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Aerogel–aerogel composites for normal temperature range thermal insulations

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ABSTRACT

Aerogel–aerogel composites are prepared by embedding highly insulating granular silica aerogel (1–2 mm, 5–58 vol.%) into ambient pressure dried resorcinol-formaldehyde (RF) aerogel. The organic RF aerogel matrix is synthesized via a sol–gel reaction of resorcinol (1,3-dihydroxybenzene) and formaldehyde in deionized water with Na_2CO_3 as the catalyst. Plates around 90 × 195 mm² with a thickness of 19–25 mm are obtained and can be processed for application by sawing and grinding. A theoretical model for the volume-based surface area was used to show that the matrix aerogel around the silica aerogel grains is affected by their presence. Composites have a density $0.19 \le \rho \le 0.27$ g/cm³ and a thermal conductivity at room temperature between 0.026 and 0.053 W/mK. Composites can be used as thermal insulation material in a normal temperature range < 200 °C due to the decomposition of the organic phase above 200 °C.

1. Introduction

A suitable thermal insulation is necessary in many application fields, for example in aerospace (airplanes, spacecraft), in ground-based vehicles, in building constructions, in air-conditioning systems or in industrial processes [1–3], to reduce costs and to reduce the emission of CO_2. Due to the global need of insulation the development of more efficient insulating products is necessary.

Aerogels have great potential to be used as thermal insulation material due to their low density (0.01–0.3 g/cm³), high specific surface area (100–2000 m²/g) and low thermal conductivity (<0.02 W/mK) owing to their highly porous (up to 99%) nanostructure [4]. The porosity and small pores of a few nanometers diameter effect the diffusive and convective gas transport and the heat conduction through the solid material, so that a very low thermal conductivity as low as 0.012 W/mK can be reached [5,6]. Commonly used thermal insulation materials are polymer foams like polyurethane (0.020–0.029 W/mK) or expanded polystyrene (0.029–0.055 W/mK), or inorganic wool (0.031–0.045 W/mK) and foam glass (0.038–0.050 W/mK) [7]. Values of thermal conductivity point out the competitiveness of aerogels in the field of insulation.

In general, aerogels are synthesized by a sol–gel reaction and the product is obtained after drying of the gel using a suitable drying method that minimizes damage of the three-dimensional solid network. Approved processes are supercritical drying (mostly with CO_2) or freeze drying [8,9]. Different aerogels are known and can be inorganic, organic or hybrids [4,9]. First aerogels were developed in 1931 by Kistler [10] who prepared silica aerogels via the sol–gel reaction of sodium silicate with hydrochloric acid and finally dried gels obtained under supercritical conditions. The massive development of organic aerogels started later in the 1980s when Pekala [11] published his work about the synthesis of resorcinol-formaldehyde (RF) aerogels. RF aerogels are obtained after the sol–gel reaction of resorcinol (1,3-dihydroxybenzene) and formaldehyde in an aqueous solution [12,13], followed by solvent exchange and supercritical drying. In 1997, Fischer et al. [14] first published ambient pressure (mostly called subcritically) dried RF aerogels by employing a lower base catalyst concentration (molar ratio resorcinol (R) to catalyst (C) R/C = 1000–1500) than Pekala did (R/C ≤ 300). In a RF solution with a low base catalyst concentration less but bigger particles are formed with a size of about a few hundred nanometers up to a few microns. The walls of the network are then strong enough to withstand the capillary forces during subcritical drying, *i.e.* evaporation of the solvent [15].

Using aerogels as insulation material is a challenge since the brittleness of aerogels complicates the handling, and the release of dust is furthermore not desired. More practicable is the use of granular aerogels instead of monolithic ones which can be fixed in a more stable matrix like polyurethane [16], melamine foams [17] or another aerogel [18,19]. The important characteristics of the granular aerogel might be best maintained by using an aerogel as the matrix. In our study, we developed aerogel–aerogel composites for the application as insulation material in a shape of plates. The present paper describes the synthesis of aerogel–aerogel composites using ambient pressure dried resorcinol-formaldehyde (RF) aerogel and highly insulating granular silica aerogel which was embedded in the RF matrix. Characterization was performed under the aspect of structural, mechanical and thermal properties.

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2. Experimental procedures

2.1. Materials

Granular, hydrophobic silica aerogel (Lumira®) was supplied by Cabot Corporation (Germany) and the particles used have diameters between 1 and 2 mm. The chemicals for the aerogel synthesis are resorcinol (>98%, Sigma-Aldrich), sodium carbonate (Na_2CO_3, puriss. p.a. ≥ 99.8%, Sigma-Aldrich) and a 24% aqueous formaldehyde solution (not buffered, VWR BDH Prolabo).

2.2. Sample preparation

A resorcinol-formaldehyde (RF) solution is prepared by dissolving 660.7 g of resorcinol (R) and 0.4240 g of the catalyst sodium carbonate (C) in 2099 g of deionized water (W). Then, 1021 g of a 24% formaldehyde solution (F) is added while stirring starting the sol–gel reaction of resorcinol with formaldehyde. The recipe contains the molar ratios R/C = 1500, R/W = 0.03761 and R/F = 0.7354. After 10 min of stirring the RF solution is divided into parts between 150 and 500 mL and filled in a sample box of 1 L capacity. The volume of RF solution depends on the intended volume fraction of granular silica aerogel. The total volume of the RF solution with the granulate material (measured with a graduated cylinder) was chosen to be 500 mL. Subsequently, the solution is stored closed to prevent evaporation of the liquid components for 7 days at room temperature and then about 6 h at 5 °C in a fridge. Granular silica aerogel (8–63 vol.%) is mixed with the RF solution to a homogeneous mixture when the solution achieves a high viscosity so that only a slight flow of the RF solution occurs when a hole is created with a spoon. At this point the gel point is not yet reached. In order to remove air bubbles from mixing the composite is placed into a vacuum chamber (<100 mbar) for 4 min. The mixing procedure is followed by gelation, aging (7 days) and drying (7 days) in an oven at 40 °C.

2.3. Characterization

Density was measured using the envelope density analyzer GeoPyc® 1360 from Micromeritics. In order to characterize the structure and the interfaces of the materials a Merlin® field emission scanning electron microscope (FE-SEM) from Zeiss was used after sputtering the samples with gold. The specific surface area was obtained using nitrogen adsorption with the analyzer TriStar II 3020 from Micromeritics and was calculated using the Brunauer–Emmett–Teller (BET) model [20]. A uniaxial compression test was performed on cubic samples (edge length about 15 mm) with a testing instrument from Latzke, and the stiffness E' was calculated from the slope of the stress-strain curve between 2 and 8% strain. The thermal conductivity was measured using the transient plane source (TPS) method realized in the Hot Disk™ TPS 2500 from Hot Disk AB. A sensor with a radius of 14.61 mm was used, and the measurement was performed at ambient pressure and at room temperature (22 ± 2 °C). The heat flow meter HFM 436 from Netzsch was used additionally to investigate the thermal conductivity at ambient pressure and at 25.0 ± 0.5 °C. The measurement was performed on samples in the dimension of 140 × 140 × 20 mm³. The thermogravimetric measurement was operated with a TG thermoanalyser TG 209 F1 Iris® (Netzsch) from 22 to 1000 °C under argon flow (20 ml/min) and a heating rate of 10 °C/min.

3. Results

3.1. Appearance and density

Aerogel–aerogel composites synthesized are light brown or ocher (RF aerogel) and contain dispersed particles which are actually transparent (silica aerogel) but appear brown due to RF. The size of the composites prepared is about 90 × 195 mm² with a thickness of 19–25 mm, and samples with the dimension of 140 × 140 × 20 mm³ were prepared additionally. Samples need a finishing treatment after preparation to smooth the surface and to process the shape desired for the application. The shape of the composite can be adjusted by sawing and grinding with fine sandpaper (mean grain size ~ 22 μm). One piece of the sample in the dimension of 80 × 59 × 19 mm³ containing 43 vol.% of silica aerogel is shown in Fig. 1 after the finishing treatment.

For the density of a composite ρ_c a simple theoretical relation

$$\rho_c = \rho_{sil}\phi_{sil} + \rho_{RF}\phi_{RF} + \Delta\rho \tag{1}$$

holds, where ρ_{sil} and ρ_{RF} are the densities and ϕ_{sil} and ϕ_{RF} are the volume fractions of the two components silica aerogel and RF aerogel and $\Delta\rho$ is a possible deviation resulting from a reaction between the components which can be neglected since no reaction occurs. Densities of composites ρ_c as the function of ϕ_{sil} are shown in Fig. 2 (squares). ϕ_{sil} is calculated from the volume of the granulate material V_{sil} with the assumption that the granular silica aerogel builds a packing density with a volume ratio of 74%:

$$\phi_{sil} = \frac{0.74 \cdot V_{sil}}{(V_{sil} + V_{RF})} \tag{2}$$

where V_{RF} is the volume of RF solution.

The graph demonstrates that values of ρ_c are between the density of the pure components silica aerogel (ρ_{sil} = 0.12 g/cm³) and RF aerogel (ρ_{RF} = 0.28 g/cm³). The lowest density (0.19 g/cm³) was obtained with the highest volume content of silica aerogel (63 vol.%); higher values up to 0.27 g/cm³ (8 vol.% of silica aerogel) are achievable with lower volume content of silica. A trend to higher density compared to the average according to Eq. (1) (dotted straight) exists.

3.2. Structural properties

Scanning electron microscopy (SEM) was performed to investigate the interfaces of silica aerogel grains and the RF aerogel matrix. In general, both aerogel structures consist of a three-dimensional network formed by small particles within nanometer scale but with the difference in average size of particles. RF particles are much larger (200–400 nm) than silica particles (<50 nm) as one can identify in the SEM images in Fig. 3. Two different SEM images are shown in Fig. 3 illustrating two different situations: in the left image (Fig. 3a) it is shown that between a silica aerogel grain (top right) and the RF aerogel matrix a gap is present. It seems that both aerogels are only partly in direct contact. In contrast to that, in the right image (Fig. 3b) one can see that both aerogels are connected with their surfaces. The interface is noticeable as a clear border without any mixed phase.

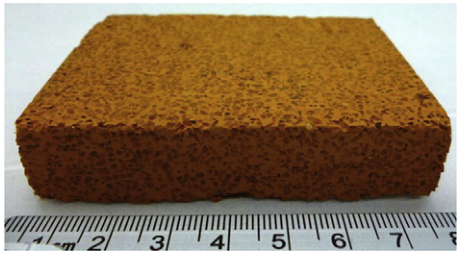

Fig. 1. Photograph of an aerogel–aerogel composite, consisting of resorcinol-formaldehyde (RF) aerogel matrix and 43 vol.% of granular silica aerogel, after finishing treatment (dimension: 80 × 59 × 19 mm³).