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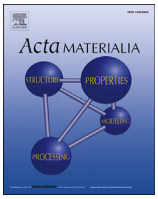

Full length article

Reinforced and superinsulating silica aerogel through in situ cross-linking with silane terminated prepolymers

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ABSTRACT

Silica aerogels have only half the thermal conductivity of conventional insulation, but their application potential is limited by the poor mechanical properties. The fragility arises from the thin necks between the silica nanoparticle building blocks. Here, we produce strong silica aerogels through co-gelation of the polyethoxydisiloxane precursor with a variety of silane terminated prepolymers that reinforce the interparticle necks, followed by hydrophobization and supercritical CO_2 drying. All prepolymers enabled the synthesis of aerogels with excellent thermal and mechanical properties, but the shortest prepolymer (~2–3 nm long) yielded the best results. The hybrid aerogels can sustain uniaxial compression without brittle rupture to at least 80% strain for all prepolymer concentrations (5–50 wt%), leading to a final strength of up to 21 MPa, an E modulus up to 3.4 MPa, and an up to 400 times lower dust release rate. In contrast to classical reinforcement strategies, the mechanical improvement does not come with a penalty in thermal conductivity, which remains between 14 and 17 $\text{mW m}^{-1}\text{K}^{-1}$. The hybrid aerogels are a unique class of superinsulating materials with superior thermal and mechanical properties and a scalable production process.

1. Introduction

The thermal conductivity (λ) of silica aerogel (12–18 $\text{mW m}^{-1}\text{K}^{-1}$ under ambient conditions) is only half that of standing air (26 $\text{mW m}^{-1}\text{K}^{-1}$) [1–4]. This extreme performance, coupled with their non-flammability, vapour open porosity and recyclability, led to the emergence of a rapidly growing industry for aerogel thermal insulation. In addition to the high cost, the poor mechanical strength, high brittleness and considerable dust release prevent a more widespread use and faster market uptake [5]. It is thus no surprise that researchers worldwide are developing new strategies to improve the mechanical properties of silica aerogels and their corresponding products.

Amongst the earliest polymer-based reinforcement strategies are the classical works by Leventis, Meador and co-workers. These classical X-aerogels [6–18] rely on the in-situ polymerization of a thin conformal coating on the silica surfaces through a post-gelation modification with isocyanate, styrene, epoxy, anhydride or acrylate monomers. Because the reinforcing agents are introduced after the gel has formed, additional solvent exchanges are required to introduce the monomers, particularly if the polymer precursor is not compatible with the gelation solvent, which is most often (m)ethanol or water. X-aerogels display a high compressive modulus (40–900 MPa) and final compressive strength (8–500 MPa), leading to high strength-to-weight ratios. However, these aerogels generally feature high densities

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($0.25–0.6\,g/cm^3$) and thermal conductivities (>30 $mW\,m^{-1}\,K^{-1}$) due to the significant mass loading with an additional polymer phase.

A second reinforcement strategy uses co-gelation of a silica precursor or sol with biopolymers [19–22], organically modified silanes (ormosils) [23–25], or silane terminated prepolymers [26–30], and we have selected this last approach in this study. Kramer et al. [26] improved the elasticity of silica aerogel by co-gelation with silanol terminated polydimethylsiloxane chains. Maleki et al. [27] incorporated short tri(m)ethoxysilane terminated linkers into a silica sol that also contained 3-(trimethoxylsilylpropyl) methacrylate. Duan et al. [28,29] reinforced silica aerogels in dimethylformamide by co-gelation with trimethoxy- and triethoxysilane-terminated polyurethane prepolymers, and a similar prepolymer was also used by Gonçalves et al. [30]. Aspen Aerogels described the synthesis of silane-terminated prepolymers through the reaction of di- and triamines with an isocyanatoalkoxysilane and their use as reinforcing agents [31,32]. Jiang et al. [33] prepared polyrotaxane-silica hybrid aerogels with reduced brittleness and increased final strength for a moderate penalty in λ (1–9 $mW\,m^{-1}\,K^{-1}$ increase), but most likely underestimated the absolute value of λ through an indirect measurement protocol, resulting for example in an unrealistically low λ value of 10 $mW\,m^{-1}\,K^{-1}$ for pure silica aerogel. In nearly all of the above described works, the co-gelation methodology leads to a moderate increase in mechanical strength at the cost of a substantial increase in λ, if λ is reported at all. One notable exception are silica-pectin hybrid aerogels with a strongly increased final compressive strength and E-modulus, but low λ (<18 $mW\,m^{-1}\,K^{-1}$) [21]. However, the silica-pectin synthesis scheme entails long gelation times and additional solvent exchanges prior to hydrophobization and gel drying because of the need for water as a gelation solvent to ensure a good compatibility with the biopolymer. In summary, no direct, scalable synthesis route exist to prepare superinsulating aerogels ($\lambda < 20\,mW\,m^{-1}\,K^{-1}$) with significantly improved mechanical properties.

Here, we introduce strong and superinsulating silica hybrid aerogels with an unprecedented combination of properties, prepared by co-gelation of an ethanol-based silica sol and silane-terminated prepolymers. This route does not depend on a post-gelation modification step typical for classical X-aerogels, but introduces the reinforcement by co-gelation with isocyanatoalkoxysilane based cross-linkers (Fig. 1; Table 1). Because the silane terminated prepolymers are fully compatible with the ethanolic gelation and hydrophobization solvent, no additional solvent exchanges are required.

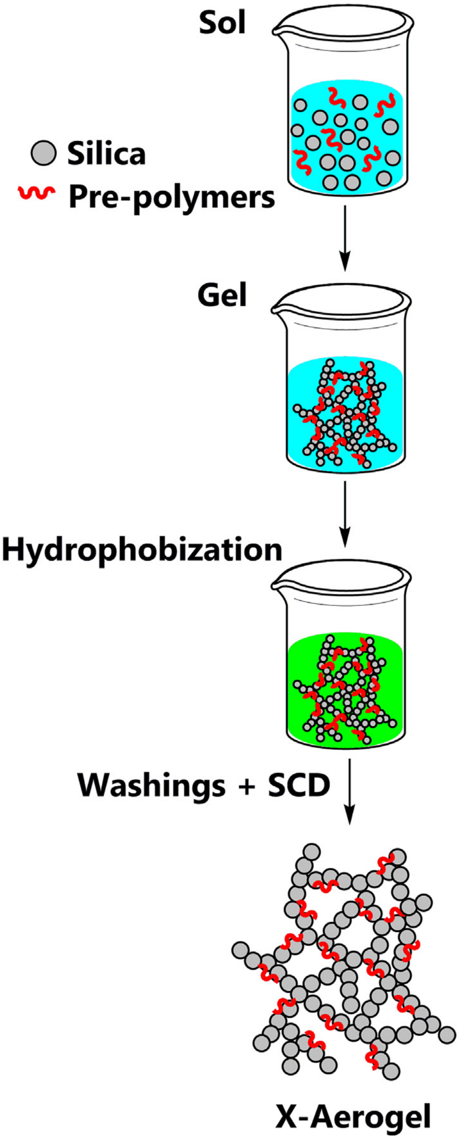

Fig. 1. Synthesis of hybrid aerogels by co-gelation. The length of the polymer chains varies from ~2 to ~100 nm depending on prepolymer type and the diameter of the primary silica particles is ~4 nm.

2. Experimental section

2.1. Synthesis of hybrid aerogels

Hybrid aerogels were prepared by co-gelation of a silica sol with different concentrations of silane terminated prepolymers, described by the prepolymer (X):SiO_2 mass ratio (Fig. 1). The silane-terminated prepolymers are of the general form $(\mathbf{R_1}O)_3$-Si-$(CH_2)_3$-(NH)-(C=O)-O-$\mathbf{R_2}$-O-(C=O)-(NH)-$(CH_2)_3$-Si-$(O\mathbf{R_1})_3$, where $\mathbf{R_1}$ is either a methyl or ethyl group and $\mathbf{R_2}$ can be a short aliphatic chain, a polyether or a natural oil polyol (NOP) based derivative. The prepolymers were either sourced commercially or synthesized by urethane formation between commercial polyols and 3-(triethoxysilyl)propyl isocyanate (Table 1 and Figure S1). In the following, we describe the synthesis procedure using the X = 0.2 hybrid aerogel as an example. The sol was prepared from a mixture of 0.36 g of prepolymer, 9 ml polyethoxydisiloxane (PEDS), a prepolymerized form of tetraethyl orthosilicate (TEOS) containing a water-to-TEOS molar ratio of 1.5 and a SiO_2 content of 20% w/w in ethanol (referred to as PEDS-P_{750E20}) [34], 21 ml denatured ethanol (F25-AF-MEK), and 1 ml distilled water prepared under constant stirring for 5–10 min at room temperature. Gelation occurred ca. 10 min after the addition of 0.36 ml 5.5 M NH_4OH in water. The gels were covered with 0.4 ml of ethanol to prevent exposure to the air, and aged at 65 °C for 24 h. The aged gels were hydrophobized by soaking in a mixture of 60 ml hexamethyldisiloxane (HMDSO), 0.24 ml concentrated hydrochloric acid (37%) and 2.2 ml ethanol at 65 °C for 24 h. After 2–4 ethanol washes, the hydrophobized gels were dried in an autoclave (Separex, France) from supercritical CO_2 (SCD).

2.2. Density and nitrogen sorption

The bulk density (ρ_{bulk}) was calculated from the sample mass and envelope volume. The skeletal density ($\rho_{skeletal}$) was obtained from the skeleton volume determined by helium pycnometry (AccuPyc II 1340, Micromeritics). Estimated uncertainties for bulk