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► **To cite this version:**

T. Woignier, Laurent Duffours, J. Primera. Porous glasses from aerogels: from organic liquid to mineral materials. *Journal of Sol-Gel Science and Technology*, 2022, 102 (3), pp.589-595. 10.1007/s10971-022-05772-6 . hal-03818038

HAL Id: hal-03818038

<https://hal.science/hal-03818038>

Submitted on 17 Oct 2022

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Porous Glasses from Aerogels : from Organic Liquid to Mineral Materials

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abstract

According to an easy sintering stage, composite aerogels are alternative ways to synthesize silica glass at temperatures ranging from 900 to 1200 °C, close to half the temperatures used for the glass melting process. The heat treatment is tailored to obtain fully densified or porous glasses. The kinetics of dimensional shrinkage is characterized during the sintering mechanism, and we confirmed that the viscous flow-sintering model also applies to composite aerogels. Porous glasses with a broad range of porosity and physical properties (mechanical strength, elasticity modulus, permeability) have been synthesized. The open pore structure is used to synthesize glass ceramics.

Keywords: silica aerogels, sintering, nanocomposites, glass, glass-ceramics.

1) Introduction

In the usual procedure for making glass, a high temperature step ensures the raw materials are melted and the amorphous structure of the liquid is preserved by the melt quenching [1,2]. However, a new method of glass synthesis is proposed in the literature, not by melting but by sintering of a silica gel [3-6]. In the "aerogel-glass method", the high temperature stages (melting and refining) are avoided, homogenization is carried out in the solution to room temperature and gelation leads to the synthesis of an amorphous medium. Subsequent heat treatments remove water, organic species, hydroxyls and porosity. The objective of the aerogel-glass method is to obtain a dense, inorganic and amorphous solid material from a solution at room temperature.

The first step is the formation of a silica gel by hydrolysis reaction of organometallic compounds like $\text{Si}(\text{OR})_4$, followed by condensation reactions [4]. The process leads to a two-phase cross-linked medium containing the solid network (silica gel) and some liquid (alcohol and H_2O). Aerogels are dried gels obtained after a supercritical drying, which eliminates the capillary forces occurring during a classical drying by solvent evaporation. [7,8]. These capillary forces transform the wet gel into a micro fissured porous solid (xerogel) which is not an efficient precursor for glass synthesis.

The "aerogel" is a solid material, amorphous and highly porous (80-99% porosity) [5] that can be transformed into silica glasses by a sequence of sintering treatments [9,10,11]. Depending on the duration of the heat treatment, porosity is progressively eliminated [11]. Silica glass and binary silicates glasses have been successfully synthesized by gelation, supercritical drying and sintering [9,12,13,14]. Previous studies show that the sintering mechanisms is described by the viscous flow Scherer's model

[9,11]. Classical silica aerogel are brittle materials [15,16] with a large pore size distribution and a fractal structure [17].

Composite aerogels were synthesized using organosiloxane compound ($\text{Si}(\text{OR})_4$) hydrolyzed in the presence of pyrogenic silica (aerosil) powder and followed by supercritical drying [18,19]. Composite aerogels are stronger, stiffer and tougher than classical aerogels because of the presence of the aerosil powder, which strengthens the porous material [20]. Moreover, the aggregation process is affected by the addition of the aerosil powder [18,21]: the porosity is changed (larger macroporosity) [14] and fractal structure is in a higher length range [21]. So classical aerogel and composite aerogels have completely different networks and we could expect different sintering behavior.

The purpose of this article is to follow the conversion of composite silica aerogels into a glass and/or porous glasses. The objective is to characterize the influence of the aerosil addition on the sintering mechanisms and on the sintering temperature. A previous study has shown a high sintering temperature (1500°C) for aerosil silica aerogel [22] and we can suppose that the sintering temperature range will be affected by the aerosil content.

In section 3.1 we will characterize the composite aerogels mechanical properties *versus* aerosil content. In section 3.2 we will characterize the sintering process by dilatometry data and kinetic studies. In the last part (section 4) we will synthesize porous glasses with different pore volumes and physical properties. We give an example where we test the composite aerogel as host matrix for the containment of nuclear wastes.

2) Experimental method

2.1. Materials (composites aerogels, glass and glass-ceramics) synthesis

Composite aerogels were synthesized using the same protocol as previously published [14,15]. TEOS was hydrolyzed with 15 mole of water ($\text{HCl } 10^{-2}\text{M}$) per mole of TEOS for 1h under stirring. Pyrogenic silica (aerosil OX 50) was added under stirring. The pH was adjusted to 4.5, which led to gelation in a few minutes. The proportion of aerosil with respect to the total silica weight, ranged from 10% to 70%. The composite wet gels were transformed into composite aerogels by supercritical drying with ethanol at 305°C and 13 MPa. The bulk density range is $0.27 - 0.42 \text{ g}\cdot\text{cm}^{-3}$ (table 1).

Dilatometry experiments characterize the sintering of composite aerogels in the temperature range $25-1200^\circ\text{C}$. Depending on the duration of the heat treatment, the pores collapse and the porosity decreases. These sintered aerogels porosity ranged from 80% to 0% (bulk density between 0.39 and $2.2 \text{ g}\cdot\text{cm}^{-3}$).

2.2. Experimental techniques

Bulk density (ρ) was determined from direct measurements of weight and from the geometric dimensions of samples. Porosity (Φ) was calculated from bulk density and skeletal density (ρ_s). The silica aerogel skeletal density, measured by helium pycnometry [9], was $\rho_s = 2 \text{ g}\cdot\text{cm}^{-3}$.

Rupture modulus (σ) and Young's modulus were measured by the three-point bending technique using an Instron 1196 mechanical testing machine (24N load cell).

Toughness (K_{IC}) was measured by the Single Edge Notched Beam technique and a_c the critical flaw size was calculated from:

$$a_c = (K_{\text{IC}} / \sigma)^2 / 1.21\pi \quad (1)$$

Permeability (D) was measured using a method of impregnation based on Archimedes' principle [16]. The samples are dipped in water and during impregnation, the height of the penetrating water, $h(t)$, increases with time. We previously showed [16] that:

$$D = \eta \Phi h^2(t)/2 \Delta P.t \quad (2)$$

Where ΔP is capillary pressure and η is water viscosity. We calculated D from the slope of the straight line $h^2(t) = f(t)$. D has the dimension of a surface and was expressed in nm^2 . The details of the technique are given in reference [19].

3 Results and Discussion

3.1. Physical properties of composite aerogels

Table 1 lists the physical properties: bulk density (ρ), porosity (Φ), rupture strength (σ), toughness (K_{IC}), flaw size (ac) and permeability (D) of the composites aerogels versus the aerosil content.

With the composite aerogel synthesis, it is possible to adjust the porosity by adding aerosil powder just before gelation [14-16]. The addition of aerosil increases the bulk density and enhance the mechanical properties (table 1): σ and K_{IC} increase with the aerosil concentration by a factor in the range 3- 4. By comparison the toughness and mechanical strength of classical aerogel (with close density) are in the range 2.5- 5KPa $\text{m}^{-0.5}$ and 150-500 KPa respectively [23,24]. Consequently, the flaw size (ac) is almost constant in the range 50 μm .

Aerosil addition also affects the aggregation process, the pore structure and pore size distribution [14-16]. It homogenizes the pore structure and increases the mean pore diameter towards the mesoporosity range (50-200 nm). An important porous feature for a following soaking process is permeability. The data in table 1 show that permeability increases with the aerosil concentration. This result is in agreement with the empirical Carman Kozeny relation: $D \propto rh^2$ [4], where rh is the mean pore size (hydraulic radius). The addition of aerosil particles increases the mean pore size [14,19], the net result being an increase in D.

% aerosil	ρ (g.cm^{-3})	Φ (%)	K_{IC} ($\text{KPa.m}^{-0.5}$)	σ (KPa)	ac (μm)	D (nm^2)
10	0.27	86.5	3.7	270	49.4	11
25	0.28	86	3.5	260	47.6	17
40	0.3	85	4.2	320	45.3	21
50	0.32	84.25	5	380	45.5	26
60	0.39	80.5	7	470	58.3	62
70	0.42	78	15	840	53.8	130

Table 1: Composite aerogels physical properties *versus* the aerosil content.

In summary, the composite aerogels set combines improvement of the mechanical properties (rupture strength and toughness), and an increase in permeability. This method produces host matrices with a large porous volume that is easily accessible by aqueous solutions.

3.2. Synthesis of silica glass from composites aerogels

The dilatometry curves shows the shrinkage amplitude ($-\Delta L/L_0$) versus the temperature (Fig 1).

Figure 1. Dilatometry curves : shrinkage amplitude ($-\Delta L/L_0$) versus the temperature for the samples CA10(—), CA40 (•••), CA50 (—•) and CA70(— —)

Dilatometer data show that the sintering increases rapidly around 900-1000 °C, near the silica glass transition temperature. For classical silica aerogels, above 800°C the sintering mechanism is described as a viscous flow process characteristic of amorphous materials [25,26]. The figure 1 shows that the sintering temperature shifts towards the highest temperature if the aerosil content increases. For example, the sintering of the CA10 begins at 500 °C and is important in the temperature range 800-900°C. For the sample CA70 the sintering is maximum in the temperature range 900-1100°C. This effect is the result of the aerosil particles that are not as active for the sintering process as classical aerogel and slow it. The small sample dilatation in the temperature range 25-500°C before sintering corresponds to the usual silica glass thermal dilatation.

Figure 2 shows the sintering data made at several temperatures in the range 850-1250°C (1hour) for the samples CA70. The data show the sharp increase in density with temperature. The shrinkage of the gel starts at 800-1000 °C. In the temperature range 1150-1200 °C, the pore volume vanishes and the bulk density is close to 2.2 gcm⁻³, the density of the silica glass.

Figure 2. Bulk density as a function of heat treatment temperature (1h) CA70

Sintering is a process by which the surface of a material reduces by mass transport. It exist two main mechanisms: by diffusion or by viscous flow. For amorphous materials, viscous flow is generally important because it is faster than the densification process resulting from diffusion. Sintering identification was obtained by studying the kinetics of shrinkage. In a previous work [9, 11], we have shown that both mechanisms are responsible for sintering of classical silica aerogels. At low temperatures, the low sintering is due to a slow diffusion process (500 to 700° C) [27] whereas at temperatures above 1000 °C, the sintering is related to a viscous flow. In the intermediate temperature range, both processes exist and overlap.

To explain the sintering of amorphous materials in a wide densification range, Scherer [25,26] has developed a viscous flow model. Scherer proposes a model describing sintering over a wide range of porosity (0-95%). In his model, a reduced time: $k(t-t_0)$ is plotted against the relative density ρ/ρ_s (Figure 3). ρ is the apparent density and ρ_s the skeletal density, t is the sintering time, t_0 is a fictitious time, and k is a constant at a given temperature.

Figure 3. Theoretical curve of the Scherer model.

Sintering identification was obtained by studying the kinetics of shrinkage. The samples are treated in an isothermal way, the apparent density is measured as a function of time and ρ/ρ_s is adjusted to the theoretical curve (Figure 3). This procedure is used to determine $k(t-t_0)$. If the model applies, the graph of reduced time versus real time shows a straight line and the slope is related to the viscosity at the temperature of interest.

We will test the Scherer model for composite aerogel and figure 4 shows the evolution of the density as a function of time for CA10 (fractal material [18,21]) and CA70 aerogel (non-fractal material [18,21]). The reduced lines $k(t-t_0)$ versus t is shown in Figure 5.

Figure 4. Bulk density of CA10 (◆) and CA70 (■) aerogel versus time at temperature 1050 °C.

Figure 5. Plot of $K(t-t_0)$ CA10 (◆) and CA70 (■) aerogels versus time (1050°C).

The results confirm some previous data [9,11,27,28] for classical silica aerogels: the sintering of composite aerogels is consecutive to viscous flow and the isothermal densification kinetics correspond to the Scherer's model. Moreover, we show that the Scherer model could also apply to fractal materials.

Because of higher mechanical properties and permeability in the following sections we will study the CA70 aerogel sample for the characterization of the aerogel-glass transformation.

3.3) Thermal analysis

Like glass, aerogels are made from amorphous silica. The main differences are the high concentrations of hydroxyl and organic groups and the high porosity. The heat treatments should eliminate these unwanted chemical species and this porosity. The thermograms obtained by differential thermal analysis (DTA) and thermogravimetry (TGA) show three temperature ranges linked to changes in the characteristics of the aerogel (Figure 6).

The large endothermic peak of DTA (25-200 ° C) is the result of the vaporization of water and alcohol. It is associated on the TGA curve with a weight loss close to 2%.

Exotherms between 250 to 500 ° C result from the oxidation of organic species. The exothermic oxidation reaction causes a weight loss of about 8-10%.

Continuous weight losses up to 1000 ° C (2%) are due to the condensation of silanol groups

Figure 6: DTA (...) and TGA (—) thermograms (CA70)

3.4) Characterization of porous glasses and dense glasses after sintering

In this section we characterize the physical properties (permeability, elastic and mechanical properties) of composite aerogel derived porous glasses versus their bulk density. Bulk density (or pore volume) are the main factors that controls the porous glass physical properties and in the literature some authors [29,30,31] propose power law evolution for elastic and mechanical properties versus bulk density or porosity.

A series of aerogels samples have undergone a sintering treatment for varying periods. The longer the duration of the heat treatment increases, the more the bulk density increases until the density of the silica glass 2.2 g cm^{-3} is reached. To obtain a fully dense material, the linear shrinkage is greater than 50%. This series of samples cover the density range from 0.42 to 2.2 g.cm^{-3} that correspond to porous glasses with porosity between 80% and 0%, respectively.

Table 2 shows changes in permeability as a function of the bulk density for partially sintered composite aerogels. The table clearly shows that D decreases considerably with sintering. As explained above, sintering proceeds first by collapsing the micropores, then for bulk density in the range $1.4\text{-}2.2 \text{ gcm}^{-3}$, the mean pore size becomes so small that permeability tends to zero. It must be noted that Klinkenberg effects is observed for the comparison of gas and liquid permeability in composites aerogels [32].

Bulk Density (gcm^{-3})	Permeability (nm^2)
0.42	130
0.44	62
0.49	21
0.54	13
0.66	7.5
0.69	7
0.79	6
0.85	4.5
0.97	3.5
1.04	2.5
1.1	2.1
1.3	2
1.4	1.2

Table 2: Porous glasses permeability *versus* bulk density

The change in mechanical properties is strongly linked to the increase in density (decrease in porosity). Table 3 shows that the elastic Young's modulus E increases by a factor of 10^4 , the mechanical strength (σ) increases by a factor of 10^3 , the toughness (K_{IC}) increases by a factor of 30 and the mechanical characteristics become identical to those of silica glass.

As explained above, during the sintering heat treatments, the microstructure of the aerogel is modified and the mechanical properties are improved. It is obvious that mechanical and elastic properties of material depends on the loading bearing fraction of solid and consequently on the density (or porosity [31]). Reinforcement of the porous glasses is thus directly related to the bulk density but also to microstructural changes. Thanks, to the viscous flow process, the heat treatment increased the connectivity and the size of the necks between particles.

The data of table 3 allow to propose simple power law evolution: for permeability $D = 2.63x^{-2.4}$, elastic modulus $E = 5704.7x^{3.6}$, mechanical strength $\sigma = 14.99x^{2.1}$ and toughness $K_{IC} = 123.61x^{2.5}$, for the set of aerogel-derived porous glasses. The same type of scaling has been previously measured for classical aerogels [29,30] but the exponents of the scaling laws are higher than the theoretical exponents for cellular solids [31]. The control of the sintering process allows preparing porous glasses with adjustable

physical properties like elastic, mechanical and permeability properties but also optical properties such as refractive index, transparency and thermal properties.

Bulk density (gcm^{-3})	E (Mpa)	σ (MPa)	K _{ic} (KPa m ^{-0.5})
0.39	35	0.47	7
0.41	300	1.45	33
0.56	760	3	70
0.75	3250	7.8	80
0.86	4580	11	155
1.1	10400	26	140
1.33	17000	38	245
1.39	23000	46	450
1.66	33000	66	200
2.07	58000	94	650
2.2	73000	95	870

Table 3 : Porous glasses mechanical and elastic properties *versus* bulk density

After the heat treatments, the material obtained is transparent and has the same physical properties as conventional vitreous silica. Optical characterizations by UV, near IR and IR spectroscopy confirm the good optical quality of the materials obtained after sintering (absence of impurities and transition metals) [9]. The only real difference is the high OH content (3000 -5000 ppm) that could lead to foaming and crystallization (cristobalite) during heat treatments at temperature higher than 1200°C [9].

3.5) Multi component glasses

It is possible to take advantage of the porous structure of the aerogel to allow the migration of salts in solution, throughout the volume of the material. The liquid phase will then be removed, and the loaded porous material (aerogel + salt) will be completely sintered, resulting in a multi-component glass. The porous structure of the aerogel is used as a volume host.

This method would make it possible to confine nuclear waste in the porosity [19,33,34]. The important characteristic is the very high chemical durability of the silica matrix that would protect nuclear waste from corrosion by water. Nuclear waste substitutes such as La and Nd were deposited in the porous structure before sintering. The final structure of the materials is that of a glass ceramic, the concentration of La and Nd of which can reach 20% by weight. The size of the La and Nd domains varies from 20 to 100 nm. This glass-ceramic material consists of La and Nd crystals embedded in a silica matrix (Figure 7). The glass corrosion rate in water of such a glass ceramic is 100 times lower than that of conventional nuclear glasses [19].

Figure 7: Glass ceramics doped with lanthanide oxide (left samples) and neodymium oxide (right samples)

5. Conclusions

This paper describes aerogels composite matrices (silica aerogel + aerosil) as precursors for silica glass and porous glasses.

The sintering model proposed by Scherer (viscous flow) is in good agreement with the sintering kinetics of the composite aerogels but the sintering temperature increases with the addition of aerosil particles. After complete sintering, the composite aerogel-derived glass exhibits mechanical properties identical to those of conventional silica glass. It is possible to control the pore volume by the sintering conditions (temperature, duration) over the large pore volume from 80 to 0%. Another interest is to use the porous volume as a host matrix to incorporate chemical species and to get glass ceramics.

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