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ABSTRACT

Aerogel is a transparent, low density, insulating material suitable for a variety of solar applications. Significant energy savings can be realized by using aerogel for a window glazing material. Other possible applications include solar collector covers, transparent insulating jackets for direct gain passive solar devices, and situations that require both transparency and good insulation. Because silica aerogel has a low density (2-10% solid), it has a thermal conductivity as low as 0.014 $W/m^{o}K$ without evacuation, and if evacuated, lower than 0.006 $W/m^{o}K$. It provides a clear view with only slight coloring due to its weak and nearly isotropic scattering of light.

This paper describes significant progress made in the past year at our laboratory in the development of aerogel. We have improved the transparency, developed new preparation methods using less toxic materials, and initiated successful experiments in drying alcogels at near ambient temperature. Optical transmission, light scattering, and electron microscopy data show that CO_2 supercritical drying of alcogels produces aerogels similar in quality to those produced by high temperature supercritical drying. These advances make the commercial production of aerogel much more feasible.

KEYWORDS

Aerogel; sol-gel processing; insulating windows; transparent insulation; porous materials; silica.

INTRODUCTION

Transparent silica aerogels are being studied because of their excellent thermal insulation properties for window glazing materials. Windows play

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an important role in the energy utilization of buildings. They allow sunlight to enter, retain heat, and provide a barrier to wind and rain. However, most existing windows are poor insulators compared to walls and are therefore responsible for major undesired heat losses. An ideal window would allow clear viewing, be capable of transmitting sunlight to provide energy gains to building interiors, and possess a thermal resistance per unit area comparable to building walls. Silica aerogel appears to be an excellent material for construction of such an ideal window [1,2].

Silica aerogel is a low-density porous material consisting of a matrix of extremely fine linked particles. Because the particles and pore sizes are very small compared to the wavelength of light, aerogel scatters light only weakly and nearly isotropically. This type of scattering does not produce distortion nor does it blur images viewed through the material. At the present state of development, aerogel samples appear slightly blue when viewed against a dark background and produce a slight reddening of transmitted images.

Due to its high porosity and small pore size, silica aerogel is an excellent thermal insulator. Nonevacuated aerogel at ambient temperature has a thermal conductivity of only 0.014 $W/m^{o}K$. Evacuated aerogel has a thermal conductivity of about 0.005 to 0.006 $W/m^{o}K$ with a low grade vacuum (0.1 atmosphere) [3]. This value may be compared with typical single and double glazings with thermal conductivities of 0.2 and 0.1 $W/m^{o}K$, respectively. There are several reasons for the low conductivity of aerogel. First, because the mean free path of the air molecules is longer than the pore size, direct gas conduction is inhibited. Additionally, silica has a low thermal conductivity and has infrared characteristics that inhibit radiative heat transfer.

Aerogel was first produced and its characteristics investigated by Kistler [4] over fifty years ago. Recent interest in aerogel resulted from the need for low refractive index materials for use in elementary particle detectors for Cherenkov counters [5-7]. Its application as a glazing material was first investigated by Schmitt [8] in 1980-82. Research on aerogels was initiated at LBL in 1981 with studies of its practicality and suitability as an insulating window material [1,2]. The goals of the study are to improve the optical and thermal properties of aerogel, develop methods to protect it from absorption of environmental moisture, discover less expensive synthesis methods, and develop a technology base for production of transparent aerogels.

PREPARATION OF AEROGEL

Silica aerogel is produced in two steps. First, a silicon alkoxide is hydrolyzed in the presence of a catalyst and a mutually miscible solvent. The product formed by the hydrolysis condenses to particles of SiO_2 that grow in size. Depending on the concentrations and pH, the particles will link together to form a semisolid material (alcogel) consisting of a matrix of extremely fine linked particles that incorporate the solvent. In the second step, the solvent is removed from the alcogel by a supercritical drying process. These processes are described in more detail in the following sections.

Hydrolysis and Gelation from Silicon Alkoxides:

Both acid and base catalyzed hydrolysis and condensation reactions give alcogels from alcohol solutions of alkoxides according to reactions:

$$Si(OCH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4CH_3OH$$

$$nSi(OH)_4 \rightarrow nSiO_2 + 2nH_2O \rightarrow \text{alcogel}$$

Silica aerogels, prepared by the base catalysis of $Si(OCH_3)_4$ have been used in Cherenkov radiation detectors [5-7]. Because $Si(OCH_3)_4$ is extremely toxic, an alternative material is highly desirable for commercial production of aerogel. A less toxic starting compound, $Si(OC_2H_5)_4$, was studied by Schmitt [8] using acid catalysis. However, these aerogels were not as clear as those produced by base catalysis of $Si(OCH_3)_4$ and tended to shrink during alcohol removal. To overcome these difficulties, it is desirable to find a method to base catalyze the hydrolysis and gelation of $Si(OC_2H_5)_4$. Schmitt [8] reported that he was unable to synthesize aerogel by base catalyzed $Si(OC_2H_5)_4$ because it gave white powdery material instead of a transparent aerogel.

We have successfully base catalyzed $Si(OC_2H_5)_4$ using ammonia and ammonium fluoride as catalysts. To obtain the desired transparency, strength, and stability of silica aerogel, a factorial design set of experiments were performed to optimize the preparation process.

Supercritical Drying of Alcogels

Alcogel is up to 98% by volume fine pores containing alcohol. The alcohol must be removed from the alcogel to obtain the aerogel material. Because the radii of the pores in the alcogel are extremely small, very high interfacial forces are generated between liquid and gas during conventional drying. Therefore, to prevent damage to the gel structure, supercritical drying under which there is no distinction between liquid and gas, and therefore no interfacial surface, is required. For methanol, the critical point is at 240°C and 8.0 MPa pressure. We have constructed a supercritical drying apparatus with computer controlled operation and data acquisition that is capable of providing conditions up to 300°C and 21 MPa. Typical supercritical drying conditions are 270°C, 12 MPa with a 0.2 to 0.5°C/min heating rate and pressure release at high temperature. These requirements make the process expensive and slow. Each drying batch requires 2 to 3 days.

We developed an alternative technique for supercritically drying silica alcogels at significantly lower temperatures [9]. Drying is done at 40°C instead of 270°C after substituting the alcohol in the gel with liquid carbon dioxide. The drying process is completed in 6 to 8 hours instead of the 2-3 days required for drying with alcohol. The lower temperature and the reduced processing times constitute major steps towards making aerogel production industrially viable. We compared the properties of aerogels dried by both the methods - CO_2 drying at 40°C and 8.3 MPa, and high temperature drying at 270° and 12 MPa - and found the gels to be similar.

RESULTS AND DISCUSSION

Light Scattering Studies

Because the transparency of aerogel is reduced by light scattering, measurements of scattering play an important part in judging its optical quality. An angular polar nephelometer was designed and constructed at LBL to study this light scattering. Scattered light is measured as a function of angle from the incoming beam and polarization. Lasers with wavelengths of

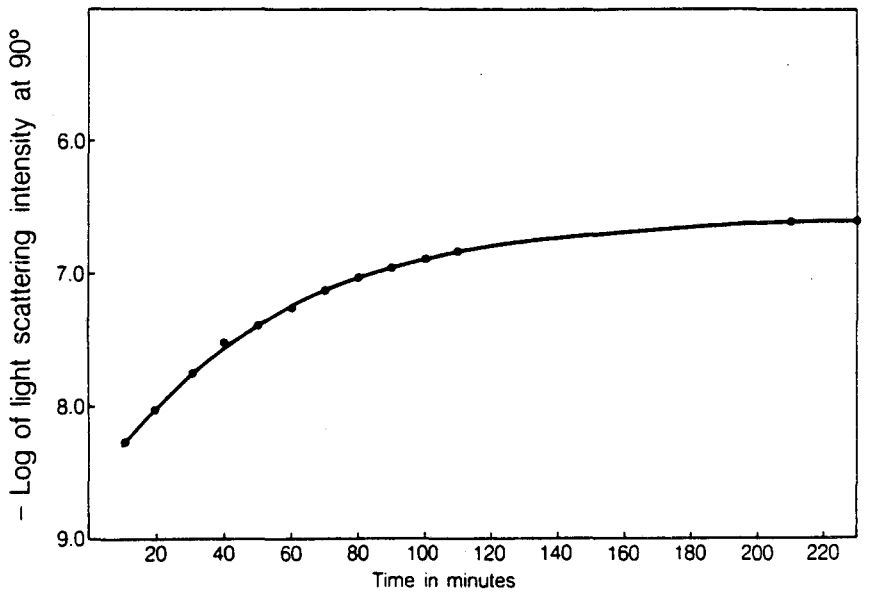

Fig. 1. Light scattering intensity of TEOS alcosol during gelation as a function of time.

425 or 633 nanometers provide collimated light. A rotating detector arm carries optics, detector, and selectable polarizers.

Results of the light scattering measurements were integrated with a scattering theory that identified the cause of scattering as due to density inhomogeneities [10,11]. Light scattering data provides an understanding of the microstructural properties of aerogel at all stages in its preparation. Measurement of scattering during the initial stages of gel formation enables us to control and optimize the parameters of particle size and density-uniformity to improve transparency. Light scattering measurements also enable us to determine the optimum time for drying and to follow the aging of the alcogel after its formation (Figure 1). Measurements before and after supercritical drying provide information about structural changes induced by drying. During removal of the alcohol, the measured light scattering intensity increases by a factor of 10 to 20 due to the change in index of refraction in the pores and shrinkage. Based on the refractive indices of alcohol (C_2H_5OH), silica, and air, it is estimated that light scattering intensity should increase by a factor of 10 in the aerogel.

Factorial Design Optimization

A series of gels were made and analyzed using a factorial design method. Experimental process parameters were varied over a wide range of conditions. Concentrations of alkoxide, water, alcohol, ammonia, and ammonium fluoride were simultaneously varied. Light scattering, optical transmission spectra, rheology, pH, shrinkage in drying, surface area of the aerogel, and transmission electron microscopy were used for the optimization.

The results were analyzed using a polynomial equation containing the various parameters. These calculations gave not only an evaluation of the significance and importance of the parameters but also the direction of change needed to optimize the process. For example, they indicated that for a better quality aerogel (one with low scattering), relatively low gelation temperatures and NH_4OH concentration should be used. Also, at gelation temperatures higher than 35°C, the light scattering quality of the aerogels cannot be improved by variation of NH_4OH. In this case, the aerogel will exhibit a large light scattering and hence a poor optical quality. A further optimization will be done to achieve the exact process conditions for the desired properties of low light scattering, high optical transparency, strength and environmental stability.

Transmission Spectra

Transmission spectra are similar for the base catalyzed aerogels dried by the high temperature and CO_2 drying method. There are minor differences in the NIR region, probably due to water in the unheated CO_2 dried sample, because in CO_2 drying, the aerogels are subjected to temperatures $\leq 40^{\circ}C$ compared to $\geq 270^{\circ}C$ in the high temperature method. Aerogels dried by the CO_2 substitution method and then heated in air are more nearly like those supercritically dried at high temperature. The transmission spectra of high temperature supercritically dried base catalyzed $Si(OCH_3)_4$ (TMOS) aerogel and CO_2 dried base catalyzed $Si(OC_2H_5)_4$ (TEOS) aerogel is shown in Figure 2.

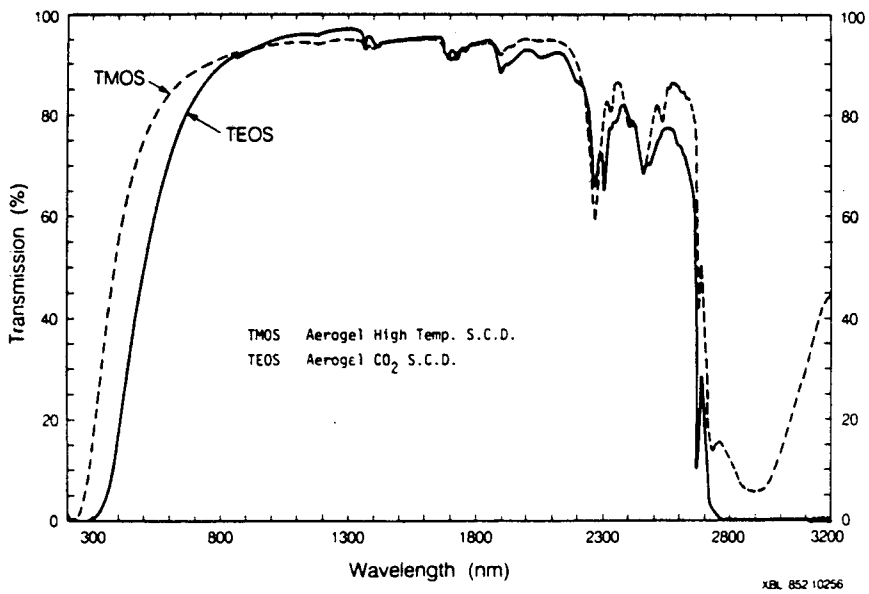

Fig. 2. Transmission spectra of base catalyzed TMOS aerogel dried by high temperature supercritical drying (S.C.D.), and TEOS aerogel dried by CO_2 method and heated to 450°C for 4-5 hours; both samples are 4 mm thick.

Reproducibility and Quality of Aerogels in CO_2 Drying

The reproducibility of aerogel is better for supercritical CO_2 drying than high temperature supercritical drying. The incidence of cracking or fracture of aerogels is significantly lower by the CO_2 method. Above all, there is a marked time saving in the CO_2 drying method, and the equipment for the CO_2 method is simpler and less expensive than that required for the high temperature supercritical drying.

SUMMARY AND CONCLUSIONS

We have made significant progress in the development of aerogel. New preparation methods using less toxic materials have been developed, and initial experiments have been successful in drying the alcogels at near ambient temperatures, making the commercial production of aerogel more feasible. Optical transmission, light scattering, and electron microscopy data show that CO_2 supercritical drying of alcogels produces aerogels similar in quality to those dried at the higher temperature. In addition, we have produced a base catalyzed $Si(OC_2H_5)_4$ aerogel similar in quality to the one prepared by $Si(OCH_3)_4$.

We have made an important step in understanding the properties of aerogel by developing an analytical framework that relates the causes of light scattering to the microstructural properties. However, further research is necessary prior to the commercial initiation of aerogel as a high performance glazing material. Methods of reducing the light scattering, improving the strength, and sealing aerogel for both evacuated and unevacuated applications are currently under investigation.

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