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## Review Article

# Aerogels in Aerospace: An Overview

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Aerogels are highly porous structures prepared via a sol-gel process and supercritical drying technology. Among the classes of aerogels, silica aerogel exhibits the most remarkable physical properties, possessing lower density, thermal conductivity, refractive index, and dielectric constant than any solids. Its acoustical property is such that it can absorb the sound waves reducing speed to 100 m/s compared to 332 m/s for air. However, when it comes to commercialization, the result is not as expected. It seems that mass production, particularly in the aerospace industry, has dawdled behind. This paper highlights the evolution of aerogels in general and discusses the functions and significances of silica aerogel in previous astronautical applications. Future outer-space applications have been proposed as per the current research trend. Finally, the implementation of conventional silica aerogel in aeronautics is argued with an alternative known as Maerogel.

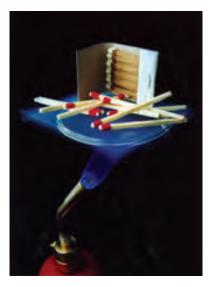
### 1. Introduction

Aerogels are nanoporous light materials consisting of an open-cell network with numerous exceptional characteristics which intrigue the intuition of scholars in various areas of science and technology. Their range of applications is almost illimitable, tracing their way in different branches such as thermal and acoustical insulation, kinetic energy absorption, electronics, optics, chemistry, and biomedicine amongst others [1-5]. Within the classes of aerogels, silica aerogel, which is the porous nanostructured form of silica dioxide, exhibits the most fascinating properties such as low thermal conductivity  $(\sim 0.015 \text{W/mK})$ , low bulk density  $(\sim 0.1 \text{g/cm}^3)$ , optical transparency in the visible spectrum (~99%), high specific surface area ( $\sim 1000 \text{ m}^2/\text{g}$ ), low dielectric constant ( $\sim 1.0-2.0$ ), low refractive index (~1.05), low sound velocity (100 m/s), and hydrophobicity [6–8]. This unique combination of characteristics is due to their microstructures consisting of nanosized

Considerable number of papers has been published during the past two decades showing not only the enthusiasm but also the scientific understanding of these nanostructures. Today, one of the most focusing areas is the modeling of

the thermal behavior of granular- and fiber-based silica aerogel and its composites [9–13]. Despite all these efforts, silica aerogel has been applied only for scientific motives in the aerospace industry. NASA has conducted many astronautical missions using this type of aerogel as a hypervelocity particle capture and thermal insulator. T  $\mbox{\sc lim}$  aviation world, both civil and military, can also be a promising market niche. For example, with the ever-increasing energy consumption and the rapidly growing interest from governments around the globe for renewable energy sources, high performance thermal insulation materials are required.

Why silica aerogel is not chosen as a candidate to resolve this problem? Why the applications remain unrealized in this sector? To the authors' knowledge, there is no available literature that discusses the potential applications of silica aerogel in the aerospace sector with regards to commercialization. This paper highlights the evolution of aerogels in general and discusses the functions and significances of silica aerogel in previous astronautical applications. Future outer-space applications have been proposed as per the current research trend. Finally, the implementation of conventional silica aerogel in aeronautics is argued with an alternative known as Maerogel.



Figur e 1: Matches on aerogel over a flame [17].

### 2. Evolution of Aerogels

Aerogel, nicknamed as the "blue smoke" or "frozen smoke" because of its cloudy appearance (see Figure 1), while believing that it is a recent invention of the nanotechnology due to its nanostructure features, is in fact a long-forsaken material developed by Samuel Stephens Kistler at his time at the College of the Pacific in Stockton, CA, USA. In 1931, he made his first publication on aerogels in nature [14] wherein he characterized an aerogel as a gel in which the liquid phase has been replaced by a gas in such a way that the solid network is being retained with only a slight or no shrinkage in the gel. The success of this process was based on one vital step of heating up the gel system in an autoclave above the critical temperatures and pressures of the liquid phase of the gel, which is known as supercritical drying. The resulted supercritical fluid was allowed to escape leaving behind a highly porous and extremely low-density material.

The first aerogel made by Kistler was silica aerogel using sodium silicate (water-glass) as the precursor of silica. Along time, he synthesized organic and metal oxides aerogels from alumina, tungsten oxide, ferric oxide, tin oxide, nickel tartrate, cellulose, nitrocellulose, gelatin, agar, egg albumen, and rubber [15]. He further extended his studies into the physical properties of silica aerogel, emphasizing on its structure, density, and thermal conductivity by varying the mechanical pressure and filling gases such as air, carbon dioxide, and chlorofluorocarbon [16].

As a result, silica aerogel was identified as the solid with the lowest heat conductivity at atmospheric pressure [18]. In 1950s, one of Kistler's patents was allocated to Monsanto Corporation for large-scale production of silica aerogels for applications such as thickening agents and thermal materials under the trademark Santocel [19]. Later, he patented the first hydrophobic silica aerogels made by silylation with trichloromethylsilane to produce water repellents [20]. Unexpectedly, Masanto's project came to an end ceasing all productions with the introduction of a relatively cheap fumed silica process

using tetrachloride in 1960s. Since then, there were no interests in aerogels due to the tedious and time-consuming procedures involved in the synthesis of aerogels and the high manufacturing cost.

Consequently, commercialization lagged behind by a long time until in 1968 when a group of researchers headed by Teichner and Nicoloan in France reformulated a simpler preparation by applying the sol-gel chemistry to silica aerogel preparation thereby replacing waterglass used by Kistler with tetramethyl orthosilicate (TMOS), an alkoxysilane, which was then removed at supercritical conditions [21]. Aerogels of silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), titania (TiO<sub>2</sub>), zirconia (ZrO<sub>2</sub>), magnesium oxide (MgO), and combinations of ZrO<sub>2</sub>-MgO, Al<sub>2</sub>O<sub>3</sub>-MgO, and TiO<sub>2</sub>-MgO were produced. While using that route, these oxides of aerogel were observed to exhibit higher values in terms of textural characteristics compared to the ones obtained through the original method. The surface area was also greater than their corresponding pure oxide aerogels [22]. This accomplishment triggered a new revolution in the science and technology world leading to intensive studies on this nanoage material. The first scientific application of aerogels was the Cherenkov radiation detector, developed by Cantin et al. in 1974. Subsequently, mass production started and several cubic meters of monolithic highly transparent tiles of silica aerogel were produced to equip the TASSO Cherenkov detector [23].

The first factory to produce blocks of silica aerogel using TMOS was established in Sweden but got devastated by an explosion due to a leak in the autoclave in the presence of methanol in 1984. The plant was rebuilt and is currently being operated by Airglass Corporation [24]. Because of its toxicity, TMOS was compelled to be replaced. Soon, Tewari and Hunt at Berkeley found tetraethyl orthosilicate (TEOS) to be a safer reagent which would not alter the quality of the aerogels [25]. But the process was not safe yet to attain mass production. Hunt continued to investigate for improvements and came up with the idea of replacing the alcohol within the gel by liquid carbon dioxide before supercritical drying because CO<sub>2</sub> is inflammable and requires a lower temperature and pressure to become supercritical [26]. This would reduce any hazard risks and increase the energy efficiency, hence resulting in a cheaper manufacturing cost. At the same time, BASF in Germany declared to have developed another CO<sub>2</sub> replacement route via sodium silicate. They marketed the product as Basogel until 1996 [4].

In 1987, the introduction of helium pycnometry for measuring the skeletal density of aerogels provided data such that the density varies with the solvent concentration, pH, and densifying heat treatment [27]. At the end of the 80's, Pekala at LLNL expanded the classes of aerogel by developing organic and carbon aerogels from an organic polymer, resorcinol-formaldehyde (RF) using the sol-gel method [28]. Tillotson and Hrubesh developed monoliths of diaphanous silica aerogel with the lowest density, 0.003 g/cm³, and of porosity up to 99.8% using a two-step acid-base process which involved the substitution of the alcohol with an aprotic solvent, by distillation, causing gelation [29]. That was the first aerogel achievement in the 90's.

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NASA has been using tiles of these aerogels for space exploration since then. Later, it was found that, by heating up a RF aerogel to temperatures of several hundred degrees Celsius in an inert atmosphere (such as nitrogen or argon), the polymer which makes up the aerogel is dehydrated leaving behind an aerogel made of carbon. Unlike silica aerogel, carbon aerogel is a conductor of electricity. It was called the aerocapacitor and characterized as an "electrochemical doublecapacitor with high-power density and high-energy density" [30, 31].

Another key development was the subcritical drying method which was devised to produce low-density silica aerogels for thermal insulation [32]. The method involved a series of aging and pore chemical modification stages to prevent drastic gel shrinkage during the fast drying at ambient pressure. The density varies between 0.15 and 0.3 g/cm<sup>3</sup> with a thermal conductivity of 0.02 W/mK at atmospheric conditions. Prakash et al. extended the ambient pressure drying (APD) method to further decrease the manufacturing cost of silica. A simple dip-coating process consisting of surface modification to induce reversible drying shrinkage was used [33]. The precursor was waterglass because of its low cost and nonflammability. The resulting aerogel was observed to have comparable density and porosity to that using the supercritical drying route. Since then, many articles were published ranging from synthesis to physical properties of silica aerogel using the APD method, indicating its advantages. However, the route alters and some approaches are more timeconsuming than others because of the lengthy process of washing and exchanging solvents [34-39].

Next was the rapid supercritical extraction (RSCE) which speeded up the supercritical heating. Experimented by John Poco at LLNL in 1996, this investigation consists of placing the sol-gel inside a pressurized mold in which the supercritical conditions were controlled in such a way to avoid unnecessary expansion and hence cracking [40, 41]. Considerable enhancement started taking place at the dawn of this millennium. In 2001, an easy, cheap, and ef Ective method was developed by Gash and Tillotson to prepare metal oxide aerogels by using epoxide-doped gelation agents provided that the corresponding metal ions should have a valency of equal or greater than +3 in their formation oxidation state. The results were promising and blocks of microporous materials with high surface areas were produced [42]. One year later, Leventis et al. developed the ultralight mechanically modified aerogels, called X-aerogels by cross-linking diisocyanates into the microstructure of silica aerogels. The strength of the latter was multiplied by 300 whilst its specific compressive strength is approximately ten times that of steel [43]. His work was extended with the assistance of other researchers to investigate the polymer cross-linking with other types of aerogel such as transition metal oxides and organics which would further broaden the applications of aerogels [44]. X-aerogels have been accomplished through the addition of a polymer as a conformal coating on the silica skeleton.

On the other hand, semiconductors made of metal chalcogenide were reported in 2005 by Mohanan et al. They used a method which consisted of oxidation aggregation of metal chalcogenide nanoparticle building blocks coupled with supercritical drying. The resulting semiconductor had a high porosity and surface area, and the characteristic quantumconfined optical properties were identical to their nanoparticle components [45]. The next year was the invention of monolithic nanoporous metal foams which possess extremely low density and high surface area of 0.01 lg/cm<sup>3</sup> and 270 m<sup>2</sup>/ g, respectively [46]. The metals selected were iron, cobalt, copper, and silver while other potential ones are still under research. Carbon nanotube aerogels were then invented in 2007 through a new synthesis method comprised of aqueousgel precursors, followed by supercritical drying and freeze drying. The nanotubes can be made more robust by doping polyvinyl alcohol which would allow them to resist a weight of 800 times heavier than their original version. They are also excellent conductors of heat and electricity [47].

Filed in 2004 and patented in 2007, Halimaton presented her method to produce pure silica aerogel via a sol-gel method followed by supercritical carbon dioxide drying. However, she used an agricultural waste product, rice husk ash (RHA), as the source of the silica (see Figure 2). The commercial term is Maerogel standing for "Malaysian-made Aerogel" [48]. The texture and physical properties of the latter have been proved to be comparable to traditional silica aerogels (see Table 1).

Maerogel is produced by first dissolving rice husk ash in aqueous sodium hydroxide at a Na2: SiO2 ratio of 1:3.33, to produce a sodium silicate solution containing from 1 to 16% by weight of SiO<sub>2</sub>. Concentrated sulphuric acid is then added to the resulting water-glass solution to convert the sodium silicate to silica to obtain a silica hydrogel. Next is the aging process which will allow the gel structure to develop. This can be for a period of up to forty days. The water is then displaced with a C<sub>1</sub> to C<sub>4</sub> alcohol, preferably methanol or ethanol to get an alcogel. The latter is subjected to supercritical drying after the alcohol is being replaced by carbon dioxide to obtain an aerogel. The supercritical extraction is preferably carried out by placing the alcogel with additional alcohol in an autoclave f tted with a thermocouple and a temperature controller and slowly raising the temperature in the autoclave until the critical temperature and pressure are reached. T le temperature may be increased, for example, at a rate of 50°C/h, for the time necessary to reach the critical temperature. After a certain time, the alcohol vapor is vented through a controlled leak by gradually reducing the pressure and temperature to atmospheric conditions. The temperature may be reduced over a period of, for example, twelve hours. The amount of additional alcohol should be such that there is sufficient alcohol in the autoclave for the critical pressure to be reached. The aerogels obtained are hydrophilic, having hydroxyl groups on their surface but can be converted to a hydrophobic form by replacing the hydroxyl groups with alkoxy groups. This may be achieved, for example, by passing methanol vapor over a heated sample of the aerogel. The methylation reaction is more advantageously to be carried out in a closed system in which the sample can be placed in a tube enclosed in an external furnace and extending between a flask containing boiling methanol and a condenser, which is connected back

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Property	Conventional aerogel	Maerogel	Comments
Apparent density	0.003-0.35 g/cm <sup>3</sup>	$0.03\mathrm{g/cm}^3$	Commonly ~0.1g/cm <sup>3</sup> for conventional aerogels; Usually 0.03 g/cm <sup>3</sup> for Maerogel
Internal surface area	$600-1000 \text{ m}^2/\text{g}$	$700-900 \mathrm{m}^2/\mathrm{g}$	
Mean pore diameter	20 nm	20.8 nm	Varies with density
Particle diameter	2-5 nm	5 nm	Determined by electron microscopy
Thermal tolerance	500°C	500°C	Shrinkage begins gradually at 500°C
Melting point	>1200°C	>1200°C	
Typical thermal conductivity	0.015W/mK	0.02 W/mK	
Coefficient of thermal expansion	$2.0 - 4.0 \times 10^{-6}$	$2.0-4.0 \times 10^{-6}$	Determined using ultrasonic techniques
Poisson's ratio	0.2	0.2	Independent of density
Young's modulus	$10^6 - 10^7 \text{ N/m}^2$	$10^6 - 10^7 \text{ N/m}^2$	Insignificant compared to dense silica
Tensile strength	16 kPa	16 kPa	For density of 0.1g/cm <sup>3</sup>
Fracture toughness	$0.8  \mathrm{kPa \cdot m}^{0.5}$	$0.8  \mathrm{kPa \cdot m}^{0.5}$	For density of 0.1g/cm <sup>3</sup>
Index of refraction	1.0-1.05	1.0-1.05	
Dielectric constant	~1.1	~1.1	For density of 0.1g/cm <sup>3</sup>
Sound velocity	100 m/s	100 m/s	For density of 0.07 g/cm <sup>3</sup>

Table 1: Physical properties of conventional silica aerogel and Maerogel.

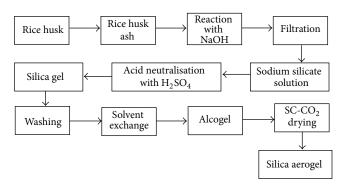


Figure 2: Schematic procedure of Maerogel preparation from rice husk.

to the flask. The temperature of the furnace may be of the order of 250°C. The samples are preferably outgassed at a temperature of about  $100^{\circ}$ C under a reduced pressure of about  $1.33 \times 10^{-5}$  kPa for at least 15 hours both before and after the methylation process [48].

Other approaches were defined using RHA at either supercritical or ambient conditions. Tang and Wang provided a preparation but the value of the surface area was lower than that using TEOS/supercritical-ethanol drying. The aerogel was not transparent, rather it was white [49]. Following that, a route which used drying process at atmospheric pressure and a temperature of 40°C was developed by Li and Wang [50]. In this method, the hydrosol was modified by a small amount of TEOS which would greatly affect the pore structure and hence other physical properties. The porosity, surface area, pore volume, and average pore size were found to be directly proportional to the amount of TEOS added while the density was inversely proportional. An optimal amount of TEOS was however achieved [51].

In 2009, the first metal aerogel was made by Leventis et al. It was an iron aerogel created by smelting interpenetrating of

resorcinol-formaldehyde and iron oxide xerogels (ambientdried aerogels). They were "ferromagnetic and superparamagnetic" materials being rich in carbon and simultaneously magnetic and metallic [52]. Recently, a superior polymerized aerogel known as polyimide aerogel has been tailored at NASA's Glenn Research Center in Ohio [53]. Polyimide gels are produced by cross-linking anhydride-capped-polyamic acid oligomers with aromatic triamine in solution and by chemically imidizing. The subsequent gels are then supercritically dried to form polyimide aerogels. These modified aerogels have densities as low as 0.14 g/cm<sup>3</sup> and surface areas as high as  $512\text{m}^2/\text{g}$  [54, 55]. The mechanical strength of this new class of aerogel is 500 times higher than the traditional silica and can provide bulk thermal and acoustical insulation. However, the thermal conductivity is increased by a certain factor because of its monolithic nature [53].

### 3. Properties of Silica Aerogels

The physical properties of an aerogel are highly dependent on its density and chemical composition. Hence, different synthesis methods will lead to dissimilar typical values for certain properties. This is illustrated in Table 1. In accordance with the scope of this article, an insight on the thermal, optical, and mechanical characterizations of silica aerogels has been provided.

3.1. Thermal Properties. T h thermal conductivity of silica aerogels has forevermore been the focal topic of researchers since the beginning. Aerogels can be synthesized into multiple forms: monoliths, grains, powders, and films, conforming to the desired application. NASA has previously used monolithic silica aerogels for the thermal insulation for space applications [56]. The total thermal conductivity  $\lambda_t$ for monolithic aerogels is attributable to three heat transfer mechanisms: solid conduction via the solid backbone  $\lambda_s$ , gaseous conduction through the gas molecules in the porous structure  $\lambda_a$ , and radiation  $\lambda_r$  [57]. Convection can be neglected in aerogels due to their nanosized pores [58, 59]. The solid structure of aerogels is made up of only a small number of silica particles tortuously interlocked in a threedimensional network with many dead-ends which therefore impedes the thermal transport [15]. Studies have shown that the heat transfer through the solid structure of an aerogel depends on its lattice structure, connectivity, and composition. Lu et al. equated the solid thermal conductivity with a factor depending on the interconnectivity of the particles and density [60]. A more convenient equation was provided by Bi and Tang et al., in which the solid thermal conductivity  $\lambda_s$  is derived by measuring the sound velocity in the aerogel [61] as follows:

$$\lambda_s = \lambda_0 \frac{\rho}{\rho_0} \frac{\nu}{\nu_0},\tag{1}$$

where  $\rho$  is the density of aerogel,  $\rho_0$  is the density of solid backbone,  $\nu$  is the sound velocity in aerogel,  $\nu_0$  is the sound velocity in solid backbone, and  $\lambda_0$  is the thermal conductivity of solid backbone. The latter is usually replaced by  $\lambda_{\rm bulk}$  to simplify the calculation as it cannot be measured straightforwardly. However, this substitution may alter the result to some extent. Nevertheless,  $\lambda_0$  can be obtained by using the kinetic theory as follows:

$$\lambda_0 = C_\nu \nu_0 \frac{\Lambda_0}{3},\tag{2}$$

where  $C_{\nu}$  is the volume specific heat,  $\nu_0$  is the mean sound velocity of the solid backbone, and  $\Lambda_0$  is the average interatomic spacing in solid backbone.

The heat transfer through the gaseous phase is dictated by the Knudsen effect which expresses the gaseous conduction in a porous medium as a function of the air pressure and the effective pore dimension [60]. The corresponding equation is as follows:

$$\lambda_g = \lambda_{g0} \frac{\Pi}{1 + \beta K_n},\tag{3}$$

where

$$K_n = \frac{l_g}{\phi},\tag{4}$$

$$I_{\text{mean}} = \frac{\kappa_B T}{\sqrt{2}} \pi d_g^2 P_g, \tag{5}$$

where  $K_n$  is the Knudsen number, a characteristic quantity for the gaseous thermal conductivity in a porous system.  $l_g$  is the mean free path of the gas molecules,  $\phi$  is the characteristic length of pores,  $d_g$  is the diameter of the gas molecules,  $\Pi$  is the porosity,  $\lambda_{g0}$  is the thermal conductivity in free air,  $\kappa_B$  is the Boltzmann constant, T is the temperature,  $P_g$  is the gas pressure, and  $\beta$  is a constant specific to the gas in the pores, usually between 1.5 and 2.0 [62].

The gaseous thermal conductivity in silica aerogels is directly proportional to the pressure and pore sizes and indirectly proportional to the density. Besides, the nanoscaled solid structure of aerogels has a significant effect on the gaseous thermal conductivity, particularly for pressures between  $0.01 \times 10^5$  Pa and  $100 \times 10^5$  Pa [63].

The impact of radiation on the overall thermal conductivity of aerogels can be substantial from ambient conditions to high temperatures (above  $200^{\circ}$ C) due to their low absorption for the infrared [10]. Radiative conductivity can be calculated by [60]

$$\lambda_r = \left(\frac{16}{3}\right) n^2 \sigma \frac{T^3}{\left[e\left(T\right)\rho\right]},\tag{6}$$

where  $\sigma$  is the Stefan-Boltzmann constant, n is the mean index of refraction of aerogel, T is the absolute temperature, e(T) is the mass specific extinction coefficient, and  $\rho$  is the density of aerogel.

It is worthwhile to note that there is an alternative approach to evaluate the effective thermal conductivity of silica aerogel  $\lambda_t$ . It uses a concept where the heat transfer mechanisms are radiation and a combined solid and gas conduction. The solid and gas thermal conductivity  $\lambda_c$  is developed based on a periodic structure, whilst the radiative conductivity  $\lambda_r$  is calculated using the diffusion approximation theory and the Rosseland equation [58, 64, 65].

The common techniques to measure the thermal conductivities of silica aerogels are hot-wire probe [69], hot disk thermal constant analysers [70], and heat-flux meters [71] or using a laser-flash apparatus [72]. However, in these techniques, the heat distribution across the aerogel under study is not uniform. Zeng et al. [73] suggested a way out where a thin-f lm heater made of a 10 nm thick gold film can be used to disperse the heat evenly. Table 2 summarizes the different approaches to predict the thermal conductivity of silica aerogels.

3.2. Optical Properties. The transparency and translucency appearances of aerogels are primarily due to Raleigh scattering, which occurs when the heterogeneities in the solid gel network are much smaller than the wavelength of visible light. The amount of light scattered from an aerogel is dependent on these structural inhomogeneities which in turn can be controlled during the supercritical extraction which dictates

Model	Author	Structure representation	Method	Comments
Empirical	Lu et al. [60] Wang et al. [67]	Ignored	Volume average as a function of density or porosity	Cannot be applied for aerogels with different microstructures
Analytical	Wei et al. [10] Lu et al. [65] Wei et al. [10]	Cubic array of nanospherical structure	Standard equivalent circuit method	Cannot represent the randomness and complexity of aerogels
	Jun-Jie et al. [66]	3D random DLCA structure	Standard equivalent circuit with improved analytical parallel-series model	Does not require any empirical parameters as input
Numerical	Spagnol et al. [68]	Von Koch snowflake fractal structure and random	Finite volume method	3D calculations are time

DLCA structure

Table 2: Approaches to predict the thermal conductivity of silica aerogels (adapted from Jun-Jie et al. [66]).

the spatial arrangements of the gel network. Rayleigh scattering is inversely proportional to the fourth power of the wavelength, that is, the shorter the wavelength of the light, the more it scatters. Therefore, when an aerogel tile is placed against a dark background, it appears slightly bluish and demonstrates a yellowish coloration when exposed to bright surroundings [74, 75]. The second source of light scattering in the visible range is due to micrometer-size imperfections of the external aerogel surface which accounts for the blurry appearance of objects viewed through a piece of aerogel [76]. On the other hand, the scattering efficiency is a function of the size of the scattering center. Thus different wavelengths will scatter with varying magnitudes. Scattering is observed to be intensified when the size of the scattering center becomes similar to the wavelength of the incident light [76, 77]. As the wavelength increases and the spectrum shifts towards the infrared range, scatterings become less significant. This phenomenon permits heat radiation to pass through the aerogel thereby increasing its thermal conductivity [78]. Many times, the optical properties of aerogels are related with their thermal properties, especially when a transparent thermal insulation system is demanded. A number of studies have been undertaken to optimize the transparency of silica aerogel without sacrificing its thermal conductivity. Danilyuk et al. [79] found that monolithic aerogel prepared using the twostep sol-gel method is more transparent than the one synthesized through the one-step approach. Venkateswara Rao and Pajonk [80] added methyltrimethoxysilane(MTMS) as a coprecursor to produce monolithic durable hydrophobic silica aerogels with high direct optical transmittance and low diffusion of light. Adachi et al. [81] synthesized new tiles of silica aerogels by adding a new chemical solvent, dimethylformamide (DMF), to improve the optical transparency in the refractive index range,  $\eta = 1.03-1.07$ . The transmission length exceeded 40 mm at 400 nm wavelength which was twice the value obtained in a previous study [82]. Bhagat et al. showed that when low density TEOS-based silica aerogels is prepared using methanol as a solvent in combination with TEOS in a two-step sol-gel process, the optical transmission is improved to some extent [83]. On the contrary, if opacity is preferred, aerogel can be rendered opaque by integrating carbon or mineral powders into its structure which will absorb the infrared and hence reducing the radiation heat transfer [84-86].

From the early age, transparent silica aerogel has been promoted as a hypervelocity particle capture for outer-space explorations because of its capacity of allowing easy detection of cosmic debris through its framework. Recently, Woignier et al. [87] investigated the effect of TEOS concentration and the addition of ammonia as a base catalysis on the optical transmission within the visible spectrum. It was found that aerogels with a higher concentration of TEOS have a wider transmission window than that with a lower TEOS concentration which affirms poor transparency in the visible range. When ammonia is added in the aerogel process, the transmission is extraordinarily enhanced in the visible range.

Another imperative optical property of silica aerogels is the index of refraction. It has been proven that the index of refraction,  $\eta$ , increases with increasing density such that

$$\eta = 1 + 2.1 \times 10^{-4} \rho,\tag{7}$$

where  $\rho$  (k gm<sup>-3</sup>) is the bulk density of aerogel [1].

It can therefore be anticipated that the refractive index for silica aerogel is very close to one, literally meaning that when light enters an aerogel, there is no reflective losses. A practical application which exploits this property is the Cherenkov detector which necessitates a medium with a refractive index close to one [88].

3.3. Mechanical Properties. Silica aerogels are known to be characteristically fragile and brittle because of the interparticle connections within the pearl-necklace-like fractal network, making them inapt for load bearing applications. Numerous investigations have been carried out to appreciate and characterize their mechanical properties, as shown in Table 3. Standard methods to characterize the silica aerogel mechanically include ultrasonic techniques, three-point bending, and uniaxial compression. The atomic force microscopy (AFM) is now commonly employed because of its capability of measuring the local elastic property of aerogels with only a small loading force. Concurrently, efforts are being concerted to improve the mechanical strength of aerogels by the addition of a second phase. One approach is through incorporating silica fibres into the aerogels. Tests have indicated that when 10% by weight of these f bres are introduced, the elastic modulus and strength are increased by 85% and

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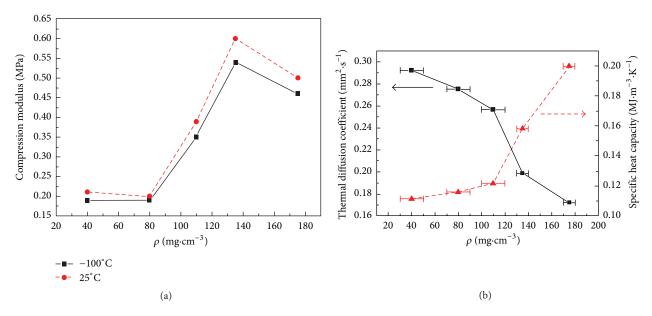
Table 3: Mechanical studies on silica aerogel.

Methodology	Author	Analysis	Approach/apparatus
	Arvidson and Scull [11]	Young's modulus, proportional limit, and yield strength	A concentric, overlapping-cylinder, capacitance extensometer is used to measure the strain
	Gronauer et al. [112]	Young's modulus	Sound velocity measurements
	Woignier and Phalippou [11 <b>3</b> ]	Young's modulus, fracture strength, and toughness	Three-point flexural and three-point bending
	Gross et al. [11]	Young's modulus and Poisson's ratio	Ultrasonic and static compression
	Scherer et al. [115]	Bulk modulus	Mercury porosimetry
Experimental	Parmenter and Milstein [89]	Hardness, compression, tension and shear on unreinforced and fiber-reinforced aerogels	Vickers and Knoop hardness test four-point bending, and a displacement-controlled Instron 1123 testing machine
	Stark et al. [116]	Young's modulus	Atomic force microscopy
	Moner-Girona et al. [17]	Hardness, Young's modulus, and elastic parameter	Microindentation measurements using a Nanotest 550 Indenter
	Martin et al. [18]	Young's Modulus	Uniaxial compression and acoustic velocity
	Perin et al. [19]	Elastic modulus and internal friction	Isostatic compression
	Miner et al. [120]	Young's modulus and nonrecoverable strain for hygroscopic silica aerogel	Low-range compression tester
	Despetis et al. [12]	Subcritical growth domain in hydrophilic silica aerogel	Double-cleavage-drilled- compression test (DCDC)
	Takahashi et al. [122]	Bending strength	Three-point bending
Numerical	Yang et al. [123]	Creep behavior of ceramic fiber-reinforced silica aerogel	Scanning electron microscope
	Hasmy et al. [124]	Wave-vector-dependent scattered intensity	Cubic DLCA fractal structure model
	Rahmani et al. [125]	Densities of states and dynamic structure factors	3D cubic DLCA fractal structure model
	Yang et al. [123]	Creep behavior of ceramic fiber-reinforced silica aerogel	Power-law creep model

26%, respectively [89]. In addition, the compressive modulus and tensile strength of aerogels can be improved by three and five times correspondingly, if 5% by weight of carbon nanofibres are implemented into the lattice structure [90]. Liquid-phase cross-linking, vapor-phase cross-linking, fibre reinforcing, and reduced bonding can enhance the mechanical properties of aerogel as well [80, 91, 92]. X-aerogels have been proven to improve considerably the fractal properties of native aerogels under both quasi-static [43, 93-97] and highimpact loading conditions [98, 99]. While their strength is superior to silica aerogels, their elasticity and flexibility properties are yet to be tailored for advanced aerospace applications such as structural components and thermal protection for small satellites, spacecraft, planetary vehicles, and habitats. Several cross-linking schemes to mechanically reinforce aerogels have been discussed in details in [100]. It is noteworthy to state that polymer reinforcement decreases the surface area of the silica aerogel by about half without altering the thermal conductivity radically [100].

Probably, the most notable application of silica aerogel in astronautics is to capture extraterrestrial materials. This is primarily because it does not constitute elements of great cosmochemical significance as well as inorganic contaminants and secondly owing to its grandiosity in trapping particles with high velocities. Yet, researchers are continually experimenting on this nanomaterial to improve its physical properties to develop a flawless kinetic shock absorber. Most of the time, the modification is made during the synthesis process as the aerogel mechanical characteristics highly depend on its bulk density [101, 102].

The mechanical and thermal properties of density-gradient aerogels for outer-space hypervelocity particle capture were analyzed by Du et al. (see Figure 3) [103]. Aerogels with densities ranging from 40 to 175 mg/cm<sup>3</sup> were prepared using a tetraethyl orthosilicate (TEOS) and ethanol-water solution as the precursor and hydrofluoric acid as the catalyst via a supercritical drying sol-gel process. Layer-by-layer gelation, sol cogelation, and gradient-sol cogelation methods were



Figur e 3: Compression modulus of aerogels with different densities at  $-100^{\circ}$ C and  $25^{\circ}$ C [103]. Relationship between thermal diffusion coefficient and specific heat capacity with density of aerogels [103].

used to prepare the density-gradient aerogels. The dynamic mechanical test showed that the Young's moduli of the aerogels at  $-100^{\circ}\text{C}$  and  $25^{\circ}\text{C}$  tend to decrease with decreasing the density with values from  $4.6\times10^{5}$  to  $1.9\times10^{5}$  Pa and from  $5.0\times10^{5}$  to  $2.1\times10^{5}$  Pa, respectively. The thermal analysis indicated that the thermal diffusion coefficients and the specific heat capacities decrease with decreasing the densities while the thermal conductivities do not change monotonically.

One weakness of aerogel as a hypervelocity capture particle could be its crack propagation which can eventually destroy the entire aerogel lattice when exposed for a long period of time. This is induced by the syneresis effect which is the continuation of the hydrolysis and condensation reactions after gelling which leads to the gel shrinkage [87, 101]. Hwang et al. observed a 10% linear shrinkage caused by syneresis during the gelation and aging procedures [104]. Woignier et al. [87] investigated the influence of the synthesis variables on the shrinkage of aerogel during preparation and delivered a good correlation on the mechanical properties with an aim to acquire an optimized aerogel for outer-space applications. It was revealed that the linear shrinkage decreases with the TEOS concentration and with increasing pH of hydrolysis solution. In addition, both elastic modulus and rupture strength of aerogels rise with a higher concentration of TEOS and hence density.

# **4.** Astronautical Applications of Silica Aerogels

4.1. Hypervelocity Particle Capture. The preliminary studies conducted at the laboratory where unmolten remnants of silicate and aluminum projectiles were fired at high speed, 7 km/s, immediately indicated the superiority of aerogel as

a hypervelocity particle capture compared to traditional dense collector media, including those exposed on the long-duration exposure facility (LDEF). The defects in these conventional collectors were their persistent melting, if not complete vaporization, which prevented any projectiles to be adhered. Hence, no analysis was possible. Researchers anticipated that this kinetic energy absorption characteristic to aerogel would boost the discoveries of extraterrestrial objects in low-Earth orbit [105].

Soon after, in September 1992, aerogels were sent on the Space Transport System (STS-47) to analyse their ability as a hypervelocity particle capture medium and endurance during launch and reentry. Five thermal insulated end covers were installed on the top of the Shuttle Get Away Special (GAS) payload canisters to hold the Sample Return Experiment (SRE) of capture cells equipped with panels of silica aerogel with dimensions of  $10 \text{cm} \times 10 \text{cm} \times 1 \text{cm}$  and densities of the order 20 mg/mL. Each GAS SRE provided a net total capture surface area of 0.165 m<sup>2</sup>. The aerogels successfully survived the launch and reentry and returned without any apparent damages. Generally, the capability of a hypervelocity particle capture is evaluated by how fast it can decelerate the highvelocity impacted particles without destroying the latter while being trapped. At least four large hypervelocity particles were captured during this preliminary mission. Later on, more than two dozens of particles were caught from STS-60 and many from others such GAS canisters [106]. One of them was the orbital debris collection experiment on Mir.

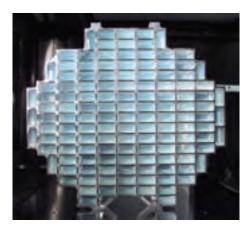
Deployed on STS-76 on March 25, 1996, and directed by Langley Research Center, the Mir Environmental Effects Package (MEEP) was equipped with an Orbital Debris Collector (ODC) made up of approximately 0.63 m<sup>2</sup> of highly porous low-density (0.02 g/cm<sup>3</sup>) silica aerogel arranged in two identical trays, Tray 1 pointing into the ram direction

while Tray 2 in the opposite direction, to collect both manmade and natural hypervelocity particles in the low-Earth orbit. The ODC was then recuperated by STS-86 after 18 months at the Johnson Space Center.

A wide range of impacts, for example, coorbing flakes, human waste materials, and cosmic dust, were extracted from the aerogel collector to analyse their compositions using SEM-EDS and TEM, and henceforth their potential origins were suggested. Two primary classes of hypervelocity impact features were revealed: long, carrot-shaped tracks and shallow pits with typical length to diameter (L/D) of 20–40 and 0.5-5, respectively. The majority were carrot-shaped tracks coming from laboratory impacts, including the presence of trapped projectile residues at their stations while the pits did not contain any measurable residues and laboratory analog due to the high impact velocities causing melting or vaporization of the projectiles. Features of intermediate morphologies between these two boundaries suggested the existence of a transitional and evolution of sequence. The third group was shallower and irregular impact tracks with aspect ratio, L/D < 0.5, formed by low-velocity impacts of coorbiting flakes and liquid droplets, all human waste products, and the result of wastewater dumps. However, aerogel could not yield reliable dynamic data for each particle, including chronological information about the collisions. Nevertheless, the unique ability of aerogel to preserve and trap unmolten residues at relatively high velocities in low-Earth orbit was confirmed compared to traditional nonporous media; those threshold velocities for vaporization were much smaller than aerogel [105, 107].

The most successful aerogel-related mission that has unveiled many scientific discoveries is probably the Stardust Mission. Launched from the Kennedy Space Center in 1999, the function of the mission was to carry a hypervelocity particle collector which would meet up with a known outer solar system body (Comet 81P/Wild 2) to capture coma samples and interstellar dust to be brought on Earth for laboratory analysis [108–11].

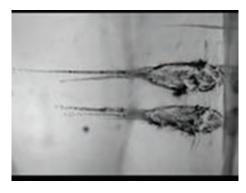
The collector, a "tennis-racket"-shaped metal frame, consisted of two grids facing in opposite direction, each of them containing one hundred and thirty cells of silica aerogel of different volumes (see Figure 4) [127]. One grid had cubes of dimensions approximately  $4 \text{ cm} \times 2 \text{ cm} \times 3 \text{ cm}$  to capture cometary particles, whilst the other grid contained aerogel tiles with dimensions  $4 \text{ cm} \times 2 \text{ cm} \times 1 \text{cm}$  to seize interstellar materials [56]. When collection was required, the collector was detached from the protective sample return (SRC) and exposed. Compared to the missions stated above, the aerogel created for that assignment had a continuous gradient density profile, starting from 10 mg/cm<sup>3</sup> at the impact surface to a higher value at the bottom depending on the type of the grid. The maximum densities were 50 mg/cm<sup>3</sup> and 20 mg/cm<sup>3</sup> for the cometary grid and interstellar grid, respectively. It was already recognized that the density depends on the ratio of the condensable silica of the solvent used in the aerogel precursor solution. That concept was exploited when the precursor solution for low-density aerogel was steadily mixed with the precursor solution density aerogel while constantly



Figur e 4: Tennis-racket collector with aerogel (Image courtesy NASA).

pumping the resultant mixture into a gradient density silica aerogel [128]. It could be anticipated that other density-dependent characteristics such as thermal, optical, acoustic, and dielectric of aerogel would vary as per the gradient profile [129]. The latter would prevent the nanopores of the silica aerogel from being damaged by the microscale particles. When the high-speed particles hit the aerogel, they f rist bumped into the low-density aerogel and, as they penetrated, the density of the aerogel increased simultaneously slowing them down. The kinetic energy was converted into mechanical and thermal energy, which in the end brought the speed to zero [130].

After the rendezvous with the comet in 2004, the collector was withdrawn to the SRC to protect the samples. Two years later, the Stardust capsule reemerged into the Earth's atmosphere and landed successfully in Utah. Once again, aerogel proved its superiority of withstanding transition from atmospheric pressure to vacuum of space without any damage though the fact that it is brittle. T his is due to the open-cell framework of aerogel which allows interstitial gases to flow out. The pathways of the impacted projectiles were clear and hence analysed since aerogel is transparent. Figure 5 shows that the comets had entered on the right-hand side and finally stopped through in the aerogel. These particles were the first materials obtained from a specified celestial body other than the Moon and were extracted delicately using a highspeed vibrating glass needle [131]. The discovery involved mainly high- and low-temperature minerals and unknown organics, leaving behind a deduction by the scientists at the Johnson Space Center that the constituents of comets were much more complex than other extraterrestrial objects, such as meteorites. Interstellar dusts were also found and extracted but none were able to be recognized [12–135]. On February 14, 2011, a recycle version of Stardust, called Stardust-NExT, was sent into the space to analyse another comet, Tempel 1, which was previously visited during the Deep Impact mission in 2005 [136]. However, the primary objective of Stardust-NExT was to obtain high-resolution pictures of the nucleus using the NAVCAM camera for further analysis. The mission was successful [137, 138].



Figur e 5: Comets trapped in aerogel (Image courtesy NASA).

In 2003, another mission was proposed based on a similar concept as the Stardust Mission of capturing sample in the outer space, known as the Sample Collection of the Investigation of Mars mission (SCIM). It was levelled as a lowbudget and low-risk program. This Mars Scout mission was designated to fly while collecting suspended dust through the upper Martian atmosphere in a silica aerogel collector which would then be directed back to the Earth to be analysed [139]. The dissimilarity between Stardust Mission and SCIM is that the latter needed to fly into the atmosphere which would cause substantial heating to the spacecraft during the capture of high speed particles. To overcome this problem, the silica aerogel collectors would be located at the aft end of the aeroshell where heat is minimal. The results of the preliminary experiments showed that the majority of the hypervelocity particles captured had preserved their physical and chemical features [140]. This mission was however precluded and was proposed again in 2006 which was again declined over the technology of Stardust. Jones investigated other potential aerogel-based collectors, for example, carbon, alumina, titania, germenia, zirconia, and niobia because of the abundance of silicate mineral present in our solar system [56]. In addition, the Raman spectrometer was proven to be a handful tool for the identification of the impact particles in aerogel [141].

Some years back, an operation known as the Material Exposure and Degradation Experiment (MEDET) was initiated in accord with ONERA, ESA, Centre National d'Etudes Spatiales (CNES), and the University of Southampton to investigate the effects of the complex low-Earth orbit space environment on material properties and material degradation due to contamination while measuring the local microparticle flux. The MEDET suite was installed on board the European Technology Exposure Facility (EuTEF). The module was launched by the STS-122 on February 7, 2008 and retrieved by the STS-128 on September 11,2009 [142, 143]. Aerogel was opted again as a passive detector to capture the micrometeoroids and orbital debris particles. Two transparent tiles of silica aerogels of size  $30 \times 25 \times 45 \,\mathrm{mm}^3$  were prepared via a sol-gel process followed by supercritical drying. The resulting bulk density was  $0.087 \pm 0.004 \,\mathrm{g/cm^3}$ . An expansive series of impacted particles including metals, glass, and mixed oxides ranging from one to several microns was

extracted from the aerogels. A study is ongoing to analyze these matter, as mentioned by Woignier et al. [87].

During the capture process of a particle, a significant amount of its kinetic energy is converted to thermal energy thereby altering or destroying its structure. Recently, a study was carried out by Jones et al. [144] to measure the temperatures experienced by hypervelocity particles during their capture in aerogels. Aggregate projectiles made up of magnetic submicron hematite were employed. The concept used was when these particles are heated above their Curie temperature (675°C) during the penetration, they lose their magnetism. Hence, the particles were fired at different velocities to acquire different temperatures upon seizure in the aerogels. Their magnetizations were then observed using an atomic and magnetic force microscopy along with an electron paramagnetic resonance. It was found that the heating of these fine particles aggregates highly depends on the location in the capture track where they come to rest. The particles which were fired with velocities up to 6.6 km/s were still magnetic. Silica aerogel, with its highly porous and transparent characteristics, remains the ideal material for hypervelocity particle capture.

4.2. Thermal Insulation. NASA extended its research on aerogel in the field of thermal insulation because of its extremely low conductivity. Silica aerogel was firstly used as an insulator on the Mars Rover, Sojourner, as part of the Pathfinder mission in 1997. The aerogel was packed in composite boxes, called Warm Electronics Boxes (WEBs), to protect the primary battery pack of the Alpha Particle X-Ray Spectrometer (APXS) from extremely low temperatures. The operational range of the battery was set to be between  $-40^{\circ}$ C to  $+40^{\circ}$ C each day with a limit of +55°C for not more than five hours. A value of 21°C was successfully achieved [145]. Being efficacious, aerogel was chosen again in the Mars Exploration Rovers, Spirit and Opportunity in 2003. Additional devices were installed in these robots, for example, Radioisotope Heater Units (RHUs) which would induce extra heat [146]. To avoid heat dissipation, aerogel was placed as a barrier to sustain a temperature variation of up to 100°C between the Martial day and night when the temperature is approximately +20°C and -99°C, respectively.

To increase the performance of the silica aerogel as an insulator, its composition was modified by doping graphite with necessary alteration in the drying process to ensure no cracking and shrinking [147]. Consequently, the transparent silica aerogel was converted into an opaque aerogel thereby inhibiting significant heat radiation thus minimizing its total heat transport. The aerogels were then shaped into relatively large panels. The two geologists, Spirit and Opportunity, were designated for a three-month operation, but the former roamed nearly seven years until March 2010 covering a total distance of 7.7 km. Opportunity, on the other hand, is still on the Martial soil and just began her in situ science investigation at "Whitewater Lake" with a Microscopic Imager (MI) mosaic, followed by the placement of the APXS [148]. The objective of the mission is to search for water on the Planet Mars [149]. Aerogel is therefore illustrated as an ultralight insulation material which not only resists relatively large

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Figur e 6: Layers in an extravehicular mobility unit (Image courtesy NASA).

temperature fluctuation but also has endurance in harsh environments.

In consequence, silica aerogels are being studied to be used in space suits which require materials with specific specifications to ensure the safety of astronauts in the harsh dust and extreme pressure and temperature conditions [150]. The actual extravehicular mobility unit (EMU) is divided into five classes of layers as shown in Figure 6. T h f rist inner layer ensures that the pressure of the suit is maintained and it is made of polyurethane-coated nylon which is in turn protected from any external pressures by the fabric-restraining dacron layer. The remaining layers form the thermal micrometeoroid garment (TMG) which primarily provide thermal and micrometeoroid protection. The TMG liner is a neoprene-coated nylon ripstop above the MLI layer consisting of f ve to seven laminates made of low conductivity aluminized mylar reinforced with nylon scrim spacers. The MLI has an overall low thermal conductivity due to the low radiation absorptivity and high emissivity on its surface and low heat conductance between the laminates. The outer orthofabric sustains tear and wear protections in addition. The present TMG is operative only in hard vacuum milieu such as low orbit and the moon where radiation heat transfer is the predominant mechanism. In the existence of an atmosphere, likewise on Mars, the MLI is ineffective due to the presence of the interstitial gases which errand convection and conduction cooling.

The performance of different potential fibrous materials were reviewed for possible space suit applications to overcome this problem [151]. It has been found that, to provide sufficient insulation, the MLI requires an effective thermal conductivity of 5 mW/mK. The 4DG fiber and aerogel interstitial void medium combination gave the best insulation performance amongst other systems with a nominal thermal conductivity of 7.5 mW/mK. This configuration consists of

a high interstitial void fraction with heat flux perpendicular to the fibers. Nevertheless, aerogel is still regarded as a capable insulation material to insulate future space suits.

In spacecraft, the accumulation of dense air, ice, water, and liquefied air within the insulation materials is of primary concern. This phenomenon is known as cryopumping. It affects the function of the insulator and therefore degrades the performance of the vehicle by increasing the heat transfer through the insulation material which increases the lift-off weight and the potential risk for damaging debris. Aerogel has been considered as a potential candidate to act as a heat shield in these cryogenic systems such as liquid-hydrogen (LH<sub>2</sub>) tanks and liquid-oxygen (LO<sub>2</sub>) feedlines because of its fully breathable and hydrophobic characteristics [12]. Furthermore, experiments in [13] have shown that liquid nitrogen (LN<sub>2</sub>) can be prevented from accumulating within the intertank of the space shuttle by using an insulation system consisting of a bulk-fill aerogel material. The key phases to assess the performance of cryogenic insulation systems are at lif tof fand reentry into the atmosphere when there are sudden changes in temperature and pressure. For example, at re-entry, the temperature of the vehicle is over thousand degrees Celsius while the LH2 and LO2 are essential to be retained below -253°C and -183°C, respectively in order to remain in the liquid form [154].

A wide variety and permutations of aerogel blankets manufactured by Aspen Aerogel Inc. and aerogel beads from Cabot Corporation have been characterized using insulation test cryostats at the Cryogenics Test Laboratory of NASA Kennedy Space Center. It was noticed that cyropumping effects were stopped beyond thermal stabilization [155]. Using these superinsulation materials, lightweight and robust vehicles can be designed which will ensure the safety of the operations.

Strangely, a manned mission to Mars has been proposed which is expected to last for nearly three years. For this, a human friendly architectural design has been planned and silica aerogel has been selected to provide the necessary thermal insulation for the f  $\phi$ ors, walls, and windows. T k conceptual design requires that a thin flexible aerogel with low thermal conductivity be used which makes Spaceloft a probable choice [156].

4.3. Cryogenic Fluid Containment. A third function of silica aerogel is to act as cryogenic fluid containment. This idea was proposed in 2004 when engineers were working on the Satellite Test of the Equivalence Principle (STEP) mission. The satellite was to be sent into the earth orbit to probe the underlying foundation of Einstein's theory, the (local) equivalence of gravitational and inertial mass [157]. The test masses and detectors were required to sustain stability from disturbances such as air drag, magnetic field, and solar pressure in order to obtain precise results [158]. This could be achieved by placing the measurement instruments in a Dewar containing liquid helium maintained at cryogenic temperatures. Silica aerogel, being highly porous and an open-cell material, was recognized to be an excellent container to store the liquid helium while simultaneously preventing any bulk flow to occur. The liquid helium coming out of the aerogel would be directed to the spacecraft thrusters along the time of the mission. An aerogel control tide was built in for the helium storage system [159]. The aerogel was firstly shaped in annular cylinders to be encircled around the cylinders inside which was the equipment. Later, it was suggested to shape the aerogel into parts, into trapezoids [56], rather than one annular cylinder to facilitate its assembly into any desired structure. The presence of aerogel in the Dewar gave rise to some doubts. One of which was whether the aerogel filled with liquid helium would survive a launch vibration environment. A test was carried out and it was found that there were no signs of damage and degradation. The STEP mission was not launched though; instead NASA selected the 2003 SMEX. The technology was however applied with success on the Gravity Probe B mission. Nonetheless, there is still an optimistic vision of bringing aerogel on STEP someday.

### 5. Evaluation of Silica Aerogels in Aeronautics

According to the Federal Aviation Regulations, Section 25.856(a), thermal and acoustical insulation should be provided by the same material while being simultaneously a fire retardant. This applies primarily for the fuselage and the current material is fiberglass batting. To hold the fiberglass in place and to protect it against contamination, insulation covers are wrapped around [160]. The common plastic covers are polyethylene terephthalate (PET), polyvinyl fluoride (PVF), and silicone-coated fiberglass for high temperature environment. Silica aerogel, being a superinsulation material and an acoustic shock-absorber, can be therefore considered as a thermal/acoustical insulator for this task. But a more realistic way to employ aerogel would be by exploiting its remarkable properties separately for thermal insulation, fire protection, and acoustics purposes in different parts of the aircraft.

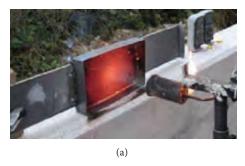
5.1. Thermal Barrier. The justification of considering silica aerogel as a thermal barrier is due to its favorable characteristics in operating temperatures, longevity, chemical (aviation fuels and lubricants) and erosion resistance, and maintenance. A simpler and lighter overall design of the thermal insulation system can be achieved which will consequently reduce the assembly cost as fewer materials are needed. More space will be available for other usages. There will be a rise in the energy efficiency because of the minimization of heat loss and hence fuel will be saved. That is, the direct operating cost will also decrease. Considering, an aeroengine, silica aerogel can be applied in two modes, depending on the temperature and environment requirements. Firstly, it could be sprayed as a thin insulative coating to protect unattainable and uneven substrate from high temperatures. The smooth and uniform layer of insulation will cause little resistance to the airflow. The thermal responses will be improved which will in turn increase the performance of the engine while the aircraf tis cruising at high altitude. Secondly, in compartments where the vibration is high, flexible light-weight blankets of silica aerogel with custom thickness can be used. They can be fastened mechanically to prevent any displacing hence interferences problems. Contrary to coatings, blankets are more resistant to contaminations and do not disintegrate easily. Their maintenance cost is also lower than that of coatings.

5.2. Fire Retardation. The fact of being an inorganic and inflammable material with a continuous operating temperature ranging from -273°C to 650°C and a high melting point of 1400°C makes silica aerogel an excellent firewall compared to the existing combustible organic coatings that cause toxic fumes when burning. The components such as pipes, wires, and electronic accessories within the fie zones of an aeroengine can be protected using thin blankets of aerogel whilst simultaneously enabling weight saving compared to conventional metal sheets. Similarly, the adjacent airframe structures will be prevented from being burnt. Aspen Aerogels has investigated on such applications where the insulation blanket made of silica aerogel with a thickness of 7 mm was exposed to a flame at temperature 100°C for at least 15 minutes (see Figures 7(a) and 7(b)). The temperature on the cold side did not exceed 150°C. Both the fire testing and the outcomes are in accordance with FAR Part § 25.1191[160] and AC 20-135 [161]. However, the product, Pyrogel 6350, has not been commercialized for aeronautical applications until now [162]. In addition, the thermal loss when the blankets are under constant vibration and gravitational stress through repeated thermal cycles is still unknown.

5.3. Acoustics. Sound waves are signif cantly absorbed through silica aerogels thus reducing the speed of propagation to 100 m/s. This is due to their extremely low Young modulus which is related to the synthesis of the aerogel, more precisely, the interstitial gas type, pressure, and density [163, 164]. Silica aerogel is now acknowledged as a promising material for acoustic matching layers of high-sensitivity airborne ultrasonic transducers for boosting of airborne acoustic waves [165]. Experiments were carried out using

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Material	Thermal conductivity (W/mK)	Acoustic absorption (dB)	Average cost (US\$)
Fiberglass	0.0345-0.0040	~5	0.2-2.8/m <sup>2</sup> [126]
Monolithic silica aerogel	0.0136-0.0038	~15	3800/m <sup>3</sup> [126]
Monolithic Maerogel	0.0200-0.099	~15	$\sim 750 - 900 / \text{m}^3$





Figur e 7: Aerogel firewall during testing. (Image courtesy Aspen Aerogel). Pyrogel 6350 installed in aircraft engine for fire protection (Image courtesy Aspen Aerogel).

different sol-gel densities of aerogels to observe the effect of the speed of sound through the aerogels. It was found that the sensitivity of a matching layer type of ultrasonic transducer (ML-UT) could reach twenty times higher than that of a conventional one. The aerogel ultrasonic transducer can be therefore incorporated into future aeronautical sensing systems for range findings. Acoustical insulation in aircraft using aerogel can also be considered based on its acoustic absorption. Forest and Gibiat found that the minimum transmission loss in granular aerogel can be 10dB higher than that of fibreglass with the same thickness [166].

5.4. Cost Analysis. The main limitation of preventing silica aerogel from commercially integrating into the aviation sector is its high cost. Is it worth now to spend on such an expensive material for space saving and lighter weight? Can there be a linear relationship between space saving and cost saving? American Airlines claimed for having saved \$422 million in operating costs through fuel savings in 2011[167]. One way to achieve this is by reducing the take-off weight, for example, by removing unnecessary items from the aircraft. In consequence, about 1 million of jet fuel gallons can be saved which would sum up to an amount of approximately \$3.63 M annually [168]. Up to now, the actual leading companies for mass production of silica aerogel are the North Americanbased industrials Cabot Corporation and Aspen Aerogels. Both of which are apprehensive with thermal insulation. The former produces silica aerogels mainly in the form of granules under the Trademark Nanogel, whilst the second one concentrates on flexible blankets, registered as Cryogels, Pyrogels, and Spaceloft. Recently, there has been Nano Hi-Tech in China which is considered to be the third player followed by some other relatively small manufacturers like EM-Power (Korea), AIRGLASS AB, and the German ROCKWOOL. Despite the existing market competition, it remains difficult to compensate the price of silica aerogel for other beneficial factors. On the other hand, it is reported that a reduction up to 80% can be attained in the manufacturing cost of Maerogel. A performance-cost comparison between fibreglass, conventional silica aerogel, and Maerogel is shown below. A performance-cost comparison between fiberglass, conventional silica aerogel, and Maerogel is displayed in Table 4.

### 6. Conclusions

Based on the above literature, it can be said that the fundamental synthesis-structure-property relationships of aerogels are now comprehended in the research community after eighty years of tremendous efforts. Different cost-effective manufacturing methods have been developed along the time to promote the commercialization of silica aerogels in various high-tech areas. In the aerospace industry, the capture effectiveness of silica aerogel as a kinetic energy absorber is already considered to be superior whilst its potential as a thermal insulator shows great promise for applications ranging from cryogenic temperatures in spacecraft to high temperatures in aeroengines. The feasibility tests of insulating space suits with aerogel show that a lower thermal conductivity is required and yet to be achieved. Silica aerogel as a fiber-reinforced blanket has efficaciously fulfilled the necessary criteria of the Federal Aviation Regulations for fire retardation in aeroengines while a profound study is still required for acoustical applications in aircraft. With the reinforcement using polymers, the mechanical properties of silica aerogels can be tailored to meet the specifications of future astronautical applications. Often in such cases, the success of the mission is more significant than the budget. However, for aeronautical implementations, the introduction of silica aerogels is questionable based on the current market manufacturing cost and the current performance of the existing materials. Maerogel, which is an ecological and green-technology material, has been proposed as a promising substitute due its relatively low cost and comparable properties with the conventional silica aerogels.

### **Conflict of Interests**

The authors have no conflict of interests to declare.

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