

Synthesis of Water-Glass-Based Silica Aerogel Powder via with and Without Squeezing of Hydrogels

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ABSTRACT: The present article describes the synthesis of water-glass-based silica aerogel powder via coprecursor method, using with and without squeezing, in drying technique. The present research was aimed to develop a simple, cost-effective, and rapid drying process, i.e., squeezing through sol-gel synthesis. The physical and textural properties of the aerogel powder synthesized with and without squeezing process via ambient pressure drying (APD) have been studied and compared. For characterization of aerogel powder, we employed Brunauer, Emmett, and Teller, Barrett-Joyner-Halenda, and field emission scanning electron microscope techniques. The experimental results showed that

the properties of the aerogel powder obtained by squeezing are superior to those dried in a furnace one. The squeeze-dried aerogel powder exhibited lower tapping density (0.126 g/cm^3) than furnace dried. Furthermore, textural investigations revealed that the aerogel powder has high-specific surface area ($752.3 \text{ m}^2/\text{g}$), high porosity, low shrinkage, and uniform pore size distribution, which is obtained by squeezing process via APD. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1675–1679, 2010

Key words: water-glass; silica aerogel; furnace drying; squeezing; BET surface area; FE-SEM

INTRODUCTION

Nowadays, silica aerogels have become very popular in the field of materials because of their attractive properties such as low-bulk density ($0.2\text{--}0.01 \text{ g/cm}^3$), high-specific surface area ($500\text{--}1000 \text{ m}^2/\text{g}$), high porosity ($>92\%$), and low-thermal conductivity ($\sim 0.02 \text{ W/mK}$).^{1,2} Consequently, in current years, aerogels have found increased interest in industries. However, the production and drying of aerogels on a large scale at reasonable cost still remain as a challenge. Bhagat et al.³ proved an effective synthesis route for the preparation of silica aerogel powder. Various drying methods are available for silica aerogels production viz., atmospheric pressure drying, freeze drying, supercritical drying, fluidized bed drying, and ambient pressure drying (APD). In our previous study, we have already reported effective and economy drying method.⁴ Extensive research efforts have been directed toward understanding the drying phenomena of different methods. However, there was no

much published literature available on silica aerogel powder drying process.

Silica aerogels have several technological applications such as thermal insulation, catalysis, drug delivery systems, gas sensors, waste water treatment, heat storage device for automobiles, particle detectors, and absorbing media for desiccation.^{5–8} However, the high production cost and drying parameters of the aerogels severely restricts the scale up and their wide exploitation in various applications.⁹ Synthesis of silica aerogels using water-glass precursor via an APD is one way to reduce its production cost. Several attempts have been made to synthesize the aerogels using this method but their commercial production is yet to be achieved. This is because of large drying time and need for modification of drying technique in bulk requirements.

The aim of this study is to find new drying method, reduce drying time, and improve the properties of aerogel powder. So far in our previous studies, there are no much reports on the drying of hydrogels via coprecursor method. Optimization and drying efficiency of silica aerogel powder from industrial point of view is very important. Therefore, in this study, we describe the drying modification of APD method. Subsequently, the physical and

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TABLE I
Physical and Textural Properties of Water-Glass-Based Silica Aerogel Powder as a Function of Drying method

Name of sample	Density (g/cm ³)	BET surface area (m ² /g)	S _{micro} (m ² /g)	V _c (cm ³ /g)	V _{micro} (cm ³ /g)	P _d (nm)
Without squeezing [FD]	0.151	704.1	299.2	1.584	1.852	25.2
With squeezing [SD]	0.126	752.3	261.5	1.228	1.580	24.3

textural properties of the consequential aerogels have been studied and discussed.

EXPERIMENTAL

Materials

The chemicals used for synthesis of silica aerogel powder are as follows. Sodium silicate (29 wt %, II Shin Chemical Co., South Korea), hexamethyldisilazane (Acros Organics, Japan), nitric acid, and *n*-hexane.

Synthesis of silica aerogel powder

The sodium silicate (SS) solution was diluted first with the deionized water, so as to obtain 5.68 wt % of silica as the starting material. The silylated hydrogels were then prepared by a coprecursor method wherein the nitric acid and hexamethyldisilazane (HMDS) were added to the SS (5.68 wt %) under constant stirring. The sol undergoes gelation in 3–5 min at room temperature (27°C). The silylated hydrogels prepared by the coprecursor method were immersed in *n*-hexane for one-step solvent exchange and sodium ion removal, which could be accomplished in 3 h. During this process, the water present in the hydrogels was given out as a consequence of surface modification by organic groups (–(CH₃)₃) present in HMDS and simultaneous intrusion of *n*-hexane into the gel resulted in the solvent exchange. The displaced pore water was then removed from the beakers and the silylated organo-gels were dried at ambient pressure in a furnace in one step and kept at 190°C for 90 min to obtain the aerogel powder. In addition, we developed another simple and rapid method for drying wet gels akin to squeezing the gel material in between filter papers, then kept in oven at 90°C for 30 min. The APD process, in which squeezing step involved is known as squeeze drying.

Characterization of aerogel powder

The N₂ adsorption measurements were made for the aerogel powder using a surface area analyzer (Quantachrome Autosorb-1) and the BET (Brunauer, Emmett and Teller) surface area and the pore volumes were calculated. The pore size distributions were estimated by the BJH (Barrett-Joyner-Halenda) method. The microstructure of the aerogel powder

was probed by a field emission scanning electron microscope (FE-SEM, JSM 6700 F microscope, JEOL). The tapping density of the silica powder was calculated from its mass to volume ratio. For this purpose, the silica powder was filled in a cylindrical column of known volume and the measurements were performed on the so-produced silica powders without evacuating them. The observations were taken five times for each sample and the average value was taken as the tapping density of the silica powder.

RESULTS AND DISCUSSION

Physical properties

The physical properties of the aerogel powder synthesized by the furnace drying and squeeze-drying techniques were summarized in Table I. The tapping density of the aerogel powder dried in the squeezing [SD] method is relatively lower than that of furnace-dried [FD] sample. Furthermore, the porosity of silica aerogel powder (with squeezing) is larger [94.2%] than the aerogels of FD (without squeezing) [93.1%]. The increased micro porosity can cause an increase in surface area. As a result, aerogel powder with lower density and larger specific surface area can be obtained using squeeze-drying process via coprecursor method. This process was mainly developed to dry the aerogels with improved properties for manufacturing of economical aerogel powder. The obtained aerogel powder showed a few micro cracks in clusters after drying through direct micro oven drying [FD] process. From Table I, it is clearly stated that the properties of the aerogel powder obtained by squeeze drying are superior to those dried in a furnace. This is due to the fact that the wet-gel gets heated nonuniformly during the furnace drying leading to the temperature gradient, which ultimately results in the shrinkage of the gel.¹⁰ On the other hand, in squeezing process, initially, the water was taken out completely from wet-gel by pressing in between filter papers, then after placing them into oven for some time leads to uniform heating to entire gels.

Textural properties

The textural properties of the aerogel powders were investigated by the standard N₂ gas adsorption

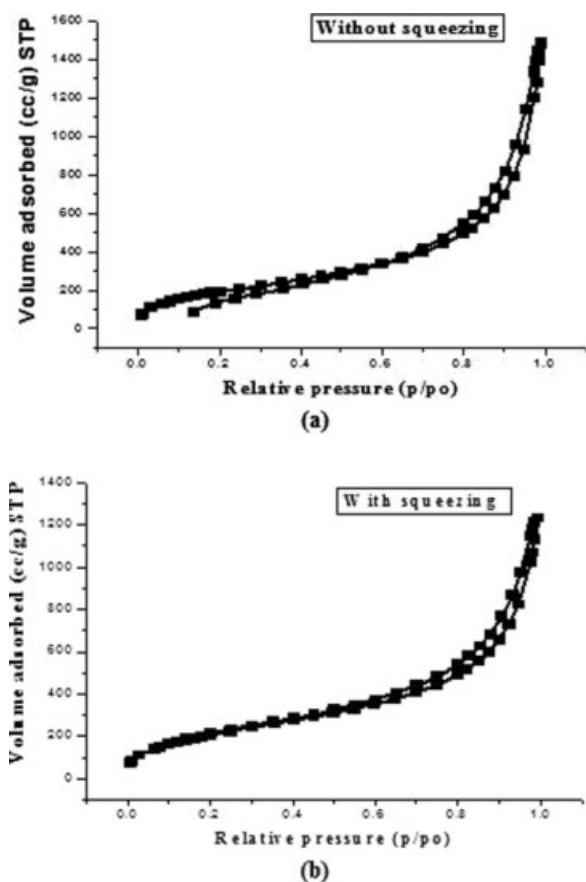


Figure 1 N_2 adsorption–desorption isotherms obtained for the silica aerogel powder synthesized by using with and without squeezing process via coprecursor method.

method using a surface area analyzer (Quantachrome, Autosorb-1). Initially, the aerogel powders were degassed at 200°C for 2 h. The specific surface area was calculated using the standard BET method. The micropore surface area (S_{micro}) was determined by the Horvath-Kawazoe method. The cumulative pore volume (V_c) was calculated from the N_2 adsorption-desorption profiles. The average pore diameters (P_d) and pore size distributions were estimated by the BJH method. All the above values are presented in Table I. From the table, it is observed that squeeze-dried aerogel powder has high-BET surface area ($752.3 \text{ m}^2/\text{g}$) than furnace-dried powder. In both cases, average pore diameter in nanometers is similar. This is understandable that the hydrogels by coprecursor method via squeezing process significantly reduces the drying shrinkage during the APD and it ultimately helps to preserve the aerogel-like properties in the final solid. The pore volume and pore size are also analyzed by BET method. The squeeze-dried aerogel powder has low-pore-volume ($1.58 \text{ cm}^3/\text{g}$) and pore size (8.4 nm), whereas pore volume and pore size were higher for

furnace-dried powder and the value is $1.85 \text{ cm}^3/\text{g}$ and 10.5 nm, respectively.

The aerogel powder with squeezing exhibits micropores in its structure with a less cumulative pore volume (V_c) of $1.228 \text{ cm}^3/\text{g}$. The average pore diameter (P_d) varied from 1.8 to 157.1 nm depending on the method of drying. Both two samples showed higher specific surface area in the range of $704\text{--}752 \text{ m}^2/\text{g}$.

The nitrogen adsorption–desorption isotherms obtained at 77 K for silica aerogel powder with and without squeezing process [SD] via APD were shown in Figure 1(a,b). From the figure, some changes have been observed in the texture of silica powder with and without squeezing. For the silica aerogel powder, i.e., with squeezing, the adsorption/desorption branches of the isotherm coincided at both ends with each other and with hysteresis loop during desorption cycle [Fig. 1(b)]. Whereas silica aerogel powder without squeezing [FD] showed isotherms coincidences at one end with hysteresis loop during desorption cycle [Fig. 1(a)]. The isotherms obtained for the both samples are of Type

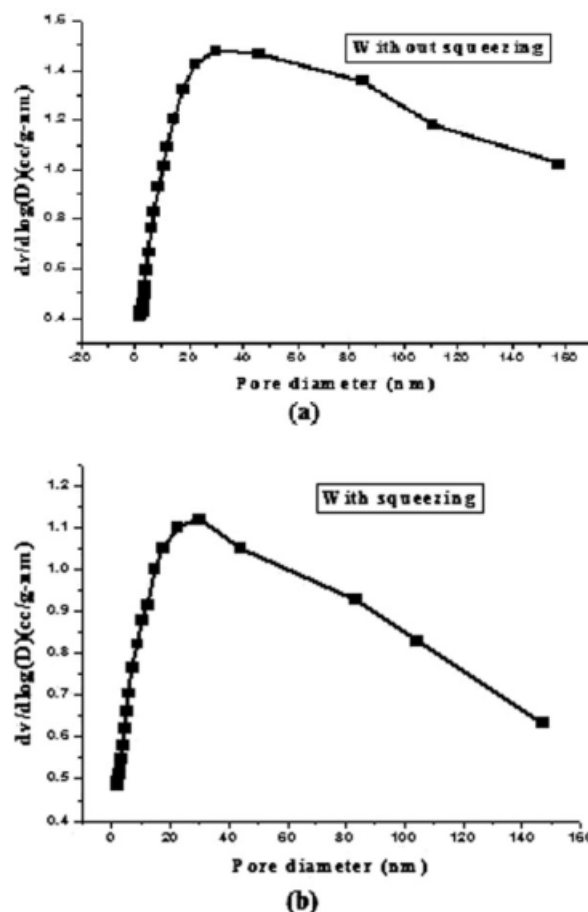


Figure 2 Pore size distribution profiles of the water-glass-based aerogel powder synthesized by using with and without squeezing process.

IV, which is the characteristic feature of the mesoporous materials.^{11,12} The desorption cycles of the isotherms showed a hysteresis loop, which is generally attributed to the capillary condensation occurring in the mesopores. The adsorption–desorption branches of the samples 1a and 1b are almost parallel and vertical over a wide range of p/p_0 showing the H₁ type of the hysteresis loop [Fig. 1(a,b)]. Such type of hysteresis loop is often associated with cylindrical mesopores open at both ends.¹³

Figure 2(a,b) depicts pore size distribution profiles of the water-glass-based aerogel powder synthesized using with and without squeezing process. The aerogel powder with squeezing process showed narrow pore size distributions [Fig. 2(b)] than without squeezing. Furthermore, small average pore sizes exhibited higher specific surface areas (Table I) compared with those powders having relatively wider pore size distributions and bigger average pore sizes [Fig. 2(a)]. The two samples [Fig. 2(a,b)] showed a pronounced peak in the mesopore region (2–160 nm), which signifies that the aerogel powder maintain mesopores in their structure even after drying them at the ambient pressure. In the powder of without squeezing [FD], the peak pore diameter shifted to a higher side (150 nm) with relatively broader pore size distributions [Fig. 2(a)].

FE-SEM analysis

Figures 3 and 4 depict the FE-SEM of silica aerogel powder with and without squeezing process, respectively. It was observed that the SEM image of furnace-dried aerogel powder showed thinner silica network with big pores (Fig. 3). The microstructure of aerogel powder comprises irregular-shaped silica

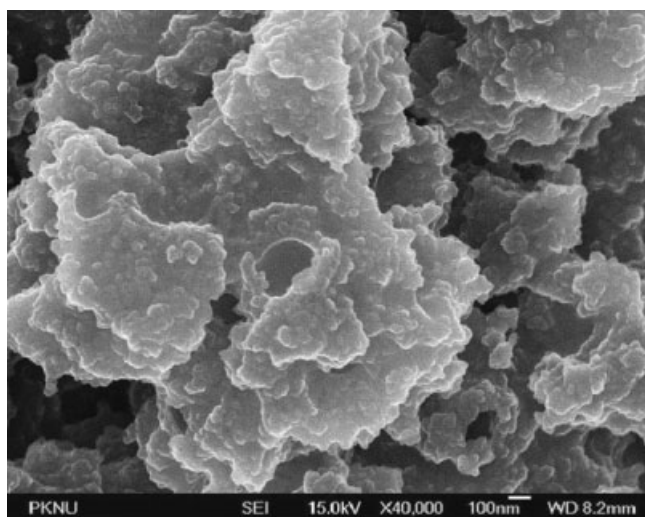


Figure 3 FE-SEM of silica aerogel powder via without squeezing process.

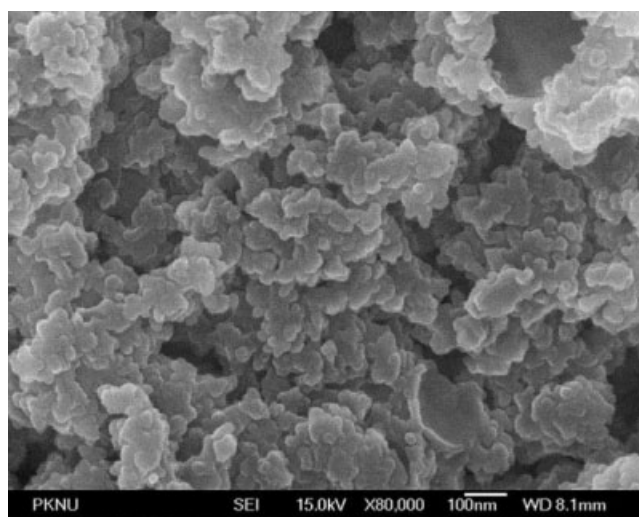


Figure 4 FE-SEM of silica aerogel powder via with squeezing process.

clusters with loose packing and also wide separation between the silica chains. This is due to the fact that the shrinkage of hydrogel to a large extent during the microwave/furnace drying at the ambient pressure and thereby losing the mesopores present in it.¹ From the Figure 4, it is evident that the aerogel powder has a three-dimensional (3D) nanoporous structure consisting of aggregation of primary particles, nearly 8–9 nm in size. The aerogel powder showed relatively denser silica network with small pores and also good interconnectivity between silica chains.

Further explorations on the various aspects of squeezing process implementation in different drying techniques and its effectiveness in the large-scale production of the aerogel powders are under process in the laboratory.

CONCLUSIONS

The silica aerogel powder was successfully prepared from water-glass via coprecursor method using drying modification, i.e., squeezing process. The obtained silica aerogel powder showed properties of 0.126 g/cm³ density, 94.2% porosity, and 752.3 m²/g higher specific surface area. Best quality silica aerogel powders, in terms of low density, high porosity, transparency, monolithicity, low shrinkage, and uniform pore size distribution have been obtained by the preparation of aerogels using squeeze-drying method. FE-SEM analysis revealed that aerogel powder has a 3D nanoporous structure consisting of aggregation of primary particles and good interconnectivity between silica chains. Based on the studies, the prepared aerogel powder in the squeeze-drying

process could be thought for thermal insulation applications.

References

1. Bhagat, S. D.; Kim, Y.-H.; Yi, G.; Ahn, Y.-S.; Yeo, J.-G.; Choi, Y.-T. *Micro Meso Mater* 2008, 108, 333.
2. Bhagat, S. D.; Kim, Y.-H.; Ahn, Y.-S.; Yeo, J.-G. *Appl Surf Sci* 2007, 253, 3231.
3. Bhagat, S. D.; Kim, Y.-H.; Moon, M.-J.; Ahn, Y.-S.; Yeo, J.-G. *Solid State Sci* 2007, 9, 628.
4. Bhagat, S. D.; Kim, Y.-H.; Ahn, Y.-S.; Yeo, J.-G. *Micro Meso Mater* 2006, 96, 237.
5. Dias, A. S.; Pillinger, M.; Valente, A. A. *Micro Meso Mater* 2006, 94, 214.
6. Jamali, M. R.; Aassadi, Y.; Shemirani, F.; Hosseini, M. R. M.; Kozani, R. R.; Farahani, M. M.; Niasani, M. S. *Anal Chem Acta* 2006, 579, 68.
7. Rao, A. V.; Hegde, N. D.; Hirashima, H. *J Colloid Interface Sci* 2007, 305, 124.
8. Tang, Q.; Xu, Y.; Wu, D.; Sun, Y. *J Solid State Chem* 2006, 179, 1513.
9. Carlson, G.; Lewis, D.; Mckinley, K.; Richardson, J.; Tilloston, T. *J Non Cryst Solids* 1995, 186, 372.
10. Bhagat, S. D.; Park, K.-T.; Kim, Y.-H.; Kim, J.-S.; Han, J.-H. *Solid State Sci* 2007, 11, 1016.
11. Li, W. C.; Lu, A. H.; Guo, S. C. *J Colloid Interface Sci* 2002, 254, 153.
12. Mohanan, J. L.; Brock, S. L. *Langmuir* 2003, 15, 2567.
13. Stengl, V.; Bakardjieva, S.; Subrt, J.; Szatmary, L. *Micro Meso Mater* 2006, 91, 1.