Boehmite nanofiber-polymethylsilsesquioxane core-shell porous monoliths for a thermal insulator under low vacuum conditions

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ABSTRACT: We demonstrate porous composite monoliths based on boehmite nanofibers (BNFs) and polymethylsilsesquioxane (PMSQ) through a designing strategy of concurrent covering and gelation. The obtained materials have BNF-PMSQ core-shell type fibrous skeletons which crosslink each other to configure a three-dimensional porous architecture. The monoliths show elastic flexibility against compression and can be dried via evaporative drying process without collapse of fine structures. Thermal conductivity under low vacuum conditions is found to be as low as that of silica aerogels at an ambient condition. Both the facile polymer/surfactant-free synthesis process and unique microstructures are expected to lead the way to new sol-gel derived materials and applications.

Monolithic porous materials have been utilized for various purposes including thermal and sound insulations, adsorption/absorption, catalysis and separation in our daily life. The production of these materials relies on several liquid-phase processes such as foaming[1], soft and hard templating[2] and phase separation[3]. The sol-gel process is employed to obtain porous monolithic materials with a well-controlled pore size in an extended size range from meso- to macro-scales. In many cases of this process, water-soluble polymers and surfactants are effective additives to control phase separation in the gelling solution.[4] By changing the starting composition and reaction conditions, a fine tuning of the phase separation leads to monolithic materials with various pore properties such as macroporous ones for separation media and mesoporous ones (aerogels and xerogels) for visible-light transparent thermal insulators.[5]

Our group has been investigating monolithic porous materials composed of organopolylsiloxanes by using a surfactant to control phase separation during hydrolysis and polycondensation reactions of organoalkoxysilanes.[6-9] In the case of polymethylsilsesquioxane (PMSQ, $CH_3SiO_{1.5}$) derived from methyltrimethoxysilane (MTMS, $CH_3Si(OCH_3)_3$), porous materials ranging from macroporous gels to mesoporous aerogels with visible-light transparency have been obtained by a fine control of phase separation with a surfactant. The PMSQ network offers mechanical flexibility and hydrophobicity, which leads to advantages in the preparation of transparent aerogels; that is, drying under ambient conditions via evaporation of pore liquid does not cause serious cracking and irreversible shrinkage but a temporal shrinkage-reexpansion (spring-back) behavior,[10,11] resulting in aerogel-like xerogels without supercritical drying.

By introducing dimethylsiloxane parts into the PMSQ network, macroporous monoliths with marshmallow-like flexibility against compression and bending have been obtained.[12] Since these marshmallow-like gels have a hydrophobic and oleophilic surface, they selectively absorb oils from water-oil two-phase systems, and can be used as efficient oil-water separation media.[13] Although the control of the phase separation offers a fine and extended tuning of pores as exemplified in these two cases, a removal of polymer/surfactant additives from monolithic gels may cause problems in processing time and complexity as well as the environmental load.
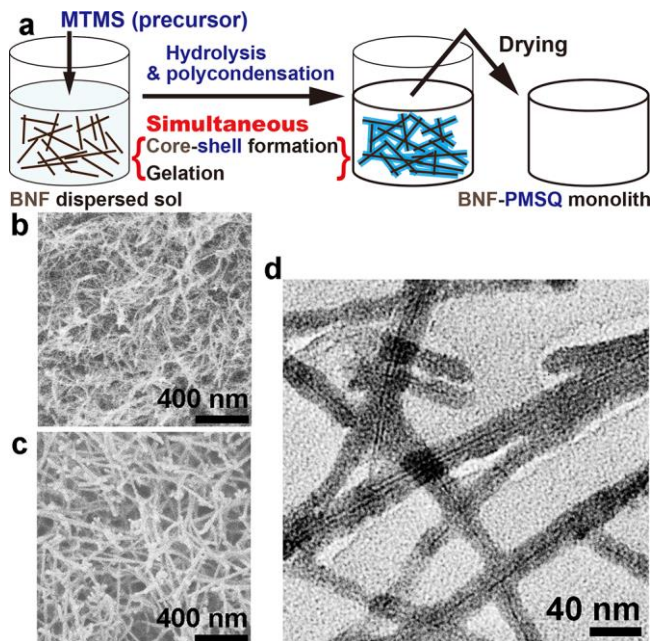
Figure 1. (a) Schematic illustration on the formation of a BNF-PMSQ monolith from BNF dispersed sol. (b) FESEM image of the BNF aerogel obtained from the BNF sol at 2.1 wt %.[15] (c) FESEM and (d) TEM images of the BNF-PMSQ monolith B2.1P5.0.

Table 1. Starting compositions and properties of BNF-PMSQ monoliths obtained in the present study.

Sample	Bulk density [mg cm^{-3}]	Porosity [%]	BET surface area [m^2 g^{-1}]	Young's modulus [MPa]
BNF aerogel^a	26.5 ± 5.0	98.9 ± 0.2	384	
B0.9P5.0	139 ± 5.3	90.4 ± 0.4	159	2.2
B2.1P5.0^b	141 ± 4.0 (180 ± 5.0)	90.7 ± 0.3 (88.1 ±0.4)	265 (146)	5.5
B4.3P5.0	152 ± 3.5	90.7 ± 0.2	279	4.0
B6.4P5.0	152 ± 4.5	91.4 ± 0.2	283	4.5
B2.1P1.0	46.6 ± 0.8	97.4 ± 0.1	405	0.69
B2.1P2.5	86.8 ± 5.2	94.5 ± 0.3	322	0.47
B2.1P7.5	193 ± 2.7	87.0 ± 0.2	273	17
B2.1P10	232 ± 2.4	84.2 ± 0.2	269	24

^{a}Obtained from the BNF sol at 2.1 wt %.[15] ^{b}The values in parenthesis indicate properties of the sample obtained via evaporative drying.

In this paper, we report a novel methodology for controlling pore properties in a monolithic gel by using a dispersed boehmite nanofiber (BNF)[14] aqueous sol instead of a polymer/surfactant (Figure 1a). The BNF sol is stable under an aqueous acetic acid condition at least for several months. Under basic conditions, however, the BNFs undergo controlled aggregation, resulting in a transparent monolithic gel. We recently have reported ultralow-

density aerogels (< 5 mg cm^{-3}) by applying this simple aggregation behavior (Figure 1b).[15] The obtained materials are highly transparent, which means BNFs form a uniform structure in the length scale of several tens of nanometers and do not contribute to strong light scattering. However, the mechanical strength is too low to handle and prepare in a shape of panels for thermal insulation. Hereby we have improved the microstructure by coating and then bonding the skeletal BNF nanofibers with PMSQ, by utilizing reactivity of hydroxyl group on the surface of BNFs with silanol groups. The resultant BNF-PMSQ composite structure forms a firm monolith in the macroscopic scale with a core-shell microstructure. From another standpoint, this process is a class of surfactant-free processes for preparing hydrophobic polymer-based materials under aqueous conditions.
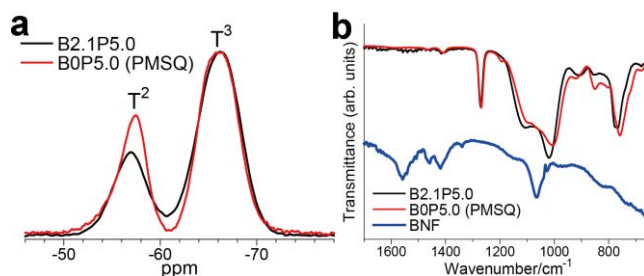

Figure 2. (a) ^{29}Si solid-state CPMAS NMR and (b) Fourier transform infrared spectra of the BNF-PMSQ monoliths B2.1P5.0 and the PMSQ precipitation B0P5.0.

The typical synthetic process is as follows: (1) mixing 12 mL of the BNF sol (x wt % of BNFs, pH = 4) and y mL of MTMS at 80 °C for 3 min, and keeping the same temperature for 24 h to promote hydrolysis and polycondensation reactions of MTMS for gelation; (2) washing with 2-propanol several times; and (3) drying under supercritical CO$_2$ at 80 °C and 14 MPa for 12 h. Table 1 shows properties of the obtained samples, where BxMy means a sample synthesized from 12 g of BNF (x wt %) and y mL of MTMS in the starting composition. Without BNFs, MTMS did not form a monolith gel but resin precipitations, which is caused by an enhanced formation of cyclic PMSQ oligomers instead of random networks under an acidic condition. On the other hand, the presence of a small amount of BNF allows a formation of translucent wet gels, which leads to low-density porous monoliths after supercritical drying. To reveal the microstructure, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) have been employed. The obtained micrographs of FESEM and TEM on B2.1P5.0 show that the skeletons of these porous materials have a fiber-like feature composed of the BNF-PMSQ core-shell structure (Figures 1c,d). Molecular-level structures are investigated by ^{29}Si solid-state cross polarization magic angle spinning (CPMAS) NMR and Fourier transform infrared (FTIR) spectroscopy on an aerogel sample B2.1P5.0 and a PMSQ precipitate from B0P5.0 starting composition. Nuclear magnetic resonance spectra in Figure 2a show that the relative amount of T^3 (CH$_3$Si(OSi)$_3$) species is higher than T^2 (CH$_3$Si(OSi)$_2$(OCH$_3$/H)) with the addition of BNF.[16] Furthermore, the absorption band by Si-O-Si species (~1100 cm^{-1} and ~1025 cm^{-1}) is increased while that by Si-OH

groups (~915 cm^{-1}) is decreased in the FTIR spectra (Figure 2b).[17] These results show that the mechanism of polycondensation reaction of PMSQ is different when there are BNFs in the starting sol. Under the presence of BNFs in the starting composition, it appears that the hydrolyzed MTMS preferentially adsorbs on and reacts with the BNF surface at an early stage, followed by homo-polycondensation on the surface. Because each of BNF and PMSQ does not form a monolithic gel alone under an acidic condition, the reaction on the surface of BNFs is essential to promote the formation of such monolithic porous structures. Although there are some reports on the formation of core-shell structure in a porous monolith, the core-shell porous structure reported here is developed through core-shell formation and gelation simultaneously, while other researchers use surface modification techniques on a preformed porous monolith.[18-20]

Figures 3a-d are FESEM micrographs of BNF-PMSQ monoliths prepared with the varied concentration of BNFs in the starting composition. The thickness of the skeletons in BNF-PMSQ monoliths becomes finer and the pore size smaller with an increasing concentration of BNFs, x. These porous monoliths with the fiber-like microstructure show elasticity against compression and completely recover their original shape from 50 % uniaxial compression (Figure 3b). With an increasing x, crosslinks between the fibers are increased and thickness of the skeletons is decreased (due to the lower PMSQ/BNF ratio), resulting in the highest compressive stress at x~2.1. (Note that the former contribution increases the hardness and the latter decreases.) Microstructure becomes coarser with increasing amount of MTMS y to the fixed concentration of BNF (Figure S1). In the range of $y > 2.5$, Brunauer–Emmett–Teller (BET) specific surface area stays almost constant (Table 1). This result shows that the most of the surface of BNF is covered with PMSQ in these conditions. In fact, although a BNF aerogel surface is hydrophilic,[15] the BNF-PMSQ monolith B2.1P5.0 exhibits water contact angle about 155° due to hydrophobicity of PMSQ on the surface and surface roughness of the fiber-like structure[21-23]. It was confirmed that the hydrophobicity is stable against water and humidity at least for several months (Figure S2, Movie S2).
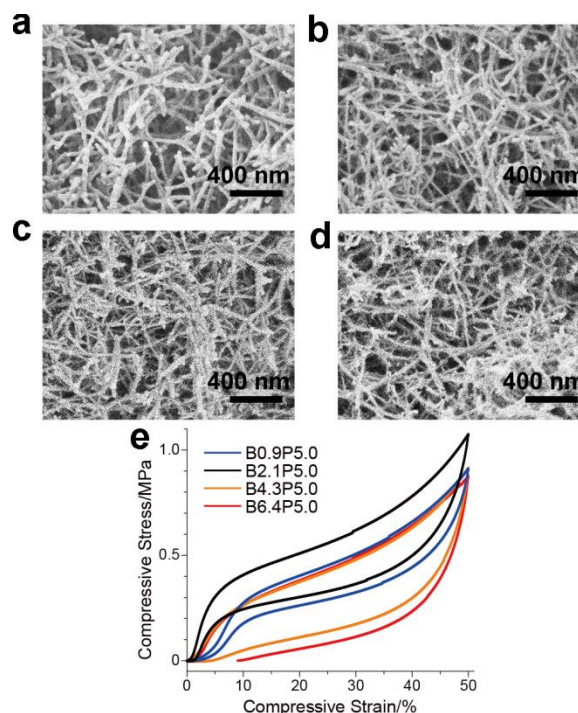

Figure 3. FESEM images of the BNF-PMSQ monoliths prepared with varied concentration of BNF; (a) B0.9P5.0, (b) B2.1P5.0, (c) B4.3P5.0, and (d) B6.4P5.0. (e) Stress-strain curves of the BNF-PMSQ monoliths against uniaxial compression-decompression.

Porous monoliths with optimized pore size and density are expected to be a high-performance thermal insulator.[24-26] Due to the moderately low bulk density (~0.14 g cm^{-3}) and the low connectivity of solid skeletons, the BNF-PMSQ porous materials can be suitable for the packing material of vacuum insulation. Thermal conductivity of these materials has been measured by the heat-flow (HF) method at ambient pressure and guarded hot plate (GHP) method at reduced pressures. At ambient pressure, thermal conductivity of a B2.1P5.0 panel is 30.0 mW m^{-1} K^{-1}, which is comparable with values of commercially available thermal insulators such as polymer foams.[27,28] Under low-vacuum conditions, the value decreases to 12.6 mW m^{-1} K^{-1} at 1000 Pa and 12.1 mW m^{-1} K^{-1} at 100 Pa. While these values are not as low as those of high-performance vacuum insulation panels, the BNF-PMSQ porous materials possess thermal insulation ability as high as that of silica aerogels[24,29,30] at a low-vacuum condition. One of the advantages in the BNF-PMSQ porous monoliths over silica aerogels is mechanical elasticity against compressive deformation. Although it is well known that supercritical drying at high pressure is necessary to obtain silica aerogel panels due to their friability, the BNF-PMSQ monoliths can be obtained via evaporative drying through the spring-back behavior (Figure 4, Movie S1) due to their compressive flexibility. The above-mentioned PMSQ xerogels also can be prepared without supercritical drying; however, surfactant is needed to tailor the fine mesoporous structure due to incompatibility of the hydrophobic PMSQ polymers with aqueous solution. The BNF-PMSQ porous monoliths rely on the different design ap-

proach of tailoring pore structure through covering and bonding nanofibers with hydrophobic polymers, in which no surfactant is needed for synthesis. In addition, similar porous materials can be obtained from vinyltrimethoxysilane and ethyltrimethoxysilane, resulting in BNF-polyvinylsilsesquioxane and BNF-polyethylsilsesquioxane porous monoliths, respectively (Table S1, Figure S3). These results suggest the possibility to cultivate new porous materials based on different organofunctional alkoxysilanes and applications such as catalyst supports, separation media and antifouling materials in addition to thermal insulators with utilizing surface functions.[31]
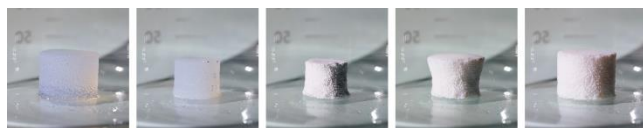

Figure 4. Photographs of the BNF-PMSQ monolith B2.1P5.0 in the course of evaporative drying at an ambient condition (left to right). See also Movie S1 in Supporting Information.

In summary, we have demonstrated porous composite monoliths based on BNFs and PMSQ through a new designing strategy of concurrent covering and gelation. Each BNF is surrounded by PMSQ networks to form core-shell type fibrous skeletons, which crosslink each other to configurate a three-dimensional porous architecture. Wet gels are obtained simply by mixing the BNF sol and MTMS in a weakly acidic condition at 80 °C, followed by ambient pressure drying via temporal shrinkage and spring-back to obtain porous monoliths without cracks. The dried monoliths show elastic flexibility against compression. Thermal conductivity under low vacuum conditions is found to be as low as that of silica aerogels at an ambient condition. The easy synthesis and drying processes and mechanical flexibility are advantageous in obtaining large-area monolithic insulating panels. In addition, if this synthesis approach is extended to other nanofiber-polymer combinations, porous monoliths with different functions and applications would be developed in the future.

ASSOCIATED CONTENT

Movies demonstrating evaporative drying and water repellency, FESEM images, water contact angle of the materials. These material are available free of charge via the Internet at http://pubs.acs.org.

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