



Small angle X-ray scattering of aerogel densification

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Abstract

Silica aerogels were densified by isostatic compression or by thermal sintering. Small angle X-ray scattering experiments show that both types of aerogels exhibit oscillations around Porod behavior at high q values. Oscillations were modified by sintering but remain unchanged by compression. According to the Babinet's principle, it is not usually possible to associate intensity change with a peculiar phase of the porous solid. However, the fact that the oscillations remain unchanged with compression, which only acts on the porous part, indicates that SAXS intensity experiments can be directly linked to the solid part. Using the Porod law [G. Porod, *Kolloid Z.* 124 (1951) 83; P. Debye, A.M. Bueche, *J. Appl. Phys.* 20 (1949) 518], the specific surface area has been estimated. Surface area of the compressed aerogels does not change with density. In contrast, the specific surface area of the sintered samples decreases markedly. The absence of shape changes of SAXS curves indicates that the mean size of the solid phase remains constant during the compression densification. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Silica aerogels; Small angle X-ray scattering; Densification

1. Introduction

Experiments have been carried out to investigate the dependence of aerogel texture on preparation parameters [1]. Both the nature of the catalyst and the silica content are the parameters which control the texture of supercritically dried gels. Other studies examined changes in aerogels texture with densification caused by thermal sintering treatment. Viscous sintering occurred on fractal [2] and non-fractal aerogels [3–13]. Small angle scattering is a very useful tool to investigate the changes in texture resulting

from viscous flow. For nonfractal aerogels exhibiting a Porod law, information about the texture has been obtained by describing the aerogel as a two phase medium [3,4]. This approach was considered to be of interest for aerogels densified by isostatic pressure [5–7]. This kind of densification performed at room temperature is assumed to be due to a compression induced by collapse of the largest pores of aerogels. Previous studies indicate that this mechanism is applicable. This paper concerns the study of the textural evolution of an initial aerogel densified using either temperature or pressure. Textural changes have been followed using small angle X-ray scattering (SAXS). Comparison between these textural changes provides details which accord with the microscopic mechanisms occurring during the density change.

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2. Experimental procedure

Silica gels were prepared from TMOS (tetramethoxysilane) under basic conditions using 1.6×10^{-2} M ammonia. After 1 week of aging at room temperature, they were supercritically dried in ethanol. They were then subjected to oxidation at 400°C overnight. The starting density was 0.186 g/cm^3 . Aerogels were sintered at a temperature between 920 to 1100°C depending on the density required. This treatment was carried out in air with heating rate of 2°C/min to 250°C followed by a 3 h plateau. Temperature was then increased to the selected temperature at which it was held for 1 h. Samples were designated PSA x where x indicates the density. PCA x refers to aerogels subjected to an isostatic pressure by means of a Hg porosimeter [5,6]. The density was calculated from the sample weight and dimensions.

Experiments were carried out on aerogel slides having a thickness less than 1 mm. Measurements were done with a high resolution spectrometer (Bonse Hart Camera). A rotating anode X-ray source with a copper target was employed. The wave vector, q , was within the range $2 \times 10^{-3} \text{ \AA}^{-1} < q < 0.2 \text{ \AA}^{-1}$.

Previous sintering experiments have demonstrated that non-fractal aerogels can be modelled by an assembly of cubic cells consisting cylinders of length, L , and radius, a [13]. SAXS results were therefore analysed assuming this structural geometry.

For low q values, using this model, the intensity, $I(q)$, is related to the wave vector by the Guinier approximation [8]:

$$I(q) = L \frac{\pi}{q} I_c(q) \quad (1)$$

with

$$I_c(q) = (\Delta\rho)^2 A^2 e - q^2 (a/\sqrt{2})^2 / 2,$$

where $\Delta\rho$ is the electronic density contrast which corresponds to ρ_s , the skeletal density of the solid, since the second phase is air. A is the cross-section of the cylinder. This equation is valid as long as the system may be regarded as dilute. For aerogels this assumption is valid. However, for highly densified aerogels the analysis must be done with caution.

At high q values, which correspond to the Porod regime [8,9], the following relation holds:

$$I(q) = Kq^{-4}. \quad (2)$$

K is given by the scattering curve and corresponds to the limit $q^4 I(q)$ when $q \rightarrow \infty$. This relation applies independently of the dilution. It expresses the sharp electron density change occurring at the solid–pore interface. The surface area per unit volume, S/V may be estimated from the relation

$$\frac{K}{Q} = \frac{1}{\pi \varphi_s \varphi_p} \frac{S}{V}, \quad (3)$$

where φ_s and φ_p correspond respectively to the volume fraction of the solid and the porous phase respectively and Q is known as the Porod invariant:

$$Q = \int_0^\infty q^2 I(q) dq; \quad (4)$$

Q is estimated from the diffusion spectrum.

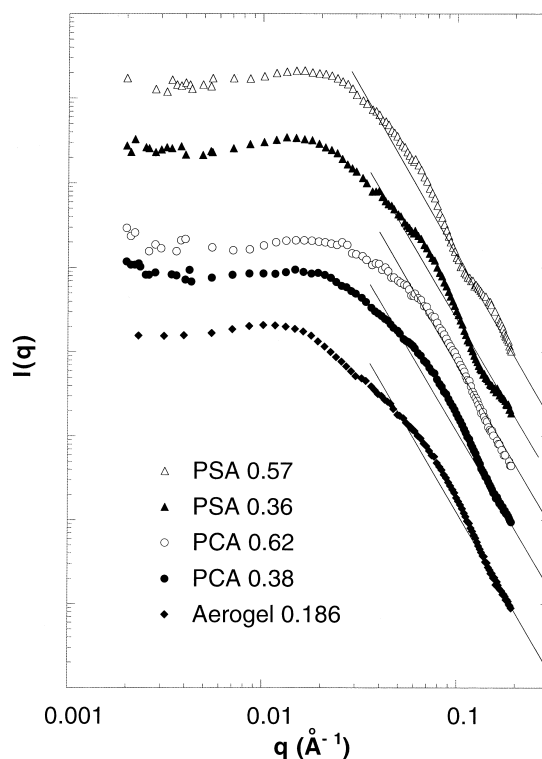


Fig. 1. SAXS intensities as a function of wave vector for the compressed (PCA) and sintered (PSA) aerogels. Initial aerogel is labelled by its density 0.186 g/cm^3 .

Another manner to express identical density contrast when passing through the interface is to define an average chord length l [8]:

$$l = \frac{4Q}{\pi K}. \quad (5)$$

The average chord length in the material may be separated between the average chord length in the solid part, l_s , and in pores, l_p , according to the following relation:

$$l = l_s \varphi_p = l_p \varphi_s. \quad (6)$$

3. Experimental results

The scattering curves are plotted on a log–log scale in the Fig. 1. They have been shifted on the intensity scale for clarity. All curves show oscillations around the slope -4 , corresponding to Porod's law. This slope has been drawn to guide the eye.

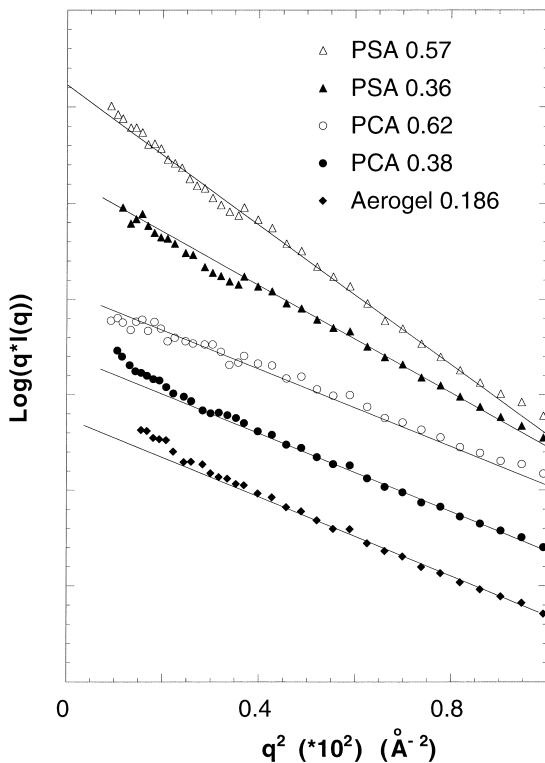


Fig. 2. $\text{Log}(I(q)q)$ as a function of q^2 for compressed and sintered aerogels. The lower curve refers to the initial aerogel.

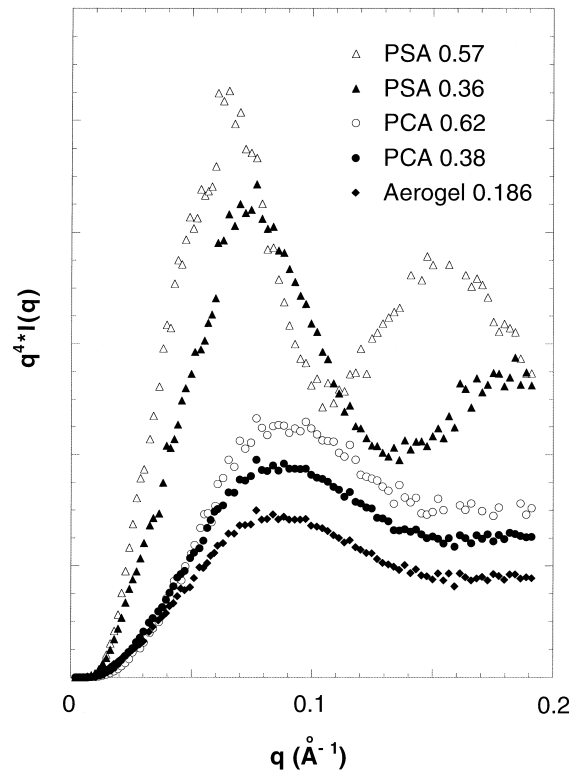


Fig. 3. Plot of $I(q)q^4$ vs. the wave vector for compressed and sintered aerogels. Initial aerogel curve is displayed at the bottom.

Samples have been selected on the basis of similar densities for comparison.

It is shown in Fig. 2, that in the intermediate q range, $\text{log}(I(q)q)$ varies linearly with q^2 . With respect to the assumption that the solid part of these aerogels can be described as cylindrical arrays, Eq. (1) applies and provides an estimate of the radius of the cylinders. It can be clearly observed that compressed aerogels curves have the same slope. This slope is not very different to that of the initial aerogels. In contrast, slopes of the sintered aerogels are closely related to aerogel densities.

Oscillations in the Porod law domain have been analyzed by plotting $I(q)q^4$ vs. q (Fig. 3). Again, curves of sintered aerogels exhibit extended oscillation in intensity which depend on the density whereas curves corresponding to compressed aerogels are identical to that of the initial aerogels. They do not seem to be modified by room temperature densification induced by pressure increases.

4. Discussion

The starting aerogel has a porosity of about 90%. In addition, the pore volume fraction of the densest aerogel (PCA0.62) is 70%. In such conditions the Guinier analysis is supposed to be valid and leads to a values reported in Table 1.

As sintering proceeds the a values increase. The radius of the cylinders grows at the expense of their length since sintering occurs at constant mass. An associated feature is a reduction in the surface area. In contrast, the radius a of compressed aerogels does not change. This result confirms that densification by compression mainly occurs through a reduction in volume fraction of pores, leaving the solid thickness of the cylinders unchanged.

Additional information is obtained from the Porod analysis. Oscillations in the Porod region can be fitted with the theoretical intensity curves given by

$$I(\mathbf{q}) = \int_0^{\infty} h(r) I_r(\mathbf{q}) dr. \quad (7)$$

$I_r(\mathbf{q})$ is the scattered intensity of cylindrical particles (cylinder form function) [8] which scales with (length, radius) r , $h(r)$ is the Gaussian distribution of the radius of cylindrical particles, and u is the half high width of this distribution. $h(r)$ is a normalised function:

$$\int_0^{+\infty} h(r) dr = 1. \quad (8)$$

According to Eq. (7), we can fit experimental results with theoretical curves. As a result, the fit gives both u and a values. Such values are given in Table 1. As previously demonstrated the cylinder

radius increases with density for sintered aerogels while it remains constant for the compressed series. Table 1 also shows that u values remain narrow with sintering.

Assuming that the skeletal density value ρ_s (2.2 g/cm³) does not change during densification the pore and the solid volume fractions were estimated for all samples. Eqs. (5) and (6) allow both average chord length in the solid and pore phases to be evaluated. The values have been plotted in Fig. 4, as a function of the volume fraction φ_p , with a 6% estimated error. Results obtained for sintered aerogels are roughly identical to those previously shown [3]. According to the model used they show that the cylinder diameter grows and corresponds with a decrease in the pore chord length. However, for the compressed aerogels, the behaviour is totally different. Here the chord length of the solid phase does not change but the decrease in the chord length for pores is very marked. This result indicates that the compression affects the pores by reducing their size. The pore chord length decrease is marked up to density of 0.4 g/cm³. However, at higher densities the slope $dl_p/d\varphi_p$ decreases indicating that the clusters resist any further interpenetration, as recently shown [10]. Some of the solid chord lengths are reported in Table 1 for comparison. They are in the same range as the radius of cylinders previously estimated.

The specific surface area given by $S/V\rho$ is related to the ratio S/V calculated from Eq. (3). ρ is the apparent density of the sample. Specific surface areas are plotted (with a 6% estimated error) as a function of φ_p in Fig. 5. They are about 10% higher than those measured by nitrogen adsorption using the BET technique. The decrease of the specific surface

Table 1
Radius of cylindrical particles (a): evolution with sintering (PSA samples)

Sample apparent density (g/cm ³)	a (Scherer model) (Å)	a and (u) (Porod) (Å)	a ($l_s/2$) (Å)	a (Guinier) (Å)
Aerogel 0.186	19	24 (4)	21	29
PSA 0.29	21	26 (4)	23	30
PSA 0.36	22	28 (3)	27	32
PSA 0.44	23	32 (3.5)	28	34
PSA 0.57	24.5	35 (4)	34	38

For PCA samples a remains constant with densification. u is the half high width of the Gaussian distribution of the radius of the cylindrical particles.

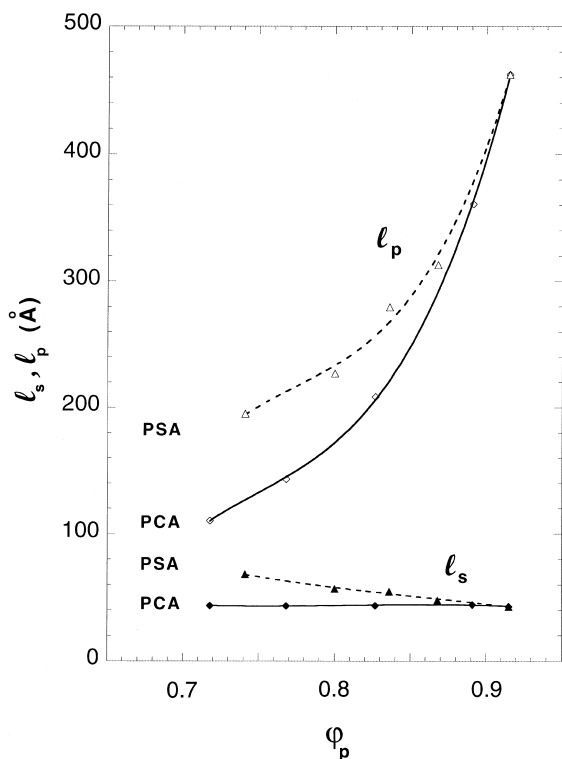


Fig. 4. Solid and pore chord lengths as a function of ϕ_p . Note that results coming from other samples of the series have been included.

area of PSA samples is linked to the transformation of the solid part which occurs thanks to the viscous flow. The fact that the specific surface area of compressed aerogels remains roughly constant clearly indicates that densification occurs without mass transport on a microscopic scale. The small decrease in specific surface area is ascribed to area lost when arms of clusters come in contact. On densification of the compressed aerogels the pore size is decreased. Largest pores collapse first. In aerogels the largest pores have a size in the mesoporous range. Their size in general does not exceed 300–500 Å as can be inferred from the low permeability of the aerogels [14].

A specific surface area evolution can also be obtained from the sintering of the Scherer model constructed with cubic cells and cylindrical particles [13]. This sintering mechanism is based on an increase of the section of such particles in association with a decrease of their length (while the mass

remains as a constant). On the basis of values of the bulk density and the specific surface area of the initial aerogel, details of the cylinder model may be estimated from Ref. [13]. This model is based on the assumption that the cylindrical particles have the same diameter. Our experimental results agree with this assumption. Moreover, this model is well suited for predicting sintering kinetics [13] as well as N_2 adsorption–desorption isotherms of aerogels [12].

The length L and the radius a of cylinders have been calculated for the initial aerogel. As shown in Fig. 5, densification by sintering using an unique cell size ($L = 193$ Å, $a = 19.5$ Å) leads to a specific surface area change which does not accord closely with the experimental results. In fact, aerogels can be better described from a distribution of length of cubic cells. Here, we have described the aerogel

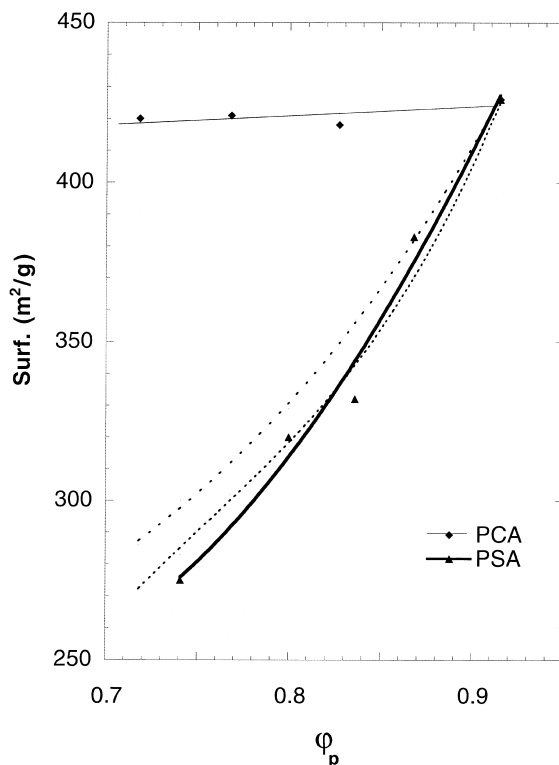


Fig. 5. Specific surface area from SAXS curves as a function of ϕ_p . (—) experimental results. (---) Calculated surface area of sintered aerogels with an one cell model, (···) with a three cell model.

texture as an assembly of three dimensional cubic cells. This arbitrary choice is used to show the influence of such a distribution on the evolution of the specific surface area with sintering. The smaller cubic cell consists of cell having a length $L/3$, the second one a length of $2L/3$ and the last one, L . The relative distribution of cells is in the ratio $1/2/1$. For this model we found $L = 240 \text{ \AA}$ and $a = 19 \text{ \AA}$. This very simple model accounts for the observed evolution of specific surface area as shown in Fig. 5.

5. Conclusion

SAXS measurements show that structural and textural evolution of the silica aerogels depends on the densification process.

Densification by isostatic compression leads to a pore size decrease while the solid phase remains unchanged.

Densification caused by sintering, results in an increase in solid particle size.

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