



Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Letter to the Editor

Dynamic spring-back behavior in evaporative drying of polymethylsilsesquioxane monolithic gels for low-density transparent thermal superinsulators

Gen Hayase^{a,1}, Kazuyoshi Kanamori^{a,*}, Ayaka Maeno^b, Hironori Kaji^b, Kazuki Nakanishi^a^a Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan^b Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

ARTICLE INFO

Article history:

Received 14 October 2015

Received in revised form 4 December 2015

Accepted 19 December 2015

Available online xxxx

Keywords:

Sol-gel

Aerogels

Xerogels

Spring-back behavior

Ambient pressure drying

Thermal insulators

ABSTRACT

Ambient pressure drying of polymethylsilsesquioxane gels via dynamic shrinkage-reexpansion has been investigated for preparation of aerogel-like xerogels and their application to thermal superinsulators. An extended aging of wet gels in aqueous solution containing precursor-derived species is found to be crucial in obtaining crack-free, monolithic xerogels with sufficiently low thermal conductivity ($13.7 \text{ mW m}^{-1} \text{ K}^{-1}$) at bulk density of 0.140 g cm^{-3} (porosity $\sim 90\%$).

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1. Introduction

Aerogels are low-density porous materials obtained via the sol-gel process and supercritical drying [1]. The chemical compositions of aerogels have virtually no restrictions; aerogels with a variety of compositions can be obtained as far as a wet gel can be prepared and the pore solvent can be removed without serious contraction by supercritical drying [2]. Various types of aerogels are therefore synthesized ranging from inorganic oxides [3–7], organic-inorganic hybrids [8–11], organic polymers [12–14] and to biomaterials [15–19] for many purposes. Silica aerogel is the most studied one due to the unique properties such as high visible-light transmittance and very low thermal conductivity [4, 20]. Since the microstructure comprising solid skeletons, composed of silica nanoparticles with ca. 10 nm in diameter and pores with several tens nanometer, is finer than the visible-light wavelengths and mean free path of the molecules in air, properties like visible-light transparency and low thermal conductivity are resulted. Aerogels are expected to be a superior substitution of existing thermal insulators, and transparent insulating window systems can be designed by sandwiching aerogels between glazing materials [21]. However, fatal mechanical friability, derived from the solid skeletons with weakly connected silica

nanoparticles and high porosity, and necessity of the supercritical drying process under high pressure hinder massive industrial productions and practical uses of silica aerogels.

Recent years, there are some reports on organic-inorganic hybrid aerogels of silica and organic polymers [11,22–25]. Those monolithic aerogels show higher mechanical properties such as compressibility and bendability, but often suffer from higher thermal conductivity and lower visible-light transmittance due to increased density and coarsened microstructure. Our group has been investigating polymethylsilsesquioxane (PMSQ, $\text{CH}_3\text{SiO}_{1.5}$) aerogels derived from methyltrimethoxysilane (MTMS) and reported transparent monolithic aerogel-like xerogels via evaporative drying [26, 27]. In comparison to silica, PMSQ has fewer siloxane bonds per silicon, which is attached to one methyl group instead, resulting in the increased flexibility. In addition, the presence of hydrophobic methyl groups causes repulsion when compressed, and the low residual silanol density suppresses irreversible shrinkage. These improved structural and mechanical features enable ambient pressure drying without collapsing the delicate pore structure to obtain aerogel-like xerogels if processed under optimized conditions. Xerogels with no significant difference in bulk density, visible-light transmittance and thermal conductivity ($\sim 15 \text{ mW m}^{-1} \text{ K}^{-1}$ or less) have been obtained [28,29]. However, there are still only a few systematic studies on the process of evaporative drying of low-density gels under an ambient condition [30–32]. In the limiting case of transparent monolithic aerogels, there is no report as far as we know, though focusing the drying process is a

* Corresponding author.

E-mail address: kanamori@kuchem.kyoto-u.ac.jp (K. Kanamori).¹ Present address: Frontier Research Institute for Interdisciplinary Sciences, Tohoku University, Aramaki aza Aoba 6-3, Aoba-ku, Sendai 980-8578, Japan.

necessary step toward further improvement of the microstructure for the practical use of aerogel-like xerogel-based transparent thermal superinsulators.

In the present paper, we synthesized PMSQ gels with different densities under the presence of a cationic surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) and observed a shrinkage-reexpansion (spring-back) behavior [30–32] in the course of evaporative drying. In addition, extended aging processes have been examined to reduce irreversible shrinkage and cracking of PMSQ gels during drying to achieve lower bulk density and higher thermal insulation.

2. Experimental procedure

The sample notations are defined as Ax and Xx, where A and X mean “aerogels” obtained via supercritical drying and “xerogel” via ambient pressure drying, respectively, and x denotes volume of acetic acid aqueous solution in the starting composition. At the starting composition of Ax/Xx, x mL of 5 mM aqueous acetic acid (Kishida Chemical Ltd., Japan), $0.3 \times x$ g of urea (Hayashi Pure Chemical Ind., Ltd., Japan), and 0.40 g of surfactant CTAC (Tokyo Chemical Ind. Co., Ltd., Japan) were dissolved in a glass sample tube, and then 5.0 mL of MTMS (Shin-Etsu Chemical Co., Ltd., Japan) was added under vigorous stirring. The mixed solution was continuously stirred for 30 min at room temperature for acid-catalyzed hydrolysis, followed by base-catalyzed gelation and aging at 60 °C in a closed vessel for 4 d. The gelation time was about 3 h in the case of A10/X10. Some of the samples were further processed by additional aging, in which wet gels were directly soaked in an “aging sol” at 80 °C for 1 d. The aging sol was prepared by the following process; (1) stirring 100 mL of 5 mM aqueous acetic acid and 3 mL of MTMS in a glass bottle for 30 min at room temperature, (2) adding 900 mL of distilled water and 5 g of urea into the bottle, and then keeping the solution at 80 °C for 24 h. The obtained gels both with and without the extended aging were then washed in a sufficient amount of methanol (Kishida Chemical Ltd.), which was exchanged with fresh one three times (at least 8 h for each duration of washing), and then in 2-propanol (Kishida Chemical Ltd.) three times in the same way to remove CTAC and other unreacted reagents. To obtain aerogels via supercritical drying, alcogels obtained in this way were dried from supercritical carbon dioxide at 80 °C, 14.0 MPa for 10 h in a custom-built autoclave (Mitsubishi Materials Corp., Japan). For evaporative drying to obtain xerogels, the alcogels were subjected to solvent exchange with *n*-heptane (Kishida Chemical Ltd.) three times, and heptane was slowly removed by evaporation at room temperature for 1 d. After drying, all aerogel and xerogel samples were heated at 110 °C for 4 h to allow further spring-back by enhancing relaxation of the deformed PMSQ network.

Bulk density was obtained by measuring the volume and weight of a carved gel. Bulk density has been measured on 3–5 samples with estimated errors of 2% (all aerogels), 4% (xerogels X8, X10 and X20) and 10% (X50 and X100). Thermal conductivity was measured with HFM 436 Lambda (Netzsch GmbH (Germany)) by measuring heat flow at the center part of the specimen with estimated error of 3–5% (including systematic error of the device). To observe shrinkage-reexpansion behaviors during the evaporative drying process, digital photos were automatically taken at intervals of 25 s. To assess the molecular-level structure of obtained siloxane networks, ^{29}Si solid-state cross-polarization magic angle spinning (CPMAS) NMR measurements were performed on an NMR spectrometer Avance III 800 (Bruker Corp. (Germany)) operated under a static magnetic field of 18.8 T. The contact time for the $^1\text{H} - ^{29}\text{Si}$ cross-polarization was fixed at 5.5 ms and the rate of sample spinning was 15 kHz. The ^{29}Si chemical shift was expressed relative to tetramethylsilane (Me_4Si) by using the resonance line at -9.66 ppm for hexamethylcyclotrisiloxane crystals as an external reference. The same equipment with a probe for liquid samples was used for ^{29}Si liquid-state NMR measurements of the aging sol prepared in deuterated water (Tokyo Chemical Ind. Co., Ltd.). The relaxation delay was set to 10 s. Fourier transform infrared spectroscopy (FTIR, FT/IR-6100TY,

JASCO (Japan)) was employed to investigate the molecular-level structures of the aerogel/xerogel and aging sol samples with an ATR attachment (ATR PRO470-H). For microstructure observations, a field emission-type scanning electron microscope (JSM-6700F, JEOL, Japan) was employed.

3. Results and discussion

Wet gels were synthesized with different ratios of the precursor methyltrimethoxysilane (MTMS) to aqueous acetic acid-urea solvent [33] in order to change density of obtained dried gels. During the observation of evaporative drying of 5 samples (Xx) with different concentrations of MTMS in the starting composition (Table 1), all samples showed three drying stages as follows (Fig. 1, and Movie S1–S5, Supplementary Material) [34,35]: (1) the whole gel shrinks by the capillary pressure on evaporation of the solvent; (2) the shrinkage rate becomes low and the gel shows critical opalescence; (3) the gel turns to transparent again and starts expanding. Fig. 2(a) displays the changes in diameter of the gels during evaporative drying, where *T* shows the normalized time when the diameter of the gel becomes minimum during shrinkage (i.e. the critical point). The shrinkage from the original shape was smaller when the gel has higher density, which is simply because the gel with higher density deforms less, given the compressive force applied by the capillary pressure is similar, i.e. the pore size is similar. Bulk density of each aerogel and xerogel is shown in Table 1. All xerogels obtained via evaporative drying do not have internal cracks (Fig. 2(b)) but have higher density than aerogels due to incomplete recovering without extended aging processes as described below.

Thermal conductivity of a porous material consists of three components; heat transfer by the gas phase, solid phase and radiation, and shows the minimum at certain density, because the contribution of the gas phase becomes higher and that of the solid phase lower with decreasing density [36,37]. In the case of PMSQ aerogels Ax, the minimum thermal conductivity was found at around bulk density of ca. 0.14 g cm^{-3} (A10, Fig. 3). Based on this data, we tried to prepare PMSQ xerogels with density ca. 0.14 g cm^{-3} via evaporative drying. However, it was hard to obtain such optimized aerogels due to the irreversible shrinkage as mentioned above.

To solve this problem, we developed an aging process in aqueous conditions. In the case of porous silica materials, the hydrothermal treatment in basic solution is effective to improve the mechanical strength by the Ostwald ripening [38]. Through this treatment, the neck part of the colloid-aggregated silica microstructure grows by the dissolution-precipitation process, and the strength and stiffness of the network are improved [39]. In addition, aging in alkoxy silanes monomer or oligomer solution was found to further improve the mechanical properties and monolithicity [40,41]. We applied this process to PMSQ wet gels with an expectation for the same effect, though the solubility of the PMSQ network would be lower as compared to silica because of the higher electron density at silicon and hydrophobicity.

Table 1

Starting compositions and properties of aerogels and xerogels obtained in the present study.

	5 mM HOAc/mL	Urea /g	CTAC /g	MTMS /g	Bulk density/g cm^{-3}	Thermal conductivity $/\text{mW m}^{-1} \text{K}^{-1}$
A8	8.0	2.4	0.40	4.8	0.167	15.3
A10	10	3.0	0.40	4.8	0.138	13.8
A20	20	6.0	0.40	4.8	0.084	15.1
A50	50	15	0.40	4.8	0.048	19.1
A100	100	30	0.40	4.8	0.040	22.4
X8	8.0	2.4	0.40	4.8	0.229	
X10	10	3.0	0.40	4.8	0.254	19.8
X20	20	6.0	0.40	4.8	0.288	
X50	50	15	0.40	4.8	0.345	
X100	100	30	0.40	4.8	0.374	
X10a	10	3.0	0.40	4.8	0.140	13.7

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