Polymethylsilsesquioxane−Cellulose Nanofiber Biocomposite Aerogels with High Thermal Insulation, Bendability, and Superhydrophobicity

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S *Supporting Information*

ABSTRACT: Polymethylsilsesquioxane−cellulose nanofiber (PMSQ-CNF) composite aerogels have been prepared through sol-gel in a solvent containing a small amount of CNFs as suspension. Since these composite aerogels do not show excessive aggregation of PMSQ and CNF, the original PMSQ networks are not disturbed. Composite aerogels with low density (0.020 g cm^{-3} at lowest), low thermal conductivity (15 mW m^{-1} K^{-1}), visible light translucency, bending flexibility, and superhydrophobicity thus have been successfully obtained. In particular, the lowest density and bending flexibility have been achieved with the aid of the physical supporting effect of CNFs, and the lowest thermal conductivity is comparable with the original PMSQ aerogels and standard silica aerogels. The PMSQ-CNF composite aerogels would be a candidate to practical high-performance thermal insulating materials.
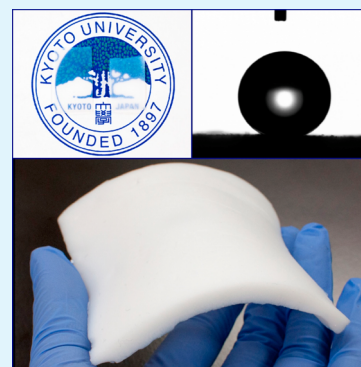
KEYWORDS: *composite aerogels, sol-gel, cellulose nanofibers, polymethylsilsesquioxane, organic-inorganic hybrids, thermal insulation*

1. INTRODUCTION

Silica (SiO$_2$) aerogels are prepared through liquid-phase processes accompanied by supercritical drying and known for their outstanding properties such as low thermal conductivity, low density, and high surface area. These are important for various potential applications, and many researchers have been studying on aerogels aiming at commercial use.[1−4] In fact, silica aerogels have been utilized in some special applications such as thermal insulators for a planetary rover, cosmic dust collectors, Cherenkov counters, and cold-resistant apparel.[5−7] Aerogels are not widely used, however, because they are too brittle to be handled without damage. This serious problem has prevented silica aerogels from prevailed practical uses for more than 80 years.

In this decade, several researchers succeeded to synthesize new silica aerogel-based materials that can be treated easier than the original ones. For instance, Leventis and coworkers have synthesized mechanically tough aerogels whose silica skeletons are laminated with organic polymers.[8] They showed good flexibility against bending deformation, but their thermal insulating properties are not reported in detail; thermal conductivity of these materials may be higher due to the partial loss of porosity. In 2007, our group reported polymethylsilsesquioxane (PMSQ, CH$_3$SiO$_{1.5}$) aerogels derived from methyltrimethoxysilane (MTMS). Aerogel-like xerogels based on PMSQ can be obtained without supercritical drying.[9−11] Although both silica and PMSQ aerogels consist of siloxane (Si−O−Si) bonds in their networks, their properties are clearly different in mechanical durability due to incorporated methyl groups; the difference corresponds to that in silica glasses and silicone resins. The organic−inorganic hybrid aerogels show high reversible elastic deformation against uniaxial compression (Figure S1 in the Supporting Information) along with excellent thermal insulation, which is as high as silica aerogels (thermal conductivity is below 15 mW m^{-1} K^{-1}).[9−12] Xerogels with properties comparable with aerogels can be easily obtained in large sizes (500 × 500 × 10 mm^3 is successful) by ambient pressure drying (Figure S2 in the Supporting Information). Although the PMSQ aerogels/xerogels show these striking features, these are still fragile against shear and tensile stresses due to fine skeletons composed of a weak linkage of nanoparticles with ∼10 nm in diameter. To obtain low-density bendable materials, we have also investigated new materials obtained from an MTMS-dimethyldimethoxysilane (DMDMS) co-precursor system. Bendable flexible materials (named as marshmallow-like gels) whose density is as low as PMSQ aerogels (∼0.1 g cm^{-3}) have been successfully obtained by ambient pressure drying.[13−15]
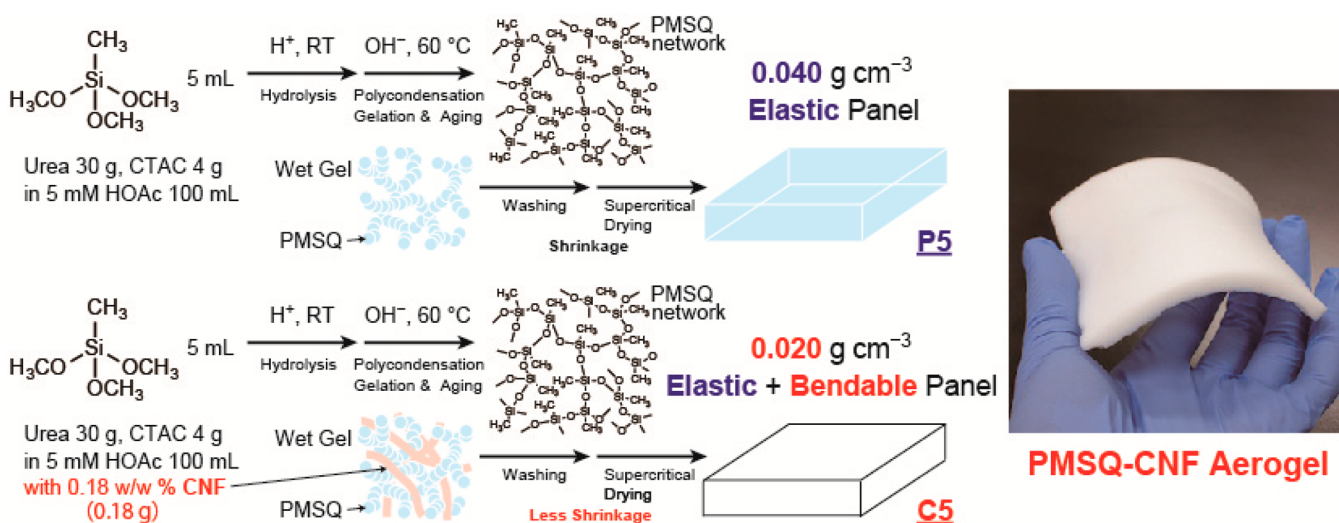
Figure 1. Preparation schemes of low-density PMSQ aerogels with and without CNFs (samples C5 and P5, see Table 1).

The skeleton and pore sizes in marshmallow-like gels are, however, much larger than silica and PMSQ aerogels, which resulted in the lost of transparency and increased thermal conductivity (~35 mW m^{-1} K^{-1}).

In another strategy, silica-bionanofiber composite aerogels have been investigated for improving the mechanical robustness. In particular, cellulose nanofibers (CNFs) have often been used because of their abundance in nature and good mechanical properties.[16−20] Due to the excellent specific tensile strength of CNFs, which are ~5 times higher that of steel wires,[21,22] these composite aerogels are expected to show higher mechanical properties and flexibility even against bending. In addition, CNFs can be obtained from scrap wood, which can reduce the environmental load in industrial productions. Their density and thermal conductivity were, however, far from those of pure silica aerogels and even comparable with conventional thermal insulators such as mineral wools, presumably because of aggregations and heterogeneous pore structures formed through strong attractive interactions by the hydrogen bonds and/or covalent bonds between silanols and hydroxyl groups of CNFs.[4,20] Previously reported silica-CNF composite aerogels were highly hydrophilic due to the abundant hydroxyl groups and high surface area, which lowers long-term stability even under an ambient condition without an additional process to impart hydrophobicity.[23,24] In this study, we have succeeded to improve the mechanical properties of the pure PMSQ aerogels, which are already advantageous in inherent hydrophobicity and the better compressive mechanical property as compared to silica, by carefully designing the process to compositing PMSQ with CNFs. The high thermal insulation ability and hydrophobicity are highly maintained in the PMSQ-CNF composite.

2. EXPERIMENTAL SECTION

Materials. Acetic acid, distilled water and urea were purchased from Hayashi Pure Chemical Industry, Ltd. (Japan). Surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) was obtained from Tokyo Chemical Industry, Ltd. (Japan). Methytrimethoxysilane was purchased from Shin-Etsu Chemical Co., Ltd. (Japan). All the chemical reagents were used as received.

Sample Preparation. To obtain cellulose nanofibers, wood powder from Radiata pine (*Pinus radiata D. Don*) sieved under 60 mesh was used.[25] Solvent extraction was first performed in a Soxhlet apparatus with a 2:1 mixture of toluene–ethanol for 6 h. Lignin in the

wood was removed using an acidified sodium chlorite solution at 70 °C for 1 h, and the process was repeated until the product became colorless. The sample was then treated in 6 wt % potassium hydroxide overnight at room temperature, and then at the same concentration at 80 °C for 2 h in order to leach hemicelluloses. Finally, a slurry of 1 wt % purified cellulose passed through a grinder (Masuko Corp. (Japan)) at 1500 rpm.

For preparation of the typical PMSQ-CNF aerogel sample C50, 2.0 g of CTAC, 15.0 g of urea, and 50 mL of 5 mM acetic acid aqueous solution with cellulose nanofibers were firstly mixed in a glass sample tube. Then, 25 mL of MTMS was added under vigorous stirring at room temperature, and stirring was continued for 30 min for hydrolysis of MTMS. The obtained sol was transferred into a tightly-sealed container, which was then placed in a forced convection oven at 60 °C for 4 d to complete gelation and aging. The obtained gels were washed with methanol several times to remove the residual surfactant and other chemicals and then solvent-exchanged with 2-propanol. The washed samples were processed with CO_2 supercritical drying at 80 °C and 14 MPa for 10 h.

Characterizations. A scanning electron microscope (JSM-6700F, JEOL, Japan) was employed to observe the microstructure. Mechanical properties of aerogels were investigated by a material tester (EZGraph, Shimadzu Corp. (Japan)). For uniaxial compression tests, carved gels (typical length × width × height was 10 × 10 × 6 mm^3) were compressed-decompressed using a load cell of 5 kN with a rate of 0.5 mm min^{-1}. For three-point bending tests, a cylindrical sample with diameter of 8 mm and length of 40 mm were put on a fixture with a 30 mm span and compressed by a wedge-shaped crosshead with 60° and 0.3 mm diameter at the point with using a load cell of 5 N at a rate of 5 mm min^{-1}. To assess the molecular-level structure of obtained siloxane networks, ^{29}Si solid-state cross-polarization magic angle spinning (CPMAS) NMR measurements were performed on an NMR spectrometer Avance III 800 (Bruker Corp. (Germany)) operated under a static magnetic field of 18.8 T. The contact time for the ^{1}H−^{29}Si cross-polarization was fixed at 5.5 ms and the rate of sample spinning was 15 kHz. The ^{29}Si chemical shift was expressed relative to tetramethylsilane (Me$_4$Si) by using the resonance line at −9.66 ppm for hexamethylcyclotrisiloxane crystals as an external reference. Thermal conductivity was measured with a transient heat flow meter HFM 436 Lambda (Netzsch GmbH (Germany)). Contact angle of water was measured with Drop Master DM-561Hi (Kyowa Interface Science Co., Ltd. (Japan)). The volume of water droplet was fixed at 3.0 μL and the contact angle was determined at 2 s after an attachment to gel surface. Thermogravimetric (TG) analysis was performed with a Thermo plus EVO (Rigaku Corp. (Japan)) instrument at a rate of 5 °C min^{-1}, while continuously supplying air at a rate of 100 mL min^{-1}.

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3. RESULTS AND DISCUSSION

Preparation and Basic Properties of PMSQ-CNF Aerogels. The PMSQ-CNF composite aerogels were obtained by a one-pot process, similar to the previously reported pure PMSQ aerogel synthesis, except for adding a diluted CNF aqueous suspension. The synthesis process is simple as shown in Figure 1. These CNFs possess uniform diameter of 15 nm, which helps making the uniform networks of composite aerogels, because the diameter is close to the size of the PMSQ nanoparticular networks (Figure 2). To obtain well-
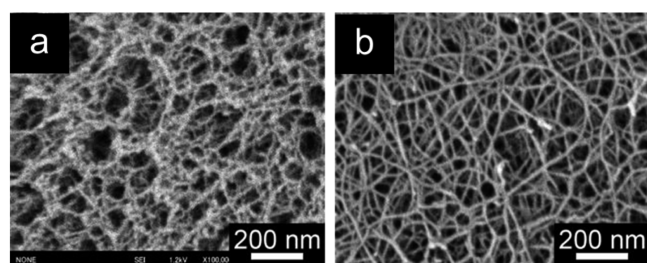
Figure 2. SEM images of (a) a low-density pure PMSQ aerogel P5 and (b) cellulose nanofibers from wood powder of Radiata pine.

defined PMSQ-CNF composite aerogels, the most important point is to avoid excessive aggregation of the PMSQ nanoparticles onto the surface of CNFs. For this purpose, the CNF solution was diluted to 0.18 w/w % in water, which is the minimum concentration to homogeneously disperse the CNFs in the sol during gelation by moderate electrostatic repulsion between PMSQ network and CNFs. Five composite aerogel panels were prepared with a varied amount of MTMS and two pure PMSQ panels without CNFs as listed in Table 1. The BET surface areas obtained by nitrogen adsorption are evaluated to be 550-750 m^2 g^{-1}, and no clear relations in density and specific surface area are found. Thermogravimetric (TG) analysis proves that oxidation of CNFs in the composite aerogel (C50) starts from ~220 °C (Figure S3 in the Supporting Information), which temperature is higher than degradation temperatures of polymer-based thermal insulators such as polyurethane and polystyrene foams.

Mechanical Reinforcement Effects by Addition of CNF into PMSQ. From the comparison between the pure PMSQ and PMSQ-CNF composite aerogels with the same amount of MTMS (i.e., samples P50 and C50), no large difference in the properties is recognized (Table 1). This means that the CNFs does not disturb the morphology of the PMSQ networks because of moderate aggregation, while silica-CNF systems show changes in physical properties through strong interaction-induced aggregation as mentioned above. In fact, uniform

fibrous networks composed of the PMSQ skeletons and CNFs are observed in SEM images (Figure 3); the PMSQ networks and CNFs are discernible due to almost the similar dimensions and good dispersity of CNFs. It is also shown by ^{29}Si solid-state CPMAS NMR and FT-IR results that the molecular-level structure of the PMSQ networks is not affected by the presence of CNFs (Figures S4 and S5 in the Supporting Information). The T^3/T^2 ratio (here T^n denotes silicon species in CH$_3$Si-(OSi)$_n$X$_{3-n}$, where X is OH or OCH$_3$) is virtually unchanged between P50 and C50, which suggests the PMSQ nanoparticles with less silanol groups compared to silica do not show extensive attractive interactions with CNFs. In FT-IR spectra, no obvious change including cyclic/polyhedral (at 1100 cm^{-1}) and linear/branched (at 1025 cm^{-1}) siloxane species[26,27] was observed between these samples.

Nevertheless, the CNFs clearly bring favorable effects on the mechanical properties of lower-density aerogels. Although the lowest density achievable in the pure PMSQ aerogels is 0.040 g cm^{-3} because of shrinkage during drying, a composite aerogel with 0.020 g cm^{-3} has been obtained (C5, Figures 1 and 3a) by introducing a small amount of CNFs as the physical support. In addition, a panel with $100 \times 100 \times 8.5$ mm^3 in dimension is bendable (Figure 1 and Figure 4a), even though the weight ratio of CNF/PMSQ is appreciably low (1:4.3 $\times$ 10^2, assuming all MTMS converted into the PMSQ networks). The bendability cannot be observed in the corresponding pure PMSQ aerogel P5. This bendable composite aerogel panel with low density is established not only by the strength of CNFs, but also by a synergetic effect with PMSQ skeletons. The PMSQ-CNF composite aerogels also show elastic behavior against uniaxial compression (Figure 4b), which is similar to the pure PMSQ aerogels reported previously.[9−11] Although compression set is relatively lower because CNFs do not possess high elasticity enough to recover the original shape, the PMSQ-CNF panels allow better handling because these panels exhibit both elasticity and bending flexibility. These are not simultaneously observed in the conventional silica, silica-CNF composites, and pure PMSQ aerogels. Further studies are underway for improving the mechanical properties of PMSQ-CNF materials to obtain aerogel-like xerogels by ambient pressure drying (see Movie S1 in the Supporting Information).

Hydrophobicity of PMSQ-CNF Aerogels. The PMSQ-CNF composite aerogels are stable against humidity without additional treatments. In the case of silica and silica-based composite aerogels, the material surface is hydrophilic and adsorbs water just as silica gel desiccants, which may collapse the pore structure due to the capillary pressure induced by adsorbed water. Cellulose nanofibers also show hydrophilicity due to their hydroxyl groups. Silica and CNFs are therefore an unsuitable combination to use under atmospheric conditions

Table 1. Starting Compositions and Properties of Typical Aerogels Obtained in the Present Study

materials	MTMS/mL	5 mM HOAc/mL	urea/g	CTAC/g	CNFs in HOAc aq./wt %	λ^a/mW m^{-1} K^{-1}	$\rho_b{}^b$/g cm^{-3}	$S_{BET}{}^c$/m^2 g^{-1}	W.C.^{d}/deg
C5	5	100	30	0.40	0.18	24.3	0.020	657	152.7
C10	10	100	30	0.80	0.18	21.7	0.039	550	152.4
C25	25	100	30	2.00	0.18	18.8	0.097	732	154.3
C50	50	100	30	4.00	0.18	15.3	0.142	525	152.7
C75	75	100	30	6.00	0.18	16.2	0.186	560	145.4
P5	5	100	30	0.40	0	22.5	0.040	601	152.5
P50	50	100	30	4.00	0	14.9	0.135	631	150.6

^{a}Thermal conductivity at an ambient condition. ^{b}Bulk density. ^{c}BET specific surface area obtained from nitrogen sorption. ^{d}Contact angle of water.
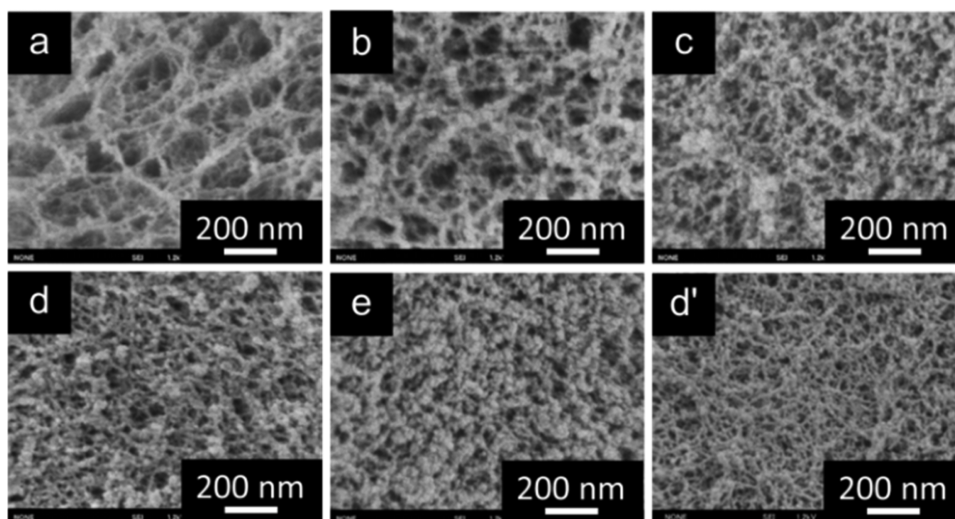
Figure 3. SEM images of PMSQ-CNF composite aerogels and pure PMSQ aerogel without CNFs; (a) C5, (b) C10, (c) C25, (d) C50, (e) C75, and (d′) P50.
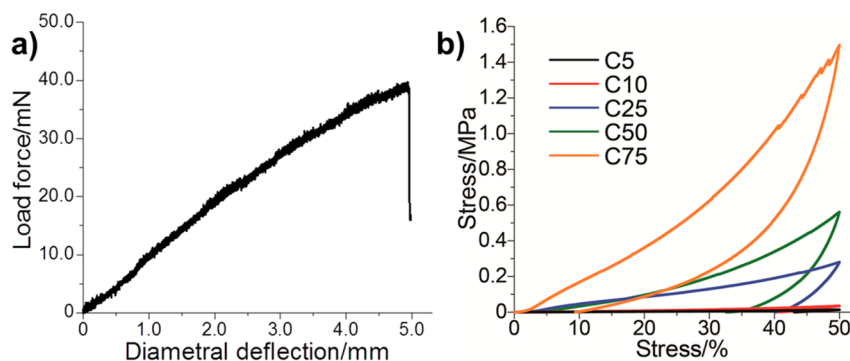

Figure 4. Mechanical properties of PMSQ-CNF composite aerogels. (a) Result of 3-point bending test on C5. A cylindrical specimen (diameter 8 mm and length 40 mm) has been used on a fixture with a 30 mm span. (b) Stress-strain curves of PMSQ-CNF composite aerogels obtained by uniaxial compression.

for long without laborious and costly hydrophobic treatments. The PMSQ network, however, is inherently hydrophobic because of the methyl groups directly bonded to each silicon and shows low surface energy such as silicone resins and poly(dimethylsiloxane) (PDMS). With an additional effect of surface roughness due to the porous morphology, the two pure PMSQ aerogels (P5 and P50) and the four PMSQ-CNF composite aerogels (C5, C10, C25, and C50) show super-hydrophobicity with the water contact angle greater than 150° (Table 1, Figure 5a and b, and Movie S2 in the Supporting Information). Although the sample C75 did not show superhydrophobicity due to a decreased length scale of surface roughness (Figure 3e), the water contact angle is still high (145.4°). In fact, all the PMSQ-CNF composite aerogels can float on water at least one month without any changes. Considering that superhydrophobic surfaces show the self-cleaning effect,[28] this is advantageous for practical uses such as low-density thermal insulating panels installed outside of buildings. With good formability and scalability as in the case of PMSQ aerogels/xerogels,[9,29] it is expected that the present composite materials can also be used for optical panels or films as reported in the dense CNF−polymer composite films,[22,30,31] because these PMSQ-CNF composite materials show acceptable light transmittance that is higher than silica−CNF counterparts (Figure 5c and Table 2).[20] By controlling the

dimension and orientation of the CNFs in the composites, there is a possibility to obtain more transparent and flexible panels.

Thermal Conductivity of PMSQ-CNF Composite and Pure PMSQ Aerogels. Thermal conductivity measurements on the PMSQ-CNF composite aerogel panels revealed that C50 shows the lowest value (15.3 mW m^{-1} K^{-1}, Figure 6). This result can be explained by the absence of morphological changes on compositing with the CNFs. Thermal conductivity of aerogel materials is mainly composed of the gas-phase conduction and the solid-phase one.[32,33] The gas-phase thermal conductivities in C5, C10, and C25 should be higher than that of C50 due to the larger pores in these samples (Figure 3), which are estimated to be longer than the mean free path of the gas molecules in air at ambient pressure (~70 nm). On the other hand, thermal conductivity of the solid phase in C75 should be higher than that of C50 because of the higher density (higher fraction of solid phase), resulting in the higher total thermal conductivity in C75. Thermal conductivity of PMSQ-CNF aerogel panels is comparable or even lower than other composite aerogels reported elsewhere[20,34] and conventional thermal insulators such as mineral wools and polymer foams (Figure 7). The poor mechanical property of the aerogels has been the highest obstacle to bring the most insulating material up to a practical application level. Through further improve-
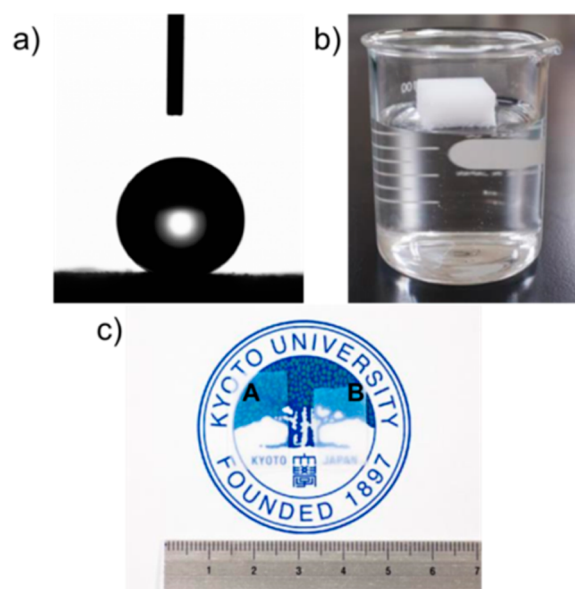
Figure 5. (a) Water drop on the PMSQ-CNF composite aerogel (C5) panel, showing superhydrophobicity. (b) Digital camera image of C50 floating on water. The PMSQ-CNF composite aerogels float on water at least for 1 month. (c) PMSQ-CNF composite aerogel sheets of (A) C10 and (B) C5, showing acceptable visible light transmittance (see also Table 2).

Table 2. Optical Properties of PMSQ-CNF Composite Aerogel Sheets[a]

| materials	thickness/ mm	transmittance at 800 nm /%	transmittance at 550 nm /%
(a) C10	5	89	84
(b) C5	10	75	54

[a]See also Figure 5c.
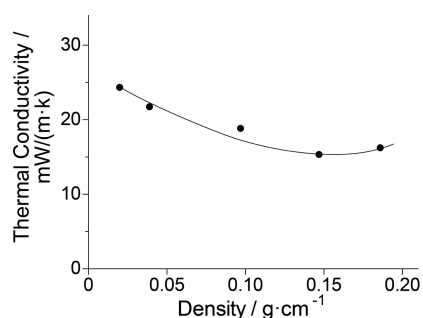
Figure 6. Relationship between density and thermal conductivity of the obtained PMSQ-CNF composite aerogels.

ment of the PMSQ-CNF materials, aerogel superinsulators with good handling and extended applicability would be realized.

4. CONCLUSION

Organic−inorganic hybrid aerogels composed of PMSQ and a small amount of CNFs have been prepared. Obtained PMSQ-CNF composite aerogels show thermal conductivity as low as pure silica aerogels and high surface area. The composite aerogel panel with the lowest density of 0.020 g cm^{-3} shows bending flexibility, which helps easy handling. The facile one-pot synthesis process for these materials is almost the same with that for pure PMSQ aerogels except adding diluted aqueous suspension of CNFs, and mechanical properties are
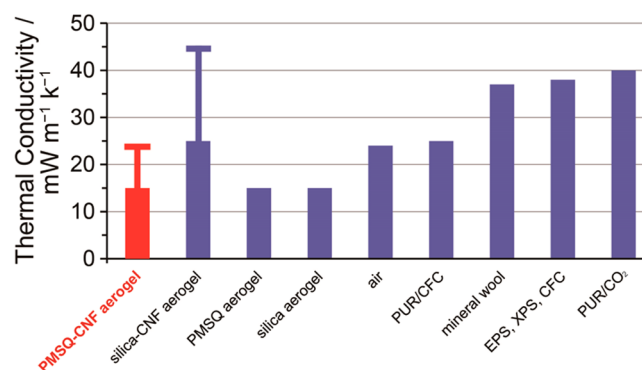
Figure 7. Comparison of the thermal insulation properties of aerogels and some commercially available insulating materials. The thin bars on the top of PMSQ-CNF aerogel and silica-CNF aerogel show the ranges of the values. PUR: polyurethane foam. CFC: chlorofluorohydrocarbons. EPS, XPS: expanded and extruded polystyrene.[4,20]

considerably improved while maintaining other pore properties. These composites show superhydrophobicity and the samples float on water at least for one month without any hydrophobizing treatments. The present composites allow applications even in outdoor environments without a change of their properties by dirt, humidity, rain, UV irradiation, and temperature change, because both PMSQ and CNFs are stable under these conditions. The present study will open up a way for practical utilization of excellent thermal insulation ability of aerogels.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Elastic mechanical properties of a pure PMSQ aerogel and a large pure PMSQ xerogels panel. Thermogravimetric analysis result and ^{29}Si CPMAS NMR and FT-IR spectra on pure and composite aerogels. Movies showing hydrophobicity and ambient pressure drying process. These material are available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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