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Silica aerogel/epoxy composites with preserved aerogel pores and low thermal conductivity

Abstract: The thermal conductivity of aerogel/epoxy composite based on the inexpensive powder form of silica aerogels by using water glass under ambient drying conditions was evaluated to investigate the relationship between the internal structure and the thermal conductivity of the composite. A high thermal conductivity was obtained for the composite fabricated by the typical liquid epoxy processing because the pores of the aerogels became filled with the epoxy resin during the processing of the composite. A new processing method for preserving the aerogel pores was then developed using ethanol evaporation, which lowered the thermal conductivity of the composite. The lowest thermal conductivity of 0.04 W/m K was obtained for the composite containing the as-received aerogel of 75 vol% with preserved pores. The preserved aerogel pores in the composite were the most significant physical factor in determining the thermal conductivity of the composite.

Keywords: aerogel; composite; epoxy; porous material; thermal conductivity.

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1 Introduction

Interests on insulating materials have increased in recent years since effective insulating materials play a key role in energy savings and efforts to address worldwide problems of global warming, oil price inflation, and carbon dioxide production. Among insulating materials, aerogels have the lowest documented thermal conductivity and thus show great promise for applications. An aerogel is a dried gel with a very high porosity (1) and was discovered in the early 1930s by Kistler (2). Silica aerogels were initially synthesized by traditional low-temperature, sol-gel chemistry (3, 4), but little further development was achieved for several decades. Silica aerogels have received significant attention in the last two decades due to their commercial potential. A silica aerogel is composed of nanosized (1–100 nm) particles with an open cell structure and has a high specific surface area (500–1200 m^2/g), low density (0.003–0.1 g/cm^3), low dielectric constant (1.1–2.0), and low thermal conductivity (0.013–0.14 W/m K) (5–8).

The excellent adiabatic capabilities of silica aerogels suggest that they have very high potential for applications in thermal, acoustic and electronic fields, particularly for thermal insulation applications such as the heat protection of space shuttles, nuclear reactors, and ordinary steam pipes (9–14). However, silica aerogels are limited in their applications as an insulation material because they are brittle and fragile under relatively low external stresses, and the fabrication of aerogel products is complicated due to the high porosity of the aerogel. There are two main research issues for silica aerogels. The first is the development of more durable silica aerogels with higher strength and stiffness. Randall et al. (15) have contributed to this topic extensively by investigating silane precursors and reinforcement with polymers, as summarized in a review article. The other one is the manufacture of inexpensive silica aerogels and silica aerogel composites for a potential market of such materials as composite parts, fibers, and textiles. Since the silica aerogel is expensive due to the high cost of the raw materials and the long drying process with super critical fluids, an appropriate processing method is required to fabricate a polymer composite based on an inexpensive powder form of silica

aerogels produced by using water glass and ambient drying conditions (8).

A polymer binding system for silica aerogels was proposed by Schmidt and Schwertfeger (16), and a material system utilizing both a thermoplastic polymer and a wet solution has been demonstrated to be a good binder for silica aerogel. The effects of wet, dry, and dual mixing on the thermal conductivity of aerogel/polyvinylbutyral (PVB) composites have been investigated, and dry mixing was shown to be more suitable than other methods (17). A thermosetting polymer has been applied to aerogel composites to improve the service temperature of the composites (18). A liquid epoxy has been used as the polymer matrix to prepare the aerogel/epoxy composite by wet mixing (19, 20), but the thermal insulation properties were not satisfactory (20). In this study, silica aerogel powder/epoxy composites were prepared with varying volume fractions of the aerogel. The thermal conductivities of the composites were measured with a heat flow meter to evaluate the insulating ability of the composites. The thermal conductivity of the epoxy composites filled with plasma-treated aerogels was also measured to investigate the relationship between the internal structure of the aerogel and the thermal conductivity of the composites. To prevent filling of the aerogel pores with the epoxy matrix, a preparation method for preserving the aerogel pores in the final composite was developed using ethanol evaporation.

2 Materials and methods

2.1 Materials

The silica aerogel powder was supplied by EM-POWER Co., Ltd. (Asan-si, Chungnam, Korea), and the procedure for synthesizing the silica aerogel is briefly summarized below. Water glass was used as the starting material, and silica sol with a silica content of 29 wt% was prepared using distilled water. For surface modification and gelation, the co-precursor method was used, in which hexamethyldisilazane and nitric acid were added to the silica sol. The hydrogel obtained by the co-precursor method was immersed in *n*-hexane at 60°C for 10 h to exchange the solvent and remove ions, including sodium. The modified gel was sequentially dried at 170°C for 20 min and 200°C for 10 min at ambient pressure. Properties of the supplied aerogel, which were related to the thermal conductivity of the composites based on the polymer matrix, are listed below. The thermal conductivity, stable temperature, density, pore volume, and porosity of the silica aerogels were 0.02 W/m K, -200°C–450°C, 0.05 g/cm^3, 35 ml/g, and 90%, respectively. As shown in Figure 1, 95% of the aerogel particles had a size between 1 and 10 μm. The pore sizes of the aerogels were smaller than 20 nm, and the average pore size was approximately 9 nm (21).

2.2 Preparation of silica aerogel powder/epoxy composites

Pristine silica aerogel powder was treated with plasma (Model BD-10AV, Electro-Technic Products Inc., Chicago, IL, USA) for 30 s to alter the structure of the aerogel, such as particle size and surface area, and to investigate the effects of the altered aerogel structure on the thermal conductivity of the silica aerogel powder/epoxy composites. The epoxy resin (YD-128) and hardener (IPDA), i.e., the diglycidyl ether of bisphenol-A and the modified aromatic amine, were supplied by Kukdo Chemical Co., Ltd. (Seoul, Korea). The silica aerogel powder/epoxy composites were

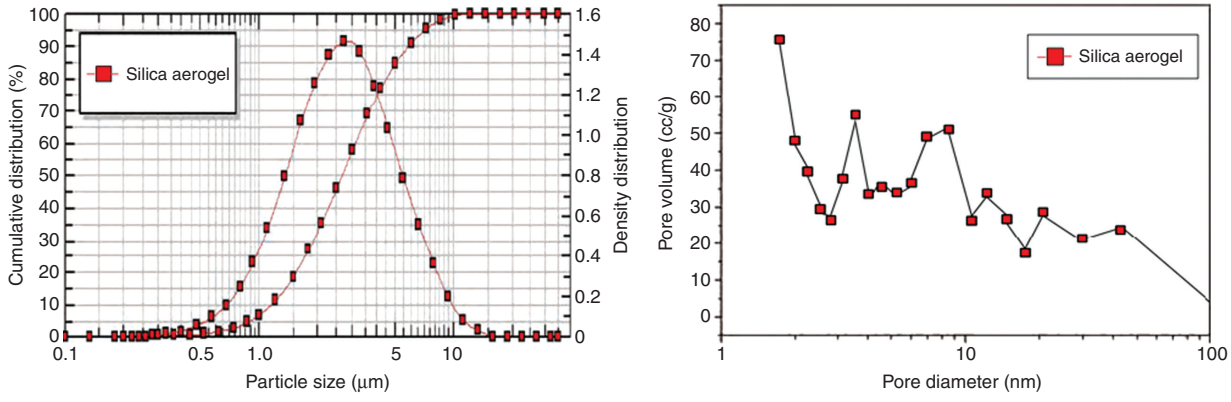


Figure 1: Particle and pore size distribution of the as-received aerogel.

prepared by mixing the aerogels with the epoxy mixture for 30 min, i.e., the epoxy resin and hardener were mixed with respect to the volume fraction of the aerogel and the aerogel type such as as-received and plasma-treated aerogels. Before the hardening of the composites, the specimens were molded for characterization by pressing the mixture at 20°C under 1.5 MPa for 5 h.

A preparation method for the silica aerogel powder/epoxy composite was developed to preserve the pores in the aerogel, as shown in Figure 2. The silica aerogels were immersed in ethanol to fill the pores of the aerogel with ethanol. A silica aerogel powder/epoxy composite with high porosity was prepared by mixing the aerogel/ethanol mixture, epoxy resin, and hardener, and then pressing the specimen at 80°C under 1 MPa for 5 h to remove the ethanol from the pores of the aerogel before the hardening of the composite.

2.3 Measurement of thermal conductivity

The thermal conductivity of the prepared composite specimen was measured with a thermal analyzer (Thermo Labo II-KES-F7, KATO TECH Co., Tokyo, Japan) that functions as a heat flow meter. The thermal conductivity was calculated using the following equation.

$$k=\frac{W\times D}{A\times\Delta T} \quad [1]$$

where W is the heat flow in watts, D is the thickness of the sample in meters, ΔT is the temperature difference between the hot and the cold plates in Celsius (°C), and A is the surface area of the hot plate (25×10^{-4} m^2).

2.4 Morphology of silica aerogel powder/epoxy composite

The as-received and plasma-treated aerogels and the fractured surfaces of the silica aerogel powder/epoxy composites were coated with platinum under vacuum for 300 s using a sputter coating machine (Sputter Coater-108, Cressington Scientific Instruments, Watford, UK). The morphologies of the as-received and plasma-treated aerogels and of the fractured surfaces of the silica aerogel powder/epoxy composite were observed with a field emission scanning electron microscope (FE-SEM, JSM-6390LV, JEOL, Tokyo, Japan) to investigate the internal structure of the aerogels and composites.

2.5 Pore characterization of silica aerogel and the aerogel powder/epoxy composite

The specific surface area, pore volume, and pore size of the aerogels and composites were measured by the Brunauer-Emmett-Teller method (BET method, ASSP 2010, Micromeritics, Norcross, GA, USA). The aerogel and composite samples were heated to 150°C and 40°C under vacuum (10^{-5} Torr) for 2 and 24 h to remove the adsorbed species, respectively. Nitrogen adsorption data were acquired at 77 K. All nitrogen adsorption/desorption measurements were equilibrated for 10 s before being recorded.

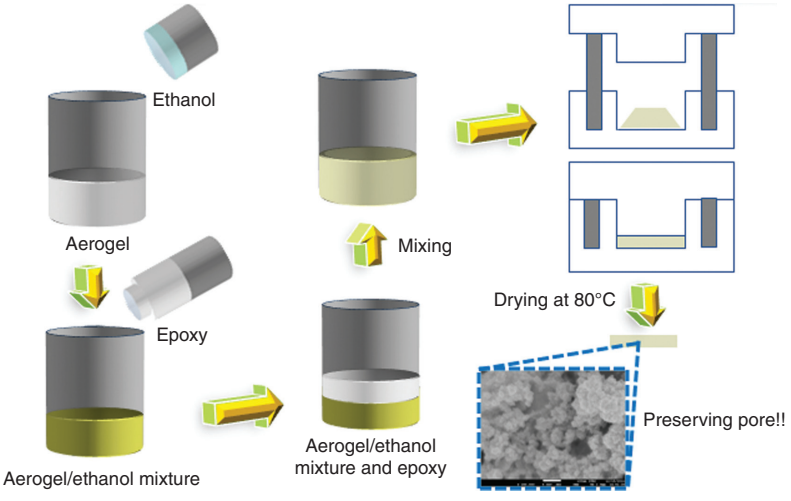


Figure 2: Schematic diagram of the processing method for preserving aerogel pores.

2.6 Density of the silica aerogel powder/epoxy composite

The density of the composites was measured at 25°C using a density-gradient column filled with carbon tetrachloride and *n*-heptane.

3 Results and discussion

The thermal conductivity of the silica aerogel powder/epoxy composite is shown in Figure 3 with respect to the volume fraction of the aerogel. The as-received silica aerogel powder/epoxy composite showed thermal conductivities from 0.11 to 0.12 W/m K, while the thermal conductivities of the plasma-treated silica aerogel powder/epoxy composite were 0.09–0.11 W/m K. The measured values were higher than expected when considering the extremely low thermal conductivity of the silica aerogel, 0.02 W/m K. The results were attributed to the fact that the pores of the aerogel were filled with the epoxy matrix as shown in the SEM images of the fracture surfaces of the composites (Figure 4A–D). Ge et al. (22) reported a similar phenomenon in which the pores of a silica aerogel were filled with an epoxy matrix when the composite was prepared with a silica aerogel and a liquid epoxy.

No obvious trend was observed in the thermal conductivity of the composite containing the as-received or the plasma-treated aerogel as the volume fraction of the aerogel was varied from 25 to 75 vol%. The results can be explained by the interfacial thermal resistance and the intrinsic thermal conductivity of the silica. First, it can be assumed that the composite consists of a biphasic material system of the silica structure and epoxy matrix because the pores of the aerogel in the composites were filled with the epoxy resin as discussed previously. Second, increasing the volume fraction of the aerogel must have generated both a larger amount of silica, whose intrinsic thermal conductivity is 1.3 W/m K, and a larger interface area between the silica structure and the epoxy matrix. Third, the conflicting results may stem from the generation of a larger interface area, which causes a decrease in the thermal conductivity of the composite, and a higher volume fraction of silica, which causes an increase in the thermal conductivity of the composite. According to Pernot et al. (23), the room temperature thermal conductivity of a single crystalline SiGe material was reduced to approximately 0.9 W/m K by engineering a set of individual phonon-scattering nanodots at the interface. Every et al. (24) reported that the thermal conductivity of zinc sulfide was lowered by the addition of sub-micron-size particles of diamond whose thermal conductivity was much higher than that of the zinc sulfide. These references obviously showed the significant effect of the interfacial thermal resistance on the thermal conductivity of the composite materials.

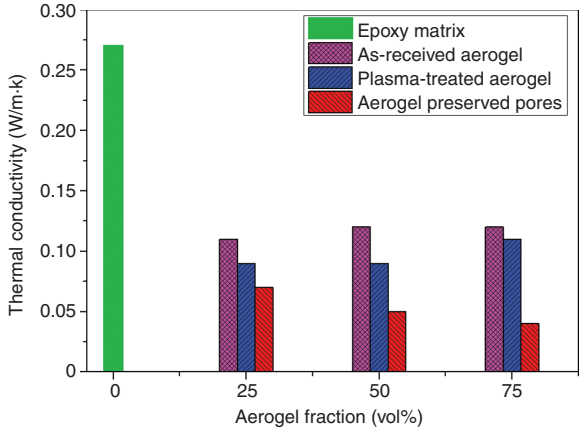


Figure 3: Thermal conductivity of the aerogel/epoxy composites with respect to the volume fraction of the aerogel.

Figure 5 shows the SEM images of the as-received and plasma-treated aerogels. The surface area of the plasma-treated aerogel is larger than that of the pristine aerogel because the size of the silica particles in the plasma-treated aerogel is smaller than that of the silica particles in the pristine aerogel. The surface areas of the as-received and plasma-treated aerogels measured by the BET method are listed in the inserted table of Figure 5. The surface areas of the as-received and plasma-treated aerogels were 614.26 and 635.45 m^2/g, respectively. Despite the changed structure of the plasma-treated silica aerogel, the thermal conductivity of the composite filled with the plasma-treated aerogel was similar to that of the composite with the same volume fraction of as-received aerogel, indicating that the structure change induced by the plasma treatment does not play an important role in the thermal conductivity of the silica aerogel composites as the aerogel pores were filled with polymer matrix.

To obtain a composite with low thermal conductivity, the pores of the aerogel should be preserved in the silica aerogel powder/epoxy composite. A new method of preparing the silica aerogel powder/epoxy composite using ethanol evaporation was developed to preserve the pores in the aerogel. Details of the procedure are explained in the experimental part and shown in Figure 2. According to the method, the ethanol prevents the aerogel pores from being filled by the epoxy during the mixing process and then vaporizes to restore the pores in the aerogel during

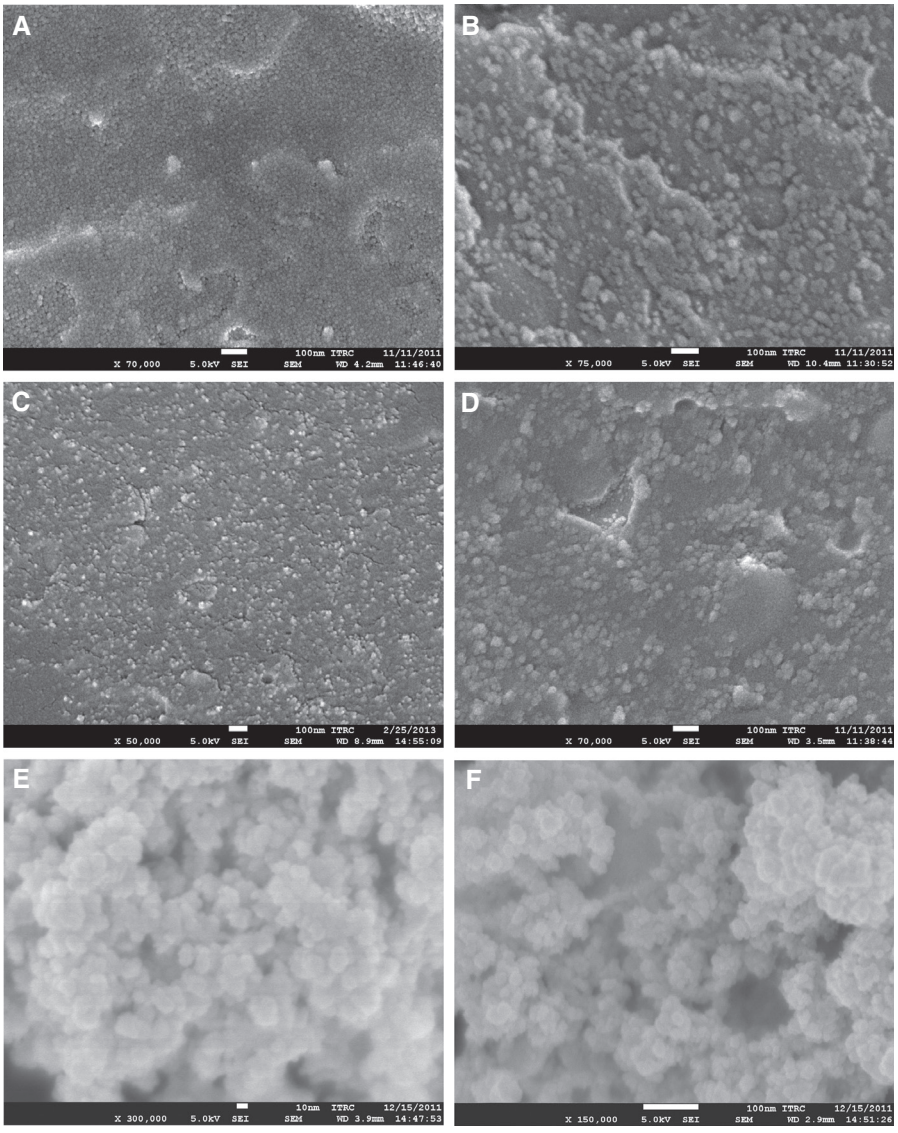
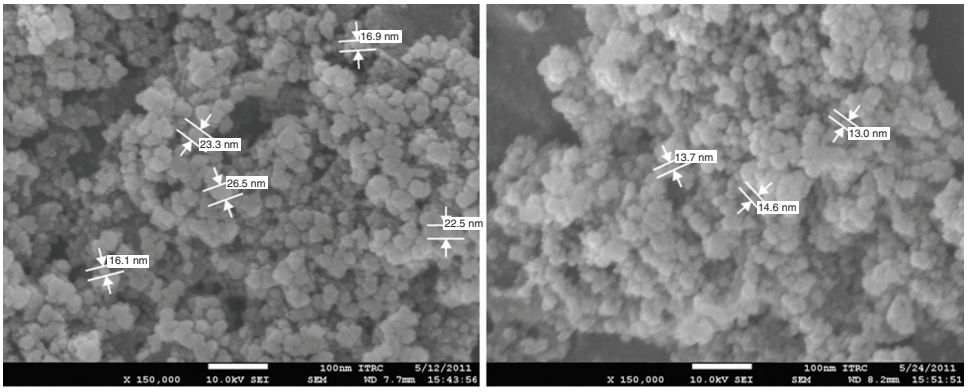


Figure 4: SEM images of the aerogel/epoxy composites with (A) as-received aerogel of 25 vol%, (B) as-received aerogel of 75 vol%, (C) plasma-treated aerogel of 25 vol%, (D) plasma-treated aerogel of 75 vol%, (E) 25 vol% preserved aerogel pores, and (F) 75 vol% preserved aerogel pores.

the hardening process. The pores of the aerogel in the epoxy composite fabricated with the new preparation method are readily identified by the SEM images shown in Figure 4E and F. From the BET results listed in Table 1, the pore volume of the composites with preserved aerogel pores was increased significantly as the aerogel volume fraction in the composites was increased. Although the aerogel pores were preserved by using the proposed processing method, some parts of the aerogel pores were still impregnated by the epoxy matrix, considering the entire pore volume of the aerogel used. The thermal conductivity of the composites with preserved aerogel pores was reduced as the aerogel volume fraction was increased in the composites. The thermal conductivity of the composite containing the as-received aerogel of 75 vol% with preserved pores was 0.04 W/m K, as shown in Figure 3. Therefore, preserving the aerogel pores in the composite had a great effect on the thermal conductivity of the composite.

4 Conclusions

The thermal conductivity of a silica aerogel powder/epoxy composite was investigated with respect to the volume



Pristine silica aerogel Plasma treated aerogel

	Pristine aerogel	Plasma treated aerogel
Surface area (m^2/g)	614.26	635.45

Figure 5: SEM images of pristine and plasma-treated aerogels. The white arrows indicate the particle size of the individual particles of the aerogel, and the surface areas of the aerogels are listed in the inserted table.

Table 1: BET results of the composites with respect to the volume fraction of the aerogel.

	Pore volume (ml/g)	Pore size (nm)	Surface area (m^2/g)	Density (g/ml)	Porosity (%)
As-received					
25 vol%	0	–	0	1.11	0
50 vol%	0	–	0	1.11	0
75 vol%	0	–	0	1.12	0
Preserved pores					
25 vol%	6.3	3–30 (average: 8.2)	122.84	0.91	18.1
50 vol%	12.5	3–30 (average: 8.4)	245.68	0.81	35.7
75 vol%	19.2	3–30 (average: 8.1)	368.52	0.73	54.8

fraction of as-received and plasma-treated aerogels. The as-received silica aerogel powder/epoxy composite displayed a range of thermal conductivity values from 0.112 to 0.123 W/m K, while the plasma-treated silica aerogel powder/epoxy composite exhibited values from 0.085 to 0.110 W/m K. The thermal conductivity of the silica aerogel composite was higher than expected because the pores of the as-received and plasma-treated aerogels were filled with the epoxy resin during the processing of the composites. The change in the silica aerogel structure induced by the plasma treatment, such as the size of the individual particle and surface area, did not play an important role in the thermal conductivity of the silica aerogel composites due to the impregnation of aerogel pores with polymer matrix. A preparation method for preserving the aerogel pores during the processing of the composite was proposed and developed using ethanol evaporation. The thermal conductivity of the composites with preserved aerogel pores was reduced as the aerogel volume fraction was increased in the composites, and the lowest thermal conductivity of the prepared composite containing the as-received aerogel of 75 vol% with preserved pores was 0.04 W/m K.

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