and the rim of composite. The rate of loss of heat of a particular plate will be proportional to the temperature difference between the disc and its surroundings, provided this temperature difference is small (Newton's law of cooling). The temperature of the three plates and the composite will increase until the rate of heat loss to the room is equal to the rate of heat generation in the electrical heater assuming the temperature boundary is uniform across the surfaces and edges for the individual parts. When this occurs equilibrium has been reached and therefore,

\[ V_1 = e_1 A_1 (T_1 - T_s) + A_2 (T_2 - T_s) + A_3 (T_3 - T_s) + A_h (T_h - T_s) \]

Where, \( e_1, e_2 = \text{Heat loss per unit area of copper and composite respectively}, T_s = \text{Ambient temperature} \)

The above Eq.2 has two heat loss constants that can be converted into single heat loss constant by using the thermal mass relationship between the copper and composite. For a body of uniform composition, thermal mass, \( C_{th} \), can be approximated by \( C_{th} = m \cdot c_p \), where \( m \) is the mass of the body and \( c_p \) is the isobaric specific heat capacity of the material averaged over temperature range in question. Thus, the equivalent thermal mass for a copper plate to aerogel composite for a constant cross section area \( (A_{xz}) \) will be as follows.

\[ (t)_{\text{copper(eq)}} = \frac{t_{\text{com}} (\rho \cdot c_p)_{\text{com}}}{(\rho \cdot c_p)_{\text{copper(eq)}}} \]

Eq.3 shows the equivalent thickness of a copper plate that will have the same thermal mass as the aerogel composite. Table 2 shows the specific heat capacities and densities of the materials used in the experiment. The specific heat capacity for the aerogel composite is estimated using the rule of mixture as shown where \( x \) is the weight fraction of the aerogels. Where there are more than two constituent materials involved in the composite, their individual weight fractions are to be accounted in the rule of mixture equation.

\[ (c_p)_{\text{com}} = x (c_p)_{\text{aerogel}} + (1 - x) (c_p)_{\text{gelatin}} \]
Table 2 – Density and Specific Heat Capacity Data

<table>
<thead>
<tr>
<th>Material</th>
<th>(c_p) (J/g-K)</th>
<th>(\rho) (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.39</td>
<td>0.89</td>
</tr>
<tr>
<td>Aerogel</td>
<td>0.7-1.15 [31]</td>
<td>0.08</td>
</tr>
<tr>
<td>Gelatin</td>
<td>1.256-3.98 [32]</td>
<td>0.8925-1.1940</td>
</tr>
<tr>
<td>F MWNT</td>
<td>0.75-0.9 Jg⁻¹K⁻¹ at 360K [33]</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Combining equations (2), (3) and (4) will yield Eq.5a that accounts for heat loss from the composite block due to the rim area and Eq.5b that does not account for the composites heat loss.

\[
e_{1\text{(with HL)}} = V[I\left[A_1(T_1 + T_3 - 2T_s)\right] + \left[A_2\left(T_2 + \frac{1}{3}T_h - \frac{4}{3}T_s\right)\right] + \left[P_{com}e_{copper(eq)}(T_4 - T_s)\right]] \quad (5a)
\]

\[
e_{1\text{(without HL)}} = V[I\left[A_1(T_1 + T_3 - 2T_s)\right] + \left[A_2\left(T_2 + \frac{1}{3}T_h - \frac{4}{3}T_s\right)\right]] \quad (5b)
\]

The amount of heat crossing the aerogel sample is the amount of heat emitted from CP3, which is,

\[
\dot{Q} = e_{1\text{(with HL)}}A_3(T_3 - T_s) \quad (6a)
\]

\[
\dot{\dot{Q}} = e_{1\text{(without HL)}}A_3(T_3 - T_s) \quad (6b)
\]

Substituting Eqs.6a and 6b into Eq.1 will yield the 1-D steady state heat transport

\[
\lambda_{com\text{(with HL)}} = \frac{[t_{com}e_{1\text{(with HL)}}A_3(T_3 - T_s)]}{A_{ycom}(T_2 - T_3)} \quad (7a)
\]

\[
\lambda_{com\text{(without HL)}} = \frac{[t_{com}e_{1\text{(without HL)}}A_3(T_3 - T_s)]}{A_{ycom}(T_2 - T_3)} \quad (7b)
\]

### 3. Results and Discussion

#### 3.1 Experiment Data

3.1.1 Distribution of Aerogel Granules

For any given sample of the aerogel granules, the average distribution of the sizes in the sample can be estimated by fitting a two-term Gaussian function as shown in Fig. 3 from the measured data given in Table 1. Therefore, the aerogel material bulk property \(\phi_a(d)\), in terms of the granule size \(d\) in a given sample can generally be estimated by the given two-term weighted Gaussian function. The coefficients for the function were resolved using curve fitting function in
MATLAB as shown in Eq. 8. For simplicity, the given two-term weighted Gaussian function herein will be expressed as \( \sum_{i=1}^{N} w_i(d_i) \).

\[
\varphi_a(d) = \frac{\sum_{i=1}^{N} \left( 0.5794 \cdot e^{-\left(\frac{d_i - 0.173}{0.03751}\right)^2} + 0.08827 \cdot e^{-\left(\frac{d_i - 0.2067}{0.07171}\right)^2} \right) \cdot \phi}{\sum_{i=1}^{N} \left( 0.5794 \cdot e^{-\left(\frac{d_i - 0.173}{0.03751}\right)^2} + 0.08827 \cdot e^{-\left(\frac{d_i - 0.2067}{0.07171}\right)^2} \right)}
\] (8)

![Graph showing distribution of aerogel granules](image)

**Fig. 3**

Weighted Two-Term Gaussian Fitted function to represent the distribution of aerogel granules in terms of size \((d \text{ cm})\)

### 3.1.2 Thermal Conductivity of Aerogel Granules

Fig. 4a shows the experimentally determined thermal conductivity of aerogel granules of various sizes plotted from the data in Annex A-1 as per Eq. 7a. The error from the difference between Eqns. 7a and 7b is approximately 3.4\%. The mean temperature \((T_m)\) is the average between CP1 and CP3. The thermal conductivity of each size of aerogel granules can be best represented as an
exponential function as shown in the figure for temperature profile from 270 to 377K. Therefore, the general equation (Eq.9) of thermal conductivity for the silica aerogels is as follows; the coefficients A and B are the constants of the respective granule size given in Table 3. The constants are resolved by curve fitting function using MATLAB.

\[ \lambda_a(d, T_m) = A(d) \times \exp[B(d) \times T_m] \]  

(9)

Table 3 – A and B Constants and R² Values of Individual Granule Size in Eq.9

<table>
<thead>
<tr>
<th>Size Range</th>
<th>Median Constants</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (mm)</td>
<td>d (cm)</td>
<td>A</td>
</tr>
<tr>
<td>1.00≤d&lt;1.40</td>
<td>0.12</td>
<td>0.0007</td>
</tr>
<tr>
<td>1.40≤d&lt;2.00</td>
<td>0.17</td>
<td>0.0011</td>
</tr>
<tr>
<td>2.00≤d&lt;2.36</td>
<td>0.218</td>
<td>0.001</td>
</tr>
<tr>
<td>2.36≤d&lt;2.8</td>
<td>0.258</td>
<td>0.0009</td>
</tr>
</tbody>
</table>

The thermal conductivity in general increases with increasing granule size and with increasing \( T_m \). In a sample lot of granules of various sizes from 1.0 to 2.8mm, the thermal conductivity can be empirically estimated as the product of two-term Gaussian function and the above exponential function for each granule size as shown in Eq.10. The general formulation in Eq.8, therefore, can be expressed for the thermal conductivity of the silica aerogels as a function of \( T_m \) and granule size. The empirically determined data is plotted in Annex A-2 as a datasheet and plotted in Fig. 4b (red line). The estimated data exhibits good correlation of the empirical formulation when compared with the measured values of mixed granules sizes. The measured values lie between 93 to 95% accuracy of the predicted equation. The 5 to 7% error is expected as it is due to the fact the only equations for 1.00 to 2.80 mm granule sizes that accounted for 95% of the particle sizes were used in the equation whereas the mixed granules have a range up to 4.00mm granules. The validated experimental data can be found in Annex A-1. Thus a correction factor of 0.93 to 0.95 can be included into Eqn.10 to account for the remaining 5% of the particle size.

\[ \lambda_{abulk}(d, T_m) = \frac{\sum_{i=1}^{N} w_i(d_i) \{ A(d) \times \exp[B(d) \times T_m] \}}{\sum_{i=1}^{N} w_i(d_i)} \]  

(10)
Fig. 4

a) Thermal Conductivity of Aerogel Granules of various sizes as a function of $T_m$; b) Experimental vs Predicted Empirical Formulation (Eqn. 10)

Fig. 5a shows the results of the experimental thermal conductivity for PG, GSA and GSA-SDS evaluated at $T_m = 320 \pm 15K$. The aerogel granules in the GSA, and GSA-SDS blocks are of mixed sizes whereas the PG blocks are purely foamed gelatin that were freeze-dried. PG blocks show higher thermal conductivity in the range of $0.100 \pm 0.04$ W/m-K for gelatin mass fraction of 0.05 to 0.5 and have a power law function in the form of $\lambda_{gel} \propto g^n$, where $g$ is the weight fraction of gelatin. Given that the thermal conductivity of PG is higher than of the aerogels, it is
expected that its addition in the composites will increase the overall thermal conductivity. The thermal conductivities of GSA and GSA-SDS composite blocks were observed to be in the range of $0.025 \pm 0.005$ W/m-K which is approximately $0.006$ W/m-K higher than the of aerogel granules. The results between the frothed and FD specimens showed insignificant difference although the FD specimens show an overall increase of $0.003 \pm 0.001$ W/m-K. However, the FD specimens offer greater consistency as the aerogel granules are closely packed under vacuum. The specimens without SDS are marginally lower but as reported previously, the GSA composites do not offer flexibility and high strain recovery [17]. The term $T_f$ account for the influence of SDS added into the composite and is ratio of the thermal conductivities of the composite with SDS and without SDS. In Fig. 5b, the addition of SDS, however, initially increases the thermal conductivity factor, $T_f$, by $1.066 \pm 0.036$ and exhibits a gradual downward slope even with increasing amount of SDS. It follows a linear function with fit $R^2=0.61$. In our previous work, the optimized mechanical properties were achieved when 0.56% SDS is added to the GSA composites. The GSA-SDS composites of various aerogel granule sizes were fabricated with 0.56% SDS to investigate the effects of the granule size on the thermal conductivity for the same temperature profile mentioned in 3.1.2 for GSA mass fraction ratios of 0.2:0.8 and 0.4:0.6 respectively (Annex A-5) is shown in Fig.6.

![Fig. 5](image)

a) Thermal conductivity of PG, GSA, GSA-SDS (both frothed and FD) specimens evaluated @ $T_m=320 \pm 5K$; b) Influence of SDS% on the $T_f$ of the composites
It is clear from Fig. 6 that the bigger granule sizes have increased thermal conductivity over the smaller ones regardless of the gelatin content following the similar trend to that of silica aerogels in Fig. 3. The bigger granules have smaller contact surface areas as compared to the smaller granules for the same silica content mass. This ultimately allows the heat transfer to be more prominent for composites with bigger granule size than the smaller ones thus having higher thermal conductivity. Comparatively, the increase in aerogel granule size increases the thermal conductivity by 0.005 W/m-K whereas the increase was 0.001 W/m-K when the gelatin content was doubled. Although, the differences were marginal, it can be said that the size of the aerogel granules had greater influence than the gelatin content in determining the thermal conductivity.

The thermal conductivity of the GSA-SDS composite blocks is a function of \( T_f \), weight fractions and thermal conductivities of constituent materials and as well as mean temperature, \( T_m \). Hence, it can be expressed as \( \lambda_{gssds} = f(T_f, \lambda_{abulk}(d, T_m), \lambda_{gel}) \). The predictive model for the thermal conductivity of GSA-SDS is shown in Eq.11 for which the thermal conductivity of the aerogels and porous gelatin were derived in the previous paragraphs.

\[
\lambda_{gssds}(d, T_m) = (1.1277 - 0.1658\alpha) \times \left[ \left( \frac{1 - g}{\lambda_{abulk}(d, T_m)} \right) + \left( \frac{g}{\lambda_{gel}} \right) \right]^{-1} \tag{11}
\]
The predictive model for GSA composites from Eq. 11 was plotted against the experimental value as shown in Fig. 7. The predictive model for aerogel granules (the red dash line) has been corrected for 5% error as shown in Fig. 4. The predictive model (green dotted line) for the GSA-SDS (20/80/0.56) composites revealed better co-relation with the experimental value with a difference of 0.004 ± 0.001 W/m-K as compared with the predictive model for GSA-SDS (40/60/0.56) (red dotted line) which exhibited a wider difference of approximately 0.006 ± 0.002 W/m-K between the experimental and estimated values. This could be attributed to the fact that the $\lambda_{gel}$ was only evaluated at only one temperature profile of 320K thus the effects due to temperature variation for the PG blocks were not accounted in the Eq. 11. This was also evident with the GSA-SDS (20/80/0.56) composites at the higher temperatures where the predictive model seems to under-estimate from the measured data. However, given that the GSA-SDS (20-80-0.56) estimation is closer to the predictive model, this configuration was used in developing the model for the GSA-SDS/FMWNT blocks. The predictive model data are presented in Annex A-6.

![Predictive model](image-url)
3.1.3 Thermal Conductivity of GSA-SDS/FMWNT Blocks

The thermal conductivity experiments for GSA-SDS/FMWNT composite blocks were carried out in the same manner as the other composites. The experimental data can be found in Annex A-7 and A-8 for various %wt of FMWNT. The lowest measured thermal conductivity 0.016 W/m-K is obtained when no SDS is added to gelatin aerogel in the ratio of 0.1:0.9 by mass. It was already reported in our previous work that at this mass ratio, the composites offer little functionality and the ability to absorb compression loads. Similar to the term \( T_f \), \( T_c \) accounts for the influence of FMWNT in the GSA-SDS composites and is expressed as \( T_c = \frac{\lambda_{cn}}{\lambda_{gasa}} \). Given that \( T_f = \frac{\lambda_{gasa}}{\lambda_{gsa}} \), substituting and equating the two expression will result in \( \lambda_{cn} = T_c \ast T_f \ast \lambda_{gsa} \).

![Fig. 8](image)

**Fig. 8**

a) Influence of both SDS and FMWCNT; b) 3D view of coupling effects of \( T_f \) and \( T_c \) with respect to SDS %wt and FMWCNT %wt

Fig. 8a shows comparison of FMWNT influence on the thermal conductivity of GSA-SDS composites as a ratio \( T_c \) with \( T_f \). The coupled effects of both \( T_f \) and \( T_c \) shown in Fig. 8a exhibit converging trends of the thermal conductivity indicating that both the FMWNT and SDS are inter-dependent on the thermal conductivity response. A surface response fitting of 2nd order polynomial function with \( R^2 =0.71 \) was plotted in MATLAB to further explore the coupling effects of \( T_c \ast T_f \) as shown in Fig. 8b. Thus, the thermal conductivity for the GSA-SDS/FMWNT composites can be expressed as \( \lambda_{cn} = f(T_f, T_c, \lambda_{abulk}(d,T_m), \lambda_{gel}) \) and can be evaluated as shown in Eq.12. The full polynomial equation for \( (T_f \ast T_c) \) is given in Annex A-8 and expressed as follows Eq.12.
\[
\lambda_{cn}(d, T_m) = (T_f \ast T_c) \ast \left[ \left( \frac{1 - x}{\lambda_{bulk}(d, T_m)} \right) + \left( \frac{x}{\lambda_{gel}} \right) \right]^{-1}
\] (12)

Thermal conductivity derived in Eq. 12 was plotted and compared with the experimental data of GSA-SDS/FMWNT composites as in Fig. 9. The predicted values of the composites differ by 0.003 ± 0.002 W/m-K which is marginally small for a temperature profile from 290 to 370K.

Fig. 9

Comparison of Experimental and Predictive Model GSA-SDS/FMWCNT composites Thermal Conductivity @ 0.56%SDS

3.1.4 Discussion

The transfer of thermal energy occurs via 3 mechanisms. They are solid conductivity, gaseous conductivity and infrared radiation. Fig. 10 shows a schematic presentation of various modes of thermal transport mechanisms in the GSA-SDS/FMWNT. In addition, the GSA-SDS and GSA-SDS/FMWNT exhibit mechanical properties similar to that of polymeric foam, and thus thermal convection within the cells shall be considered as an additional component in deriving total thermal conductivity, which can be represented by Eq. 13.
\[ \lambda_T = \lambda_s + \lambda_g + \lambda_c + \lambda_r \]  

Where,  
- \( \lambda_T \) is the total thermal conductivity  
- \( \lambda_s \) is the thermal conduction via solid  
- \( \lambda_g \) is the thermal conduction via gas  
- \( \lambda_c \) is the convection within the cells  
- \( \lambda_r \) is the radiation through cell walls and across the cell voids  

Minimizing any of the four components of the thermal conductivity will effectively reduce the porous material’s overall thermal conductivity.

![Diagram of thermal transport mechanisms](image)

**Fig. 10**
Schematic representation of the various modes of thermal transport mechanisms in GSA-SDS and GSA-SDS/FMWNT composites

Solid conductivity, \( \lambda_s \), is an intrinsic property of a specific basic material. Silica aerogels possess a very small fraction of silica mass (approximately 1 to 2\%\) as compared to the overall volume. These extremely light nanoparticles are arranged in a 3D amorphous network with many dead ends essentially reduce the thermal transport through solid conduction. Moreover, silica itself is a poor conductor of heat. The spaces not occupied by solids are filled with air or gas which accounts for almost 99\% of the total volume in the silica aerogels.
The gas conductivity, $\lambda_g$, likewise is inhibited by both the aerogels and porous gelatin network as the gas molecules have limited space to vibrate and move randomly. Gaseous convection, $\lambda_c$ in the aerogels has major influence on the overall thermal conductivity; it is primarily affected by the ratio of the mean free path length of the gas molecules to that of the free space and porosity of the aerogel as reported by Zeng et al. [34]. It was reported that if the mean free path of a particular gas is longer than the pore diameter of the aerogel, the gas molecules will collide with the walls and amongst themselves at a higher rate transferring the thermal energy to the solid particles which already has low intrinsic conductivity. Unlike foams, the aerogel $\lambda_c$ can be reduced further by simply sealing them in commercially available storage vacuum bags [35]. The aerogel granules were purchased commercially with an average pore size of 20nm is deemed reasonable and adequate. For the gelatin foamed network that binds the aerogels, the Grashof, $Gr$ number is an important consideration in convective thermal transport. It describes the ratio of the buoyant force driving convection to the viscous forces opposing it when it is greater than 1000. It is a function of the cell size, temperature difference of gas across one cell, volumetric expansion of gas, density and dynamic viscosity of the gas and finally the acceleration due to gravity [36]. The minimum cell size is determined to be 10mm when $Gr$ number is set to 1000 and given that the aerogels are nano-materials with the particle sizes in the range of 0.1mm to 4.0mm and the gelatin network to be in the similar range, the contribution of $\lambda_c$ should be suppressed completely as reported by Baxter and Jones [37].

The open pores allow thermal transport of gas through the material. At low temperature, radiative thermal transport, $\lambda_r$, is low; however, at high temperature radiation transport becomes dominant and should be suppressed. This can be accomplished by adding carbon which is an effective absorber of infrared radiation. The maximum operating temperature of the GSA-SDS and GSA-SDS/FMWNT composites is approximately 180 to 200°C. Although, the silica aerogels can withstand higher temperature, the gelatin network and the binding capacity will deteriorate beyond the operating temperature. Even though, all experiments were carried out below the maximum operating temperature, FMWNT are added nevertheless to study the influence on the overall thermal conductivity at temperatures below 200°C.
Thus, the thermal conductivity in our works is limited to heat transfer through the solid and gas of the composites and most importantly the development of predictive model based on the aerogel granule sizes. The thermal conductivity of the aerogels regardless of their irregular shape and size can be expressed as an empirical relation with respect to their mean granule size, and aspect ratio as shown in Fig. 4. The experimental results of mixed granules showed excellent co-relation with the empirical formula given in Eq.10. This forms the basis of expanding the equation to include the effects of other material constituents, namely gelatin, SDS and FMWNT. While it is generally accepted that thermal conductivity increases with the increasing temperature, the infusion of addition material also affects the heat insulating performance of the aerogel. In the current study, rule of mixture equation to account for the effects of gelatin, SDS and FMWNT is used, which have been expanded to include the aerogel granules distribution function (i.e. two-term Gaussian function).

The PG blocks thermal conductivity were evaluated in the same corresponding proportions and were used in rule of mixture equation as shown previous section. The effects of SDS were charted as a ratio of composites ($T_f$) with SDS and without SDS as shown Fig. 8a. Similarly, given the extremely small amounts of FMWNT used in the composite, the ratio of composites with CNT and without CNT ($T_c$) is also shown in the same figure. These ratios were tabulated from the experimental data and a functional relationship derived as a result. While, the composites have higher thermal conductivity as compared to the neat aerogel granules, it is interesting to know that addition of SDS reduces the mean thermal conductivity of the composites. Furthermore, the inclusion of FMWNT, showed $T_cT_f$ for composites without SDS which is approximately 0.7 and 0.85 for 0.042 wt% and 0.084 wt% respectively. In addition, it was also observed that the coupled effects of FMWNT and SDS showed an increasing trend that eventually converge towards values that are similar to GSA-SDS. This can be seen from the experimental results of GSA-SDS/FMWNT of 0.033 wt% CNT @ 0.56 wt% SDS annotated by the yellow cross on Fig. 8a. Thus, to achieve lower thermal conductivity, it is best not to use SDS in the mixture. However, as previously reported [17, 38] in our works, without SDS the composites offer little flexibility and application due to brittleness of aerogel granules.

The coupled function of $f(\alpha, CNT) = T_c * T_f$ is a 2nd order polynomial function. The
optimal values of the SDS and FMWNT can then be determined using the 1st and 2nd derivative test that is commonly used in determining the saddle points and the critical points. Setting $\frac{\partial f}{\partial a}$ and $\frac{\partial f}{\partial cnt}$ to zero will yield the optimal values of SDS and FMWNT which can be solved simultaneously. Substituting these values into the expression $|H| = \left[\frac{\partial^2 f}{\partial a^2}\right]\left(\frac{\partial^2 f}{\partial cnt^2}\right) - \left(\frac{\partial^2 f}{\partial a\partial cnt}\right)^2$ will determine whether the critical points will give the maximum or minimum. The coupled function is optimized when $\frac{\partial^2 f}{\partial a^2} > 0$ and $|H| < 0$. The derivation and the associated calculations for the above test are illustrated in Annex A-8. The coupled function is optimized when SDS %wt and FMWNT %wt are 0.323%wt and 0.0303%wt respectively produce $T_c \times T_f = 0.93$. The above statement translates to the possibility of achieving 7% lower thermal conductivity using this configuration of SDS and FMWNT as compared to the composite fabricated without the additives, i.e. GSA composite. While some of the experimental results showed even lower values using FMWNT, it does not represent the consistency achieved with other proportions of SDS and FMWNT in the composite.

The predictive model was validated with two additional specimens of the 0.134 wt% SDS-0.0167 wt% FMWNT and 0.134 wt% SDS-0.0534 wt% FMWNT. The predictive model and the experimental data for validation were plotted as shown in Fig. 11 which clearly showed that the predictive model in Eq.12 reasonably offers good measure of approximation to the experimental values. Thus, the use of the predictive models presented in this paper in for the thermal conductivity to provide close to 94.3% ± 2.4% accuracy to the experimental values.

4. Conclusions

The thermal conductivity of the silica aerogel with various granules sizes was evaluated in a specific temperature profile under room conditions. The thermal conductivity generally increased with the increase in the granule size and it was also the same for the composite blocks. A converging trend, however, was observed in the performance of the composites when SDS and FMWNT were added.
Validated Thermal Conductivity of 0.134% SDS - 0.0167% CNT (black) and 0.134% SDS - 0.0534% FMWCNT (yellow) with the predictive model (Eqn. 12) showing lower values of approximately 7% as compared to GSA (red).

The predictive models were developed from the numerous experiments carried out with gelatin, SDS and FMWCNT in various proportions and in terms of the granule sizes. A coupled function, $TcTf$, based on 2nd order polynomial function were derived from these experimental data and included in the predictive model. The model was validated and showed that a reduction of 7% in thermal conductivity was achieved using GSA-SDS/FMWNT over the GSA composites. The predictive models developed in this paper offers good estimation to the experimental values within approximately 94.3 ± 2.4% accuracy. The predictive models can be tabulated as a data sheet in a number of ways and presented in terms of temperature profile, granule size, various composition of gelatin, SDS and FMWCNT.
Comparison of GSA-SDS-CNT, GSA-SDS, GSA-CNT and GSA composites specific Thermal Conductivity [in Wm$^2$/kg-K] with other commercial thermal insulators

The composites developed and discussed in this paper offer extremely good thermal insulation performance to weight ratio as compared to many commercially available thermal insulators such as foams and wood as shown in Fig. 12. This work not only highlights the invention of a new composite thermal insulator, but also exhibits reduction in the thermal conductivity with the doping of highly conductive FMWNT. This unusual phenomenon resulting from the interaction of FMWNT with the GSA-SDS composite blocks may open doors to many future applications of MWNT.

Acknowledgement

The first author gratefully acknowledges Nanyang Technological University (NTU) for PhD scholarship as well as the financial and other support to this research.
References