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Effect of drying method on the structure and porous texture of silica-polybutadiene hybrid gels: Supercritical vs. ambient pressure drying

Mahnaz Shahzamani [a,*], Rouhollah Bagheri [a,*], Mahmood Masoomi [a], Majid Haghgoo [b], Akram Dourani [b]

[a] Department of Chemical Engineering, Isfahan University of Technology, P.O. Box: 84156-83111, Isfahan, Iran
[b] Space Transportation Research Institute, Iranian Space Research Center, Department of Nanotechnology & Nanoscience, Tehran, Iran

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ABSTRACT

Drying methods can strongly affect the structure, pore size and morphology of organic–inorganic aerogels. In this study, the textural properties of silica-polybutadiene hybrid gels which were dried in supercritical condition (aerogels) were compared with those dried in ambient pressure condition (xerogels). The silica-polybutadiene wet gels were synthesized by two-step sol-gel process using different amounts of silane functionalized polybutadiene latex nanoparticles (0, 10, 30 and 50 wt.%). In order to decrease the surface tensions in silica pore network, the resulting gels were modified with hexamethyldisilazane (HMDZ) before drying. Nonetheless, high volume loss was observed in ambient pressure drying. The supercritical dried aerogels indicated lower density ranged from 0.08 to 0.24 g/cm^3 and higher porosity from 96.1 to 79.6% comprised to those dried in ambient pressure condition. Supercritical drying could avoid polymer particles aggregation, leading to a wider pore distribution including larger pores and higher pore volumes (ranging from 4.38 to 1.48 m^3/g). Moreover, a different non-rigid structure was found from nitrogen sorption isotherms in supercritical condition.

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1. Introduction

Aerogels are a class of hyperporous nanostructure material with desired properties, such as low density and high specific surface area, leading to low thermal conductivity and low dielectric constant. The unique properties of these materials make them convenient for manufacturing of thermal and acoustic insulators, catalyst supports, adsorbents, sensors, supercapacitors and fuel cells [1–6].

Aerogels are normally synthesized by conventional sol-gel process which is followed by drying the wet gels, without collapsing the gel solid network [7,5]. The drying of the wet gels is the most important step in the synthesis of aerogels that affects their pore structure and textural properties [8]. During drying under atmospheric conditions, concave liquid/vapor menisci form at the exterior surface of the gel. As the liquid stretches to cover the solid, tensile stress appears in the liquid and compressive stress is imposed on the solid network. Such capillary pressure gradient is able to collapse most part of the pore volume [9–12]. Capillary pressure of a fluid in a porous network depends on pore fluid/vapor surface tension, γ, contact angle that the meniscus makes with pore wall, θ, and characteristic capillary size, r_c, which is related to the pore size, r_p. For cylindrical pores, the magnitude of the capillary pressure is $P_c = -2\gamma\cos(\theta)/r_c$ [13].

At small pore size, the capillary pressure will be enormous and hence a collapse of the gel structure can take place. The increase in stiffness and large pore size pulls down the capillary pressure during drying, leading to a low density structure [14,5]. The cracking of aerogels is a major problem in drying of aerogels. In the initial stages of drying, evaporation of solvent from micropores creates an overall drying stress and local differential stresses which lead to cracks in the aerogels [15,16]. To avoid cracks and maintain the high porosity several strategies were developed: drying in supercritical condition, surface modification and strengthening the gel network to dry in ambient pressure conditions, and freeze drying [17]. In supercritical conditions, surface tension disappears along with the capillary pressure gradient built up in the pore walls. Thus, the potential collapse of the pore volume due to capillary forces was avoided [8,11]. Another approach is to modify the surface characteristics of the wet gels from hydrophilic to hydrophobic using reagents with hydrophobic reactive agents [18,19]. Strengthening the gel structure through aging [17,20] or hybridization with polymers [21,22] is an attempt to reduce capillary forces. Another technique is freeze drying in which the gel liquid is first frozen and thereafter dried by sublimation [11,17].

Attempts have been made to synthesize hybrid aerogels with high flexibility, strength and superhydrophobic properties [23].

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* Corresponding authors.
E-mail addresses: m.shahzamani@ce.iut.ac.ir (M. Shahzamani), bagheri@cc.iut.ac.ir (R. Bagheri).

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Incorporation of rubber latex nanoparticles, as flexible organic components, in the gel structure, would be a solution to overcome the capillary pressure during drying. These rubbery particles can act as an impact modifier and hinder crack propagation in the fragile structure of the network. Fidalgo et al. [24] reported the synthesis of silica-polymer hybrid aerogels using polybutyl methacrylate particles. These hybrid aerogels were dried at ambient pressure conditions but it showed a considerable shrinkage (i.e. ~70%). Evan et al. [25] also presented a novel silica-polymer hybrid aerogels using rubber latex particles (i.e. styrene-butadiene rubber) at supercritical condition. In our previous work [26], the monolithic silica-polybutadiene hybrid gels were successfully synthesized under ambient pressure drying with relatively high porosity (~86%). The effect of different synthesis conditions on their structure and mechanical properties were also studied. However in some cases, the resulting hybrid aerogels demonstrated large volume shrinkage especially at low silica sol concentration. This work was conducted specifically to understand the drying behavior and investigate the shrinkage in these kinds of hybrid gels. In order to avoid the capillary forces in silica phase, the resulting hybrid gels were silylated with Hexamethyldisilazane (HMDZ) before drying. With this strategy, the role of polybutadiene particles would be studied more properly.

The aim of this work is to compare the structural and morphological properties of the obtained hybrid silica-polybutadiene monoliths using ambient pressure and supercritical drying which leads to producing hybrid "xerogels" and "aerogels", respectively. The effect of these drying methods on the structure, porosity, pore size and morphology along with oil adsorption capacity of silica-polybutadiene hybrid aerogels in different content of polybutadiene latex were investigated.

2. Experimental

2.1. Materials

Polybutadiene latex (PBL) used in this work (~40 wt.% solid cont., particle diameter ~90 nm, pH = 8.5) was supplied from Ghaed Basir Petrochemical Company, Iran. Silane coupling agent namely, bis[3-(triethoxysilyl) propyl] tetrasulfide (TESPT, Si69) was received from Evonik Degussa Company, Belgium. Tetraethylorthosilicate (TEOS, 98%), hexamethyldisilazane (HMDZ, 98.5%), ammonium hydroxide (25%) and oxalic acid were supplied from Merck Company. 2-propanol and n-hexane (from Arman Sina Company) as solvent and deionized water were used in this work.

2.2. Preparation of silica-polybutadiene hybrid aerogels and xerogels

Fig. 1 illustrates the preparation of silica-polybutadine hybrid xerogels and aerogels schematically. The process can be divided into two steps: synthesis of hybrid wet gels and drying.

2.2.1. Synthesis of hybrid wet gels

The hybrid gels were synthesized by a two-step acid/base catalyzed hydrolysis and condensation of TEOS and silane functionalized polybutadiene latex (Si-f-PBL) [26]. Polybutadiene latex nanoparticles were modified with TESPT in the presence of zinc oxide as an activator in a process like pre-vulcanization [27]. In the first step, the TEOS and 2-propanol were mixed with oxalic acid in water with the molar ratio of 1:12:6.23 × 10^{-5}:3.75 and stirred for 30 min followed by keeping for 24 h at room temperature to complete hydrolysis. The hydrolyzed solution of TEOS was then mixed with different amounts of Si-f-PBLs (0, 10, 30 and 50 wt.%) to achieve a homogenous mixture. The resulting mixture was neutralized with ammonia (0.1 M) and after stirring for 30 min poured into molds and left to gel at room temperature. The wet gels were aged in a solution of ammonia (0.5 wt.%) in 2-propanol/H_2O (4:1) mixture for 24 h at 60 °C. The solvent of the gels was exchanged with 2-propanol three times at a 12 h interval, then 2-propanol was replaced with n-hexane three times every 12 h at 60 °C. To silylate the surface of the wet gels, they were immersed in 7 wt.% HMDZ in hexane at 50 °C for 24 h. After silylation, the solvent was exchanged two times with hexane to remove unreacted HMDZ.

2.2.2. Drying of hybrid wet gels

Two drying methods were employed to convert the resulting wet gels into hybrid solid gels: (1) ambient pressure and (2) supercritical drying. In the first method, the wet gels were dried in an oven for 24 h at 60 °C followed by 4 h at 80 °C at atmospheric pressure. To obtain aerogels, supercritical drying of the samples was carried out at 313 K and 20 MPa, i.e. above the critical point of CO_2, by a supercritical dryer.

2.3. Characterization

The bulk density of the samples (ρ_b) was determined by measuring their weight and volume. The average value of ρ_b was recorded for three samples. The nominal structural density of the samples ($\rho_s = g/cm^3$) was determined by He pycnometer with a micromeritics Accupyc 1330 instrument. The porosity and the pore volume of the samples

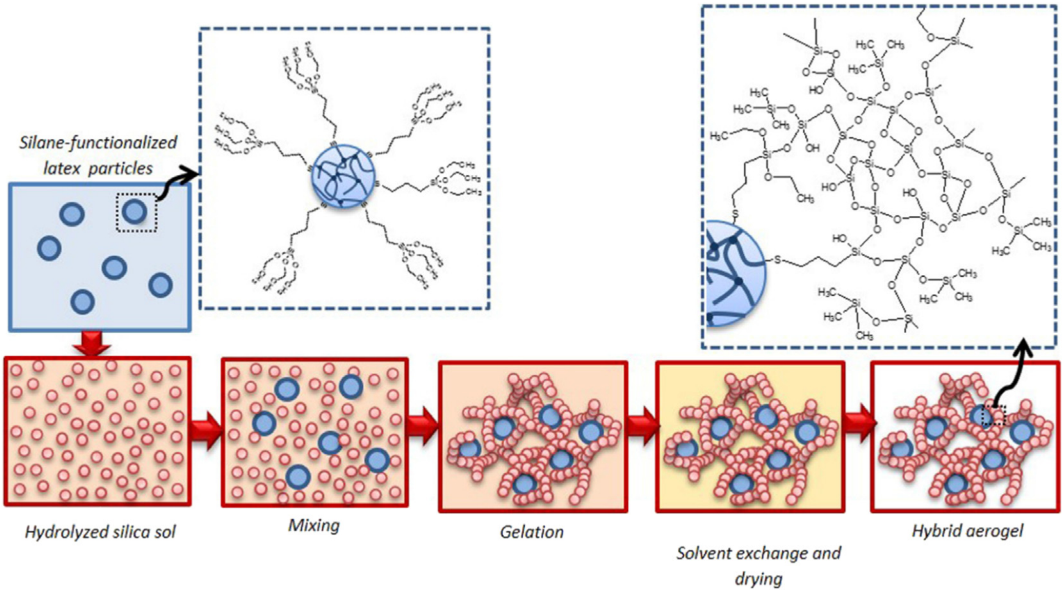

Fig. 1. Schematic process diagram of silica-polybutadiene hybrid xerogels and aerogels and their structures.

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