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# An overview on silica aerogels synthesis and different mechanical reinforcing strategies

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ABSTRACT

Silica aerogels are lightweight and highly porous materials, with a three-dimensional network of silica particles, which are obtained by extracting the liquid phase of silica gels under supercritical conditions. Due to their outstanding characteristics, such as extremely low thermal conductivity, low density, high porosity and high specific surface area, they have found excellent potential application for thermal insulation systems in aeronautical/aerospace and earthly domains, for environment clean up and protection, heat storage devices, transparent windows systems, thickening agents in paints, *etc*. However, native silica aerogels are fragile and sensitive at relatively low stresses, which limit their application. More durable aerogels, with higher strength and stiffness, can be obtained by proper selection of the silane precursors, and constructing the silica inorganic networks by compounding them with different organic polymers or different fiber networks. Recent studies showed that adding flexible organic polymers to the hydroxyl groups on the silica gel surface would be an effective mechanical reinforcing method of silica aerogels. More versatile polymer reinforcement approach can be readily achieved if proper functional groups are introduced on the surface of silica aerogels and then co-polymerized with appropriate organic monomers. The mechanical reinforced silica aerogels, with their very open texture, can be an outstanding thermal insulator material for different industrial and aerospace applications.

This paper presents a review of the literature on the methods for mechanical reinforcing of silica aerogels and discusses the recent achievements in improving the strength and elastic response of native silica aerogels along with cost effectiveness of each methodology.

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## 1. Introduction

Silica aerogels are materials with unique properties such as high specific surface area (500–1200 $m^2.g^{-1}$), high porosity (80–99.8%), low density (~0.003–0.5 $g.cm^{-3}$), low thermal conductivity (0.005–0.1 W/(mK)), ultra low dielectric constant ($k = 1.0–2.0$) and low index of refraction (~1.05) [1,2]. Due to their such unusual characteristics, much attention has been given to silica aerogels in recent years for their use in several technological applications including Cherenkov radiators in particle physics experiments [3] and thermal insulation materials for skylights and windows [4]. Silica aerogels have also been used for making heat storage devices used in window defrosting and as acoustic barrier materials [5]. Other aerogels have been demonstrated as battery electrodes [6], catalyst supports [7], and oxygen and humidity sensors [8] and adsorbents for environmental clean-up [9] due to their large internal surface areas and facile changing of their surface chemistry. The low values of thermal conductivity and the very low density make silica aerogels attractive materials for a number of aerospace applications. One example involves insulation around the battery packs in the Mars Sojourner Rover to protect its electronic units [10]. More robust and flexible aerogels are being considered to insulate extra-vehicular activity (EVA) suits for future manned missions to Mars [11]. Aerogel composites are the only materials that come close to meet the requirements for EVA suit insulation [12]. Robust aerogel composites are also considered as insulation materials of inflatable decelerators for entry, descent, and landing (EDL) applications for future space missions on Mars [13].

It should be noted that aerogel applications in space are not all limited to thermal insulation. Indeed, silica aerogels can also be applied to collect aerosol particles [14], to protect space mirrors or to design tank baffles [15,16]. However, these applications of silica aerogels have been restricted because of their extreme fragility and poor mechanical properties and hygroscopic nature [17]. Therefore, with the purpose of expanding the application range of aerogels, while fully retaining their outstanding properties, mechanically more robust aerogels are needed.

Different methods have been explored to improve the mechanical properties of silica aerogels such as structural reinforcement using flexible silica precursors in silica gel backbone [18–21], conformal

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coating of silica backbone via surface cross-linking with a polymer [22–26], and dispersing carbon nanofibers in the initial sol of silica aerogel [27]. In principle, to improve flexibility or elastic recovery in silica aerogels, it is required either to include organic linking groups in the underlying silica structure or to cross-link the skeletal gel framework through surface silanol groups by reacting them with monomers/polymers.

Since the silica aerogels consist of silica particles that are connected to each other via only Si–O–Si stiff bonds, the compounding of the silica aerogel with polymer leads to an increase of the connection points between the silica particles, with the formation of extra strong –(C–C–) covalent bonds between these particles [28]. Therefore, such methodology leads to an increase of the strength of the reinforced silica aerogels over native silica aerogels [29]. Thus, the objective of such compounding with organic polymers is to provide an aerogel with good compressive strength to be able to adapt to the design of components and to adsorb the energy involved in shock compressions [14,15,30,31]. However, manufactured aerogels are not strong enough to be reshaped and must be casted to the final forms during synthesis and processing [32]. But, it has been proven that elasticity/flexibility can be significantly enhanced in non cross-linked aerogels by altering the chemical nature of the silica backbone. For example, for TMOS/BTMSH-derived aerogel, with densities bellow 0.06 $g.cm^{-3}$, it was possible to bend by 50° the material without breaking it [33]. Additionally, Kramer *et al.* [34] demonstrated that an addition of up to 20% (w/w) poly(dimethylsiloxane) in (TEOS)-derived aerogels resulted in rubbery behavior with up to 30% recoverable compressive strain. Shea and Loy [35] have developed hybrid aerogels from bridged polysilsesquioxanes, using building blocks comprised of organic bridging groups attached to two or more trialkoxysilyl groups via nonhydrolyzable carbon–silicon bonds. All of these methods proved to be different ways of tuning mechanical properties to the application requirements.

As it is indicated by Fricke [36] and Pekala *et al.* [37], due to the tradeoff between mechanical properties (*e.g.* Young's modulus or maximum strength) of silica aerogels with their density, the most straightforward methods of mechanical reinforcing of silica aerogels result in increasing the density and therefore increasing the thermal conductivity [38–40]. This is caused by the increase of the total amount of material used for the production of the gel matrix, due to the need of increasing the total number of connection points within the silica aerogel. The most recent achievements involve the preparation of aerogels with approximately three order of magnitude improvement in their maximum compression strength at break with only doubling the density and thermal conductivity [29]. Therefore, the purpose of this review is to provide an overview about versatile methods to impart higher strength or stiffness to silica aerogel monoliths with minimum increase of their density and thermal conductivity.

General physical and chemical issues involved in the synthesis of silica gels were explained in books [41,42]. Additionally, many reviews on aerogels, with particular focus on silica aerogels, have already been published [1,43–47], which give a more specific and complete description about the aerogels' processing, properties and applications. For the purpose of strengthening the mechanical properties of silica aerogels, different possible strategies of surface chemistry modification of aerogels, followed by compounding their surfaces with appropriate organic polymers, namely epoxide [48,49], polyurea [50], polyurethane [33,51], polyacrylonitrile [22], and polystyrene [52,53], are reviewed by Leventis *et al.* [26,54], and more recently by Meador *et al.* [29,32].

The present review is composed by two parts: firstly, a general history of silica aerogels with chemistry beyond their methods of synthesis and the principles of the drying techniques is given; secondly, an extensive study of very recent published works about the development of silica aerogels with improved mechanical properties is presented, with particular emphasis on recent advanced methods for preparing class II hybrid polymer–silica aerogels. The main objective is to review the possible physical and chemical existing methodologies to improve the mechanical properties of silica aerogels, which were not under scope of studying by the previous authors. Additionally, the present review surveys the use of different kinds of nanofiber networks, including polymeric [55–57], ceramic [58,59] and carbon nanofibers [58], in order to develop the free standing silica with improvements on skeletal maintenance of native silica or even polymer reinforced aerogels. Finally, the future trends for development of flexible and bendable hybrid thin sheets of silica aerogels are addressed, being these materials suitable for folding or wrapping around different space assemblages, such as around the electronics and battery packs in the Mars Sojourner Rover [10]. Moreover, the development of smart silica aerogels using shape memory polymers [60] is also mentioned as a major future development and is described in the last part of the present review.

## 2. Sol–gel chemistry

Generally, a nanostructured solid network of silica is formed as a result of a hydrolysis and condensation process of the silica precursor molecules, in which siloxane bridges (Si–O–Si) are formed. Such reactions are equivalent to a polymerization process in organic chemistry, where bonds between the carbon atoms of organic precursors lead to linear chains or branched (cross-linked) structures [61].

The manufacturing process to form silica aerogels comprises two steps: the formation of a wet gel by sol–gel chemistry, and the drying of the wet gel. Originally, silica wet gels were made by Kistler in the early 1930s [62,63] through the condensation of sodium silicate (also termed as waterglass). However, the reaction formed salts within the gel that needed to be removed by many long and laborious repetitive washings steps [64]. In following years, Teichner's group extended this approach to prepare optically transparent monoliths using tetraalkoxysilanes ($Si(OR)_4$) as the silica source [65]. The key of this process was to use an alcohol (*e.g.* methanol or ethanol), thus, the need for the tedious water to alcohol solvent exchange was eliminated [65–69]. This reduced the time required to make a final dried aerogel to approximately one day, which was a drastic reduction relatively to Kistler's original method. Presently, with the further developments of the sol–gel process, different alkoxysilane derivatives are used all together and with different solvents, which are needed for the homogenisation of the mixture and control of concentrations. Although, when switching from a protic to an aprotic (hydrocarbon) medium, alcohols are ideal intermediary solvents, as their bifunctional nature (polar/non-polar) promotes miscibility of water and the organic phase. But, surprisingly, the choice of the alcohol has a tremendous effect on pore structure and therefore also on final material properties [70–72]. The indication of different gelation solvents and related methodologies applied by different investigators, along with the different properties of the resulting aerogels, is reviewed by Soleimani *et al.* and Siouffi [47,73].

Due to the rapid development of sol–gel chemistry over the last few decades, the majority of silica aerogels are prepared today using silicon alkoxides as precursors [74–80]. The most common of the silicon alkoxides are the tetramethylorthosilicate (TMOS, $Si(OCH_3)_4$) and tetraethylorthosilicate (TEOS, $Si(OCH_2CH_3)_4$) [42], with common chemical formula of $Si(OR)_4$, that lead to the aerogels called “Silica”. Many other alkoxides [81], containing various organic functional groups linked to silicon, can be used to give different properties to the gel. They have a general formula $R'_XSi(OR)_{4-X}$ $(1 \leq X \leq 3)$, being mono, di and trifunctional organo silanes, which lead to the aerogels named as “orgonosilsesquioxanes” [78]. Other common organo silica precursors with chemical formula of $(OR)_3SiR'Si(OR)_3$ in which R′ is an alkyl, aryl or alkenyl bridge group between two elements of silica, lead to the “bridged organosilsesquioxane” products [19,35,82,83]. Alkoxide-based sol–gel synthesis avoids the formation of undesirable salt by-products, and allows a much greater degree of control of the final

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