

AEROGEL DRYING

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Aerogel materials possess a wide variety of exceptional physical properties due to their unusual morphologies. Aerogels are extremely porous, very high surface area materials obtained from the drying of organic or inorganic gels.

Polymer-based (organic) aerogels are predominantly based on formaldehyde / resorcinol, formaldehyde / melamine, polyurethanes and polyisocyanurates systems. Carbon aerogels are derived from selected organic aerogels pyrolysed in an inert atmosphere. Inorganic aerogels are mainly composed of metal oxides or mixture of metal oxides and silica-based materials.

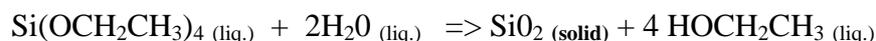
Aerogel vocabulary

In general, aerogels are prepared from gels, which in turn can be produced from organic monomers for organic aerogels and from inorganic salts or metal alkoxides for inorganic aerogels [1]. In the preparation of the gels, a first step is the preparation of a colloidal form of the material or Sol, which is called an “aquasol” if the liquid phase is water, “alcosol” if the liquid phase is an alcohol. Gels are formed from Sols. If the liquid which permeates the pores of the resulting is water, the gel is termed an “aquagel”. If it is an alcohol, the gel is termed an “alcoagel”. If a gel is dried by normal means, such as exposing to ambient conditions or placing it in an oven, the product is termed as “**xerogel**”. The other way to dry the gel in order to produce **aerogel** is by a supercritical procedure.

Preparation of organic and inorganic gels

An example of inorganic aerogels : silica aerogels

The most famous example of inorganic gel is based on silica material (it is the first aerogel prepared : Kistler 1931). With the rapid development of sol-gel chemistry over the last few decades, the vast majority of silica aerogels prepared today utilise silicon alkoxide precursors. The most common of these are tetramethyl orthosilicate (TMOS, $\text{Si}(\text{OCH}_3)_4$), and tetraethyl orthosilicate (TEOS, $\text{Si}(\text{OCH}_2\text{CH}_3)_4$). However, many other alkoxides, containing various organic functional groups, can be used to impart different properties to the gel. Alkoxide-based sol-gel chemistry avoids the formation of undesirable salt by-products, and allows a much greater degree of control over the final product. The balanced chemical equation for the formation of a silica gel from TEOS is:



The above reaction is typically performed in ethanol, with the final density of the aerogel dependent on the concentration of silicon alkoxide monomers in the solution.

After gelification, the gel is left undisturbed in the solvent for a long period of time (at least 48 hours) because the silica backbone of the gel still contains a significant number of unreacted alkoxide groups. In fact, hydrolysis and condensation can continue for several times the time needed for gelation. The alcogel is then submitted to supercritical drying.

Organic aerogels

The preparation of organic aerogels is rather similar to the procedure here above described. We can illustrate the preparation of organic aerogels with the example of the resorcinol / formaldehyde (RF) material. Resorcinol (1,3-dihydroxy benzene) and formaldehyde are mixed in a 1:2 molar ratio, respectively. Distilled water is used as a solvent to control the final gel concentration. After forming a homogeneous solution, sodium carbonate is added as a based-catalyst, and the mixture is cast into the desired shape (in a high pressure cell) and cured at 85°C. Then cross-linked RF gel is exchanged with acetone and subsequently dried with supercritical carbon dioxide.

Supercritical drying process

The final, and most important, process in making aerogels is **supercritical drying**. This is where the liquid within the gel is removed, leaving only the linked aerogel network. The process can be performed by venting the solvent above its critical point (generally high temperature) or by prior solvent exchange with another solvent (CO₂) followed by supercritical venting (lower temperatures).

The idea is to eliminate the solvent from the sol-gel without generating a two-phase system and the related capillary forces. This is possible through compressing and heating the sol-gel above the critical pressure and temperature of the solvent (for CO₂ : T_c = 31°C, P_c = 7.4 MPa) and then by decompressing it down to atmospheric pressure and cooling it down to room temperature, maintaining the solvent in gas phase without any condensation.

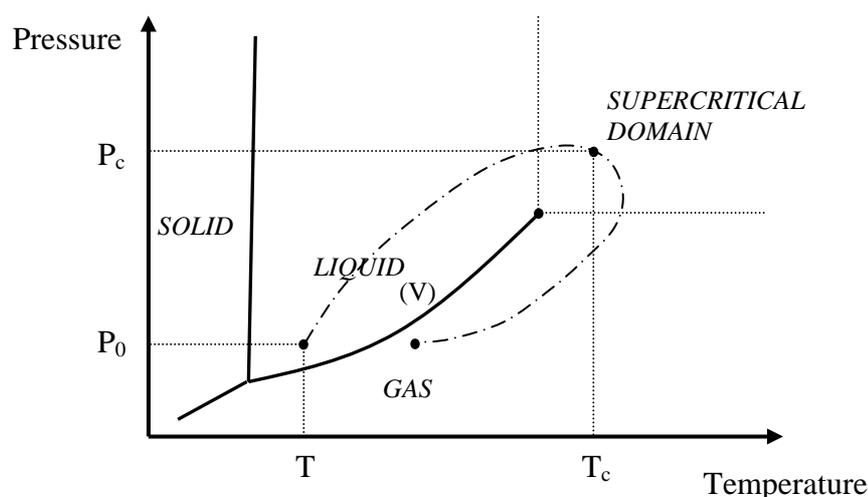


Figure 1 : Supercritical drying procedure

Referring to figure 1 representing a pressure / temperature curve, it is easy to understand that the sol-gel mixture (point A at room pressure and temperature) can be pressurised and heated to reach supercritical state (point B) and then depressurised and cooled to reach again room conditions (point C); during this operation, the solvent vaporisation curve (V) is never crossed: so, at no time any two-phase solvent system appears, and finally, only a low pressure solvent vapour is present in the porous aerogel that is further filled with air by diffusion as the aerogel is highly porous with open pores.

Practically, for silica gels in ethanol, the supercritical drying using CO₂ is as follows. The sol-gel is placed in the autoclave and charged with additional ethanol to prevent air drying of the sol-gel. The system is then pressurized to at least 5-6 MPa with CO₂ and cooled to 5-10°C. Liquid CO₂ is then flushed through the vessel to start the ethanol extraction. The vessel is gently heated and pressurized over the critical temperature and pressure. Then, supercritical fluid is flushed through the vessel until ethanol has been totally removed from the vessel and from within the gel. The system can be held in these conditions for several hours depending on the thickness of the gel. A slow release of CO₂ is then started until the pressure reaches ambient pressure.

Physical properties of Aerogels

As implied by the name, aerogel is mostly air. It is the lightest existing solid material, as it can have a surface area as high as 1,000 m² per gram. Aerogel is one of the few existing materials that can be both transparent and porous. It also makes an excellent thermal insulator [2].

Morphology of aerogels

A common feature of all aerogels are open, ultra small inter-connected pores with a diameter below 100 nm. The majority of pores are called mesopores (mean diameter between 2 and 50 nm) and few pores with lower diameter (<2 nm) called micropores and upper diameters (>50 nm) called macropores. For example in silica aerogels, the mean pore diameter is circa 20 nm and the primary particle diameter is about 2 to 5 nm. This leads to a very low apparent density of 100 kg.m⁻³, an internal surface area of 600 to 1000 m².g⁻¹ and a typical solid percentage of 5%, what means a 95% of volume free space!

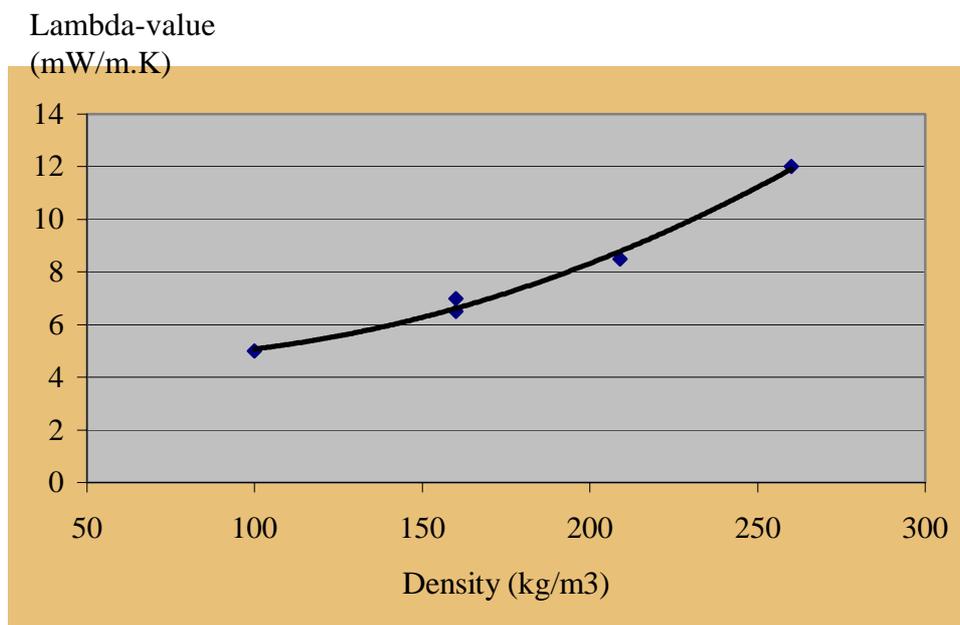
Thermal properties

Thermal energy transfer through an insulating material occurs through three mechanisms ; solid conductivity, gaseous conductivity, and radiative (infrared) transmission. The sum of these three components gives the total thermal conductivity of the material. Solid conductivity is an intrinsic property of a specific material. For dense silica, solid conductivity is relatively high (a single-pane window transmits a large amount of thermal energy). However, silica aerogels possess a very small (1-10%) fraction of solid silica. Additionally, the solids that are present consist of very small particles linked in a three-dimensional network (with many "dead-ends"). Therefore, thermal transport through the solid portion of silica aerogel occurs through a very tortuous path and is not particularly effective. The space not occupied by

solids is normally filled with air (or another gas) unless the material is sealed under vacuum. These gases can also transport thermal energy through the aerogel by convection or conduction. The pores of silica aerogel are open and allow the passage of gas (albeit with difficulty) through the material. The final mode of thermal transport through silica aerogels involves infrared radiation. A advantage of silica aerogels for insulation applications is their visible transparency (which will allow their use in windows and skylights). However, they are also reasonably transparent in the infrared (especially between 3-5 microns). At low temperatures, the radiative component of thermal transport is low, and not a significant problem. At higher temperatures, radiative transport becomes the dominant mode of thermal conduction, and must be dealt with.

A typical silica aerogel has a total thermal conductivity of approximately 17 mW/m.K at atmospheric pressure. A major portion of this energy transport results from the gases contained within the aerogel. By lowering the gas pressure in the matrix (< 0.1 mbar), the conductivity can be decreased to 8 mW/m.K. At high temperature (above 200°C) the radiative component of thermal conductivity becomes important and must be suppressed. By adding a component to the aerogel (generally carbon black), the conductivity is reduced from 17 to 13.5 mW/m.K at ambient pressure and from 8 to 4.2 mW/m.K under vacuum.

Thermal transport can also be reduced by lowering the aerogel density as shown on the following graph of the thermal conductivity (at a pressure of 0.1 mbar) of a polyurethane-based organic aerogel (monolith form) [3] versus the density.



Graph 1 : Thermal conductivity versus density

Optical properties [4]

Aerogels are often transparent and the best example is silica aerogel. This property not appears so strange if you take into account the structure of the material which is in fact glass (see figure 2). The transparency arises because the aerogel microstructure has a small scale compared to the wavelength of light and because there is a small amount of scattering in the

visible (the material displays a slight bluish haze when an illuminated piece is viewed against a dark background and slightly reddens transmitted light). The material transmits about 88% of the integrated solar spectrum (thickness of 10 mm) and its index of refraction is between 1 and 1.05 which is very low for a solid. Hence, this material has many possible applications such as insulation in windows and solar collector, windows in firewalls...



Figure 2 : Transparency of silica aerogel

Other properties

All of the aerogel varieties have unusual acoustic and mechanical behaviour, which could be exploited for various applications. For example in acoustics, aerogels are implied in sound absorption (anechoic chambers) and in the construction of efficient ultrasonic devices. Aerogels also absorb kinetic energy by plastic and elastic deformations and are used to collect particles like cosmic or cometary dust during experiments in space (Nasa's Stardust Project).

The metal oxide and organic aerogels are excellent dielectrics and are used for microwave electronics and high voltage insulator. On the other hand, carbon aerogels are electrically conductive, so they have applications as electrodes for batteries and capacitors. Some metal oxide exhibit superconducting properties.

The high porosity ($> 85\%$) and very large surface areas ($> 400 \text{ m}^2\cdot\text{g}^{-1}$) available in aerogel materials, lead to applications as filters, absorbing media for desiccation and waste containment, encapsulation media, and hydrogen fuel storage. Aerogels have been recognized for many years as excellent catalysts and catalyst supports.

Industrial development

As shown here above, aerogel materials have demonstrated an incredible versatility of applications and not only at the lab scale. For example, using the transparency and insulation properties, large panels for windows are now available on the market. The Swedish company Airglass AB is able to provide panels with a standard size of $60 \times 60 \times 2 \text{ cm}^3$.

Petroleum industry is now interested by insulation capabilities of aerogels for the tubings in oil or gas wells. A first demonstration on a gas well of Elf Petroland in the Netherlands occurs in 1999 as part of the European R&D project "Thermogelf". In this process, synthesis of the silica alcogel was performed directly around the tubing to be insulated and then dried with supercritical carbon dioxide. In spite of an uncompleted drying operation, a considerable production and flow stability gains occurred : the average output flow is now multiplied by 2.4! Insulation of pipes and tubings will probably with aerogel powders which are easier to produce and handle. The high fluidity of aerogel powder permits the filling of the tubes.

Until recently, aerogels were considered prohibitively expensive (around 5000 Euros/m³ for powder of silica aerogels for example), but the constant progress achieved in the chemical processes involved and the development of aerogel applications are likely to bring about significant reductions in cost, especially with optimised processes operated at very large scale [5].

References

- [1] R.J. AYERN, P.A. IACOBUCCI, Reviews in Chemical Engineering, Vol. 5, 1988, 158-193.
- [2] J. PHALIPPOU, R. VACHER, Aerogels 5. Proceedings of the Fifth International Symposium on Aerogels (ISA-5) Montpellier, France. 8-10 September 1997.
- [3] G. BIESMAN, D. RANDALL, E. FRANÇAIS, M. PERRUT, Journal of Non-Crytalline Solids 225 (1998), 36-40.
- [4] L.W. HRUBESH, Journal of Non-Crytalline Solids 225 (1998), 335-342.
- [5] M. PERRUT, E. FRANÇAIS, US Patent 5,962,539, 1999 ; European Patent 97.107604.7, 1997.