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Effect of mixing on thermal and mechanical properties of aerogel-PVB composites

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Silica aerogels were synthesized via solvent exchange/surface modification of wet gels from waterglass using IPA/TMCS/*n*-Hexane solution. The densities, porosities, and specific surface areas of the aerogel were in the range of 0.128–0.153 g/cm^3, 93–95%, and 598–795 m^2/g, respectively. Aerogel-PVB composites were manufactured by hot pressing. Aerogels were crushed and mixed with PVB. Three mixing methods were performed. The aerogel-PVB composites had densities of 0.19–1.09 g/cm^3, and thermal conductivities of 0.03–0.12 W/(m · K). Density and thermal conductivity can be controlled by aerogel volume fraction and the mixing method. The modulus of rupture of aerogel-PVB composites was in the range of 0.15–46.5 MPa. © *2003 Kluwer Academic Publishers*

1. Introduction

Because silica aerogels have lowest thermal conductivity (<0.02 W/(m · K)), lowest dielectric constant (1.1–2.2), low density (0.003–0.35 g/cm^3), and high specific surface area (500–1200 m^2/g), silica aerogels have numerous applications in various areas such as thermal insulation, low-dielectrics for ICs, catalyst, and so on. Among proposed applications, silica aerogels have been intensively investigated as potential candidates for possible application as a thermal superinsulation [1–3].

Silica aerogels provide a total thermal conductivity of about 0.02 W/(m · K) under ambient conditions due to the extremely high porosity leading to a very low solid thermal conductivity. Due to weak strength resulting from high porosity, silica aerogels can not be applied to conventional insulation. M. Schmidt *et al.*, therefore, proposed aerogel-polymer binding system [4].

In this work, we prepared silica aerogels via ambient drying using IPA/TMCS/*n*-Hexane solution and manufactured aerogel-PVB composites by hot pressing. In addition, the effects of mixing methods such as dry, wet, and dual mixing on thermal/mechanical properties were investigated.

2. Experimental procedure

The overall experimental procedure for synthesizing aerogel-PVB composites is shown as a flow chart in Fig. 1.

2.1. Preparation of silica aerogels

Silica sols were prepared with waterglass (Young-il Co., Korea) as a starting material. About 0.7 liter of waterglass solution (SiO_2 contents 8 wt%, Na_2O:SiO_2 mole ratio 1:3.3) went through an ion exchange column (8 cm in diameter, 40 cm in length) filled with 1 liter of Amberlite (Rohm & Haas, France). The collected silica sols had a pH in the range of 2.6–2.8.

For gelation, 1.0 M NH_4OH solution was added to the silica sol. The sols, which had pH values ranging from 3.5 to 5.0 with increments of 0.5, were stirred for 30 seconds respectively, and then transferred into polypropylene molds (30 mm in diameter). After gelation in closed molds, the wet gels were aged at 50°C for 1 d in D.I. water in order to strengthen the gel structure.

In this experiment, three solvents [isopropyl alcohol (IPA; Yakuri, Japan), trimethylchlorosilane (TMCS; Lancaster, U.K.), and *n*-Hexane (Duksan Co., Korea)] were used for the solvent exchange/surface modification as described in previous paper [5]. The modified wet gels were dried at 50°C for 1 h and 230, 430°C for 1 h in air.

2.2. Preparation of aerogel-PVB composites

Aerogel particles and PVB particles were mixed by three methods (dry, wet, and dual mixing) as shown in Fig. 2, and then via hot pressing of the mixture of crushed aerogel particles and polyvinyl butyral (PVB; B76, Solutia Inc., USA) at 150°C under 0.28 MPa, the aerogel-PVB composites were obtained.

2.3. Characterization

Apparent density was determined by weighing samples of known dimensions. The microstructure of silica aerogel was observed by scanning electron microscopy (SEM) (Model H4200, Hitachi, Tokyo, Japan). The surface area of silica aerogel was determined using the Brunauer-Emmitt-Teller (BET) method (Model Gemini 2375, Micromeritics

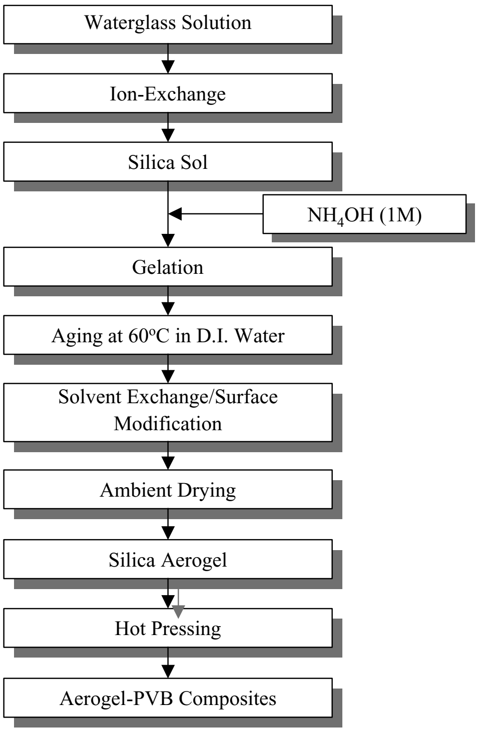

Figure 1 Overall experimental procedure.

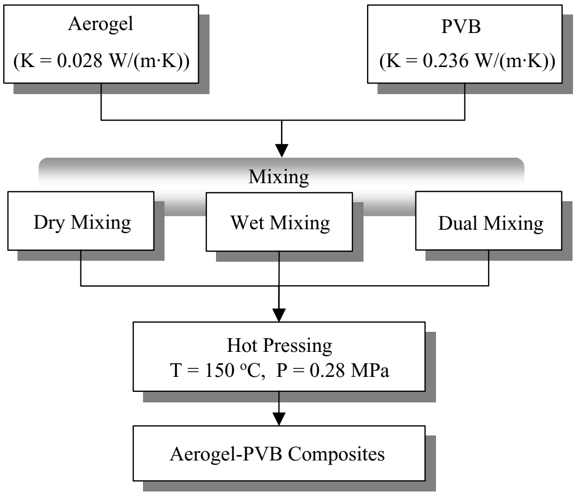

Figure 2 Preparation of aerogel-PVB composites.

Instrument Group, Norcross, GA). The thermal conductivity of aerogel-PVB composites, like in Fig. 3a, were measured by a hot disk thermal constants analyzer (Model TPA-501, Hot Disk Inc., Sweden). Samples with dimensions of 36 mm × 4 mm × 3 mm (KS L 1591) for mechanical tests were pressed at 150°C under 0.28 MPa, as shown in Fig. 3b. The strength of rupture was measured by a universal testing machine (H10K-C, Hounsfield Test Equipment, U.K.), using a three-point bend fixture with a span of 20 mm and a crosshead speed of 0.5 mm/min.

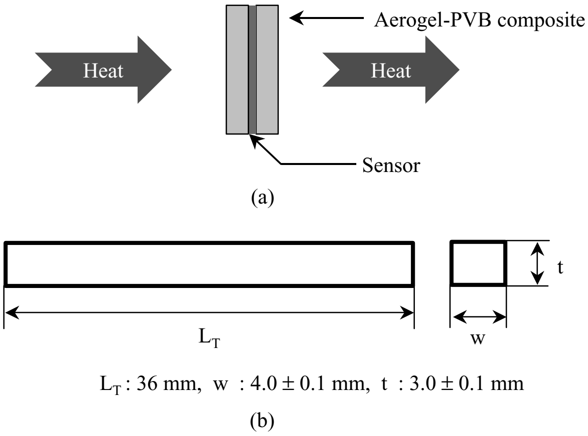

Figure 3 Typical sample shape: (a) thermal conductivity and (b) mechanical strength.

3. Results and discussion
3.1. Properties of aerogels
Silica aerogels, synthesized by the ambient drying process using an IPA/TMCS/*n*-Hexane solution, showed a density of 0.128–0.153 g/cc, porosity of 93–95%, and specific surface area up to 795 m^2/g. In particular, the hydrophobic property was maintained up to 350°C. It shows that the silica aerogels, based on waterglass using an IPA/TMCS/*n*-Hexane method, have no great differences in comparison to aerogels synthesized by the general method—via a supercritical drying technique from alkoxides.

Figs 4, 5, and 6 show that variations of pore size distribution, according to heat-treatment. Fig. 4 shows the pore size distribution of xerogel dried at 25°C after surface modification. Xerogel had pore sizes mainly in the vicinity of 2 nm, and the amount of N$_2$ adsorption is very small. However, the pore size distribution of hydrophobic aerogel dried at 25°C was shown in Fig. 5. Due to the effect of springback, pore size distribution of hydrophobic aerogel dried at 25°C was broad, and the amount of N$_2$ adsorption was much greater than that of xerogel dried at 25°C. The pore size distribution of hydrophilic aerogel dried at 450°C is shown in Fig. 6. The pore size distribution of hydrophilic aerogel dried at 450°C can be depicted in a similar fashion

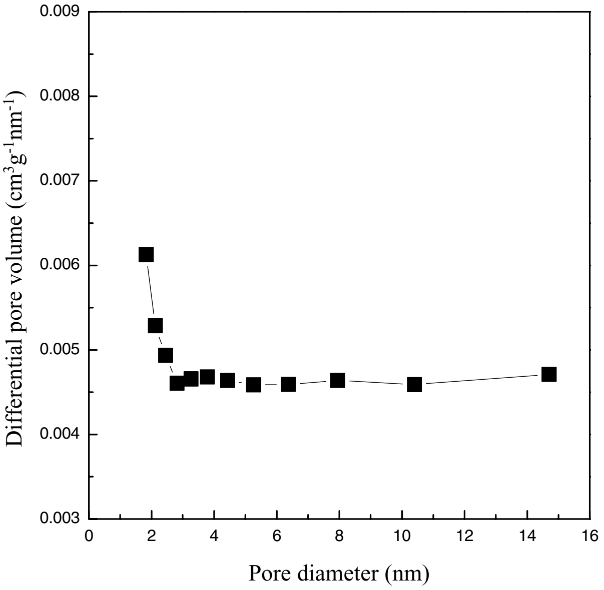

Figure 4 Differential pore volume versus pore diameter for xerogel dried at 25°C by the BJH method.

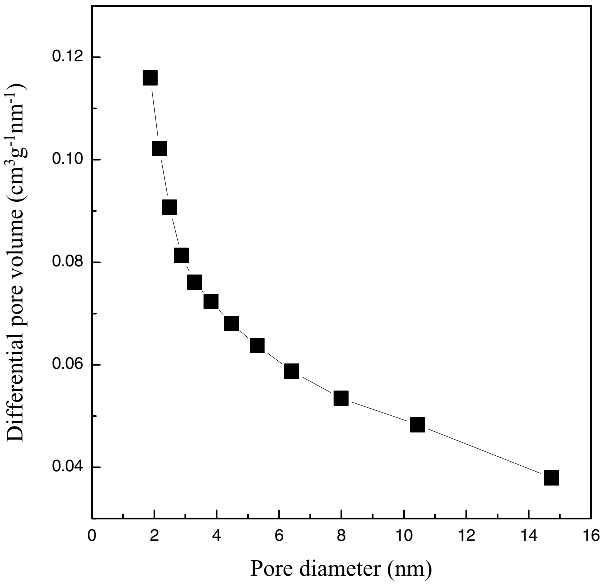

Figure 5 Differential pore volume versus pore diameter for hydrophobic aerogel dried at 25°C by the BJH method.

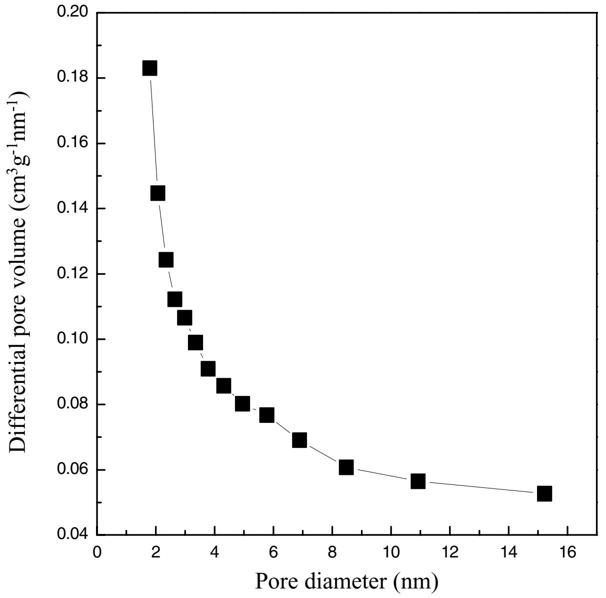

Figure 6 Differential pore volume versus pore diameter for hydrophilic aerogel dried at 450°C by the BJH method.

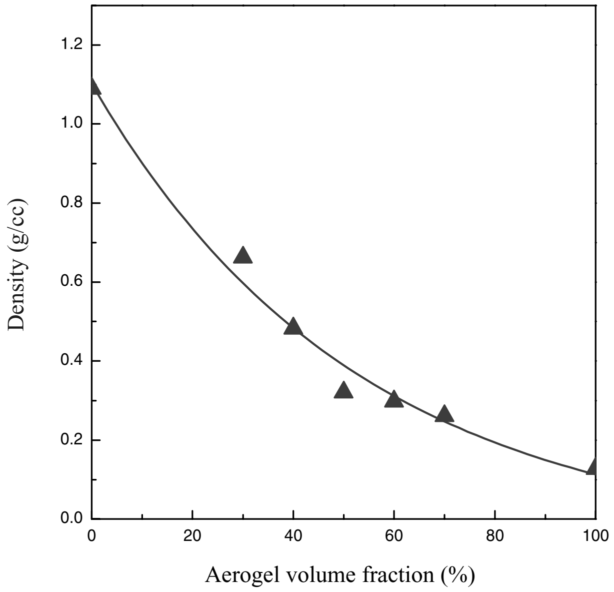

Figure 7 Density versus aerogel volume fraction (Dry Mixing).

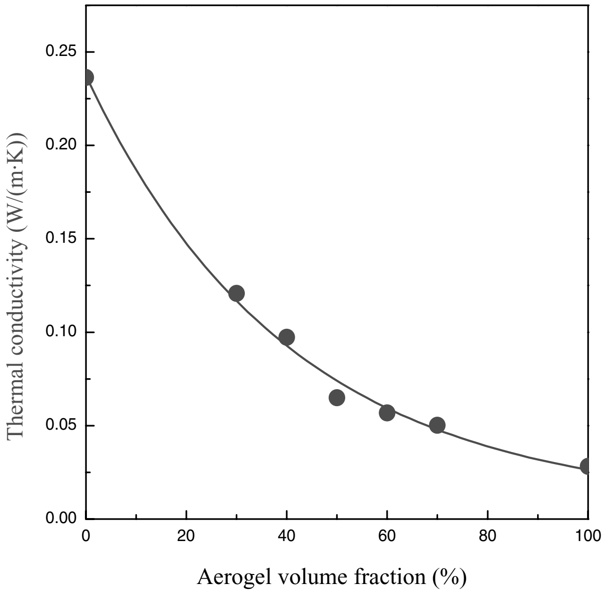

Figure 8 Thermal conductivity versus aerogel volume fraction (Dry Mixing).

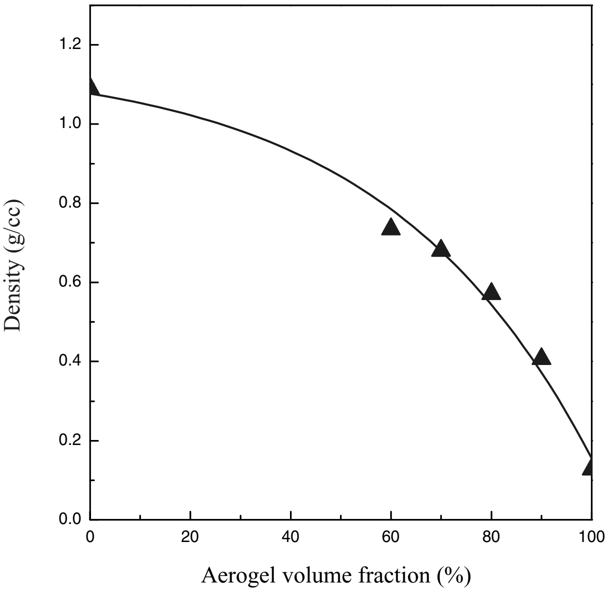

Figure 9 Density versus aerogel volume fraction (Wet Mixing).

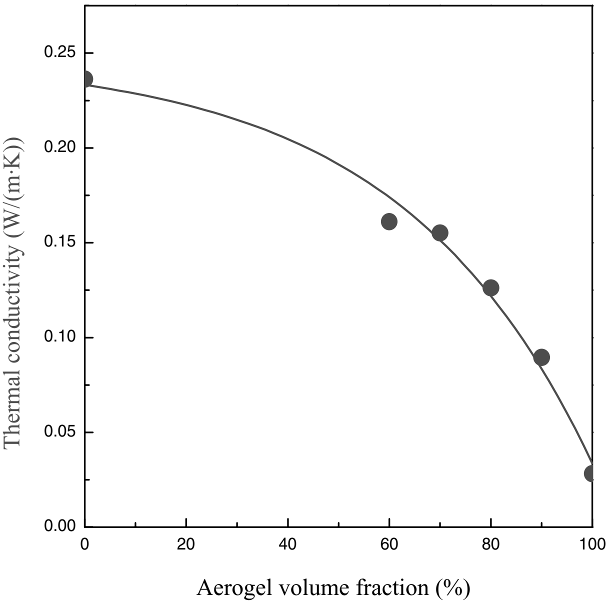

Figure 10 Thermal conductivity versus aerogel volume fraction (Wet Mixing).

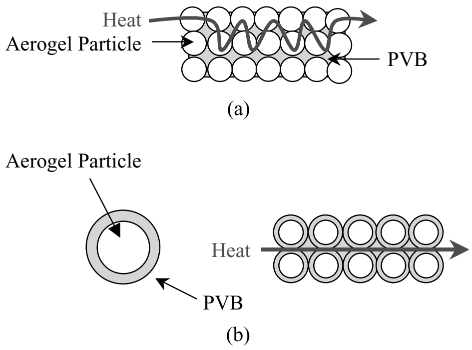

Figure 11 Schematic diagram of the effects of mixing on heat transfer.

to that of hydrophobic aerogel dried at 25°C, but the amount of N_2 adsorption of hydrophilic aerogel was larger than that of hydrophobic aerogel, caused by removing the -$(CH_3)_3$ species. The specific surface areas of xerogel, hydrophobic aerogel, and hydrophilic aerogel were 41.4, 621.9, and 794.8 m^2/g, respectively.

3.2. Effect of mixing on properties of aerogel-PVB composites

Silica aerogels were crushed and mixed with PVB powders (dry mixing). The mixtures were pressed

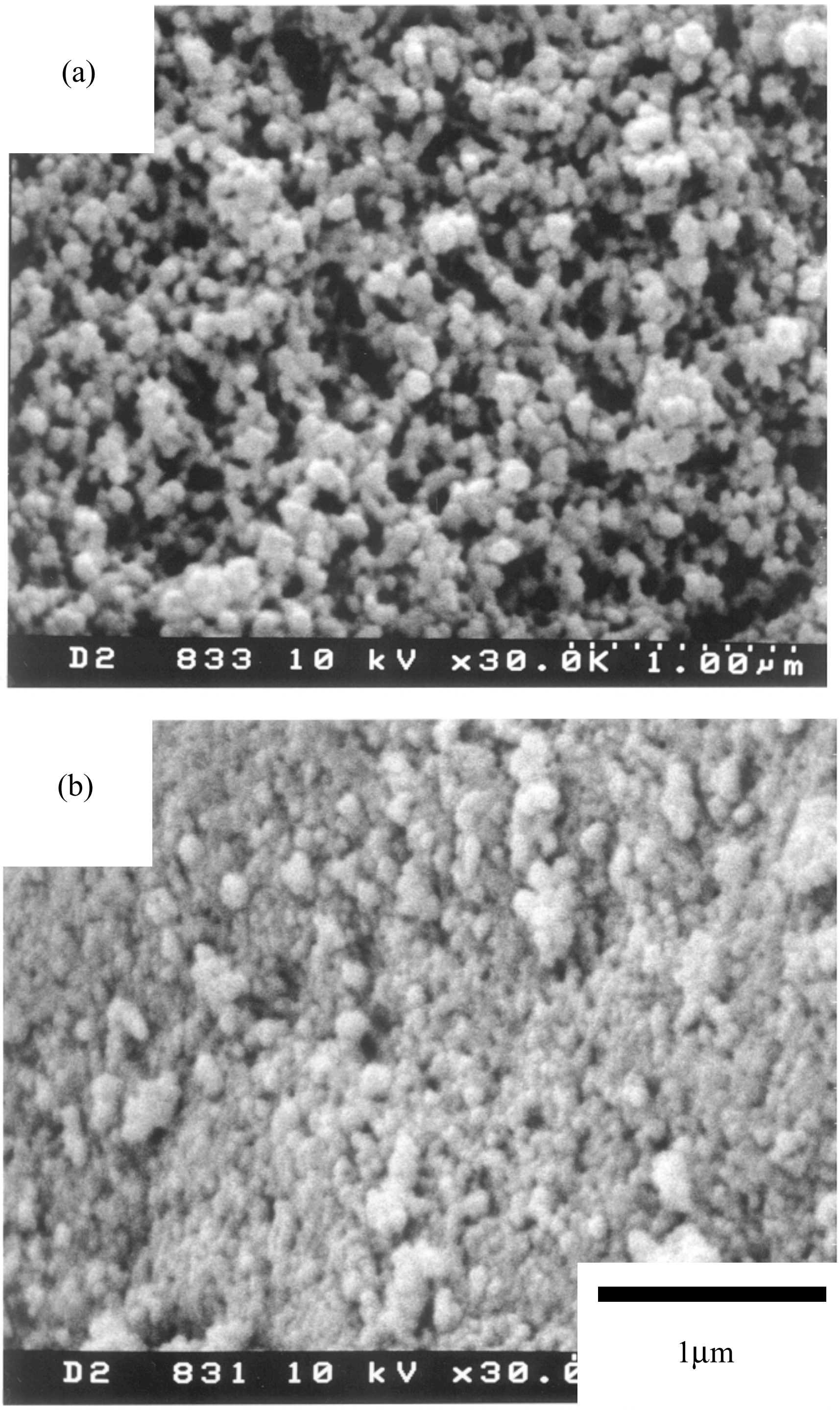

Figure 12 SEM micrographs of (a) aerogel and (b) aerogel coated with PVB.

at 150°C under 0.28 MPa. Figs 7 and 8 show the density and the thermal conductivity of the aerogel-PVB composites as a function of aerogel volume fraction in dry mixing. As the aerogel volume fraction increased (∼70 vol%), thermal conductivity significantly decreased (conduction heat transfer would occur mainly through aerogel particles, as shown in Figs 5–14a). Because of a different density however (d_{PVB}:0.235 g/cm^3 > d_{aerogel}:0.128 g/cm^3), it was difficult to mix homogeneously; as well, an original composite shape containing the aerogel above 70 vol% could not be obtained by hot pressing.

Therefore, in order to homogeneously mix aerogel particles with PVB, PVB powders were first dissolved in toluene and then hydrophilic aerogel particles, which were heated at 450°C, were added to the PVB-toluene solution (wet mixing). After drying the mixture, aerogel-PVB composites were fabricated by hot pressing. In this case, the surface of the aerogels was coated with PVB, and then homogeneous mixing was possible. The density and the thermal conductivity of the aerogel-PVB composite as a function of aerogel volume fraction in the case of wet mixing are shown in Figs 9 and 10. As the aerogel volume fraction increased (∼90 vol%), thermal conductivity decreased. Thermal conductivities were found to be higher than those of composites using dry mixing. This can be explained by the fact that since the surface of aerogel particles was coated with PVB in the PVB-toluene solution, the heat transfer through the continuous PVB phase might be dominant, in comparison with the heat transfer through the discontinuous aerogel phase, as shown in Figs 11 and 12. Fig. 12 shows uncoated aerogel particle and aerogel coated with PVB. Fig. 12a shows a 3-dimensional structure including many pores but Fig. 12b shows PVB integrates in pores of aerogel particle. Because of integration of PVB, wet mixed aerogel-PVB composites have higher thermal conductivity and lower mechanical strength than dry mixed aerogel-PVB composites (see Figs 8, 10, and 15).

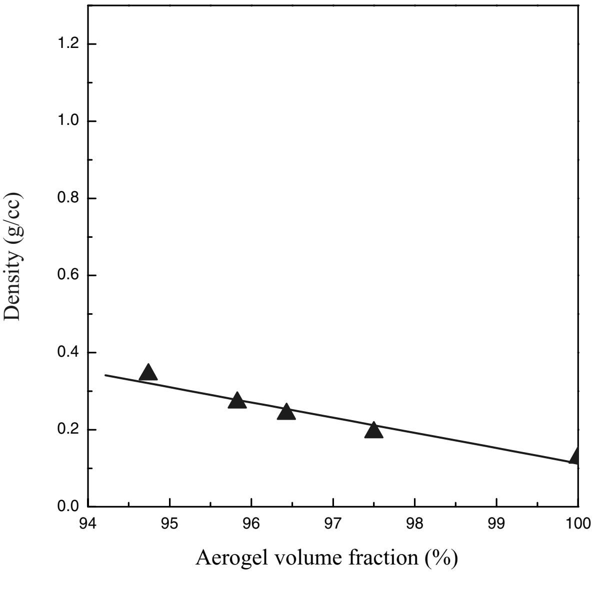

Figure 13 Density versus aerogel volume fraction (Dual Mixing).

In order to solve the problems of dry/wet mixing, the aerogel particles coated with PVB and uncoated aerogel particles were mixed and pressed (dual mixing). As can be seen in Figs 13 and 14, dual mixing solves problems such as inhomogeneous mixing in dry mixing, and high thermal conductivity in wet mixing. The density and the thermal conductivity of composites were low and an original shape containing aerogel above 94.7 vol% could be obtained by hot pressing. Congruently, the homogeneous composites containing 97.5 vol% of aerogel particles could be obtained, and they had very low thermal conductivity (0.037 W/(m · K)) similar to that ((0.028 W/(m · K)) of pure aerogel.

Fig. 15 shows the mechanical strength of the aerogel-PVB composites. The modulus of rupture of aerogel-PVB composites decreased as aerogel volume fraction increased. The modulus of rupture of composites using dry mixing is higher than by using wet mixing (aerogel

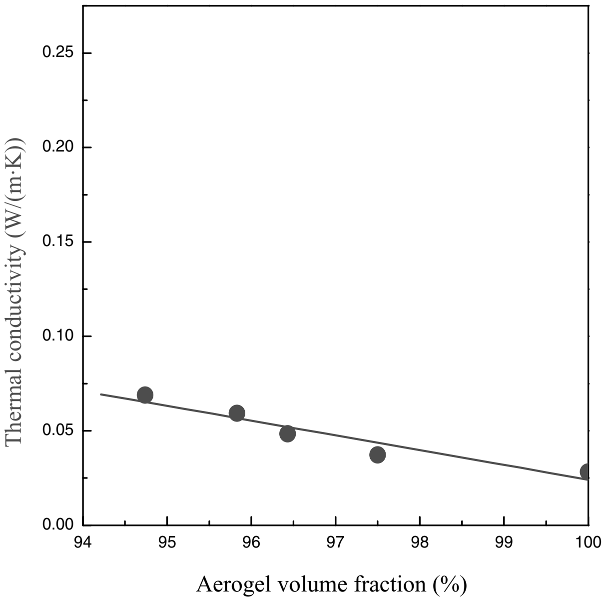

Figure 14 Thermal conductivity versus aerogel volume fraction (Dual Mixing).

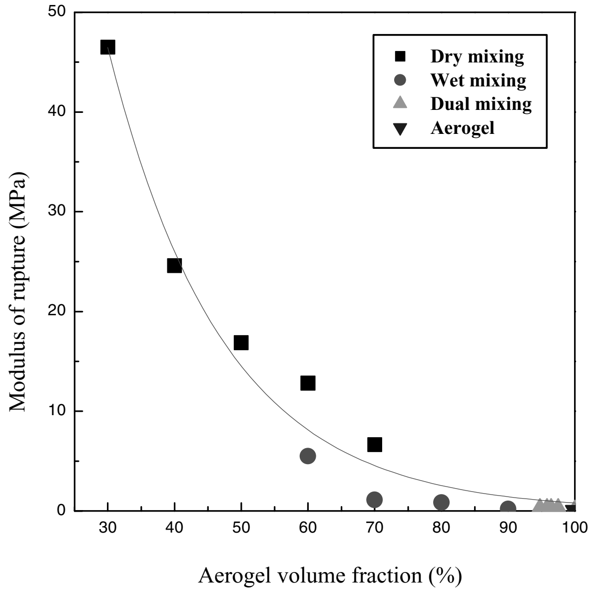

Figure 15 Mechanical strength of aerogel-PVB composites.

volume fraction: 60 and 70 vol%). This phenomena can be explained in that PVB coated aerogel particles connected at the neck and composites using wet mixing had weaker than those using dry mixing (see Fig. 11). In the case of dual mixing, composites have a low value of modulus of rupture because the PVB volume fraction is very small in comparison with that of dry/wet mixing.

4. Conclusions

1. Silica aerogels synthesized by the new ambient drying technique using an IPA/TMCS/*n*-Hexane solution showed properties of 0.128–0.153 g/cm^3 density, 93–95% porosity, and $\sim$795 m^2/g specific surface area.

2. In the case of aerogel-PVB composites using dry mixing, heat transfer would occur mainly through aerogel particles. However heat transfer in the composites using wet mixing would occur mainly through PVB. Thermal conductivity of wet mixing composites was found to be higher than that of dry mixing composites.

3. When using dual mixing, homogeneous aerogel-PVB composites containing more than 97.5 vol% aerogel could be synthesized, and their thermal conductivities were reduced to 0.037 W/(m $\cdot$ K).

4. The mechanical strength of aerogel-PVB composites were decreased as aerogel volume fraction increased and the composite showed property of 0.15–46.5 MPa the modulus of rupture.

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References

1. L. W. HRUBESH and J. F. POCO, *J. Non-Cryst. Solids* **188** (1995) 46.
2. L. W. HRUBESH, *ibid.* **225** (1998) 335.
3. S. H. HYUN, J. J. KIM and H. H. PARK, *J. Amer. Ceram. Soc.* **83**(3) (2000) 533.
4. M. SCHMIDT and F. SCHWERTFEGER, *J. Non-Cryst. Solids* **225** (1998) 346.
5. C. J. LEE, G. S. KIM and S. H. HYUN, *J. Mater. Sci.* in press.

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