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Silica Glass from Aerosil by Sol-Gel Process: Densification and Textural Properties[1]

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Sol-gel processes allow the synthesis of inorganic materials from solutions of molecular precursors. These precursors can be either organic, inorganic, or a mixture of the two. The aim of this work is the preparation of aqueous solutions consisting of Aerosil OX 50 (fumed silica) using small amount of additives like ammonium fluoride NH_4F (less than 2%), which are dried at room temperature in order to obtain monolithic gels. These are then densified at temperatures below 1200°C and sintered at 1300°C in order to obtain pure silica glass. The textural properties evolution of these gels is investigated as a function of temperature by thermal analysis (mass loss, shrinkage, and density) and scanning electron microscopy.

KEY WORDS: Aerosil; properties; silica glass, sol-gel; texture; thermal analysis.

1. INTRODUCTION

Glasses and ceramics have always been obtained from powders reacted at high temperatures, mostly above 1000°C, and then put into different needed physical forms [1–4].

During the last decade, new approaches of synthesis and elaboration known as "sol-gel processing" have been proposed. These procedures make use of hydrolysis reactions and polycondensation at low and medium temperatures. They consist of dissolving into a solvent one or many reactive species which react to form the gel [5, 6]. Then, the solvent is eliminated to obtain a rigid gel. Finally, the gel is packed to obtain a solid product. The

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product obtained using this technique is identical to the one obtained by the classical method of melting [7–10]. Among the techniques of preparation of a gel, two are widely used. The first technique uses colloidal chemistry based on the destabilization of the dispersion of fine particles maintained in suspension by Brownian motion. The second technique makes use of the polymerization of alcoxydes to obtain a lattice. Using these techniques, a large number of new materials have been manufactured. Worldwide research groups showed a great interest in the physical properties of these materials in order to derive the appropriate technological applications [11–17].

The present paper is mainly concerned with the preparation of homogeneous solutions from Aerosil OX 50 and NH_4F by applying the sol-gel process, the study of their conversion on glass, and the following of their textural evolution by different experimental techniques.

2. EXPERIMENTAL

2.1. Raw Materials

The Aerosil is amorphous ultra-fine silica obtained by hydrolysis in a flame of a chlorosilane. By modifying the production parameters, it is possible to manufacture different quantities that are characterized by the size of their particles and specific surface. The average primary particle size is between 7 and 40 nm, and the corresponding specific surface area varies between 380 and 50 $m^2 \cdot g^{-1}$. Initially and because of the presence of silanol groups on the surface of their particles, the synthetic silica are hydrophilic. The swapping of these silanol groups with organic ones leads to products that are generally hydrophobic which behave differently at the time of their utilization [18].

The precursor used in this investigation is an Aerosil of the Type OX 50 supplied by “Degussa.” It possesses a relatively weak specific surface ($50\,m^2 \cdot g^{-1}$) and an average particle size of 40 nm. These particles are spherical in shape, have a smooth surface, and have no pores. They include groups of silanol and siloxanes on their surfaces. The former groups confer the hydrophilic property of the Aerosil, and the latter being in greater quantity constitute the reason for the very inert character of this synthetic silica.

2.2. Preparation of Gels

Gels are prepared from mixtures of the Aerosil OX 50, ammonium fluoride (NH_4F), and distilled water according to the experimental procedure

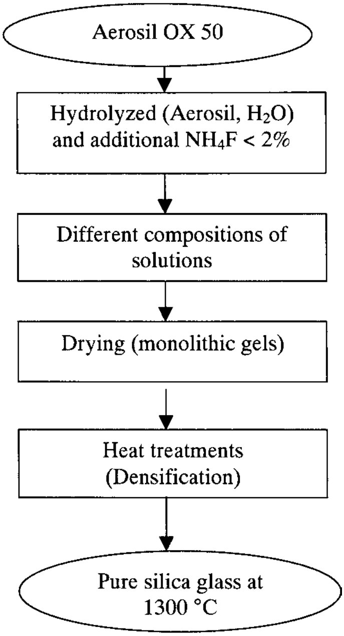

Fig. 1. Schematic of sol-gel process for the preparation of glasses.

presented in Fig. 1. The achieved suspensions possess low viscosities ($\eta < 50\,\mathrm{mPa \cdot s}$) that allow an easy transfer into the different molds used. They may also be used as thin films [19].

In order to produce monolithic gels having a relatively short gelation time, several solutions ($\mathrm{Aerosil + NH_4F + H_2O}$) have been prepared by varying the Aerosil concentration from 10 to 40% and the NH_4F from 0.5 to 2% of the total mass used. Each solution is poured into 13 quartz tubes (each tube contains $10\,\mathrm{cm^3}$ of solution), then dried at ambient temperature and in an electric oven at 50°C. After drying, the gels with 10, 20, and 40% of Aerosil presented failures (samples cracking); only the solutions of 30% Aerosil gave monoliths gels (no failures).

Consequently, in this study, only three solutions (three compositions) of 30% Aerosil with different concentrations of NH_4F (0.8, 1, and 1.2%) have been used because they give monolithic gels.

These concentrations have resulted in different times of gelation (90, 60, and 30 min). Therefore, the compositions of the three solutions is the same ($\mathrm{Aerosil + NH_4F + H_2O}$), only the time of gelation has changed. The solutions used in this investigation are reported in Table I.

Table I. Compositions Based on Aerosil Concentrations and NH_4F

Samples	Aerosil (%)	NH_4F (%)	Time of gelation (min)
1	30	0.8	90
2	30	1	60
3	30	1.2	30

2.3. Drying of Gels

The major problem in the preparation of gels lies in drying (i.e., the elimination of the liquid phase) because that may lead to failures in these gels, making them unusable. There are mainly two types of drying: classical drying and hypercritical drying [20–22].

Classical drying is used in this work. The solutions are initially dried at ambient temperature for several hours, then in a furnace at 50°C. The aspect of the obtained monolithic gels is presented in Fig. 2.

The samples are removed from the tubes and placed on refractory supports, and put into an electric furnace at different temperatures with a heating speed of $5°C \cdot min^{-1}$; at 100°C intervals (100 to 1300°C), a sample is removed from the furnace to be weighed (mass loss) and to measure its shrinkage (Figs. 3 and 4). The removed samples from the furnace did not show any failures (no cracking).

2.4. Classical Drying

Classical drying leads to the appearance of a dry solid called xerogel through the evaporation of the liquid phase at atmospheric pressure and ambient temperature. This type of drying can be divided into two distinct regimes. In the first, the reduction of the gel volume is equal to that of

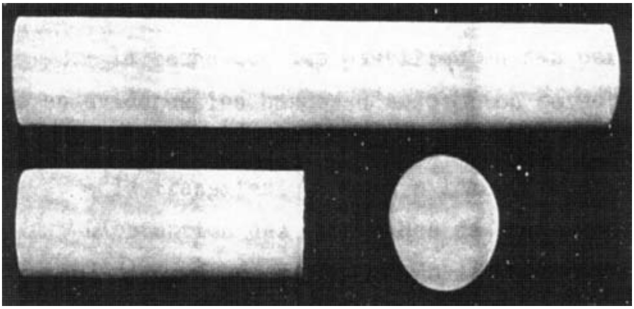

Fig. 2. Aspect of monolithic gels.

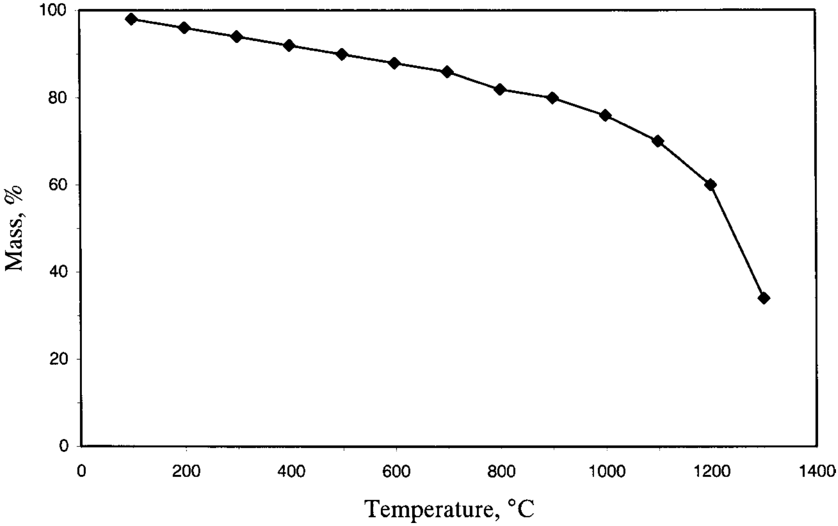

Fig. 3. Mass loss of the Aerosil gel during heat treatment.

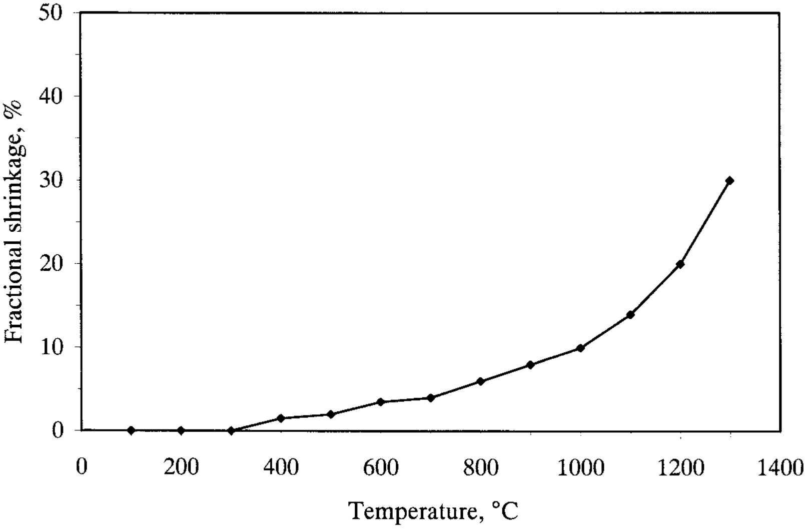

Fig. 4. Linear shrinkage of the Aerosil gel during heat treatment.

the evaporated solvent. During the second regime, capillary forces appear (through the creation of the liquid-gas interface) due to the fact that the volume of the evaporated solvent is greater than the volume lost by contraction. The capillary forces are given by the Laplace equation [21]:

$$P = -\frac{2\gamma_{\mathrm{LV}} \cos \theta}{r} \tag{1}$$

where γ_{LV} is the energy of the liquid-vapor interface, r is the radius of the pore, and θ is the angle of contact.

These forces compress the gel structure and can lead to its destruction. This drying is, therefore, difficult to perform. The gels obtained through the application of such drying are found to be hard materials whose porosity can reach 50%. The porosity is defined as the ratio of the porous volume to the total volume. The obtained gels present an important structural and textural difference with regard to the initial gel, and this is mainly due to the great volume shrinking obtained at the time of the evacuation of liquid from the solid phase.

3. RESULTS AND DISCUSSION

In order to study the textural evolution of these gels according to temperature, only one solution (13 samples) has been used because the composition is the same for the three solutions (Table I).

Thermal analysis (loss of mass, shrinking, and density), as well as scanning electronic microscopy, are used to characterize the gels and to investigate the gel-glass conversion.

3.1. Loss of Mass and Shrinking of Samples

Diverse thermal treatments have been applied to the samples in order to evaluate the loss of mass of the obtained gels and their shrinking.

The loss of mass as a function of temperature is determined through the relation:

$$P(\%) = 100[(m_0 - m_1)/m_0] \tag{2}$$

where m_0 is the mass of the raw sample and m_1 is the mass of the treated sample.

The shrinking is determined through the measurement of the shrinkage of the sample volume (measurement of the diameter) after every thermal treatment. The evolution of the loss of mass and shrinkage as a function of temperature is presented in Figs. 3 and 4, respectively.

A significant variation of these two parameters is noticed. The maximum mass and shrinkage are both reduced by approximately 70 and 30%, respectively. This is mainly caused by the thermal dehydroxylation of the gels, which leads to the destruction of the initial hydrophobic nature of the samples. The elimination of water by thermal polycondensation:

$$\text{Si–OH} + \text{HO–Si} \rightarrow \text{Si–0–Si} + \text{H}_2\text{0}$$

is essentially responsible for the loss observed between 400 and 1000°C.

The glass of pure silica is obtained through an operation of sintering at approximately 1300°C. This sintering is of the viscous flow as demonstrated by the investigation carried out by Close [22] on the silica powder. The X-ray diffraction curve shows the amorphous character of this silica glass obtained after sintering. It is found to be identical to the curves published in the specialized literature [1–3].

3.2. Density

The variation of the density of gels as a function of temperature is measured through the relation:

$$\rho = m/v \tag{3}$$

where m is the mass of the sample and v is the volume.

Measurements of gel density as a function of applied thermal treatment show a significant increase that varies from $0.13\ \text{g}\cdot\text{cm}^{-3}$ ($130\ \text{g}\cdot\text{l}^{-3}$) [16] for the raw Aerosil OX 50 to the theoretical value of the glass, i.e., $2.2\ \text{g}\cdot\text{cm}^{-3}$ at 1300°C. This variation is a consequence of the densification of the gels, i.e., the elimination of water from the structure and the pores. It is important to remember that according to measurements of BET carried out on treated samples [19], the increase of the density as a function of thermal treatment leads to a significant reduction of the specific surface area of these gels. This obtained result agrees well with the literature [14, 15].

3.3. Observations Using SEM

The application of the scanning electron microscopy (SEM) shows the porous texture of the Aerosil gels. The porous texture of the initial Aerosil OX 50 is demonstrated through the observations carried out through the application of transmission electronic microscopy (TEM) and presented in Fig. 5. It is found that the average size of the fumed silica particles is of the order of 40 nm.

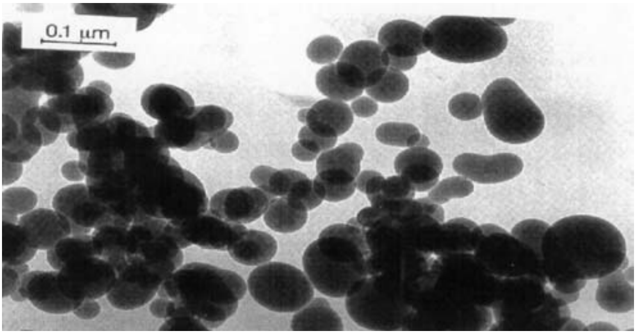

Fig. 5. TEM picture of Aerosil OX 50.

Figure 6 is the result of the application of the SEM technique on a sample dried at ambient temperature over some hours. It clearly shows the reduction of pores to the gain of silica aggregations that have an average size of the order of 200 nm.

The size of silica aggregations of the 13 samples has been measured from the SEM pictures [17]. The size of these silica aggregations increases according to heat treatment; the densification of these gels increases with temperature and leads to a reduction of the pore size.

4. CONCLUSION

The use of Aerosil as precursors in aqueous solution has led to monolithic gels that have been densified at temperatures below 1200°C and then sintered at 1300°C obtaining pure silica glass. These silica monoliths are found to be solids amorphous to X-ray diffraction.

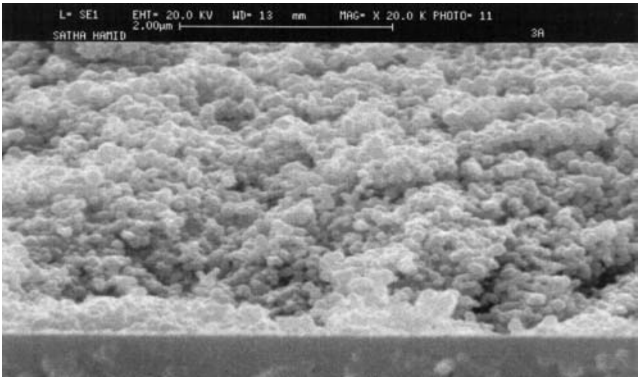

Fig. 6. SEM picture (texture) of gel at ambient temperature.

To be transformed into glass, an initial thermal treatment is applied to the gels in order to eliminate as much water as possible from the structure. The loss in mass and the shrinking of samples vary with temperature to reach 70 and 30% at 1300°C, respectively. This result seems to be the consequence of the densification of gels as shown by the observations obtained through the application of scanning electronic microscopy.

The density of gels evolves with temperature from $0.13\ \mathrm{g \cdot cm^{-3}}$ (raw Aerosil) to the theoretical value of pure silica glass $2.2\ \mathrm{g \cdot cm^{-3}}$ at 1300°C. Silica glasses obtained through heating at constant speed are transparent, and possess physical and optical properties identical to those of vitreous silica obtained by application of the traditional method.

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