



Nanostructured interpenetrated organic-inorganic aerogels with thermal superinsulating properties



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ABSTRACT

Organic-inorganic composite aerogels were synthesized via a facile one-step impregnation of a wet hydrophobic cellulose II matrix with polyethoxydisiloxane solution followed by in situ NH_4OH -catalysed formation of a nanostructured mesoporous silica network. The silica phase was subsequently hydrophobised with hexamethyldisilazane. By tuning synthesis conditions, organic-inorganic composite aerogels with various morphology (from meso- to macroporous), specific surface area (from 200 to 850 m^2/g) and hydrophilic-hydrophobic balance (from fully hydrophilic to highly hydrophobic) were prepared after supercritical CO_2 drying. The obtained organic-inorganic aerogels are monolithic, resistant to humidity and thermally superinsulating with the thermal conductivity 0.021–0.022 $\text{W}/(\text{m}\cdot\text{K})$ in room conditions.

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1. Introduction

Aerogels are known to be lightweight (density $< 0.2 \text{ g}/\text{cm}^3$) materials with open porosity; they are usually mesoporous with high specific surface areas up to 800–1000 m^2/g . Aerogels are synthesized via sol-gel route either from organic (polymer, e.g. resorcinol-formaldehyde or polyurethane) [1–3] or inorganic (typically, SiO_2) [4] systems. In most of the cases the drying of gels is performed with supercritical (sc) CO_2 to prevent pore collapse because of the high surface tension created between the evaporating liquid and the vapor phase. Some aerogels are thermal “superinsulating” materials defined as those having thermal conductivity below that of air in ambient conditions, i.e. 0.025 $\text{W}/(\text{m}\cdot\text{K})$ [5]. The most performing are mesoporous resorcinol formaldehyde [6] and silica [5] aerogels with the thermal conductivity as low as 0.012–0.015 $\text{W}/(\text{m}\cdot\text{K})$ in room conditions. This unique property is due to their low density and pore sizes below the mean free path of air molecules which is around 70 nm in standard conditions (i.e. 25 °C and 1 atm), together with a tortuous and nanostructured solid backbone. Such ultra-low thermal conductivity makes aerogels very promising materials for lowering energy losses using thin components in buildings', pipelines' or refrigerators' insulation. Despite this extraordinary property, silica aerogels are not yet widely used because of mechanical fragility and relatively high production cost, and resorcinol-formaldehyde because of their toxic synthesis route.

Recently, we reported on new bio-aerogels prepared from pectin: “Aeropectin” has thermal conductivity between 0.018 and 0.020 $\text{W}/(\text{m}\cdot\text{K})$ at ambient conditions and is mechanically much stronger than silica aerogels (plastic deformation without breaking up to 70–80% strain) [7]. However, as pectin is intrinsically hydrophilic, Aeropectin adsorbs moisture from the air leading to an irreversible collapse of the pores and associated densification after capillary condensation. Another thermal superinsulating bio-aerogel, from nanofibrillated cellulose [8], should also suffer from the same drawback.

Several ways are reported to improve the mechanical properties of silica aerogels. One involves the modifications of silica phase itself, for example, i) using methyltrimethoxysilane (MTMS) or methyltriethoxysilane instead of tetraethoxysilane (TEOS) [9,10], or ii) via a cross-linking way [11,12], i.e. functionalization of silica with organic (e.g. amines) moieties followed by “growing” of an organic matrix, leading to formation of cross-linked organic-inorganic aerogels, or by using interpenetrating network approach (silica gelation inside the macropores of polystyrene gel or gelation of polystyrene in the silica gel) [13]. An interesting “one-pot” approach was reported in ref. 14: silica and pectin solutions were mixed, silica phase hydrophobised and dried with sc CO_2 resulting in superinsulating, hydrophobic and mechanically strong aerogels. Another way is to use “composite” approach, i.e. to reinforce silica matrix i) with dispersed “fibers” (for example, sepiolite with high aspect ratio) [15] or ii) by impregnation of silica sol in a non-woven fibrous matrix which leads to the formation of so-called blankets [16]. It must be underlined that this “composite” processing route allows maintaining the global cohesion of the mineral matrix after subcritical drying but does not reinforce the silica aerogel itself. All these different routes generally allow

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improving the mechanical properties of silica aerogels but are often accompanied by an increase of thermal conductivity mainly because of i) the creation of huge macroporosity (e.g. Ormosil), ii) too important densification (cross-linking approach) or iii) phonon transport of heat along the “added” fibers (composite approach). Recently, cellulose nanofibrils, which possess excellent mechanical properties, were used as a fibrous network to reinforce silica aerogels: it was either bacterial cellulose [17], or nanofibrillated cellulose (NFC) [18,19]. In the first case bacterial cellulose fibrous mat was freeze-dried before being impregnated with silica-based sol and then freeze-dried again to obtain dry composites: despite the improved compression properties, the superinsulation property of silica aerogels was “lost”: the thermal conductivity of composite aerogels varied from 0.030 to 0.037 W/(m·K) with the lowest value obtained for pure bacterial cellulose aerogel. When nanofibrillated cellulose was used, two approaches were taken, both leading to very interesting results: i) NFC was dispersed as suspension in MTMS-based sols and the resulting gels were dried with sc CO₂: hydrophobic and bendable aerogel composites with a thermal conductivity ranging from 0.015 to 0.025 W/(m·K) were obtained [18] and ii) NFC was silylated, freeze-dried, impregnated with silica sol and dried with sc CO₂, resulting in thermal conductivities from 0.014 to 0.020 W/(m·K) and improved, as compared to the reference silica aerogel, mechanical properties [19].

In this work, we took another approach: as a background, we used our previous results obtained on the synthesis of cellulose II aerogel, so-called Aerocellulose [20,21]. Aerocellulose is prepared via cellulose dissolution, coagulation and drying with sc CO₂, and Aerocelluloses of various shapes, from cylinders [20] to flat disks and beads [22] can be made. Before drying, wet coagulated cellulose can be impregnated with silica sol followed by silica gelation in the pores of cellulose matrix. This approach was recently reported in refs. 23–25, where TEOS or sodium silicate (Na₂SiO₃) was used. For the case of TEOS, the specific surface area of composite aerogel increased significantly, indicating clearly the formation of nanostructured silica in the pores of cellulose [23]. However, thermal conductivity of composite aerogels increased from around 0.025 W/(m·K) for the neat Aerocellulose to 0.030–0.045 W/(m·K) for composite aerogels, and their mechanical properties slightly decreased as characterized by uniaxial compression [23]. When sodium silicate was used for the impregnation, the specific surface area remained the same or even slightly decreased from 320 m²/g for the neat Aerocellulose to 270 m²/g for the composite aerogels, and a thermal conductivity was not reported [24]. A decrease in the thermal conductivity for composite aerogels to 0.026–0.028 W/(m·K) vs 0.033 W/(m·K) for the neat Aerocellulose and improved mechanical properties were reported in ref. 25. To the best of our knowledge, no thermal superinsulating properties were reported for cellulose II based neat or organic-inorganic aerogels. Several reasons can be given: too high conduction of cellulose solid phase, presence of a non-negligible fraction of large macropores and also cellulose hydrophilicity which induces aging and thus increases the thermal conductivity through densification of the matrix.

In the present work we first functionalise cellulose to obtain a hydrophobic matrix to avoid posterior cellulose aging due to moisture adsorption. Wet coagulated functionalised cellulose is then impregnated with TEOS-based sol and dried with sc CO₂. We demonstrate that hydrophilic-hydrophobic properties of the so-obtained composite aerogels can be tuned by hydrophobisation of each phase. Composite aerogels were characterized in terms of density, morphology, specific surface area as well as mechanical properties and thermal conductivity.

2. Experimental section

2.1. Materials

Microcrystalline cellulose Avicel (“cellulose” in the following) with a degree of polymerization of 180 (as given by the manufacturer) and hexamethyldisilazane (HMDZ) (98% purity) were purchased from Sigma Aldrich. Triphenylmethyl chloride (98%

purity), dimethylacetamide (DMAc) (99% purity), lithium chloride (99% purity), NH₄OH (35 wt% aqueous solution), methanol, dimethylformamide (DMF), NaOH, absolute ethanol and pyridine (purity >95%) were purchased from Fisher Scientific.

Polyethoxydisiloxane (PEDS) was in the prepolymerized form of TEOS, prehydrolyzed under H₂SO₄ catalysis in ethanol, with SiO₂ concentration of 20 wt% in ethanol; it was kindly provided by ENERSENS, Bourgoin-Jallieu, France.

Cellulose was dried in a vacuum oven (50 °C, 50 mbar) for two hours before use. All other solvents and chemicals were used as received.

2.2. Drying

All samples were dried with sc CO₂ as described previously [7,25]. Briefly, the samples were placed in a 1 L autoclave containing ethanol to avoid solvent evaporation. The system was pressurized at 50 bars and 37 °C with gaseous CO₂. Ethanol was purged with CO₂ and the system was pressurized at 80 bars and 37 °C. The dynamic washing step with 5 kg CO₂/h was carried out for 1 h. The system was then let in a static mode for 1–2 h at the same pressure and temperature; dynamic washing was performed with the same CO₂ output for 2 h. The system was then slowly depressurized at 4 bars/h and 37 °C and cooled down to room temperature [26].

2.3. Characterization

FTIR spectroscopy was performed using a Bruker Tensor 27 TGA-IR with OPUS 5.6 software. Air was measured as reference and set as the baseline.

Sample densities were measured with powder pycnometer Geopyc 1360 from Micromeritics.

The morphology of the samples was studied using high resolution scanning electron microscope (SEM) SEM-FEG Zeiss Supra 40. Samples were coated with a 7 nm platinum layer on a QUORUM Q150T rotating metallizer before observations.

Philips XL30 environmental scanning electron microscope coupled with Energy Dispersive Spectroscopy (EDS) was used to study silicon distribution inside the composite aerogels.

Specific surface area was determined using BET treatment of N₂ adsorption isotherms at 77 K on ASAP 2020 apparatus from Micromeritics. Samples were degassed for 300 min at 70 °C before analysis. Although sorption isotherms were recorded over the full range of relative pressure, significant in-situ deformation effects were observed; therefore no pore size distribution was calculated [27].

Elemental analysis for carbon was performed at the Service Central d'Analyse, CNRS, Villeurbanne, France, by atomic absorption spectroscopy using a Microanalyzer CHN, allowing calculation of the degree of substitution in modified cellulose.

Water contact angle θ(H₂O) measurements were performed with a Krüss Drop Analyzer DSA 100 goniometer and Drop Shape Analysis software.

For water vapor uptake measurements, the sample was placed in controlled climate chamber from Binder at 20 °C and 20% relative humidity (%RH) for 24 h and the mass m_0 and volume V_0 of the sample at this “dry point” were recorded. The sample was then submitted to 30 °C and 80%RH for 30 h (time needed for weight and volume stabilization as it will be shown in Results section), and sample weight H_m and volume H_v change were recorded as a function of time:

$$H_m(\text{wt}\%) = \frac{m_t - m_0}{m_0} * 100 \quad (1)$$

$$H_v(\text{vol}\%) = \frac{V_0 - V_t}{V_0} * 100 \quad (2)$$

where m_t and V_t are sample weight and volume at time t , respectively,

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