The effect of embedding highly insulating granular aerogel in cellulosic aerogel

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ABSTRACT

We investigate aerogel–aerogel composites to develop new materials for thermal insulation applications with reduced fragility and without release of dust. Two different kinds of highly insulating silica aerogels (SiO_2) were embedded into a cellulosic aerogel: a high-density ($0.25 \, g/cm^3$) tetramethylorthosilicate (TMOS) based and a low-density ($0.15 \, g/cm^3$) waterglass based hydrophilic granular silica aerogel which are added to the salt hydrate melt of 59 wt.% calcium thiocyanate and 2 or 3 wt.% of cellulose during the synthesis of a cellulosic aerogel. The silica aerogel species show a different behavior regarding the interaction with the cellulose network in the composite examined by scanning electron microscopy. With the synthesis method we were able to produce non-fragile aerogel–aerogel composites and a strong stiffening effect regarding Young's modulus was achieved compared to pure aerogels. Density obtained is 0.04–$0.15 \, g/cm^3$ and thermal conductivity reached is between 0.04–$0.05 \, W/mK$.

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1. Introduction

An efficient thermal insulation for example in vehicles, in building constructions, in air-conditioning systems or in industrial processes is required in order to reduce costs and to reduce the emission of CO_2. Aerogels are promising candidates for the application as thermal insulation material due to their properties of low thermal conductivity about $0.015 \, W/mK$ and low density (0.01–$0.3 \, g/cm^3$) caused by their nanoporous structure [1–3]. These characteristics underline the competitiveness of aerogels with commonly used insulation products as 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–$0.050 \, W/mK$) [1]. Silica aerogels (SiO_2) are a material not causing additional risk in thermal insulation because they are inflammable and stable at high temperatures ($\approx 1000 \, °C$). They can therefore be applied as crucible material for example for aluminum alloys [4]. According to Folgar et al. [5] no significant structural changes are observed for hydrophilic aerogels between 25–700 °C but higher temperatures (>700 °C) causes densification of the material and a substantial decrease in pore volume. Hydrophobic silica aerogels can be converted into hydrophilic ones from thermal treatment because surface methyl groups ($-CH_3$) oxidize completely at a temperature above 430 °C [6,7].

The inorganic silica aerogels are synthesized via a sol–gel process and supercritical drying of the gel which was first published 1931 by Kistler [8,9], who used an aqueous sodium silicate solution (waterglass) and hydrochloric acid. Other routes contain the polymerization of alkoxysilanes $(SiOR)_4$ (e.g., tetramethylorthosilicate, TMOS) in a mixture of an organic solvent with water through hydrolysis and a condensation reaction [10].

Pure silica aerogels are mostly fragile and tend to release dust on handling. Therefore, in industry a trend may be observed that granular silica aerogel instead of monolithic ones are used and are then applied for the synthesis of particulate composites to obtain a stable product. The matrix can be polymers like polyurethane [11–13], melamine foam [14] or other aerogels [15,16] in order to maintain best the important characteristic properties of aerogels.

A potential matrix for particulate composites is cellulosic aerogel which is an interesting organic material since it consists of the re-growing and non-hazardous bio-polymer cellulose. The synthesis of cellulosic aerogels is not a classical sol–gel reaction as it is for inorganic aerogels. The synthesis is a combination of dissolution and regeneration of cellulose followed by a suitable drying method (freeze drying, supercritical drying) to avoid considerable shrinkage yielding eventually a non-dusty and open porous material [17]. In addition to the drying method, the important step to produce cellulosic aerogels is the formation of a gel by using a suitable

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solvent agent. Jin et al. [18] first described the synthesis of aerogels from raw cellulose by using as solvent a calcium thiocyanate ($Ca(SCN)_2$) hydrate melt according to Kuga [19] in which the bio-polymer in solution builds a nanofibrillar felt structure while cooling below 80 °C. Other routes include the use of the systems NaOH/water or NMMO/water [20–22]. In all cases pure cellulosic aerogels usually have density between 0.04 and 0.3 g/cm^3; lowest values for thermal conductivity were 0.029–0.032 W/mK reported by Nguyen et al. [23].

The present paper describes the synthesis of aerogel–aerogel composites consisting of cellulosic aerogel as the matrix embedding highly insulating granular silica aerogel. Two different silica aerogels available on the market were tried and the usage of cellulosic aerogels as the matrix is evaluated. Characterization was performed under the aspect of structural (density, SEM), mechanical (compression test) and thermal properties (thermal conductivity).

2. Experimental

2.1. Materials

Chemicals used for the synthesis of cellulosic aerogels are calcium thiocyanate $Ca(SCN)_2 \cdot 4H_2O$ (95%, Sigma–Aldrich) and cellulose powder (cellulose fibers, medium, Sigma–Aldrich) obtained from cotton linters. The mean degree of polymerization (DP) of cellulose fibers is 201 as determined at the Institute for Textile Engineering, ITA, RWTH-Aachen using the Cuoxam method based on the change in viscosity of cellulose DP in Cuoxam solution. Low-density and hydrophobic granular silica aerogel (Lumira® aerogel particles) is supplied by Cabot Corporation (Germany) and high-density and hydrophilic monolithic silica aerogel is from Airglass AB (Sweden). The washing step of the composite gel is performed with ethanol (96%, denatured, Th. Geyer).

2.2. Synthesis

2.2.1. Preparation of granular silica aerogel

Low-density (0.15 g/cm^3) waterglass based, hydrophobic silica aerogel (LD-silica) grains supplied by Cabot Corporation have average diameter of about 0.5–5 mm which were separated by sieving with mesh sizes of 0.25, 0.5 and 1 mm. In order to get hydrophilic grains necessary for the preparation of aerogel–aerogel composites they were thermally treated at 600 °C for 3 days. Hydrophobic organic groups (methyl groups) oxidize during the thermal treatment and hydrophilic grains are obtained.

Tetramethylorthosilicate (TMOS) based and hydrophilic high-density (0.25 g/cm^3) silica (HD-silica) aerogel monoliths from Airglass AB are crushed with hands and the grains generated are sieved in the same way the LD-silica grains were separated. Since silica aerogel grains are already hydrophilic no thermal treatment is necessary.

An easy electrical conducting test of 10 mL granular material in 150 mL deionized water (3.0 μS/cm) was performed to test if any impurity exists in the pores of silica aerogels. The conduction changed to 13 μS/cm with HD-silica and to 6 μS/cm with LD-silica aerogel indicating a certain amount of water soluble residual impurities remained after synthesis of silica aerogels. In the HD-silica (TMOS based) probably residual ammonia used as catalyst [24] is still present in the pores, whereas in the LD-silica (waterglass based) impurities in terms of sodium chloride is possible. Sodium chloride are generated from waterglass and hydrochloric acid added to initiate the sol–gel process [25].

2.2.2. Synthesis of aerogel–aerogel composite

The synthesis of the composites is similar to the synthesis of pure cellulosic aerogels [26] but with an additional step. Firstly, 1.137 g or 1.705 g of cellulose and 49.0 g of $Ca(SCN)_2 \cdot 4H_2O$ are filled into a beaker and mixed with a stirring rod. 7.8 mL of deionized water is then added resulting in a suspension with 59 wt.% of $Ca(SCN)_2$ and 2 or 3 wt.% of cellulose. The suspension is heated up to 110 °C with an oil bath and is stirred frequently and carefully with the stirring rod. As soon as the salt is melted 1, 2 or 3 wt.% of granular silica aerogel related to the complete approach is added still stirring with the rod. After 20 min of heating the viscosity of the melt increases having then a consistency of honey and a clear solution in which no cellulose powder can be seen is obtained. We assume that at this point cellulose is completely dissolved. The hot solution is then filled into a sample box (polypropylene) and the surface is covered by ethanol. While cooling below 80 °C cellulose starts to regenerate and builds a nanofibrillar felt structure. After 24 h the gels are released from boxes and are washed several times with ethanol using a Soxhlet extractor to remove the salt from pore space. The washing step is finished when the test with Fe^{3+} ions does yield a colorless solution what proofs the absence of SCN^- ions qualitatively. The presence of SCN^- ions leads to a dark red solution caused by the red complex $[Fe(SCN)_3(H_2O)_3]$ and shows that the salt is not yet removed. After sufficient washing the gels are dried with supercritical CO_2 performed in an autoclave developed by Eurotechnica GmbH (Germany). At 55 °C and with 90 bar supercritical CO_2 circulates through the system and removes ethanol from pore space. The solvent is extracted and collected in a separate vessel so that CO_2 can be recycled. When no more ethanol is obtained in the collection vessel the pressure is slowly and completely released with 0.3 bar per min.

2.3. Methods

Bulk density was measured with the envelope density analyzer GeoPyc® 1360 and skeletal density was determined using the helium pycnometer AccuPyc® II 1340 both from Micromeritics. Specific surface area was obtained from nitrogen adsorption measurement with the analyzer TriStar® II form Micromeritics by using the BET method. In order to characterize the structure and the interfaces of the grains and the matrix a field emission scanning electron microscope (FE-SEM) Merlin® from Zeiss was used after sputtering the sample with gold. Fourier transform infrared spectroscopy (FTIR) was performed with a Bruker–Tensor 27 instrument. The thermal conductivity was obtained from HotDisk™ method with the thermal constants analyzer type TPS 2500. The radius of the sensor was $r = 6.403$ mm. A uniaxial compression test was realized with a compression machine from Latzke (Germany) on cubic samples (edge length about 15 mm) implemented with a pressure gauge with a maximum of 500 N. Young's moduli were calculated from slopes of stress–strain curves.

3. Results and discussion

3.1. General properties

Aerogel–aerogel composites consisting of a cellulosic aerogel matrix and granular silica aerogel appear white (Fig. 1) similar to pure cellulosic aerogel but with a difference in haptic. In contrast to cellulosic aerogels the composites release dust while cutting due to the loss of silica grains. Cellulosic aerogels are easily deformable with fingers what is hindered if silica grains are embedded in the matrix.

Fig. 2 shows the density ρ of the composites as a function of volume fraction of silica φ_{silica} compared to the pure materials