

Ambient drying silica aerogel coatings modified with polyethylene glycol

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Hybrid silica aerogels modified with polyethylene glycol (PEG) were successfully fabricated on the large window glass by an ambient drying process after solvent exchange and surface modification. Surface cracking was effectively prevented by adding PEG, which acted as a drying control chemical additive. The particle size of silica aerogel increased with the addition of PEG, while the pore size and volume decreased. The thermal conductivity and transmittance increased and decreased with further PEG modification more than 20 wt%, respectively, which is detrimental to aerogel applications. Although physical properties of silica aerogels were found to be good regardless of PEG content, tailored properties such as thermal conductivity and transmittance were observed for the aerogels with 10 wt% PEG. Modified hybrid surfaces of the silica/PEG aerogels were hydrophobic, exhibiting specific surface area of ~ 1028 m²/g, total pore volume of ~ 1.2 cm³/g, average pore diameter of ~ 5.5 nm, penetration ratio of $\sim 70\%$, and thermal conductivity of ~ 0.02 W/mK.

Key words: Silica aerogel, Polyethylene glycol (PEG), Sol-gel, Ambient drying, Drying control chemical additive (DCCA), Hybridization.

Introduction

Silica aerogels are a mesoporous substance consisting of a few to ten-nanometer pores in a 3-dimensional network structure. They have become quite popular because they possess a wide variety of exceptional properties such as high porosity of $\sim 99\%$, high specific surface area of 1000 m²/g, low density of 0.003 g/cm³, low permittivity of ~ 1.1 , low dielectric constant of 1.0~2.0, low refractive index of 1.05, and very low thermal conductivity of 0.01 W/mK. Due to their unique characteristics, silica aerogels can be used in a wide area such as ultra-light weight materials, super thermal insulation, acoustic insulation, chemical catalysts, ion exchange resins, noise reduction, drug delivery systems, ultra-low dielectric materials in electronics and optical fields [1-10]. Actually, a transparent silica aerogels have been used as a Cerenkov counter since the early 1970s [4]. In addition, aerogels can be used for the measurement of environmental pollution and the detection of biochemical responses as a chemical sensor or biosensor [5].

Aerogels were first reported by Samuel Stephens Kistler in 1931 via supercritical drying of wet gel using silica alkoxide or sodium silicate (water glass) solution [4]. The aerogels did not draw to a particular attention after that because his method was tedious and time-consuming procedure. Recently, many researchers had

rediscovered the importance of the aerogels in the 1970s. Investigations into the possibility of their commercial uses such as sky light have been actively pursued [11, 12]. Silica aerogels are mostly manufactured by a supercritical drying method, but this method contains the problems of cracking and low transmittance. The efforts to improve a transmittance and strength of the aerogel adapting various kinds of drying control chemical additive (DCCA) have been made to solve those problems. The supercritical drying method for the preparation of silica aerogels is still studied, but a few results were reported [13-15].

This study is focused on the ambient drying method, because the supercritical drying method generally involves a processing risk since high temperature and pressure are applied to dry the wet gel, resulting in size limitation. For large-area coatings, the ambient drying method has a high advantage since aerogels can be prepared by a lower drying temperature under air atmosphere [16]. For the effective energy saving application, silica aerogels have been studied in various areas, including smart glazing, solar ponds and skylight jackets against cold weather. In this study, the silica aerogels modified with PEG are investigated to minimize crack formation by employing an ambient drying method, which is not well documented until now for successful large-area coatings.

Experimental

A modified two-step sol-gel process was performed [17, 18]. In the first step, tetraethylorthosilicate, TEOS (Si(OC₂H₅)₄, Aldrich, USA) and isopropanol (IPA,

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(CH₃)₂CHOH, Junsei, Japan) were mixed for 1 h, and then 0.1 mol of HCl was added for 1 h to accelerate hydrolysis. In the second step, 0.15 mole of NH₄OH was slowly added to promote a polymerization of the silica sol. PEG 1000 (H(CH₂CH₂O)_nOH, Daejung, Korea), as DCCA, was added during the stirring of the sol in 10 wt% interval at a ratio of 0-40 wt% to TEOS. The final molar ratio of the TEOS:IPA:H₂O:HCl:NH₄OH was 1:3:4:1.80 × 10⁻³:8.12 × 10⁻³. The viscosity of the solution was measured by a Brookfield viscometer (programmable DV-II). In the case of the film type, the solution was applied to the cleaned window glass substrate. The wet silica sols were changed to a gel state by leaving them for 1 h at an ambient temperature. The gel samples were put in the chamber for maturation and solvent exchange to strengthen the network structure of the gel. The aerogel samples were surface-modified with trimethylchlorosilane (TMCS). Then, the aerogel films were dried for 24 h at room temperature in the air.

Specific surface area, average pore size, and pore distribution were measured at 77.3K by the BET method (ASAP 2010 automated volumetric analyzer). FT-IR (Infinity Gold FT-IR 60AR, Thermo Mattson, USA) and ESEM (XL-30 EDAX, Philips, Netherlands) were performed. Thermal conductivity was measured by a heat flow method (EKO HC-074-314), where the sensors were attached at a top and bottom of the sample with setting temperature of 35 °C at the bottom and 15 °C at the top.

Results and Discussion

The effect of surface modification with 6% TMCS to n-butanol was compared with the aerogels prepared by

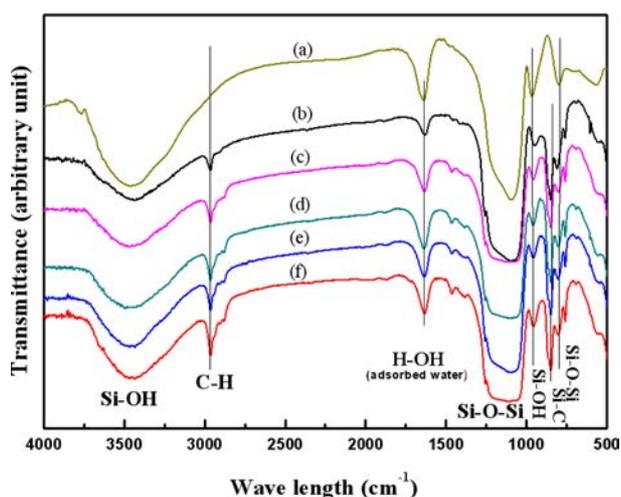


Fig. 1. FT-IR spectra of the silica aerogels as a function of the PEG additive/TEOS ratio: (a) the hydrophilic gel sample without surface modification treatment, and (b)-(f) the hydrophobic gels prepared by surface modification; the PEG content is from 0, 10, 20, 30 to 40 wt%, respectively.

n-butanol only without surface modification. Comparison between Fig. 1(a) unmodified gel and 1(b) modified gel reveals that the absorption peaks located at 3468 cm⁻¹ and ~962 cm⁻¹ appear due to vibrations of hydrogen-bonded Si-O-H groups. The 1634 cm⁻¹ peak is due to adsorbed water. Fig. 1 shows the FT-IR analysis of the silica aerogels with 0-40 wt% of PEG as DCCA. Si-OH stretching mode and asymmetric Si-O-Si stretching vibration mode were observed near the wavelengths of 3400 cm⁻¹ and 1100 cm⁻¹, respectively. The peaks located at 2970 cm⁻¹ indicate the C-H stretching mode, which suggests that the hydrophobic aerogel of CH₃-O is well compounded due to the surface modification of the silica aerogel. The enhanced hydrophobicity is obtained with increasing the PEG content. Such a hydrophobic surface modification makes ambient drying possible without cracking by controlling condensation time due to low surface tension of pore fluid solvent in gel.

The primary mechanism for the surface modification with TMCS, which is directly substituted with OH on the gel surface, is shown in the reaction formula (1) [19]. TMCS was known to be an effective surface modifier due to its good reactivity with Cl.



SEM images of the silica aerogels with PET as a function of additive/TEOS prepared by ambient drying are shown in Fig. 2. The thickness was about 80 μm regardless of the PEG content. No appreciable difference in microstructure was detected for the aerogels having PEG up to ~20 wt%. They show a well 3-dimensional network structure. However, the uniformity of the particle size was raised dramatically with increasing the PEG content more than 30 wt%. In contrast, the adhesion strength and cohesion of the aerogel particles with a strong surrounding of aerogel particle and a network structure were improved with increasing the PEG content. Silica aerogel particles tightly attached on the surface of glass substrate were

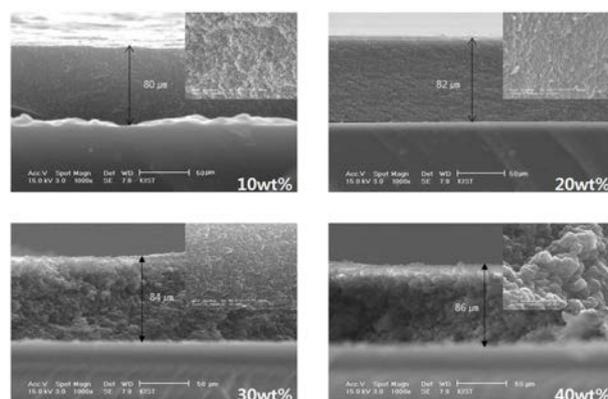


Fig. 2. SEM images of the silica aerogels with different amount of PEG addition.

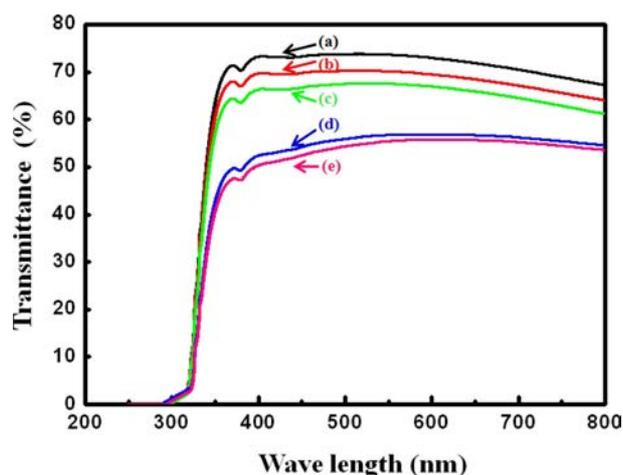


Fig. 3. Transmittance of the silica aerogel coatings modified with PEG: (a) 0, (b) 10, (c) 20, (d) 30, and (e) 40 wt%, respectively.

observed.

Fig. 3 shows the transmittance of silica aerogel samples. A 75% transmittance was detected for the silica aerogels with no PEG. Transmittance began to decrease from 75%, 65~70%, to 50~55% with increasing PEG content from 0, 10~20 wt%, to 30~40 wt%. The transmittance reduction is due to chlorosis caused by the presence of PEG. The PEG addition may raise the particle size, leading to light scattering. However strength of networking between silica particles in the silica aerogel can be enhanced due to stabilization of coatings of the silica aerogel by the PET hybridization [15]. Although uniform surfaces of aerogels were obtained, the optical transmittance reduction was detrimental to aerogel application.

The results of the BET measurement, particle size, thermal conductivity, and overall heat transmission are listed in Table 1. Total pore volume, specific surface area, and average pore diameter increased with increasing the PEG content up to 20 wt% and then decreased with further PEG addition. The addition of PEG to a certain amount helps strengthening of the network structure of the aerogel, but an excessive addition of PEG causes a decrease in pore volume, specific surface area, and average pore diameter since the PEG covers or blocks up the pores of the aerogel.

The aerogel particles are not overtly changed. They show only little difference in size up to 20 wt% PEG addition. However, dramatic increase in size was detected with further PEG doping more than 30 wt%, as summarized in Table 1. Although the small addition of PEG gives a negligible reduction in the physical properties of aerogels without hampering the absence of crack, higher PEG addition results in dramatic increase in particle size and thermal conductivity. Thermal conductivity of the silica aerogel films was measured by equation (2): [20]

$$1/K_m = t_a/K_a + t_s/K_s \quad (2)$$

where, K_m , K_a , K_s , t_a , and t_s are total thermal conductivity, thermal conductivity of aerogel, thermal conductivity of substrate, aerogel thickness ratio to the total thickness, and substrate thickness ratio to the total thickness, respectively. Thermal conductivity of silica aerogels was in the range of 0.020 to 0.057 W/mK. Thermal conductivity was close to 0.020 W/mK for a pure silica aerogel, implying that the silica aerogel films in this study are within a permutable range for smart glazing application. It increases with increasing the amount of PEG. Aerogel's pore is similar to or smaller than mean free path of molecule in a high temperature so that heat cannot be conducted well through gas phase. It cannot be conducted by solid phase efficiently since it has a low density. However, as the PEG content increases, pore size and particle size decreases and increases, respectively, resulting in high thermal conductivity.

The overall heat transmission (U) was calculated by equation (3) [21].

$$U = 1/[R_i + R_1 + R_2 + \dots + R_o] \quad (3)$$

Where, R_i , R_o , R_1 , and R_2 are thermal resistance of inside surface, thermal resistance of outside surface, and thermal resistance of constitutes, respectively. The calculated overall heat transmittances were in the range of 1.54 to 1.55 W/m²K. These values are effective to save the energy of ~43% compared to a common pair glass (2.7 W/m²K), and of ~11% to a low-emission glass (1.73 W/m²K). Such a low thermal conductivity and

Table 1. Physical properties of the silica aerogels with the PEG addition.

PEG (wt%)	Total pore volume (cm ³ /g)	Average pore diameter (nm)	Specific surface area (m ² /g)	Particle size (nm)	Thermal conductivity (W/mK)	Overall heat transmission (W/m ² K)
0	1.2	5.5	923	6.5	0.020	1.54
10	1.2	5.5	1028	6.7	0.020	1.54
20	1.4	5.6	1042	8.27	0.020	1.54
30	0.6	3.1	830	12.69	0.045	1.55
40	0.5	2.9	682	18.33	0.057	1.55

overall heat transmission values are obtained for the aerogels having 90% porosity due to a lack of circulation and convection of air confined in the pores. When adapting this processing, in particular, net structure of wet gel was not contracted even during dry process. Therefore, it is conceivable that the tailored aerogels having PEG less than 20 wt% and pores larger than 5 nm are effective to the aerogel applications.

Conclusions

In the present study, hybrid silica aerogel coatings modified with PEG were prepared. The hydrophobic silica aerogels with 10 wt% PEG exhibit a specific surface area of $\sim 1028 \text{ m}^2/\text{g}$, an average pore size of $\sim 5.5 \text{ nm}$, a pore volume of $\sim 1.2 \text{ cm}^3/\text{g}$, and a thermal conductivity of 0.02 W/mK , respectively. The plat pair glass coated with this film shows a transmittance of $\sim 70\%$ and an overall heat transmission of $\sim 1.54 \text{ W/m}^2\text{K}$. However, further PEG doping causes decrease in pore size and total pore volume as well as increase in particle size, resulting in high thermal conductivity. In the present study, the silica aerogels with PEG are successfully prepared by the sol-gel and the ambient drying methods, which are applicable to thermal insulation for large-area smart glazing.

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