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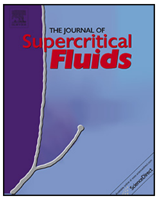

Effect of polymer molecular weight and deposition temperature on the properties of silica aerogel/hydroxy-terminated poly(dimethylsiloxane) nanocomposites prepared by reactive supercritical deposition

D. Sanli[a], C. Erkey[a,b,*]

[a] *Department of Chemical and Biological Engineering, Koç University, 34450 Sariyer, Istanbul, Turkey*
[b] *Koç University TÜPRAŞ Energy Center (KUTEM), Koç University, 34450 Sariyer, Istanbul, Turkey*

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ABSTRACT

Monolithic nanocomposites of silica aerogels with hydroxy-terminated poly(dimethylsiloxane) (PDMS(OH)) were prepared by reactive supercritical deposition technique. The depositions were performed by using PDMS(OH) having two different molecular weights ($M_n = 2750$ g/mol and 18,000 g/mol) and at three different temperatures (313.2 K, 323.2 K, 333.2 K) and the effects of deposition temperature and polymer molecular weight on the properties of nanocomposites were investigated. The polymer uptake of the nanocomposites was found to increase with increasing deposition temperature indicating faster reaction rates at higher temperatures. PDMS(OH) molecules with lower molecular weight were homogenously distributed throughout the cylindrical composites. On the other hand, the samples that were deposited with high molecular weight PDMS(OH) were not homogenous with a higher polymer concentration near the surface than at the center. The pore volumes and BET surface areas of the nanocomposites decreased upon deposition of the polymer. The reductions in pore volumes were higher by a factor of two than the volume of the deposited polymer indicative of blocking of pores. Moreover, the compressive modulus of the nanocomposite was found to be more than three times greater than the compressive modulus of the native silica aerogel.

1. Introduction

Silica aerogels are nanostructured materials that have been attracting considerable attention due to their unique and intriguing properties such as low density, transparency, high surface area, high porosity and low thermal conductivity. More importantly, their properties can be tailored for a specific application either by manipulation of the synthesis parameters during the sol–gel process or by post-treatment of the synthesized aerogels [1–4]. Another important feature of silica aerogels is that they can be obtained as monoliths in any size and shape. Due to these favorable properties, silica aerogels have been utilized or under investigation for various applications such as thermal insulation, adsorption, nuclear waste storage, electrochemical energy storage and catalysis [5].

A significant fraction of the recent studies on silica aerogels are associated with the development of composites of silica aerogels with various polymers. Polymers can be incorporated into aerogels by generally following three different routes. One way is to add the polymer to the sol mixture before gelation occurs, i.e. during the hydrolysis or condensation steps of the sol–gel process. Composites of silica aerogels with poly(2-vinylpyridine) [6], syndiotactic polystyrene (sPS) [7] and polyethylene glycol (PEG) [8] constitute some examples to this technique where the gelation of the sol occurs in the presence of the polymers chains. An alternative route involves the reaction of the polymer molecules with the surface groups of the silica aerogel, which is carried out after the formation of the solid gel network. The aerogel surface can be functionalized to include specific chemical groups, which constitute active sites for further reactions and are used for the attachment of the polymers. Thus far, there have been many studies on the modification of the silica aerogel surface with various silane-based compounds having different functionalities [9–11]. For instance, amine groups have been introduced to the silica aerogel surface by co-condensation of TEOS or TMOS with bis(trimethoxysilylpropyl)amine (BTMSPA)

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[*] Corresponding author at: Department of Chemical and Biological Engineering, Koç University, 34450 Sariyer, Istanbul, Turkey.
E-mail address: cerkey@ku.edu.tr (C. Erkey).

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[10] and 3-aminopropyltriethoxysilane (APTES) [11–13]. These amine groups have further been employed for the reactions with isocyanates to yield a coating of polyurea on the aerogel surface. Amine functionalized silica gel surfaces have additionally been reacted with different epoxy compounds to yield epoxy-reinforced materials [11,12,14]. Such surface functionalization techniques have also drawn significant interest for the preparation of chromatographic sorbents of various types.

As a third alternative, polymers can be added to the reactant mixture during the synthesis and can directly participate in the co-condensation reactions with the hydrolyzed precursor molecules. This method requires specific polymers that can undergo co-condensation reactions with —OH groups of the hydrolyzed silane precursors. Poly(dimethylsiloxane) (PDMS) with hydroxyl end groups (PDMS(OH)) is one of the rare polymers that can participate in such reactions. Kramer et al. synthesized for the first time a composite of PDMS(OH) with silica aerogel by reacting the polymer with hydrolyzed TEOS [15]. Being a water-insoluble polymer, PDMS is not soluble in the conventional reactant mixture (ethanol, water and TEOS) for synthesis of silica aerogels and the addition of the polymer into this mixture causes phase separation. The immiscibility of the polymer with the sol mixture results in non-homogenous composites with two different phases; silica gel network with polymer aggregates on the surface [16,17].

It is well known that many silane compounds have appreciable solubility in $scCO_2$ [18–22], which can be exploited for development of composites of silica aerogels with silicone-based polymers. We recently demonstrated that PDMS(OH) forms miscible mixtures with $scCO_2$ at mild temperature and pressures [23]. Subsequently, monolithic composites of silica aerogels with PDMS(OH) were developed by reactive deposition of the polymer from $scCO_2$ and PDMS(OH) with a number average molecular weight of 2750 g/mol was found to chemically react with the surface —OH groups of silica aerogel and became covalently attached to silica aerogel surface upon deposition. Moreover, the polymer molecules were homogenously distributed throughout the aerogel sample and formed a thin layer with a thickness of ~1 nm on silica aerogel surface [24].

In this study, monolithic composites of silica aerogels with PDMS(OH) were prepared by reactive deposition of the polymer from $scCO_2$. The depositions were carried out at three different temperatures by utilizing PDMS(OH) with two different molecular weights. The effects of deposition temperature and polymer molecular weight on the properties of silica aerogel–PDMS(OH) nanocomposites were investigated. Mass uptakes were measured gravimetrically and ATR-FTIR measurements were performed to analyze the chemical groups in the composites. The mass uptakes, transparencies and homogeneity of the composites that were prepared with low and high molecular weight PDMS(OH) were compared. N_2 adsorption/desorption analyses were used to analyze the pore properties of the composites. Additionally, the compression tests were carried out in order to quantify the mechanical properties.

2. Materials and methods

2.1. Materials

Tetraethylorthosilicate (TEOS) ($Si(OC_2H_5)_4$) (98%) was purchased from Alfa Aesar (USA). Ethanol (C_2H_5OH) (99.9%) was purchased from Merck (Turkey). Hydrochloric acid (HCl) (37%) was obtained from Riedel-de Haen (Germany) and ammonium hydroxide (NH_4OH) (2.0 M in ethanol) was obtained from Aldrich (USA). Hydroxy-terminated polydimethylsiloxane (PDMS(OH)) ($H(C_2H_6OSi)_nOH$) of two different number average molecular weights (M_n = 2750 g/mol and M_n = 18,000 g/mol) with 99.9% purity were purchased from Sigma Aldrich (USA). The chemicals were used as received. Carbon dioxide (CO_2) (99.9%) was purchased from Messer Aligaz (Turkey).

2.2. Synthesis of silica aerogels

Silica aerogels were synthesized by a two-step sol–gel procedure using TEOS as the silica precursor. The schematic representation of the two-step sol–gel process that was utilized as the synthesis procedure is depicted in Fig. 1. At the initial stage, TEOS is hydrolyzed with water for 40 min in the presence of ethanol as the co-solvent and HCl as the acid catalyst. Subsequently, NH_4OH was added to the sol mixture to adjust pH value to 5.5. At this pH, the condensation reactions accelerate which eventually lead to the gelation of the sol mixture. Before gelation, the solution was poured into cylindrical molds having a diameter of 1.1 cm. After gelation, the so-called alcogels were aged in an equi-volume mixture of water and ethanol at 323 K for 24 h. Before supercritical drying, solvent exchange with pure ethanol was performed in order to replace the pore solvent. Lastly, ethanol was extracted from the pores with supercritical CO_2 at 313.2 K and 90 bar. As a

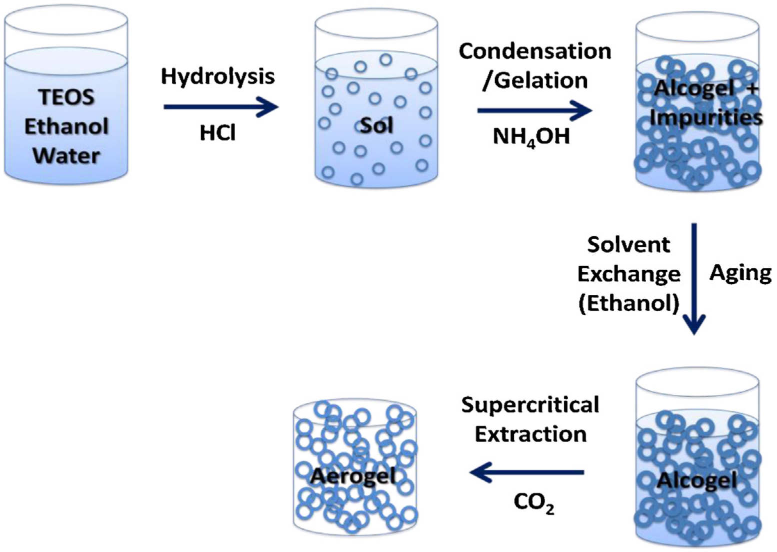

Fig. 1. Processing steps for the synthesis of silica aerogels.