

Chapter 2

Aerogels Today

2.1 Introduction

The term “aerogel” is not a name associated with a specific mineral or material with a specific formula, but rather a term that encompasses certain materials with unique geometry and structure. Aerogels are a special class of nanoporous solids with complex interconnectivity and branched structure of a few nanometers. It comes in variety of forms, colors, and shapes from monolithic to powders. Aerogels have very little solid component and almost made up of 99.8 % of air which gives the product an almost ghostly appearance.

Aerogels are synthesized via sol-gel technique, where the liquid in a gel is removed above its critical temperature and pressure and replaced with air, thus forming a skeletal solid (i.e., networked structure). At the critical parameters, there is no liquid–vapor phase, and thus no surface tension present on the gel. This allows the gel matrix to remain intact without large shrinkage (Rao et al. 2005).

2.2 Aerogels Today

Earlier, aerogels were made from silica. In this modern era, technological advancement has made it possible to make aerogels from various materials. Alumina aerogels which appear in rust-like color were synthesized via hydrated aluminum salts, and aluminum alkoxides have tremendous potential for high-temperature storage systems and catalysts (Zu et al. 2011). Carbon aerogels are used as super-capacitors in electronic circuits and battery-powered portable device providing bridging power for days (Juzkow 2002). Aerogels have been studied as a superinsulator used in embedded garments for cold water diving by the US Navy (Nuckols et al. 2005). Similar work by Erik et al. (2006) to determine performance of aerogel blanket coupled with synthetic foam revealed having 35 % greater thermal resistance

compared with underwater pipeline insulation. Aerogels made from plants' cellulose fiber extract have shown to be flexible, transparent, and possess good mechanical toughness (Kobayashi et al. 2014). Hybrid aerogels made as a result of combining two or more constituent materials are fast creating a niche in science for specific applications. CNT-graphene composites decorated with sodium alginate have potential application in heavy metal ion detection (Wang et al. 2015). Aerogels made from chalcogens, the column of elements on the periodic table beginning with oxygen, such as sulfur, selenium, cadmium, and platinum are called chalcogels. Scientists have shown that chalcogel preferentially absorbs heavy metals and pollutants such as mercury and lead from water (Bag et al. 2007). AeroSand, a ceramic-based core material using resorcinol-formaldehyde (RF) aerogel as a binder for foundry sand (Ratke and Brück 2006) is an example of industrial application of the aerogels today. Recent works by Hong et al. (2013) on synthesizing silica aerogel with freeze cast porous zirconia ceramics revealed high compressive strength with reasonably low thermal conductivity ranging from 0.041 to 0.098 W/m-K. The varied applications in several industries from building and construction to dielectrics in integrated circuits are explicitly detailed in a review paper by Gurav et al. (2010).

2.3 Market Outlook

While the prospects and potential of aerogels seem exuberating, researchers are still hesitant to put these varieties of aerogels for commercial and business use. The most practical use of aerogels now is thermal insulation. Insulation materials made of aerogels are gaining popularity in the United States and the coldest regions of Europe. Besides thermal insulation, aerogels are also used for acoustic and optical insulation (Gibiat et al. 1995; Schmidt and Schwertfeger 1998) in the buildings. Allied Market Research has done an extensive coverage on the global aerogel market, which in 2013 was valued at \$221.8 million. It is estimated to reach \$1896.6 million by 2020 with a reported compound annual growth rate (CAGR) of 36.4 %. The report evaluated that recyclability, reusability, and fire protection will be key drivers for upswing in commercial success for the aerogels providing thinner and lighter alternatives to convectional insulation materials as described in Fig. 2.1. Koebel et al. predicted that aerogel-based thermal superinsulators market will grow more rapidly than the "conventional" insulators for at least a decade up to the point when markets will begin to saturate (Koebel et al. 2012). The main drawbacks for aerogels are the high cost of production and the ever-changing global economic conditions. Even so, with advancing methods and technology, the production cost of aerogels is expected to reduce from US\$4000 to US\$1500 per cubic meter (Koebel et al. 2012).

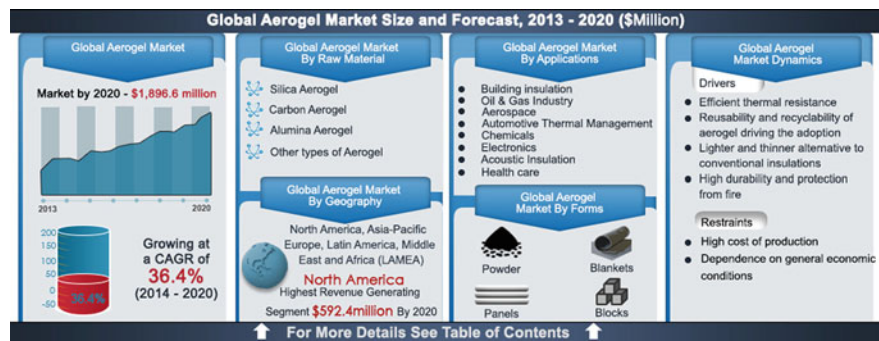


Fig. 2.1 Global aerogel market size (Source Allied Market Research)

2.4 Silica Aerogels

Silica aerogels are probably the most researched and investigated aerogels amongst the class of aerogels. They are primarily prepared via the solution-gelation (sol-gel) chemistry technique. This technique basically involves two steps: 1) formation of the wet gel and 2) drying of the wet gel with an intermediate aging process. The first step involves hydrolysis of silicon alkoxide precursors, suitable solvents, catalysts, and water stirred into a homogenous solution (Pajonk 1998). This forms colloidal dispersion of particles and over a period of time the solution will form a three-dimensional grid of solid and liquid phases. This process is called *gelation*. Gesser and Goswami (1989) described the process of sol-gel as shown in Fig. 2.2 in their paper in great details.

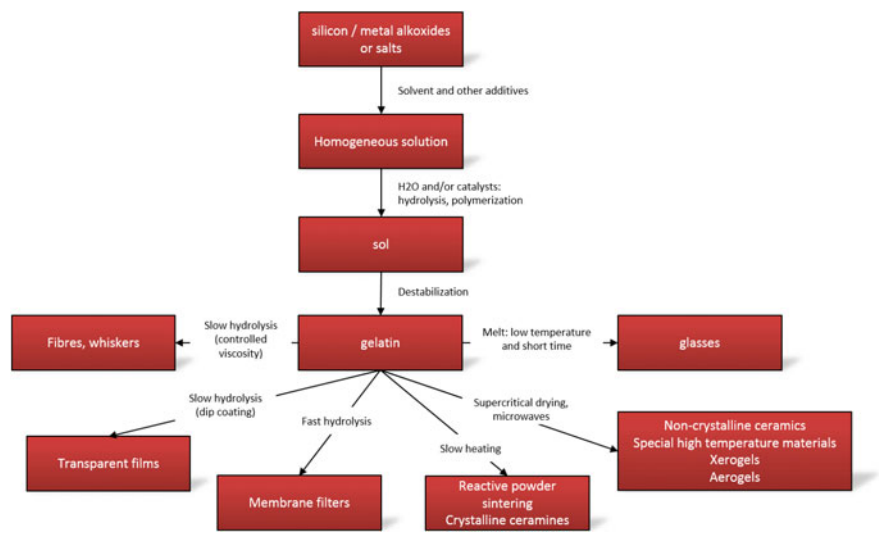


Fig. 2.2 Sol-gel process redrawn from Gesser and Goswami (1989)

The gel formed could be of polymer chain-like or colloidal-like gel depending on the pH value of the medium used. The solvent will then be distilled leaving a viscous fluid that is redissolved in an alcohol-based liquid such as ethanol (Gerard 2006). It would take a few cycles to accomplish complete wash out of the residual solvent and water when redissolving in alcohol. The second step involves drying. This is a critical step in the making of aerogel as the properties of the material are greatly influenced by pressure and temperature as explained previously (Lee et al. 1995). This step generally purges the remaining liquid in the pores and at the same time prevents the gel structure from collapsing. Figure 2.3 explains the general steps involving the production of aerogels. The aging process can be considered as the intermediate step between gelation and drying process (Lee et al. 1995).

Over the decades since it was first discovered, researchers have studied extensively to improve the properties of the final product and as well as reduce the high cost of production by synthesizing with alternative materials (Morris et al. 1999). The evolution of the silica aerogels over the past three decades will be discussed in the following sections.

2.5 Evolution of Silica Aerogels

Soleimani Dorcheh and Abbasi (2008) reviewed the properties and characterization of silica aerogels since its invention in the 1930s. They had categorically written about the evolution of silica aerogels in each of the key processes and the corresponding improvements that were made in producing these aerogels safely and effectively. The flowchart in Fig. 2.3 shows the general processes involved in the synthesis of aerogels.

2.5.1 Formation of Wet Gel

Silica aerogels are available in variety of forms such as powders, chunks, granulates, and others. Their properties can be customized to suit the applications required. The basis for the formation of wet gel is through hydrolysis in sol-gel technique using varying molar ratios of precursors, solvents, and catalysts.

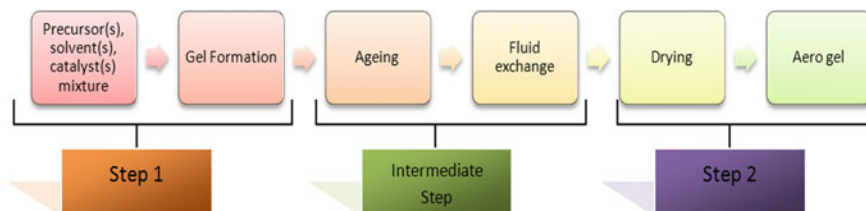


Fig. 2.3 Overview of key processes in making aerogels

2.5.1.1 Precursors, Solvents, and Catalysts

The precursors used in the sol-gel technique are mainly silicon alkoxides that possess high degree of purity. Many of these silicon derivatives are used in various types of solvents and catalysts to produce silica aerogels. Each of these produces varying degrees of physical, thermal, mechanical and optical properties in the aerogels. Some of these precursors used are Tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), polyethoxydisilane (PEDS), methyltriethoxysilane (MTES), and many others (Rao et al. 2003, 2005; Soleimani Dorcheh and Abbasi 2008; Wei et al. 2011). However, they are very expensive and hazardous materials that are known to cause blindness.

The current commercial synthesis of silica aerogels is produced using water-glass (sodium silicate) solution by ambient pressure drying (Lee et al. 2002; Bhagat et al. 2007a, b). Water glass is cheap and has high stiffness and large pore size (Lee et al. 2002). Typical solvents used are ethanol, methanol, acetone, and to a small degree, ethyl acetate. Catalysts are added in the sol-gel technique to control the rate of gelation. The catalysts used in the preparation are acid catalysts, base catalysts, or two-step acid–base catalysts (Lee et al. 2002; Bhagat et al. 2007a, b, c). The pH levels and duration of gelation process needs to be monitored and controlled in order to achieve optimal results. Generally, it has been reported that base catalysts or two-step acid–base catalysts produce better quality silica aerogels in terms of uniform distributions (Lee et al. 1995), reduced shrinkage, and increased ability for cross-linking (Bhagat et al. 2007a, b).

2.5.2 Aging and Fluid Exchange of Wet Gel

The “ageing” process has great influence on the microstructure, porosity, surface area, pore size, and volume shrinkage of the aerogel. The effects of prolonged aging duration and concentration were studied by various researchers (Rao et al. 2005, Bhagat and Rao 2006; Mahadik et al. 2012). The period of aging has significant effects resulting in increased optical transmittance, density, and surface area with increased strength and stiffness.

2.5.3 Drying

Drying determines the nature of the final product and it is governed by surface tension of the gel. Volume shrinkage is most evident in this step as the pressure and temperature play important roles. Three types of drying method have been employed by researchers: supercritical drying (SCD), ambient pressure drying (APD) and freeze drying (FD).

2.5.3.1 Supercritical Drying (SCD)

High-temperature supercritical drying (HTSCD) was first used by Kistler in 1931, and is still being used widely for silica aerogel production (Gesser and Goswami 1989, Hunt et al. 1991). HTSCD is carried out using any organic solvent such as methanol or ethanol placed in an autoclave raising the temperature slowly resulting in corresponding pressure increase.

Thereafter, the pressure is adjusted to reach above the critical pressure of the solvent and kept constant for a period of time. The solvent or fluid is then vented slowly at constant temperature resulting in pressure drop. When the ambient pressure is reached, the autoclave is cooled down to room temperature (Rao et al. 2003). The biggest disadvantage using this method is the potential fire hazard that the solvents pose due to the high operating temperature and pressure (Gerard 2006). An alternative means called low-temperature supercritical drying (LTSCD) utilizes liquid CO₂ since it has a critical point that is very near to the ambient temperature (Bhagat and Rao 2006, Soleimani Dorcheh and Abbasi 2008). The silica aerogels produced in this manner are less expensive but usually hydrophilic (water absorbing), though they can be modified to be hydrophobic via surface functionalization (Bhagat and Rao 2006).

2.5.3.2 Ambient Pressure Drying (APD)

APD is seen with great interest as both HTSCD and LTSCD are considered relatively expensive processes. APD is a cheaper alternative process that involves surface chemical modification, manipulating the contact angle, and network strengthening with a silylating agent (Rao et al. 2005). Silylation is carried out in the water phase of gel, which involves the replacement of Si–OH groups by the hydrolytically stable Si–R (R-alkyl) groups through oxygen bond, thereby resulting in the hydrophobic aerogels (Lee et al. 2002, Rao et al. 2005, Bhagat et al. 2007a, b, c). Figure 2.4 shows the silylation process of the silica aerogel. An interesting feature of silylation is the “spring back” (Fig. 2.5) phenomenon. The trimethylsilyl (TMS) groups that are introduced during the silylation process effectively terminate further interaction between the solid structure and the solvent. Thereafter, the gel begins to shrink during



Fig. 2.4 Silylation process of silica aerogel (Soleimani Dorcheh and Abbasi 2008)

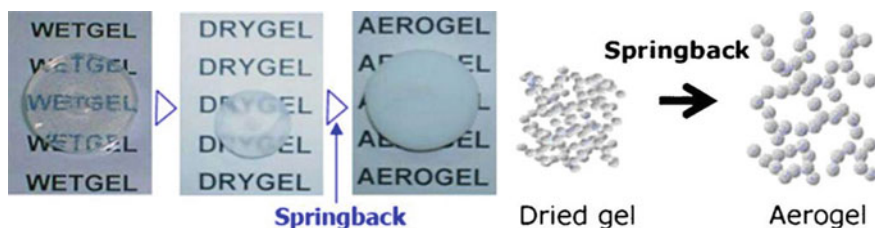


Fig. 2.5 "Spring back" phenomenon (Rao et al. 2005)

the drying process due to capillary forces since this is treated at ambient pressure. However, when the liquid phase within the gel starts to evaporate, the chemically inert surface silyl groups prevent further infusion of liquid.

Hence, the gel is able to re-expand as shown in Fig. 2.5. Rao et al. (2005) prepared two-step acid–base ambient pressure-dried silica aerogels successfully. He reported that aerogels obtained from APD have improved properties in terms of low thermal conductivity, low density, high porosity, and high optical transmittance than aerogels produced by HTSCD.

However, the realization of finished product takes about four to seven days and require enormous amount of solvents and materials. Therefore, it is too costly for large-scale production of silica aerogels. Bhagat et al. (2007a, b) investigated the effect of using co-precursors on water-glass solution for rapid surface modification. He and his co-workers had reduced the processing time (one day) using trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDZ) on water-glass solution and reportedly showed improvement in properties such as low density and higher thermal stability of up to 500 °C (Bhagat et al. 2007a, b, c). Rao et al. (2003) investigated the effect of thermal degradation of $\text{Si}-(\text{CH}_3)_3$ groups on the surface of silica aerogels which are stable up to 325 °C.

Nevertheless, thermal stability ranges between 325 and 500 °C, beyond which the inert TMS groups on the surface will oxidize and revert back to $\text{Si}-\text{OH}$ bonds (Rao et al. 2005; Bhagat et al. 2007c) and thus become hydrophilic. Many researchers have tried using other precursors with silylation agents to improve overall qualities of the APD processed silica aerogels, but water-glass-derived aerogels remain the best and most feasible for commercial production (Soleimani Dorcheh and Abbasi 2008).

2.5.3.3 Freeze Drying (FD)

Solvents of low expansion coefficient and high sublimation pressure are usually used in FD. Similar to SCD, FD works on the principle of non-capillary pressure between the liquid and gas phase. The liquid is frozen and then sublimed under

vacuum (Arndt et al. 2007). Although this technique offers a safer route to obtaining aerogels, FD is not extensively used (Tamon et al. 2001). Hyun et al. successfully developed nanoporous silica films with low dielectric constant using the FD method (Hyun et al. 2000). A major setback of FD is crystallization of the solvent in the pores tends to destroy the network structure in aerogels thus inhibiting cracks. FD also requires prolonged aging than other drying process for stabilization of the network (Daoussi et al. 2009). Despite the shortcomings, FD is used in the current works as one of the methodologies in the binding treatment of the silica aerogel composites fabrication as it is safer and hassle free. This will be discussed in detail in Chap. 3.

2.6 Concluding Remarks

Aerogels are fast becoming a niche material, which will be seen as a significant global commodity in the near future. The expected rise in the market value of aerogels could see greater involvement, investment, and collaboration from various industries to achieve commercial success for diversified applications. Silica aerogels are the most researched aerogels that offer the diversity for commercial application. This has been aided by the reduction in production and manufacturing costs. Commercially, available silica aerogels are synthesized under ambient conditions negating the need for expensive equipment. However, main drawbacks of silica aerogels are brittleness and low mechanical properties. Strengthening methodologies of silica aerogels by addition of fibers, resins, and other materials as a composite will be the highlight in the next chapter.

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Silica Aerogel Composites

Novel Fabrication Methods

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