# SILICA-AERO. Production of lightweight Silica Aerogel Fibers for excellent heat insulating application

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Aerogels are today the lightest solids and the best thermal insulating materials in the world. Silica aerogels are the most common aerogels. On one hand, silica is inorganic, fire proof and thermal stable up to 900 °C; one the other hand, the material is brittle and rigid. Due to their brittleness combined with the ultrahigh porosity of aerogels (over 80 %), silica aerogels are very difficult to process into a product. Commonly lightness is a required characteristic in transport sectors like aircraft, spacecraft or automobile. Due to the vibrations, it is difficult to use aerogels in these sectors. It is already possible to make brittle materials flexible. Glass, ceramic and carbon fibers are nowadays used for several applications in the form of flexible textiles and fabrics. Aim of this paper is to introduce a new developed process for the production of silica aerogel fibers. The fibers have been successfully produced and showed the same porosity and pore structure like in their corresponding bulk material.

## 1. Introduction

### 1.1 Silica Aerogel – material properties

Aerogels aresynthetic porous ultralight materials deriving from a gel, in which the liquid component of the gel have been replaced by a gas (Alemán et al., 2007). Aerogels are characterized by a very high porosity (80-99.8 %) (Dorcheh and Abbasi, 2008). Because of that they have a low density as well as a high thermal insulation capacity. Due to these properties, there are several potential applications of aerogels from a wide range of disciplines. One of the best known applications of silica aerogels is certainly the use as a particle collector in the space test "Stardust" in the early 2000s (NASA, 2004). Silica aerogels are particularly interesting since they have an inorganic character and high temperature stability. Among the different aerogels which have been developed during the last years, silica aerogels have the advantage that the precursor used for the preparation is relatively inexpensive. Due to the already mentioned high porosity and a mean pore diameter of 20-40 nm, silica-based aerogels are used as drug delivery systems (Smirnova, et al., 2004). The high porosity is accompanied by a large specific surface area. In figure 1 the silica aerogel monolith, its nanostructure and a schematic representation of a pore are shown. Due to their excellent specific surface area, they are also suitable as catalysts or as carrier material for catalysts (Schneider and Baiker 1995). Because of their low thermal conductivity ($0.02$ W m$^{-1}$ K$^{-1}$) further possible applications are the use as insulation material, for example, resorcinol-formaldehyde based aerogels are already used in transport containers for temperature-sensitive medicines and organs. In addition to the thermal insulation capability, silica aerogels have a dielectric constant of 1.1 and can thus also be use as electrical insulators. (Dorcheh and Abbasi 2008).
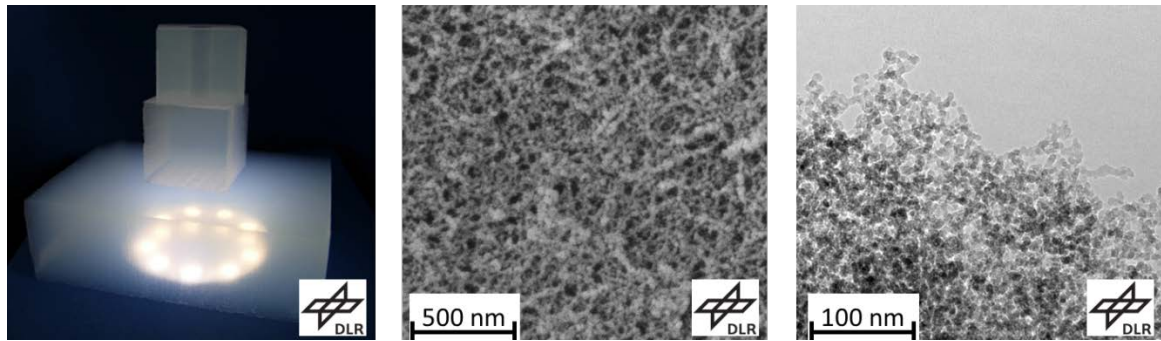
*Figure 1: Silica Aerogel (left), SEM picture of its nano-structure (middle) and TEM-picture of its pore (right).*

## 1.2 Silica aerogel – synthesis

The synthesis of silica aerogels takes place through a sol-gel reaction. In a first step a silica source (e. g., tetraethyl orthosilicate TEOS), ethanol, water and catalyst are mixed together. In general, various silicon alkoxides can be used as silica source. The most common is tetraethyl orthosilicate (TEOS) that is preferred to tetramethyl orthosilicate (TMOS) which produces methanol during the process. TEOS is first partially hydrolyzed in a mixture of ethanol, water and hydrochloric acid and then reacts further in a polycondensation reaction. The hydrolysis and the condensation are shown in figure 2. (Brinker and Scherer, 2013)
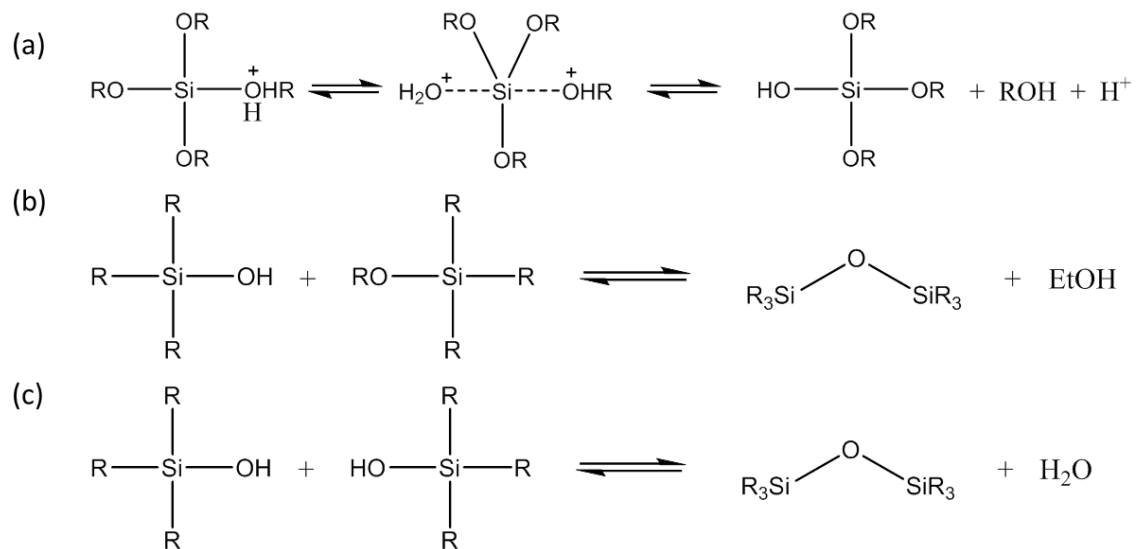


*Figure 2: Hydrolysis (a), Alcohol-condensation (b) Water-condensation (c) (Brinker and Scherer, 2013).*

The polymerization reaction is a multistep reaction. The first step consists in the formation of dimers and other short-chain oligomers. Long-chain polymers are produced only during the further course of reaction. During polymerization the viscosity increases and the sol changes into a wet gel firstly. This is converted into an aerogel in the last step of the process by *e.g.* supercritical drying. In figure 3 the process steps from solution to silica aerogel are shown.
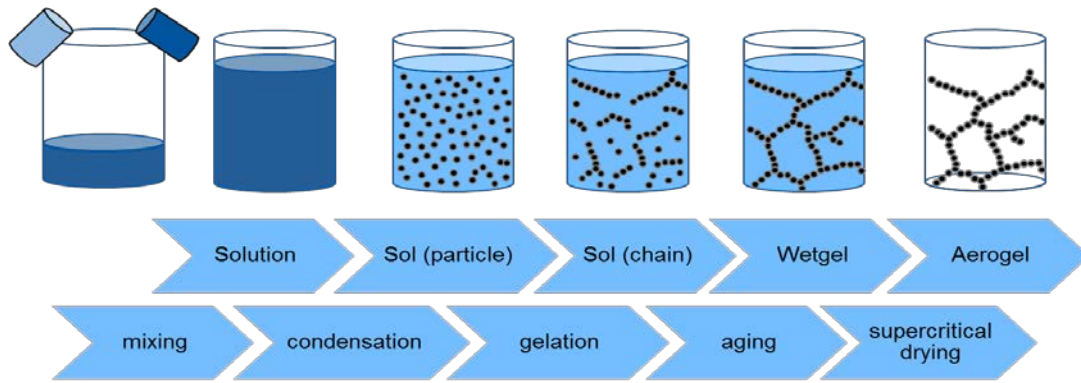
*Figure 3: Process steps from solution to silica aerogel*

### 1.3 Aim of this study

While the sol-gel process has already been extensively investigated, the production of silica aerogel fibers is largely unexplored. Several materials have already been converted into a fibrous structure. Especially brittle materials like glasses, ceramics, graphite and rock showed high flexibility and vibration resistance in their fibrous state. Aim of this study is to determine the feasibility of spinning fibers made of silica aerogel.

## 2. Experimental

In order to produce a silica aerogel monolith the viscosity changes of the sol plays a minor role  but in order to fiberize the material an appropriate viscosity range is required. In a first step the focus of this work was put on the preparation of the sol. Its success was determined by obtaining a filament in air. In a second step, the hardening process of the filament, corresponding to the gelation and aging of the fiber in a coagulation bath was under research. At least after the supercritical drying from wet gel stage to aerogel fibers the material properties were determined; in particular its porosity and its pore structure.

### 2.1 Material

Based on the state of the art, several formulations have been tested to select a sol that is able to be fiberized and a suitable coagulation bath. The most important parameters were TEOS (Aldrich 98%), ethanol, distilled water, catalyst and their molar ratios. The ratio between TEOS and HCl was fixed on a constant value (HCl / TEOS 0.01).

After TEOS was dissolved in ethanol a solution of water and HCl and ethanol was added. The mixture was heated for a defined time until a certain viscosity was reached. Subsequently, the vessel was closed and stored until its usage.

Figure 4 shows the area of investigation within a ternary diagram (TEOS/water/EtOH) in order to determine the right composition for the fiberization process.
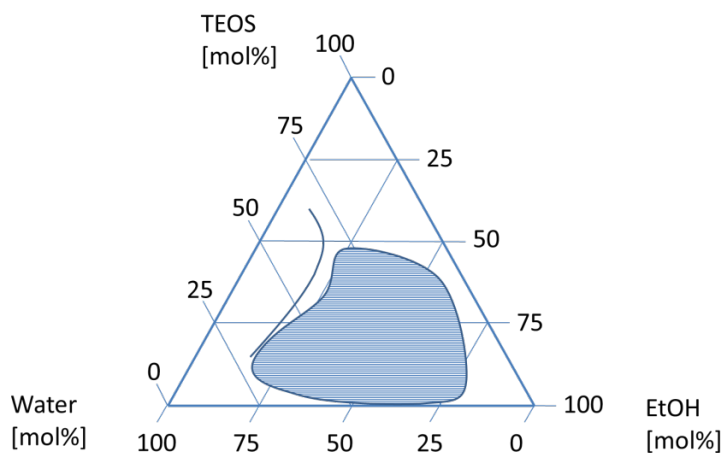


*Figure 4: Area of investigation (TEOS, water, EtOH)*

## 2.2 Fiberization process

The spinning plant is shown in figure 5 and consists of three main elements: A nozzle, a coagulation bath and a winder. The sol is pushed by a metering pump through the nozzle and flows into the coagulation bath where the polymerization is completed. The wet gel fiber is continuously drawn by a winder on a bobbin. At the end of the fiberization, the bobbin has been put in EtOH to remove unreacted compounds and to wash the fibers free of coagulant and water necessary before supercritical $CO_2$ extraction for drying can be carried out.
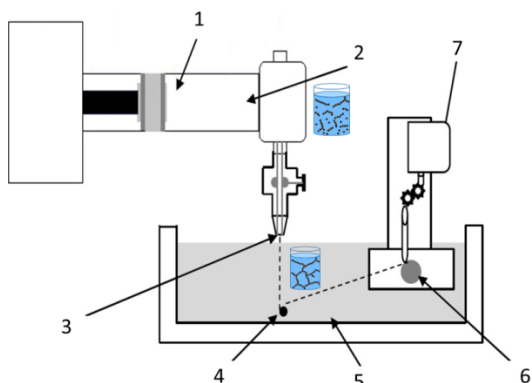


*Figure 5: Laboratory spinning plant for the fiberization of silica wet gel.1. Metering pump; 2. Heating; 3. Nozzle Head; 4. Guide; 5. Fiber; 6. Bobbin; 7. Gear Head.*

## 2.3 Supercritical drying

The last step is the shrinkage-freedrying of the wet gel. Figure 6 shows a phase diagram. The transition states of supercritical drying and freeze drying are marked. During supercritical drying the liquid in the gel pores transforms into a supercritical fluid. The inherent null surface tension of supercritical fluids allows to avoid the pore collapse due to capillary forces. Supercritical drying can be classified into high-temperature supercritical drying, the solvent in the gel is directly forced beyond its critical point (needs high temperatures) and  in contrast low temperature supercritical drying, which describes a method where the pore solvent has to be soluble in supercritical $CO_2$ to be directly extracted at more moderate temperatures and pressures .
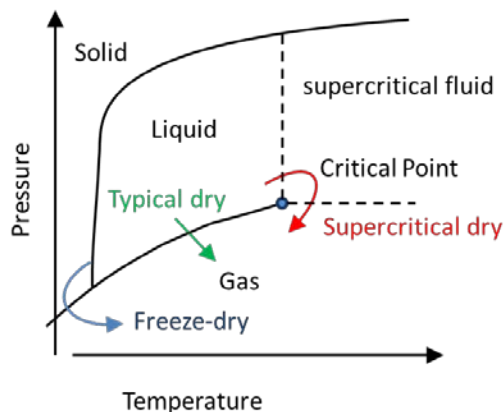


*Figure 6: Phase diagram and representation of different drying processes; redrawn from (Meyer, 2004)*

## 3. Results

### 3.1 Process ability to fibers

 A sol with the required physical properties (fiberization viscosity) could be produced.
In figure 7 the results of the fiberization process in relation to the sol material with the focus on the ratio between TEOS, water and EtOH are shown. The central part of the investigated area presents the best processability. The other two areas are characterized by materials with unsuitable viscosity or inhomogeneus gelation.
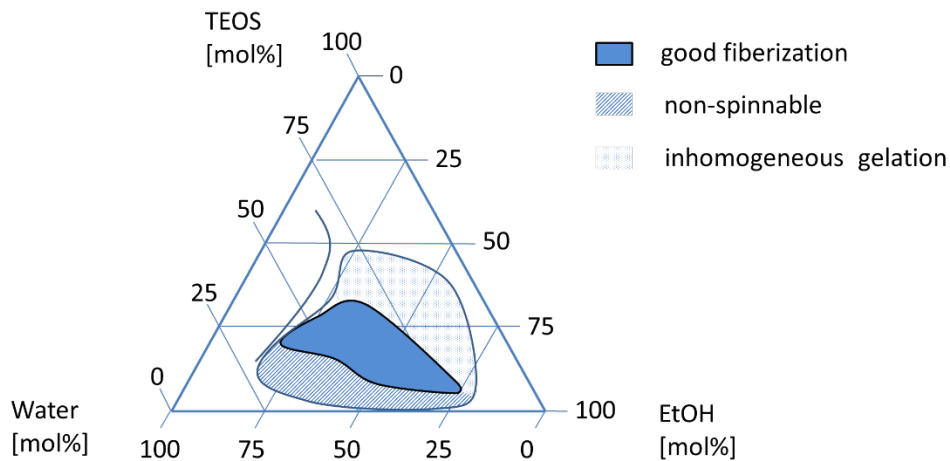
Figure 7: Ternary plot (TEOS / water / EtOH) and composition's area with good fiberization properties

The filament has been successfully drawn in air without any formation of droplet in a viscosity range optimized for spinning. Several coagulating baths have been tested. For example 1-Amino-2-propanol, sodium carbonate and hexamethylenediamine allowed to drawn the fiber at several velocities under 10 m/min.

## 3.2 Porosity / Structural properties

The fibers have been successfully dried in a supercritical dryer and their structure was investigated. From a first analysis a fiber diameter of over 50 µm (figure 8) was measured. The diameter along the fiber is not constant along the fiber and presents particles as well as scratches on the surface that are related to an inhomogeneous spinning process through the nozzle into the coagulation bath.
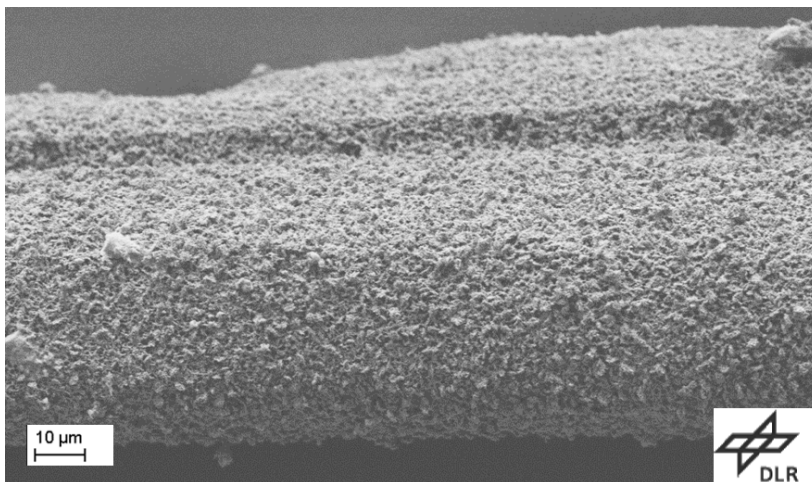


Figure 8: Silica Aerogel fiber surface after supercritical drying

A deeper optical analysis of the surface shows that the fiber has the same structure as a silica aerogel monolith. The fiber exhibits a sponge organization with constant nanoparticles and pores (figure 9).
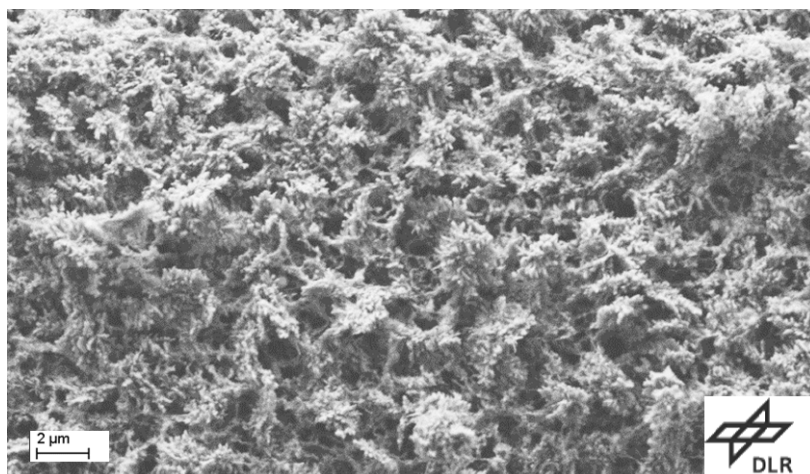
*Figure 9: surface pore structure of silica aerogel fiber.*

Based on the BET method, a specific surface area of 755 m²/g was determined. The pores have been measured by BJH methods and are in average 6 nm. These results are comparable with the porosity and pore diameter of silica aerogel monolith materials. But in contrast to the smooth surface of monolithic silica aerogels additional bigger pores of 200 nm to 1 µm are observed by SEM.

## 4. Conclusion

For the first time silica aerogels have been fiberizated and their morphology corresponds in parts with monolithic aerogels. The production process consists of two steps: the fiberization of a sol through a coagulation bath until the formation of a silica wet gel fiber and secondly the elimination of the liquid inside the pores of the fiber by supercritical drying.

Even the fibers did not reach a continuous diameter below 15 µm, necessary to be mechanically flexibel, the process was successfully tested. The material was coagulated into a structure that preserved its porosity during the drying process.

The fiberization of silica aerogel offers the possibility to use a super light and super thermal insulator by balancing the brittleness of the material with the flexibility of the fiber. The potential applications range over several sectors, from aerospace (lightness by high temperatures and vibrations), to chemical processes (catalyst, reactive filtration) to the more common construction and automotive industry.

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