Journal of Non-Crystalline Solids 481 (2018) 622–626

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Preparation of compressible silica aerogel reinforced by bacterial cellulose using tetraethylorthosilicate and methyltrimethoxylsilane co-precursor

Mengmeng Cai, Sameera Shafi, Yaping Zhao*

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Minhang District, Shanghai 200240, China

ARTICLE INFO

Keywords:
Silica aerogel
Bacterial cellulose
Composite
Insulate

ABSTRACT

Silica aerogel is one of the most attractive insulation materials but has not been broadly applied yet because of limitation of its fragile nature. In this work, we synthesized a compressible bacterial cellulose/silica aerogel composite from the co-precursor of tetraethylorthosilicate and methyltrimethoxylsilane by a two-step acid-base catalyzed sol-gel method followed by supercritical CO_2 drying. This aerogel composite possessed a series of excellent properties: standing the considerable strain, high resilience, dust-free, low density of 0.066 g/cm^3 and low thermal conductivity of 0.0292 W/(m·K) along with hydrophobicity with a water contact angle of 147°. Weight loss analysis indicated that the thermal stability of the as-prepared composites was about 270 °C which primarily depended on the thermal stability of the bacterial cellulose. These outstanding properties were attributed to the Interpenetration Polymer Network structure formed via the co-precursors and the bacterial cellulose and the excellent fabric of the aerogel retained by the supercritical CO_2 drying. The results suggest that the as-prepared aerogel composite has potential applications as a suitable insulation material with dust-free and resilience.

1. Introduction

Low thermal conductivity materials have attracted increasing interest because they have broad applications in heat insulating area. The most remarkable material is silica aerogel which was firstly prepared in 1931 by Kistler using water-glass as starting material followed by supercritical CO_2 drying [1]. The silica aerogel has hierarchical nanoporous structure accumulated by nano-colloid particles (dimensions from 5 to 10 nm) with a "pearl necklace"-like morphology and is considered as a new state of matter which is different with the three states of material because of the high porosity of 90% [2]. Therefore, it shows unique properties such as low density, big surface area, visible-light transparency, tiny refractive index and low acoustic velocity, and has been applied in electrical, thermal, optical, chemical area and so on [3–7].

However, the application of the pure silica aerogel as an insulating material is limited because of its fragile property caused by the pearl-necklace-like structure [4,8–11]. In order to reinforce aerogels, polymers, such as polyuria [12], poly(methyl methacrylate) [13], poly(urethane urea) [14] were used to strengthen aerogel via chemical cross-linking. But the preparation process is complicated. Using micro- or nanoscale objects as filler or substrate for binding aerogel [15–17] was a straightforward and efficient process. Li [18] made flexible silica aerogel composites by adding aramid fibers, of which the bending modulus reached to 1.4 MPa. In the same way, Li [16] prepared aerogel/ceramic composites by using polycrystalline mullite fiber, of which the Young modulus was 18 MPa. However, the composite has a dust-release defect due to the weak connection of the fiber with the silica. Recently, the formation of Interpenetration Polymer Network (IPN) structure through combining silica with 3D network nanofiber was reported to solve the dust issue because the much more active site of 3D nanofiber could react with the silica [19]. Also, the skeleton of the 3D network scaffold provided a continuous framework to binding mesoporous silica. Nanofiber network structure significantly improved the mechanical strength of the silica aerogel composites: its compressive modulus and maximum compressive strength reached to 8 MPa and 25 MPa, respectively [19–23]. Bacterial cellulose (BC) is a kind of 3D web-like network nanofiber which has incredible Young's modulus of 138 GPa and tensile strength of at least 2 GPa. It can reduce the brittleness of the silica aerogel by forming a chemical bond with silica via its vast hydroxyl groups [24,25]. Nevertheless, the published papers on a study on the preparation of nanofiber/silica aerogel composite are few. Especially, there is no report on the synthesis of BC/silica aerogel composite using two types of silica source as a co-precursor.

The objective of this work is to prepare the BC/silica aerogel composite with dust-free, low thermal conductivity, hydrophobic and

---

* Corresponding author.
E-mail address: ypzhao@sjtu.edu.cn (Y. Zhao).

https://doi.org/10.1016/j.jnoncrysol.2017.12.015
Received 4 October 2017; Received in revised form 23 November 2017; Accepted 4 December 2017

excellent mechanical performance. Tetraethylorthosilicate (TEOS) and methyltrimethoxylsilane (MTMS) are selected as co-precursors and the BC as 3D network nanofiber. A two-step acid-base catalyzed sol-gel method followed by supercritical CO_2 drying was applied to make the composite. The morphology, structure, mechanical and thermal properties were characterized and tested using SEM, FTIR, universal tensile testing machine, and thermal constants analyzer.

2. Experiment

2.1. Materials

TEOS, absolute ethanol, hydrochloric acid, ammonia, and sodium hydroxide were all purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and were analytical reagent. MTMS with purity of 95% was bought from Beijing Innochem Science & Technology Co., Ltd (Shanghai, China). Bacterial cellulose (BC) was purchased from Hainan Yida Food Industry Co., Ltd (Guangzhou, China).

2.2. Method

2.2.1. Preparation of dried BC

The wet BC was cut into 4 cm × 2.5 cm × 1 cm pieces and immersed in deionized water for 2 h, and then neutralized with sodium hydroxide for 2–3 h at 50 °C, followed by washing for several times to neutrality by deionized water. The dried BC was obtained by pre-freezing the pretreated wet BC in liquid N_2 and then dried through freeze drying.

2.2.2. Preparation of hydrophobic BC/silica aerogel

Hydrophobic BC/silica aerogel was prepared by a two-step acid-base catalyzed sol-gel followed by supercritical CO_2 drying method. First, the TEOS (2.8–5.6 mL) and MTMS (1.8–3.6 mL) precursors were dissolved in absolute ethanol (EtOH) (21.9–43.8 mL), in which 1.4 mL water was added, with magnetic stirring for 10 min to obtain the mixture solution of TEOS-MTMS-EtOH. The molar ratio between TEOS and MTMS, and among TEOS, MTMS, EtOH, and water are listed in Table 1. Then, 0.1–0.2 g BC matrix was immersed in the mixture solution and continuously stirred for 1.5 h at 50 °C. The amount of the mixture solution was enough to embed all BC. Next, the pH of the mixture was adjusted to 3 using 0.3 mL ~ 0.7 mL hydrochloric acid with a concentration of 0.5 mol/L and stirred for hydrolysis for 4 h at 50 °C. After that, 0.8 mL ~ 1.2 mL aqueous ammonia with a concentration of 6.0 mol/L was added to the mixture to regulate its pH to 8 for condensation. Finally, the formed gel was aged for 12 h in EtOH and followed by drying using supercritical CO_2. The drying procedure is similar to the previously published paper [26]. Briefly, the wet gel (the composite) was placed in the pressure vessel, and the air of the vessel was replaced by CO_2 in three times. Then, pump CO_2 into the vessel until the pressure reached 7.4 MPa (above the critical point of CO_2). After that, start to increase the temperature of the vessel. After the pressure and the temperature reached the desiring value (12 MPa and 40 °C), start to vent out the CO_2 from the vessel and record the time while maintaining the drying conditions. After drying 4 h, take the samples out from the vessel for characterization later.

2.2.3. Characterization

Morphologies of the as-prepared samples were characterized by field emission scanning electron microscope (Nova Nano SEM450 with an accelerating voltage 10 KV). All the samples were coated with platinum by a sputter coater (1.2 kW, E-1045, Hitachi, Japan) for the 60s. Fourier transform infrared spectrometer (FTIR) was recorded on a Spectrum 100 instrument by KBr sample holder method to characterize the chemical bonds of BC and the composites. The thermal conductivity of the BC/silica aerogel composites was measured through a hot-wire method with a thermal constants analyzer TC300E at 25 °C. The thermal gravimetric analysis was made by using TGA Q5000IR with a heating rate of 20 °C/min from 50 °C to 600 °C in the air. The surface hydrophobicity of the BC/silica aerogel composite was determined using a Kruss DSA30 droplet scanning analysis (DSA Germany) at a static analysis mode, and the droplet was 5 μL. The stress-strain curves and the cyclic compression test were measured by Zwick/Roell Z020 machine at room temperature. All samples were cut into a cylinder shape (height is 10 mm, the diameter is 20 mm).

The bulk density of the BC/silica aerogel (ρ_0) was obtained by measuring the weight and volume of the composite. The calculating formulation of the composite porosity (%) is shown as follows [18]:

$$\text{Porosity\%} = \frac{(1/\rho_0) - (1/\rho_a) - (1/\rho_b)}{(1/\rho_0)} \times 100$$

Herein, ρ_a and ρ_b are the skeletal density of the silica aerogel of $= 2.1\ \text{g/cm}^3$ and the skeletal density of the dried BC matrix of $= 1.59\ \text{g/cm}^3$, respectively [15,27], each sample was measured in triplicate. The errors of the data measurement shown in Table 1 were derived from three times of measurement. However, the error value was minimal suggesting our measurement was good in terms of accuracy.

3. Results

3.1. Analysis of morphology and physical properties of the composites

Table 1 lists the preparation conditions and partial results of the BC/silica aerogel. Fig. 1 displays the morphologies of the as-prepared composite. The ratio of the Si/EtOH influences the physical properties and the structure of the composite. When the ratio reduced, the density of the composite decreased while its porosity increased as shown in sample 1, 2, and 3 of Table 1. It can be seen from the inset pictures of Fig. 1A–C that the structure of the composite became loos and the size of the pores increased with the ratio reduction, which is consistent with the change trend of the density and porosity. The skeleton of the composites became more compact when the ratio of MTMS and TEOS increased as shown in the inset pictures of Fig. 1B, D, and E. Also, the

Table 1
The condition and result of the preparation of the BC/silica aerogel composite.

Sample	TEOS/MTMS[a]	Si/EtOH/H_2O[a]	Density (g/cm^3)	SiO_2 content of the as-prepared sample %	Porosity %	Thermal conductivity (W/m·K)[b]
1	1/1	1/10/2	0.118 ± 0.009	89.3 ± 0.4	87.0 ± 1.0	0.0309 ± 0.0005
2	1/1	1/15/2	0.086 ± 0.003	87.4 ± 0.3	90.5 ± 0.3	0.0306 ± 0.0006
3	1/1	1/20/2	0.066 ± 0.002	83.9 ± 0.3	92.7 ± 0.2	0.0292 ± 0.0003
4	1/0.5	1/15/2	0.058 ± 0.002	81.4 ± 0.1	93.6 ± 0.2	0.0303 ± 0.0005
5	1/2	1/15/2	0.122 ± 0.003	88.8 ± 0.1	86.5 ± 0.3	0.0315 ± 0.0003
6	0/1	1/20/4	0.100 ± 0.010	88.6 ± 0.9	88.9 ± 1.1	0.0351 ± 0.0004
7	0	0	0.010 ± 0.001	0	99.4 ± 0.1	0.0315 ± 0.0002
8	1/1	1/20/2	0.080 ± 0.004	100	96.2 ± 0.2	0.0257 ± 0.0008

[a] Molar ratio.
[b] The thermal conductivity of the air was 0.027 W/m·K.