INVITED PAPER: FUNDAMENTALS OF SOL-GEL AND HYBRID MATERIALS PROCESSING

How elastic moduli affect ambient pressure drying of poly (methylsilsesquioxane) gels

Mamoru Aizawa [1]

Abstract

To understand which properties of wet gels decide whether they can be dried under ambient pressure or not, the author prepared fifty-six gels from solutions of different mass ratios of tetra-functional tetramethoxysilane (TMOS), tri-functional methyltrimethoxysilane (MTMS) and difunctional dimethyldimethoxysilane (DMDMS). These gels were dried under ambient pressure, and the mechanical properties of the wet gels were investigated by uniaxial compression test. The stress-strain curve of the wet gels was composed of two parts (the 1st and 2nd parts) with different slopes. When the ratio of the 1st and 2nd parts (E_{2nd}/E_{1st}, EM ratio) exceeded 2.3, the gel was dried without crack accompanying spring-back to obtain a dried gel with bulk density lower than 0.2 g/cm^2. This finding means that the elastic modulus of a wet gel is a good criterion to predict whether or not they can be dried under ambient pressure without cracking to obtain a xerogel whose properties are close to the aerogel counterpart. Choosing a starting composition from fifty-six formulas, which gives the highest EM ratio, the author obtained a crack-free and transparent aerogel monolith with the dimension of $300 \times 300 \times 8$ mm^3 through ambient pressure drying.

Graphical abstract

$300 \times 300 \times 8$ mm^3 aerogel monolith with 81% light-transmittance under ambient pressure drying.
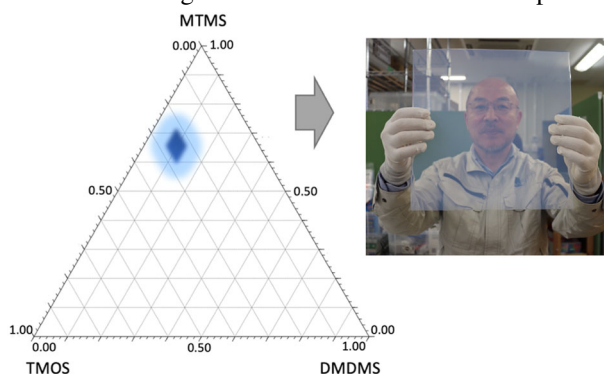
Highlights

- Aerogels were obtained from three-component system; TMOS, MTMS and DMDMS.
- While MTMS formed the main network, TMOS improved transparency and DMDMS affected elastic moduli of the gel.
- A $300 \times 300 \times 8$ mm^3 crack-free aerogel monolith was obtained under ambient pressure drying.
- Elastic modulus of the wet gel was an important factor for successful ambient pressure drying.

✉ Mamoru Aizawa
aizawa@hiiragilab.jp

Hiiragi Laboratory Inc., Nishisenouchicho 40, Kitashirakawa, Kyoto 606-8255, Japan

1 Introduction

Hüsing and Schubert defined aerogels as materials in which the typical structure of the pores and the network

of wet gels is largely maintained while the pore liquid is replaced by air [1].

Since the first preparation of aerogels by Kistler [2], regarding silica or organically modified silica aerogels, they have been utilized for relatively specialized applications. The Cherenkov counters use transparent, low bulk density aerogel tiles as a medium to efficiently detect charged elementary particles [3]. Aerogels also have other excellent properties such as very low thermal conductivity [4], which has been desired in the architecture field. Aerogels were also proposed to be used in the terraforming of Mars [5]. Sunlight passed through transparent and insulative aerogel tiles, which was enough to melt the ice on Mars.

In a more common sector, there have been some projects to improve our living environment on the earth. Although it had not been in practical use, some consumer use applications have been examined. From 1995 to 2005, HILIT and HILIT + projects were carried out [6], in which the aerogel glazing was made under vacuum conditions. It showed a U-value (the rate of transfer of heat through matter) of 0.66 W/(m^2 K) which was comparable to the triple layered gas- filled glazing units [7]. Despite the excellent result, the aerogel glazing has not been commercialized yet. While aerogels combine attractive properties for the architecture field, they suffer from high cost, most of which comes from the drying process. Due to the capillary force, silica gels are easily shrunk and collapse during drying [8]. As Kistler employed for his process, supercritical drying is ideal to minimize the capillary force during drying. However, the apparatus for supercritical drying is very expensive due to the need for constructing a pressure-durable system. Thus, the aerogels obtained through supercritical drying are inevitably expensive. Prakash et al. instead proposed a novel process to obtain aerogel thin film under ambient pressure without using the supercritical process [9], in which they prepared the thin film with pulverized wet gels and dried under ambient pressure. Transparent poly(methylsilsesquioxane) aerogel monoliths prepared under ambient pressure were first reported by Kanamori et al. in 2007 [10]. The mechanical properties of poly (methylsilsesquioxane) aerogels was discussed from the point of view of its porous morphology [11]. At that time, the planar size of aerogel monolith that can be prepared in their process was as small as 100×100 mm^2, while the industrially meaningful monolith size is larger than 300×300 mm^2, according to an interview with glass sheet manufacture officials. Aizawa reported a 1 square foot ($300 \times 300 \times 10$ mm^3) monolith prepared under ambient pressure in 2017 [12].

Drying of a wet gel by evaporation encounters significant deformation by the capillary force [13]. In the case where the pore diameter of the gel is 50 nm, the surface tension of the n-hexadecane, an example of drying solvent, is 27.6 mN/m and the contact angle is 24.4° [14], the capillary force is calculated to be around 20 N/mm^2 from the Young-Laplace equation.

Meanwhile, according to the brittle fracture mechanism [15], the fracture strength of a conventional silica-aerogel is 0.5 N/mm^2, which is too low to withstand the capillary force. However, if the gel is flexible enough to deform its shape without fracture, its volume decreases and its bulk density increases in the course of drying. As the higher density leads to the higher fracture strength, the gel can withstand the capillary stress at this stage. When the gel sprung back to its original shape, one could obtain an aerogel under ambient pressure drying [16].

Then, what is the required mechanical properties to obtain aerogels from ambient pressure drying? Nakanishi and Kanamori's group reported that the mechanical properties of the gels are improved by modifying their molecular framework [17–19]. Li et al. reduced the silanol groups of silica gels and prepared low density aerogels [20].

The author prepared 56 gels which were made from solutions of different mass ratios of tetra-functional tetramethoxysilane (TMOS), tri-functional methyltrimethoxysilane (MTMS) and difunctional dimethyldimethoxysilane (DMDMS), and investigated their mechanical properties. As an evaluation criterion of successful ambient pressure drying toward aerogels, here the author claims with no-cracks, bulk density <0.2 g/cm^3 and light transmittance >40% as aerogel. Furthermore, by choosing the highest EM ratio, an aerogel monolith with the size of $300 \times 300 \times 8$ mm^3 were prepared.

2 Experimantal

2.1 Chemicals

TMOS was purchased from Tama Chemicals Co., Ltd., Japan. MTMS was purchased from DuPont Toray Specialty Materials K.K., Japan. DMDMS was purchased from Tokyo Chemical Industry Co., Ltd., Japan. Pluronic PE-9400 was purchased from BASF Japan Ltd., Japan. 30 wt% aqueous solution of n-hexadecyltrimethylammmonium chloride (Quartamin 60W) was purchased from Kao Corp., Japan. Alkoxysilanes TMOS and MTMS were distilled under reduced pressure before use, and DMDMS was used without further purification. The surfactant PE-9400 was diluted to 20 wt% with water and filtrated with a 0.4 μm membrane filter.

Methanol, 2-propanol (IPA) and n-heptane were purchased from FUJIFILM Wako Pure Chemical Corp., Ltd., Japan. Each of those solvents is guaranteed grade.

2.2 Preparation of gels

The compositions of TMOS, MTMS and DMDMS are listed in Table 1. First, 4.10 g of the PE-9400 aqueous

Table 1 Composition and properties of wet and dried gels

Sample number	Mass ratio			Wet gel			Dried gel		
	MTMS	TMOS	DMDMS	Elastic modulus [N/mm^2]		E_{2nd}/E_{1st}	Bulk density d [g/cm^3]	Degree of spring-back, d_{ideal}/d	Transmittance at 550 nm, T[%]
				E_{1st}	E_{2nd}				
1	1.00	0.00	0.00	0.46	1.02	2.21	0.13	0.85	76.31
2	0.95	0.05	0.00	0.53	1.28	2.41	0.13	0.85	76.51
3	0.95	0.00	0.05	0.56	1.17	2.09	0.14	0.79	64.49
4	0.90	0.10	0.00	0.51	1.38	2.68	0.13	0.85	80.33
5	0.90	0.05	0.05	0.39	1.13	2.91	0.13	0.85	75.92
6	0.90	0.00	0.10	0.35	0.97	2.76	0.14	0.79	43.72
7	0.85	0.15	0.00	0.36	1.36	3.81	0.12	0.92	83.20
8	0.85	0.10	0.05	0.35	0.92	2.62	0.12	0.92	81.77
9	0.85	0.05	0.10	0.63	1.20	1.89	0.13	0.85	66.33
10	0.85	0.00	0.15	0.23	0.59	2.60	0.17	0.65	17.77
11	0.80	0.20	0.00	0.24	0.77	3.21	0.12	0.92	85.70
12	0.80	0.15	0.05	0.40	1.56	3.91	0.13	0.85	83.88
13	0.80	0.10	0.10	0.50	1.14	2.27	0.12	0.92	75.09
14	0.80	0.05	0.15	0.41	0.87	2.12	0.14	0.79	45.98
15	0.80	0.00	0.20	0.21	0.31	1.47	0.27	0.41	1.12
16	0.75	0.25	0.00	0.33	1.18	3.55	0.11	1.00	81.65
17	0.75	0.20	0.05	0.73	1.28	1.74	0.13	0.85	79.12
18	0.75	0.15	0.10	0.37	1.27	3.41	0.13	0.85	76.11
19	0.75	0.10	0.15	0.33	0.97	2.90	0.13	0.85	68.39
20	0.75	0.05	0.20	0.30	0.80	2.68	0.18	0.61	15.82
21	0.75	0.00	0.20	0.17	0.26	1.50	0.37	0.30	0.08
22	0.70	0.30	0.00	0.52	1.16	2.23	0.11	1.00	85.82
23	0.70	0.25	0.05	0.48	1.28	2.64	0.11	1.00	84.36
24	0.70	0.20	0.10	0.13	0.92	6.88	0.13	0.85	83.17
25	0.70	0.15	0.15	0.48	1.19	2.48	0.13	0.85	72.15
26	0.70	0.10	0.20	0.32	0.91	2.85	0.15	0.73	55.39
27	0.70	0.05	0.25	0.22	0.51	2.29	0.27	0.41	1.53
28	0.70	0.00	0.30	0.02	0.00	-----	0.56	0.20	0.00
29	0.65	0.35	0.00	0.29	1.09	3.76	0.12	0.92	82.61
30	0.65	0.30	0.05	0.27	1.10	4.13	0.12	0.92	81.58
31	0.65	0.25	0.10	0.35	0.92	2.62	0.11	1.00	91.26
32	0.65	0.20	0.15	0.32	1.01	3.21	0.12	0.92	77.02
33	0.65	0.15	0.20	0.31	0.81	2.63	0.15	0.73	55.34
34	0.65	0.10	0.25	0.27	0.60	2.22	0.23	0.48	5.31
35	0.65	0.05	0.30	0.14	0.27	1.92	0.43	0.26	0.05
36	0.60	0.40	0.00	0.33	1.24	3.75	0.11	1.00	65.55
37	0.60	0.35	0.05	0.34	1.09	3.20	0.11	1.00	78.86
38	0.60	0.30	0.10	0.47	1.18	2.50	0.12	0.92	87.69
39	0.60	0.25	0.15	0.59	1.39	2.36	0.13	0.85	75.21
40	0.60	0.20	0.20	0.35	1.07	3.10	0.13	0.85	68.66
41	0.60	0.15	0.25	0.40	0.79	1.96	0.18	0.61	12.74
42	0.60	0.10	0.30	0.14	0.34	2.36	0.36	0.31	0.28
43	0.55	0.45	0.00	0.30	0.73	2.44	0.13	0.85	53.05

Table 1 (continued)

Sample number	Mass ratio			Wet gel		E_{2nd}/E_{1st}	Dried gel		
	MTMS	TMOS	DMDMS	Elastic modulus [N/mm^2]			Bulk density d [g/cm^3]	Degree of spring-back, d_{ideal}/d	Transmittance at 550 nm, T[%]
				E_{1st}	E_{2nd}				
44	0.55	0.40	0.05	0.53	1.34	2.52	0.12	0.92	70.91
45	0.55	0.35	0.10	0.26	1.00	3.88	0.12	0.92	58.62
46	0.55	0.30	0.15	0.68	1.43	2.10	0.12	0.92	70.98
47	0.55	0.25	0.20	0.60	1.45	2.42	0.13	0.85	65.19
48	0.55	0.20	0.25	0.44	1.02	2.31	0.18	0.61	46.31
49	0.55	0.15	0.30	0.28	0.63	2.29	0.28	0.39	1.74
50	0.50	0.50	0.00	0.33	1.01	3.05	0.17	0.65	36.70
51	0.50	0.45	0.05	0.59	1.13	1.91	0.13	0.85	58.79
52	0.50	0.40	0.10	0.12	0.88	7.43	0.11	1.00	55.83
53	0.50	0.35	0.15	0.30	0.85	2.83	0.12	0.92	53.26
54	0.50	0.30	0.20	0.41	1.19	2.88	0.13	0.85	67.31
55	0.50	0.25	0.25	0.52	1.04	2.00	0.13	0.85	58.63
56	0.50	0.20	0.30	0.52	0.91	1.77	0.21	0.52	9.10

solution, 0.14 g of Quartamin 60 W, 3.96 g of 5 mM acetic acid aqueous solution and 1.00 g of urea were put in a 50 mL polystyrene beaker (inner diameter is 40 mm) and stirred for a few minutes until urea was dissolved. Three kinds of silicone alkoxides (total amount was 2.50 g) were mixed and added simultaneously in the beaker and the solution was stirred for 1 h at room temperature. The beaker was then covered with a plastic wrap and placed in a thermostatic oven at 50 °C and then at 60 °C for 4 h to allow gelation to obtain a coin-shaped gel. The obtained gel was cooled to room temperature, covered with 5 mL of water to prevent drying and covered with the wrap again. The beaker was put in a closed container filled with water to a depth of 1 cm. The water was added to the container to prevent the gels from being dried. The container was placed in a thermostatic oven at 80 °C for 72 h to complete the aging.

The resultant gel was placed in a stainless steel container equipped with a glass condenser and rinsed with a fivefold volume of methanol for 8 h. This process was repeated for 5 times with fresh methanol. Next, the liquid for the rinse was changed to a mixture of IPA/n-heptane = 1/3 (vol/vol), and stirred for 8 h. Finally, the gel was rinsed with a fivefold volume of n-heptane for 8 h twice. Then the gel was placed in a container covered with gas permeative sheet and was dried at the evaporation speed of 30 g/[(100 g of wet gel)·d]. Finally, the dried gel was heated at 250 °C for 30 min to ensure the spring-back and to burn off the residual additives.

Three pieces of coin-shaped gels were prepared in each composition. Two of them were taken aside after gelation and rest of them was dried.

2.3 Mechanical test on wet gel

Stress-strain (S-S) curves were obtained on each wet gel using a material tester (EZGraph, Shimadzu Corp., Japan). A 200-N load cell was used with the loading speed of 1 mm/s. Elastic modulus was measured up to 200 N/mm^2. The S-S curve of No.24 was shown in Fig. 1, which consists of two parts (the 1st and the 2nd parts) with different slopes. Although the 2nd part of the S-S curve did not go through the origin, E_{2nd} was calculated from its slope for convenience. The ratio of elastic moduli of the 1st and 2nd parts (E_{2nd}/E_{1st}, EM ratio) were listed in Table 1.

2.4 Preparation of a $300 \times 300 \times 8$ mm^3 aerogel monolith

Employing the No. 24 composition (MTMS:TMOS: DMDMS = 7:2:1), which showed the highest EM ratio among those showing light-transmittance of 80% or higher, an aerogel monolith with the size of $300 \times 300 \times 8$ mm^3 was prepared. The procedure was almost the same with that for the coin-shaped samples except the amount of the raw materials. A large square-shaped container for gelation was custom-made with transparent polypropylene sheet. The whole process is illustrated in Fig. 2.

2.5 Characterization of dried gel

The values in this section were averaged over at least three measurements.

Bulk density of each dried gel was calculated from its volume and weight. Light transmittance of each dried gel was measured with a UV-Vis spectrometer (V-750, JASCO Corp., Japan.) at 550 nm and normalized to the value through 10-mm-equivalent thickness by the Lambert-Beer equation (denoted as T).

The aerogel monolith with $300 \times 300 \times 8$ mm^3 aerogel monolith was furthermore characterized as follows.

Thermal conductivity was measured with a heat flow meter (HFM 436 Lambda, NETZSCH-Geratebau GmbH, Germany). Thermal analysis was conducted by thermogravimetry-differential thermal analysis (TG-DTA, Thermo Plus Evo2, Rigaku Corp., Japan) under the ambient atmosphere. Mean pore size was measured with Tristar II, Micromeritics Instrument Corp., USA. Microstructure was observed with field emission scanning electron microscopy (FE-SEM, Regulus-8220, Hitachi High-Tech Corp., Japan) on the sample sputter-coated with osmium.
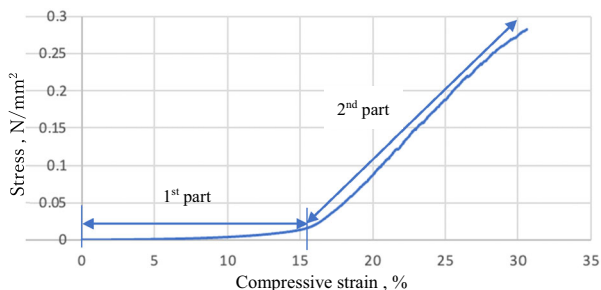
Fig. 1 Stress-Strain curve of a wet gel of No.24 showing different elastic moduli in 1st and 2nd parts. The sample size was 30 mm in diameter and 10 mm in thickness

3 Results and discussion

3.1 Preparation of gels

The elastic modulus of the wet gels, bulk density and transparency of the dried gels are listed in Table 1.

Each dried gel showed different density and transparency. The bulk density of the aerogels fell below 0.2 g/cm^3 when the EM ratio was above 2.3. The transparency of the aerogels exceeded 40 % when the EM ratio was above 3.1 as shown in Fig. 3.

Each of three silicon alkoxides has their own role. The EM ratio of the wet gels, the transparency and the bulk density of the resultant aerogels are optimized by adequately determining the ratio of the three precursors each other. While tri-functional MTMS formed the main molecular framework, tetra-functional TMOS contributed to improving the transparency and decreasing the bulk density of the dried gel. Its optimal ratio was 0.2 to 0.3. Difunctional DMDMS also contributed to improving the transparency and to increasing the EM ratio. Its optimal ratio was 0.05 to 0.15, which was lower than TMOS. Addition of DMDMS at ratios >0.15 prevented the spring-back of the dried gel, but TMOS buffered this ill effect.

During the ambient pressure drying, wet gels shrunk due to the capillary force. Many of them stayed shrunk even after completing drying, resulting in high bulk density dried gels. However, wet gels prepared from the optimized precursor ratios, in addition to the optimized reaction conditions, spring-back from their temporarily shrunk state to their original volume and shape. Ambient-pressure-dried aerogels were thus obtained. When the dried gel recovered its original volume, its density or d_{ideal} should be 0.11 g/cm^3. The degree of spring-back was defined as d/d_{ideal}. The author found that the EM
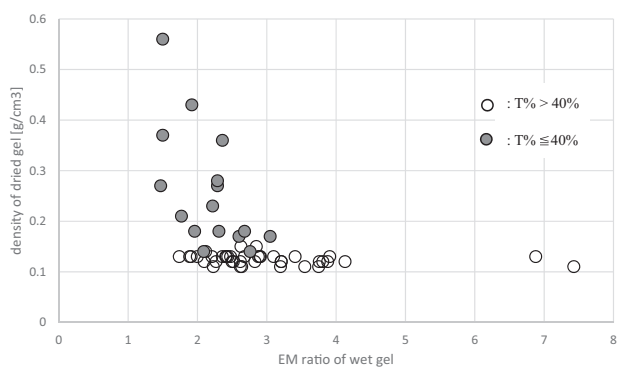
Fig. 2 Whole preparation process of aerogel monolith with $300 \times 300 \times 8$ mm^3 dimension

Fig. 3 Relationship between EM ratio of wet gel and density of dried gel
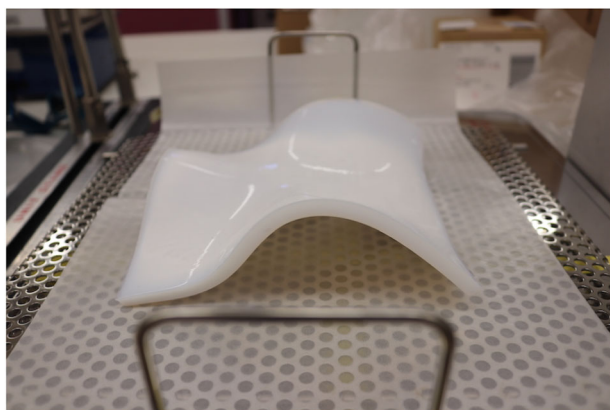
Fig. 4 Appearance of $300 \times 300 \times 8\ mm^3$ gel during spring-back

Fig. 5 Appearance of $300 \times 300 \times 8\ mm^3$ aerogel monolith obtained by ambient pressure drying
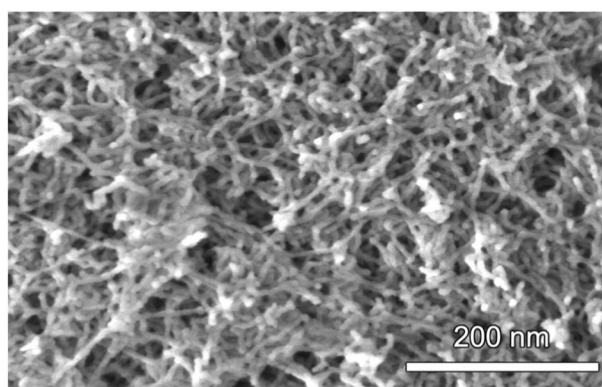
Fig. 6 Microstructure of $300 \times 300 \times 8\ mm^3$ aerogel monolith observed under FE-SEM

ratio of 2.3 was the threshold for the spring-back behavior and successful drying toward aerogels. At the first stage or the constant rate period of drying [21], in which evaporation occurred only from the material surface, the elastic modulus of the wet gels ($\sim E_{1st}$)should be low enough to deform without fracturing by the capillary force. The elastic modulus of the second stage of the falling rate period ($\sim E_{2nd}$), in which the menisci thrust into the material body, might reflect the degree of spring-back.

3.2 Preparation of a $300 \times 300 \times 8\ mm^3$ aerogel monolith

Larger size gels as well as coin-shaped gels could be dried under ambient pressure. However, unlike small and round-shaped gels [13], large and rectangular-shaped gels drastically deform especially during the spring-back as shown in Fig. 4. Sometimes the drastic deformation led to cracking of the gel. In many cases, however, those gels regain their original shape and transparency. Using a little different type Pluronic surfactant, 2 out of 50 gels were cracked during spring-back. Rest of them were crack-free and transparent.

A crack-free and transparent aerogel monolith was obtained as shown in Fig. 5. The side length was 295 mm,

which was 98.3% of the size of the wet gel. The bulk density of the sample was 0.13 g/cm^3. The above discussion in "3.1 Preparation of gels" on the coin-sized gels held true even for the larger size gel.

The microstructure observed with FE-SEM is shown in Fig. 6, in which fibrous skeletons in $ca.$10 nm form the three-dimensional pore structure with pore size of 20–60 nm. Transmittance T of the aerogel was 81%, which is close enough to the corresponding small-size aerogel (83%). Its thermal conductivity was 12.0 mW/(m K). Decomposition temperature of the aerogel, the first exothermic peak temperature in the DTA curve, was 498.4 °C. The exothermic peak temperature matched with that where the weight decreases started in the TGA curve.

4 Conclusions

Fifty-six gels which were made of different TMOS, MTMS and DMDMS ratio, and investigated whether or not they can

be dried under ambient pressure without cracking to obtain a xerogel whose properties are close to the aerogel counterpart.

The S-S curve of the wet gel consisted of two parts and when the EM ratio exceeds 2.3, the dried gel's bulk density falls below $0.2\,g/cm^3$. It means that EM ratio predict wet gel become aerogel or not under ambient pressure drying.

The author also investigated how those three kinds of silicone alkoxides affect the EM ratio of the wet gels, the transparency and the bulk density of the resultant aerogels. While tri-functional MTMS formed the main molecular framework, tetra-functional TMOS contributed to improving the transparency and decreasing the bulk density of the dried gel. Difunctional DMDMS also contributed to improving the transparency and to increasing the EM ratio. Too much addition of DMDMS prevented the spring-back of the dried gel, but TMOS buffered this ill effect. Employing the No. 24 composition (MTMS:TMOS:DMDMS = 7:2:1), which showed the highest EM ratio among those showing light-transmittance of 80% or higher, a crack-free aerogel monolith with the size of $300 \times 300 \times 8\,mm^3$ was successfully prepared.

Compliance with ethical standards

Conflict of interest The author declares no competing interests.

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