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Facilitated fabrication of high strength silica aerogels using cellulose nanofibrils as scaffold

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ABSTRACT

Monolithic cellulose nanofibrils (CNF)-silica composite aerogels were successfully prepared by immersing CNF aerogels into a silica solution in a two-step sol-gel process (initial hydrolysis of tetraethyl orthosilicate (TEOS) followed by condensation of silica particles). Aerogels were characterized by SEM, BET surface area test, bulk density and silica content analysis, FTIR spectroscopy, and compression test. The form of SiO_2 existing in the composite aerogel was the spherical individual particles coated on CNF fibrils. The pH value of condensation solution was found to have great influence on the properties of the composite aerogels. By varying the pH value of condensation atmosphere from 8 to 12, the bulk densities of composite aerogels were able to be linearly increased from $0.059\,g\,cm^{-3}$ to $0.29\,g\,cm^{-3}$, and the silica content in the matrix sharply jumped from 3 wt% to 79 wt%. The porosities of the aerogels remained very high, between 85 and 96%, and the surface area of the composite aerogel reached up to $700.1\,m^2\,g^{-1}$. The compression properties of the composite aerogel improved greatly compared with those of the silica aerogel, about 8–30 times higher. Moreover, the compressive strength of the composite aerogel prepared in this work greatly exceeded the conventional insulation materials found in the recent commercial market, and without substantial increases in thermal conductivity. Hence, the findings of this research offer a promising application for composite aerogels and give a theoretical basis for developing new advanced materials.

1. Introduction

Silica aerogels have gained significant attention due to their unique properties, such as high specific surface area ($500–1200\,m^2\,g^{-1}$), high porosity (80–99.8%), low density ($0.003–0.5\,g\,cm^{-3}$), extremely low thermal conductivity ($0.005\,W\,m^{-1}\,K^{-1}$), and prominent heat insulation qualities (Carraher, 2005; Fricke & Emmerling, 1992; Fricke, 1988; Kim, Hyun & Park, 2001). Their existing and potential applications are in a wide variety of technological areas, such as thermal insulation, acoustic insulation, catalyst carriers, absorbents and others (Fricke, Schwab & Heinemann, 2006; Soleimani Dorcheh & Abbasi, 2008). But they also have some weaknesses, such as low strength, poor toughness and great brittleness (Chen et al., 2010; Gao et al., 2009), which limit their practical engineering application as super-thermal insulation materials. To mitigate these defects, some methods have been reported in the literature to enhance silica aerogels' mechanical properties (Leventis, Sotiriou-Leventis, Zhang, & Rawashdeh, 2002; Randall, Meador, & Jana, 2011). Aging of wet gel (Ma, Roberts, Prévost, Jullien, & Scherer, 2000; Meador, Capadona, McCorkle, Papadopoulos, & Leventis, 2007), hybridization (Huang, Orler, & Wilkes, 1987; Kramer, Rubio-Alonso, & Mackenzie, 1996; Yim, Kim, & Yoo, 2002), and compounding with different polymeric systems (Leventis, 2007) are among the most common techniques. Because some existing chemistry and processing technologies are too expensive and may require the use of toxic compounds (Patel, Purohit, & Suthar, 2009), it is important to find an available and eco-friendly method to sustainably develop better characteristics in these aerogels.

One approach is to strengthen the silica aerogel by reinforcing it with fiber homogeneously dispersed into the skeleton of the silica

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through chemical and mechanical mixing (Shao, Zhang & Cheng, 2014). So far, in corporation of commercially available or laboratory developed fibrous supporting materials (such as glass fiber (Kim, Lee & Kim, 2008), mullite fiber (Dong, Li, & Yuan, 2006), aluminum silicate fiber (Yang, Ni, Liang, Xu, & Xu, 2007), carbon fiber (Meador et al., 2008), polymer fiber (Li, Yalcin, Nguyen, Meador, & Cakmak, 2009; Zhang et al., 2006), and so on) into the aerogel systems has been quite effective in improving the mechanical properties of aerogels.

Cellulose is not just any polysaccharide biopolymer; it is present in plant cell walls as a primary reinforcement for load bearing (Sehaqui, Salajková, Zhou, & Berglund, 2010). In particular, cellulose nanofibrils (CNF), which have a hierarchical open-pore structure and remarkable mechanical properties (Ali & Gibson, 2013; Cheng, Wang, & Harper, 2009). CNFs are abundant, available, and renewable, characteristics that make them a prime candidate for reinforcing silica aerogels. Very recently, research on cellulose-based materials has proposed the use of CNFs for the reinforcement of silica aerogels. To simplify and lower the cost of synthesizing composite aerogels, >one-pot" preparation (Demilecamps, Reichenauer, Rigacci, & Budtova, 2014), water glass as a silica source (Liu, Yu, Hu, Liu, & Liu, 2013), and a non-supercritical drying process (Sai et al., 2013) have been reported. The flexible precursor PMSQ, prepared with CNF, has been found to yield hybrid aerogels with high flexibility and superhydrophobicity (Hayase et al., 2014). And using forced flow induced by a pressure differential method when silica is impregnated into the cellulose phase has allowed an enormous decrease in the impregnation times as well as stiffer composite aerogels (Demilecamps, Beauger, Hildenbrand, Rigacci, & Budtova, 2015). The modification of cellulose (such as maleic anhydride modified NFC (Wong, Kaymak, Tingaut, Brunner, & Koebel, 2015) and MTMS modifying the NFC surface (Zhao et al., 2015)) has ameliorated the compressibility and stiffness of silica aerogels.

The sol-gel process plays a vital role in the preparation of composite aerogels. Parameters such as the reaction time, the concentration of the silica source (Raabe et al., 2014), the temperature, the stirring rate, and the ratios of precursor to solvent to water (Guzun et al., 2014) all have a great influence on the properties of composite aerogels. In addition, the environment in which silica particles are formed will control the shapes that the silica takes and its relationship with the cellulose matrix. Thus, the condensation process is of great importance when designing silica aerogels to be interpenetrated into nanocellulosic scaffolds. So far, there has been no study of the relationship between the condensation process of silica particles and the properties of cellulose-reinforced silica aerogels.

The objective of this study was to synthesize cellulose-silica aerogels by a sol-gel process to improve the mechanical properties of the aerogels. Herein, a simple, low cost and low risky drying method: the ambient pressure drying method was chosen to promote material shaping. The effect of the pH value during the condensation process on the microstructure and the mechanical properties of the CNF-silica aerogels is examined. The morphology, specific surface area, density, FTIR analysis results, mechanical properties, and thermal conductivity were tested and are discussed. Finally, the potential usefulness of CNF-silica composite aerogels in insulation materials is discussed.

2. Materials and methods

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98% purity), hydrochloric acid (HCl, 12.1 M), ammonium hydroxide (NH_4OH, 1.0 M), ethanol (anhydrous, histological), *n*-Hexane (≥95%, environmental grade), trimethylchlorosilane (TMCS, 98%) were purchased from Fisher Scientific (USA) and used as received. Cellulose nanofibrils (CNF, solids 2.95%) were purchased from The University of Maine Process Development Center (Orono, ME, USA). Cross-linker KymeneTM resin (Ashland Hercules Inc., USA) was purchased and added into the nanofibril cellulose suspension. Distilled water was used for all preparations.

2.2. Preparation of silica aerogels

Silica aerogels were prepared using the following two-step catalysis sol-gel process. Tetraethyl orthosilicate (TEOS) was used as the silica precursor, HCl as the acid catalyst, and NH_4OH as the base catalyst. In the first step, a solution was prepared by mixing TEOS, ethanol, water, and HCl with the molar ratio $1:3:1:7 \times 10^{-4}$. After 90 min stirring of the first-step solution at 60 °C, ethanol, water, and the base catalyst were added to the mixture. NH_4OH was added drop by drop in order to decrease the rate of the condensation reaction. The following molar ratios were used: C_2H_5OH: H_2O was 5:2.6, and the NH_4OH was added until it adjusted the pH value of the whole solution to 8. The two-step molar ratios are listed in Table S1. After a few minutes of magnetic stirring, the mixture was poured into plastic cylindrical molds. After becoming >solid", the samples were transferred to another container for gelation (2–3 h). Then the wet gel was immersed in ethanol for further gelation and aging at 50 °C for 24 h (Fig. S1). During the gelation of the wet gel, further condensation reactions occurred that strengthened the silica gel. Subsequently, the silica gel was kept in the ethanol bath at room temperature for 2 days to remove any impurities or water remaining in its pores. The ethanol solution was refreshed every 24 h.

Before the drying process, the wet silica gel needed surface modification to avoid structural cracking during the drying. To start the modification, the gel underwent solvent exchange with *n*-hexane at 25 °C for 2 days, and the *n*-hexane was refreshed every 24 h. The surface modification was proceeded by immersing the wet gel in TMCS (10%, v/v)/*n*-hexane solution at room temperature for 24 h. Then the modified wet gel was washed with *n*-hexane to remove the excess TMCS at room temperature for 24 h. Finally, the wet gel was dried in the oven under ambient pressure: 5 h at 80 °C.

2.3. Preparation of cellulose-silica composite aerogels

The cellulose nanofibrils (CNF) aerogels were prepared according to a procedure previously published by our group (Meng et al., 2015). The CNFs were centrifuged to a 5% solid concentration and mixed with cross-linker resin (5 wt% of solid CNF). The CNF aqueous suspension was poured into a plastic mold (contains several grids, the size of each grid is 58.0 mm in length, 42.6 mm in width, and 43.7 mm in height, Fig. S2). Then the mold was placed into liquid nitrogen for 4 min rapid freezing, followed by freeze-drying in a vacuum lyophilizer (Labconco, Inc., Kansas City, MO) at a temperature of −51 °C for 3 days. The samples were oven-heated at 120 °C for 3 h to promote cross-linking in order to form a three-dimensional network.

When the CNF aerogels were done, the next step was to synthesize the CNF-silica aerogels. The CNF aerogels were entirely immersed in the first-step solution of the sol-gel process for 10 min and then immersed for 10 min in the second step solution (adding different amounts of NH_4OH to get the pH values of the solutions to 8, 10, and 12) to induce silica condensation. The composite aerogels prepared at the different pH values were labeled C-S-pH8, C-S-pH10, and C-S-pH12, respectively. The subsequent aging process, solvent exchange, surface modification, and ambient