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Lightweight superinsulating Resorcinol-Formaldehyde-APTES benzoxazine aerogel blankets for space applications

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ABSTRACT

The purpose of this study was to develop an easy to handle, light, superinsulating material for space application. A benzoxazine organic-inorganic hybrid aerogel blanket was developed in a one-pot sol-gel synthesis. Crosslinking between a resorcinol-formaldehyde matrix and a (3-Aminopropyl)triethoxysilane (APTES) matrix was confirmed by the presence of oxazine rings. The polyethylene terephtalate mat used as blanket core limited shrinkage compared with the organic matrix alone, provided mechanical reinforcement, and allowed obtaining very low apparent density materials of high user convenience. The materials' characteristics (morphological, thermal, chemical and hydric) were found to depend on the sol formulation. Blankets featured apparent densities as low as 0.03 g cm^{-3}, low water weight uptake (1.65 wt.%) in humid conditions (80% HR and 20 °C) or thermal conductivities as low as 0.019 W m^{-1} K^{-1} in room conditions.

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1. Introduction

For obvious reasons, the demand for innovative energy-saving materials is growing. Although the building sector remains the main interested party for new energy-efficient materials, other applications are concerned as well. In space (full vacuum conditions, $P < 10^{-5}$ mBar), for instance, heat transfer occurs by solid conduction and/or by radiation only. Insulation is generally provided by Multi-Layer Insulation (MLI), based on a stack of multiple thin reflectors with very low infrared emissivity. MLI are presently the most efficient technical solution, with performances far above those of any other thermal insulation materials with comparable mass and envelope [1]. However, when the pressure differs from zero, MLI performance decreases rapidly. The thermal conductivity of a typical MLI blanket may increase by two orders of magnitude between full vacuum conditions (in spacecraft thermal control conventionally defined as $P < 10^{-5}$ mBar = 0.001 Pa) and a pressure of 1 mBar (100 Pa). For cargo modules or manned or unmanned compartments in ascent/(re-)entry vehicles or on Mars surface where an atmosphere is present, MLI becomes less efficient and alternative materials are needed [2].

Aerogels have been known for many years as the solids presenting the lowest thermal conductivity at ambient pressure ever measured [3], with conductivities as low as 0.012 W m^{-1} K^{-1}. Therefore, aerogels are very promising candidates to solve above-mentioned issues MLI face i.e. in environments where convection and gas conduction take place. In order to be used for space applications aerogels have additionally to present a low apparent density, be easy to handle and to shape. In this

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context, the aim of the present work was to develop new aerogel materials presenting a favorable compromise regarding thermal conductivity (<0.03 W m^{-1} K^{-1}) and apparent density (<0.05 g cm^{-3}).

Silica aerogels are the most widely known type of thermally insulating aerogels. Even so, they are rather fragile materials, even if tuning their sol-gel synthesis parameters allows improving mechanical properties, like compressive strength, significantly [4]. Several promising composites have already been developed and are presently commercialized (so-called silica-based blankets) but remain elements releasing much powder. Today, many studies are thus dedicated to reinforcing the mechanical properties of silica aerogels. One promising method currently studied involves via organic-inorganic hybridization [5], as organic aerogels are known to possess better mechanical properties than their silica counterparts [6]. Various interpenetrated networks have been synthesized at lab-scale based, for instance, on coupling silica with polyurethane [7] or with bisphenol [8,9]. One of the main methods studied within the aerogel community for enhancing an aerogel's mechanical properties is based on cross-linking (i.e. covalent coupling between organic and mineral matrices after chemical grafting of silica [10]. However, this synthesis process involves several steps. Recently, research on "one-pot" processing methods has begun to emerge [11,14]. Among the different studies on this topic, several focus on coupling silica with resorcinol-formaldehyde (RF). The main purpose of these studies was to produce organic-inorganic materials as precursors to silicon carbide [11–14]. These materials are developed for different applications such as high temperature structure materials or support or carrier for catalytic applications. No studies have been done to prepare and to evaluate these organic-inorganic materials for thermal superinsulation, nor on the addition of a mat to reinforce the final blanket. Therefore, we have carried out a systematic study of the synthesis parameters' influence on the effective thermal conductivity versus apparent density, parameters particularly important for space applications. We selected a RF-APTES aerogel blanket route permitting to combine multiple advantages like:

- contribution of RF aerogel well known to be the most insulating organic aerogel [15].
- simple processing i.e. "one pot" synthesis limiting the number of synthesis steps,
- synthesis of benzoxazine materials which are materials prepared from phenols, formaldehyde, and primary amines [16] used in a variety of applications in the industry of composites, coatings, adhesives, the manufacturing of encapsulants [17] because of their capability to exhibit thermal and flame retardant properties [18] of phenolics along with mechanical performance and molecular design flexibility,
- possibility of obtaining both low density and low thermal conductivity necessary for special applications like space travel,

Blanket-type samples were prepared by impregnating a mat with a mix of resorcinol, formaldehyde and APTES. We observed the influence of the mat on the properties of the final material by comparing the characteristics of the final material either containing a mat core or without a mat core (aerogel). We varied systematically the sol-gel composition to obtain blankets with different characteristics in order to meet the specifications for space travel in terms of apparent density and thermal conductivity for pressures above zero.

2. Experimental

2.1. Materials

Resorcinol (R), formaldehyde (F) (37% w/w aqueous solution) and ethanol (99.9%) were purchased from Fischer Scientific while (3-Aminopropyl)triethoxysilane (APTES) was obtained from Alfa Aesar. All reactants were used as received. An ultra-porous non-woven fibrous polyethylene terephtalate (PET) mat from 3 M France Thinsulate type P60 was used as blanket core.

The synthesis of resorcinol - formaldehyde - APTES aerogels is inspired by recent publications of Ye et al. [12] and Kong et al. [11]. We studied blanket-type samples and cylinder-shaped aerogels (without mat support). Blanket-type samples were prepared by impregnating a PET mat with a mix of resorcinol, formaldehyde and APTES in ethanol. We changed molar ratios F/R (n_F/n_R) and APTES/R (n_{APTES}/n_R), as well as the mass fraction of reactants in solvent ($\%_{solid}$) systematically to obtain aerogels with different characteristics. Gelation occurred generally after several hours at 60 °C. Gels have been washed in ethanol, cured at 60 °C for two days and subsequently left to age at ambient temperature for 5 days before supercritical CO_2 drying ($T < 40$ °C, $P > 85$ bars, $Q \sim 6$ $kgCO_2/h$, $t > 4$ h).

2.2. Materials characterization

2.2.1. Textural characterization

Nitrogen sorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 automatic apparatus. Prior to measurement, samples were pre-treated under secondary vacuum at 100 °C for 10 h for sufficient removal of adsorbed impurities. BET specific surface area, S_{BET} (± 5 m^2 g) was calculated from the N_2-adsorption isotherms. Total pore volume Vt (± 0.05 cm^3 g^{-1}) was determined at a relative pressure of 0.988. Pore size distribution is calculated applying the Barret-Joyner-Halenda method to the desorption branch of the isotherm. To determine the microporosiy, t plot with Harking-Jura correlation is used with $0.54 < t < 0.8$ nm.

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