Surfactant-free Aqueous Fabrication of Macroporous Silicone Monoliths for Flexible Thermal Insulation

Gen Hayase*

International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki Tsukuba, Ibaraki 305-0044

E-mail: gen@aerogel.jp

Gen Hayase

Gen Hayase received Ph.D. Degree from Kyoto University in 2014. After a year of JSPS research fellow at Kyoto University, he worked as an assistant professor at Tohoku University from 2015 to 2019. He has been an independent researcher at National Institute for Materials Science since November 2019.

Abstract

Hydrophobic silicone macroporous materials prepared in an aqueous solution by the sol–gel method have been considered for various applications such as separation media, heat insulators, and liquid nitrogen adsorbents. In the conventional preparation process, surfactants are used to suppress phase separation to obtain a uniform bulk material. However, a large amount of solvent and time is required to remove them before drying, which hinders industrial-scale synthesis. By copolymerizing tetra-, tri-, and bifunctional organosilicon alkoxides in an aqueous acetic acid–urea solution, flexible macroporous silicone monoliths were successfully obtained. The marshmallow-like monoliths recovered their original shape even after 80 % uniaxial compression and significant bending and water repellency. The thermal conductivity of those materials was ~0.035 W m^{-1} K^{-1} and did not increase even under 60 % uniaxial compression. This characteristic property can be used for thermal insulation on surfaces with various shapes and in confined spaces under harsh conditions.

Keywords: porous monoliths, silicone, thermal insulation

1. Introduction

Researchers are increasingly investigating the use of porous materials as heat insulators owing to growing interest in global warming and energy issues. Historically, unglazed bricks, felt, and cork have been used as porous insulators, and recently, foamed polymers such as polyurethane, styrene, and phenolic resins, as well as glass wool, are often used.[1] Those heat-insulating materials have different advantages and disadvantages in terms of heat and weather resistance and degradation over time, and they are used differently depending on the target application. As a superinsulating material that is far superior to existing ones, aerogels have long attracted the attention of researchers.[2-5] In recent years, there are some reports of flexible aerogels that overcome the brittleness that has been a problem for decades.[6-10] However, the industrial use of aerogels is still quite limited due to its still poorer handling and much higher production cost than existing insulation materials. Because the market penetration of aerogel is expected to take some time, there is a need to develop insulation materials that are not as good as aerogels but are more efficient to use than existing materials.

This study investigates polyorganosiloxane (silicone) monolithic macroporous materials that exhibit high thermal insulation with excellent weatherability and processability. Silicones are generally characterized by low thermal conductivity not found in ceramics and chemical stability not found in organic polymers (specifically, they are not degraded by oxygen or water vapor).[11-13] Further, they are flexible even when dense, and become more flexible when produced with a porous structure such as foam. By taking advantage of its softness, silicone foam is already widely used in cushioning materials and soundproofing materials. The macroporous silicone materials produced by the sol-gel method have higher application potential than silicone foam. Macroporous silicone monoliths, we have reported and called marshmallow-like gels (MGs), are obtained by copolymerizing organosilicon alkoxides in an aqueous solution sol-gel reaction.[14, 15] These materials are fabricated by controlling the phase separation using a surfactant in an aqueous solution system, and have a structure with a framework diameter of several micrometers and a pore diameter of several tens of micrometers. Unlike porous silica (SiO_2) and silsesquioxane ($RSiO_{1.5}$) materials, which also contain siloxane bonds produced by a similar reaction, silicones are highly flexible and resistant to compressing and bending, and therefore do not collapse easily. Their chemical properties and sponge-like flexibility have been exploited for realizing a wide range of practical applications such as liquid phase (oil-water) separation,[15] liquid repellency,[16, 17] liposome fabrication,[18] sound absorption,[14] thermal insulation,[19] and liquid nitrogen adsorbents[15, 19]. However, there are still some problems that need to be improved for mass production and lower cost.

Although not limited to the MG case, using an aqueous sol–gel system to fabricate hydrophobic macroporous materials is disadvantageous because a surfactant must be used in the starting sol. Even though the preparation of gels by aqueous reactions can be easily scaled up while maintaining homogeneity, the need for surfactant removal as a pretreatment for drying remains a significant problem. The larger the volume of the desired monolithic xerogel, the longer it takes to remove the surfactant owing to slower liquid diffusion inside the macroporous material. Cationic surfactants, which are also used for sterilization, are known to be cytotoxic. The generation of waste liquids containing large amounts of surfactants is undesirable because it harms the environment. Organic solvents could be used instead of an aqueous solution for the reaction; however, this would increase process costs. For realizing widespread use, therefore, completing the chemical reaction in

a simple aqueous solution system remains desirable.

In previous studies, liquid-phase synthesis of porous silicone monoliths without using surfactants has been proposed by adding nanomaterials, copolymerization of alkoxides containing ionic groups, and processes using emulsion templates.[20-22] However, these methods have had problems such as the inability to achieve high flexibility and non-uniform microstructure. In this light, I propose a method for preparing flexible porous silicones in an entirely aqueous solution system by adding hydrophilic tetrafunctional alkoxides to the MG precursors. Alkoxides with different organic groups are known to have different hydrolysis rates and undergo different polycondensation reactions.[23] This study aims to find the appropriate conditions under which multiple alkoxides can react uniformly and prepare samples of the order of several hundred milliliters. The microstructure and mechanical properties of the obtained samples are investigated, and their thermal conductivity is measured to evaluate thermal insulation properties.

2. Experimental

2.1 Materials

The silicon alkoxides tetramethoxysilane (TMOS, $Si(OCH_3)_4$), methyltrimethoxysilane (MTMS, $CH_3Si(OCH_3)_3$), and dimethyldimethoxysilane (DMDMS, $(CH_3)_2Si(OCH_3)_2$), and the cationic surfactant *n*-hexadecyltrimethylammonium chloride (CTAC), were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Acetic acid, urea, and methanol were purchased from Kanto Chemical co., Inc. (Japan). All reagents were used as received.

2.2 Sample Preparation

On a 25 mL scale, *x* mL of TMOS, *y* mL of MTMS, and *z* mL of DMDMS were added to 15 mL of 5 mM aqueous acetic acid solution containing 5.0 g of urea. The mixture was stirred for 15 min to hydrolyze the alkoxides. After the sol became homogeneous, it was transferred to an airtight container and allowed to stand at 80 °C for 24 h for gelation (within 1–3 h) and aging. The obtained wet gels were washed by immersion in water and underwent solvent exchange to methanol, following which they were subjected to evaporative drying. The resulting gel was named MG*x*-*y*-*z*. Figure 1 and Table 1 show the fabrication process and the combinations of alkoxides tested in this paper.

As a reference sample, a gel with the surfactant CTAC was also prepared. In this case, 1.0 g of CTAC was added to a starting composition of MG0-3.0-2.0, and methanol was used for all washes; this sample is called MGref hereafter.

2.3 Characterization

The bulk densities were calculated based on the respective measured weights and volumes with an error margin of approximately 5 %. The microstructures were observed using a scanning electron microscope (SEM; TM3000, Hitachi High-Technologies Corp., Japan). The thermal conductivity was measured using a heat flow meter (HFM 446 Lambda Small, Netzsch GmbH, Germany) for sample panels with 110 mm × 110 mm × 10 mm. The temperatures of the top and bottom heat plates were set at 25 °C and 15 °C, respectively, and the thermal conductivity at an average temperature of 20 °C was measured. For highly flexible samples, the thermal conductivity was measured while compressing and deforming the sample from a thickness of approximately 20 mm to 5 mm within the original weight range of the device. Uniaxial compression tests were performed using a universal/tensile tester (EZ-SX, Shimadzu Corp., Japan) and a 500 N pressure gauge. For measurements, the sample was cut into a 15 mm × 15 mm × 8 mm rectangle piece. Young's modulus was calculated from stress changes under compressive strains of 5.0–10.0 %. The water droplet contact angle was calculated by capturing images using a self-made device fabricated using Raspberry Pi 4 and Camera Module V2. The images were analyzed using the Image J plug-in Contact Angle.[24-26] The photographs required for the calculations were taken by dropping 10 μL of water on a smooth cut surface of the samples. Fourier transform infrared (FTIR) spectra were recorded using IRSpirit-L (Shimadzu Corp., Japan) with an attenuated total reflection (ATR) attachment QATR-S. A total of 100 scans of samples were recorded at a resolution of 4 cm^{-1}. A moisture meter MOC63u (Shimadzu Corp., Japan) was used to measure the moisture content. Each sample was heated at 110°C for 1 h. Thermogravimetric–differential thermal analysis (TG–DTA) was performed using Thermo Plus EVO2 TG8122 (Rigaku Corp., Japan) at a heating rate of 10 °C min^{-1} with air at a rate of 100 mL min^{-1}.

Table 1. Molar ratio of each alkoxide in the starting composition and physical properties of the obtained MG samples.

Sample	TMOS [%]	MTMS [%]	DMDMS [%]	Bulk density [g cm^{-3}]	Thermal conductivity [W m^{-1} K^{-1}]	Young's modulus [kPa]
MG0.5-3.5-0.5	10.7	77.9	11.4	0.100	0.0329	11.2
MG1.0-2.0-2.0	19.2	39.9	41.0	0.092	0.0360	8.3
MG1.0-2.5-1.5	19.2	50.0	30.8	0.096	0.0327	10.2
MG1.0-2.5-2.0	17.4	45.3	37.2	0.106	0.0324	9.8
MG1.0-3.0-2.0	16.0	49.9	34.1	0.140	0.0344	26.5
MG1.0-3.5-1.0	17.5	63.8	18.7	0.118	0.0343	14.3
MG1.0-3.5-1.5	16.0	58.3	25.7	0.125	0.0349	20.2
MG1.0-3.5-2.0	14.8	53.7	31.5	0.125	0.0340	25.1
MG1.0-4.0-1.0	16.1	66.8	17.1	0.125	0.0343	27.9
MGref	0	59.4	40.6	0.108	0.0324	6.1

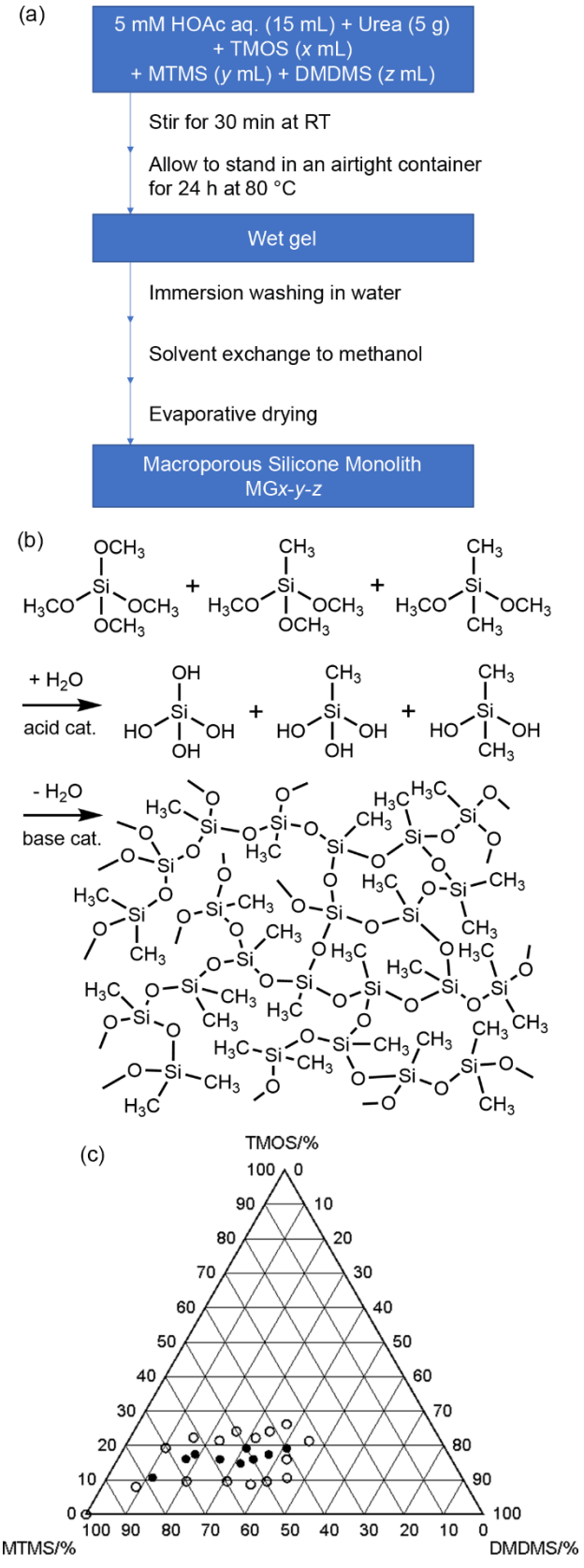

Figure 1. (a) Flowchart of sample preparation. (b) Schematic reaction diagram. (b) Sample compositions tested in this paper. The compositions indicated by the black circles yielded MGs with a homogeneous structure and flexibility to recover their original shape after 80 % uniaxial compression.

3. Results and Discussion

3.1 Preparation and characterization of MGs by surfactant-free process

In previous studies, MGs were prepared by adding the tri- and bifunctional silicon alkoxides MTMS and DMDMS, respectively, to an aqueous solution with a surfactant ratio of approximately 3:2 and then hydrolyzing and copolymerizing them in a two-step acid–base reaction to obtain a uniform gel.[14] When the same reaction was conducted without the surfactant, the phase separation of the organosiloxane oligomer, which became more hydrophobic with polymerization, could not be suppressed, and a bulk gel could not be obtained. If TMOS, which has no hydrophobic methyl group, was added instead of the surfactant to make the oligomer hydrophilic, phase separation would less likely occur before gelation. However, because the tetrafunctional silicon alkoxide uses all bonds to form a network, the resulting gel tends to be hard and brittle. Therefore, a range of microstructures and mechanical properties similar to those of MGs were investigated by finely varying the composition ratio of the three silicon alkoxides used for copolymerization.

The efficient hydrolysis and polycondensation of silicon alkoxides to form a three-dimensional network are realized commonly through a two-step acid–base reaction.[23, 27-30] The same reaction was used in this study; however, its conditions had to be optimized. The precursors TMOS, MTMS, and DMDMS have different numbers of methyl groups bonded covalently to silicon, resulting in different hydrolysis and polycondensation rates of the alkoxy groups. The difference of reaction rates must be minimized to form a uniform organosiloxane network using the three alkoxides. In our previous study, gels were obtained relatively easily using dilute acetic acid/ammonia water as the acid/base in the system with a surfactant.[31] However, the reproducibility of the method with TMOS was low when the fabrication scale was increased. Through various adjustments, the reproducibility was secured independently of the scale by increasing the temperature to 80 °C rapidly after the hydrolysis of the precursor using the acid for using ammonia derived from the hydrolysis of urea as a base.

Figure 1 and Table 1 show the compositions of silicon alkoxides and their physical properties. These alkoxides were prepared as homogeneous gels with a viscoelastic phase separation structure[32] similar to MGref and flexibility (viscoelasticity) to return to the original shape over time after 80 % uniaxial compression. All these compositions could be easily scaled up to more than 100 mm × 100 mm × 10 mm (100 mL), which is the sample size required for thermal conductivity measurements with low error. These flexible panels can be bent and will not tear when wrapped around a pipe with a diameter of 10 mm, for example. However, because the samples deformed under their own weight, it was not possible to ensure reproducibility in the three-point bending measurement. The Young's modulus of MGs was higher with the addition of tetrafunctional alkoxide TMOS in the coprecursor and lower with increasing the percentage of bifunctional alkoxide DMDMS. Although flexibility is a characteristic property of MG, the samples with low Young's modulus showed poor handling before evaporative drying, because they contained liquid inside that can reach many times their weight. Highly flexible samples with a thickness of several centimeters (e.g., MG1.0-2.0-2.0) sometimes collapsed under their weight if not immersed in liquid.

Here, the physical properties of an MG1.0-2.5-1.5 sample are described in detail as a representative composition. Figure

2a shows a photograph of the resulting 500 mL sample. In previous studies, MGref samples of several hundred milliliters required immersion in alcohol for several days to remove the surfactant within. This is because the hydrophobic part (alkyl group) of the surfactant tends to stick to the hydrophobic silicone surface and diffuses slowly. If the rinsing process were incomplete, the dried sample would shrink or not exhibit its original properties. By contrast, for the MG1.0-2.5-1.5 sample, the acetic acid and urea used in the reaction were immediately washed away by immersing in warm water; this significantly reduced the time required for drying. Although the precursor compositions were different, MG1.0-2.5-1.5 had a viscoelastic phase separation structure similar to that of MGref (Figures 2b and S1) and showed high flexibility against compression and bending. Despite the addition of TMOS to make the siloxane oligomers hydrophilic during the reaction, the MG1.0-2.5-1.5 cut surfaces all showed high water repellency with a water drop contact angle of 151.7° (Figure 2c). At the same time, because of its lipophilicity, the bulk of MG1.0-2.5-1.5 was able to separate oil (organic solvent) from water in the same way as previously reported using MGref (Figure 2d and Movie S1).[15, 31] The maximum amount of heptane absorbed was ~6.4 times its weight, and the MG could be reused by squeezing out the absorbed liquid. However, FTIR measurement results showed unreacted silanol (Si-OH), which has hydrophilicity, at approximately 900 cm^{-1} in all samples prepared using TMOS (Figures 3a and S2).[29] Although it is difficult to examine precisely, the silanol on the surface of the microstructure is assumed to have decreased during aging, and some remains only inside the skeleton. In the moisture meter measurement, MG1.0-2.5-1.5 released only about 1.8% of its weight of water, also suggesting that the material has few surface hydrophilic groups. Although only a simple test was conducted, these monoliths were not affected by weak acids, weak bases, or organic solvents at around 100 °C within a few days.

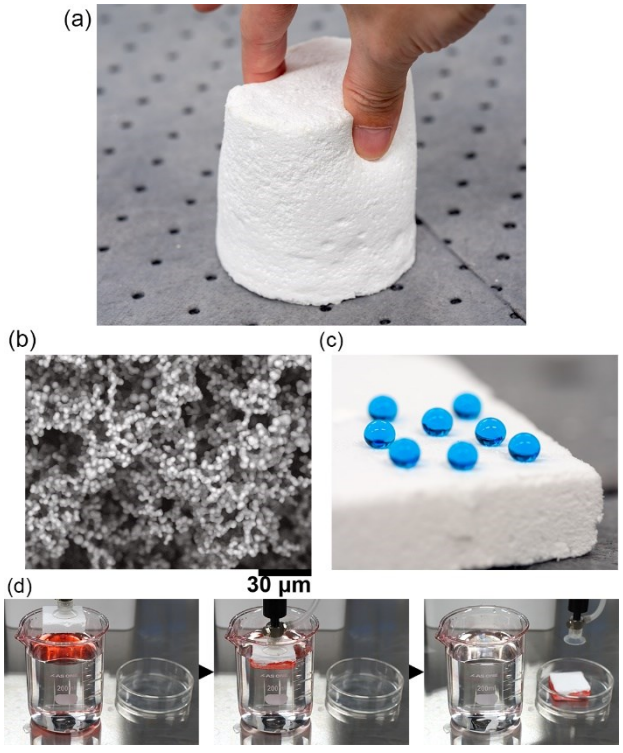

Figure 2. (a) Appearance of MG1.0-2.5-1.5 fabricated at 500 mL scale. (b) SEM image of MG1.0-2.5-1.5. (c) Water repellency of MG1.0-2.5-1.5. Water was stained with methylene blue. (d) Removal of heptane (colored with Oil Red O) from water utilizing the hydrophobic/lipophilic properties of MGs. The whole process can be seen in Movie S1.

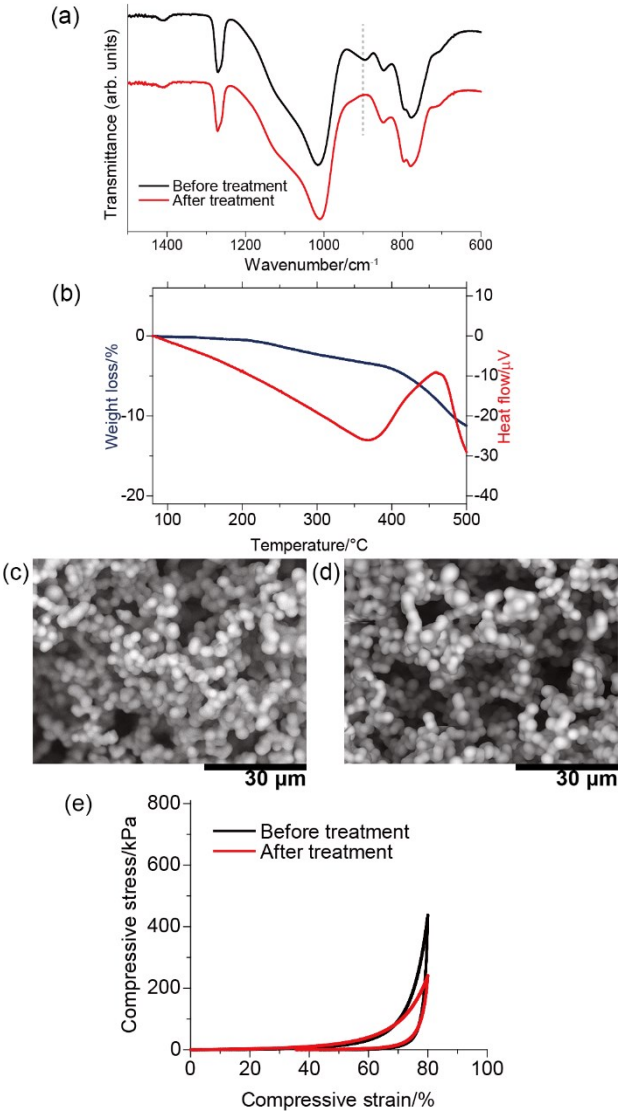

Figure 3. (a) Changes in FTIR spectra before and after heat treatment of MG1.0-2.5-1.5. After treatment, the obvious peak of the silanol group at ~900 cm^{-1} disappeared. (b) Thermogravimetric–differential thermal analysis (TG–DTA) curve of MG1.0-2.5-1.5. SEM images of MG1.0-2.5-1.5 (c) before and (d) after the heat treatment. There was no noticeable change in the diameter or morphology of the skeleton. (e) Change in the uniaxial compressive stress–strain curve before and after the heat treatment.

Heat treatment was applied to induce reactions between the residual silanol groups to form a more stable siloxane framework.[33] Thermogravimetric–differential thermal analysis

(TG–DTA) measurements were performed to determine the heat treatment temperature. A slight dehydration reaction was observed at 200 °C, followed by the oxidation of methyl groups at approximately 360 °C (Figure 3b).[29, 34] From this result, the bulk sample was heat-treated at 300°C for 2 hours, and then FTIR measurement was performed. In the obtained spectrum, the Si-OH peak (~900 cm^{-1}) was no longer seen. However, SEM observations of the microstructure before and after heat treatment did not reveal any noticeable change, and no loss of flexibility in compression or bending occurred. Since the decrease in silanol groups did not affect the physical properties much, it can be said that heat treatment is not essential. To investigate the heat resistance, the heat treatment at 300 °C was extended to 24 h; however, the results remained unchanged. By contrast, with heat treatment at 350 °C, the methyl groups of MG1.0-2.5-1.0 were oxidized gradually, resulting in the loss of flexibility and brittleness after 24 h.

3.2 Thermal conductivity change in MGs by compressive deformation

Silicone is a polymer with low thermal conductivity, and macroporous silicone monolith MGs exhibit high thermal insulation properties. All MGs produced in this study have low thermal conductivities of 0.032–0.036 W m^{-1} K^{-1}; these conductivities are comparable to those of commercially available high-performance thermal insulators. Even if the thermal conductivity is at the same level, silicones have much higher thermal and chemical stability than ordinary organic polymers and glass fibers. They do not degrade over long periods, even in environments with rapid temperature changes or high humidity. Unlike polymer foams, MG does not use an enclosed gas, so there is no reduction in thermal conductivity due to gas exchange. As a flexible silicone material, MGs can be expected to be applied as an excellent insulator that flexibly fits objects with complex shapes even in harsh environments. To investigate the change in thermal conductivity during deformation, measurements were performed while the MG was compressed uniaxially. Owing to the limited range of pressures that the thermal conductivity measurement system can apply to the sample, a panel sample with much higher flexibility was prepared by increasing the amount of acetic acid–urea solution to alkoxides by a factor of 1.67 in the starting composition of MG1.0-2.5-1.5 (Figures 4a, S3 and Table S1). When the compression of the sample started, the thermal conductivity decreased for a while (Figure 4b). This is because the pore diameter reduced due to compression, thereby suppressing the heat momentum exchange of the gas inside the pores and reducing the thermal conductivity of the gas phase.[35-37] For a compressive strain above 40 %, the thermal conductivity increased with increased compression because the effect of the increase in bulk density on the thermal conductivity of the solid phase became more considerable than that of the decrease in the thermal conductivity of the gas phase. For a compressive strain of approximately 60 %, the thermal conductivity did not become higher than that of the uncompressed sample. The unique feature of MGs is that the monoliths do not lose its heat insulation properties and mechanical properties due to repeated deformation (Figure S4). This is expected to lead to special heat insulation applications, such as filling in small spaces where maintenance is complex.

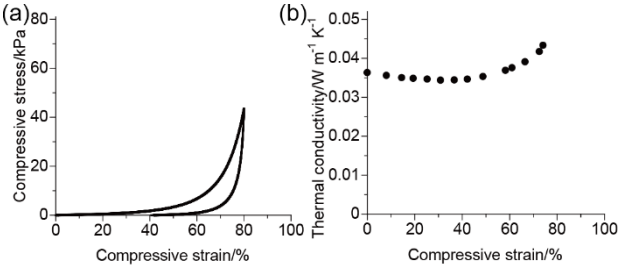

Figure 4. (a) Uniaxial compressive stress–strain curve and (b) thermal conductivity change of the higher flexible MG under uniaxial compression.

4. Conclusion

Macroporous silicon monoliths were prepared by the reaction of tetra-, tri-, and bifunctional silicon alkoxides, TMOS, MTMS, and DMDMS, respectively, as co-precursor in dilute aqueous solutions of acetic acid and urea. The obtained macroporous monolithic materials were sufficiently flexible to recover their original shape even after 80 % uniaxial compression and bending. Their cut surface showed high water repellency with a water droplet contact angle above 150°. When the obtained samples were heat-treated at temperatures above 200 °C, the unreacted silanol groups created siloxane bonds, making the material stable even at 300 °C for 24 h. The materials kept a low thermal conductivity of approximately 0.035 W m^{-1} K^{-1}, even when they were significantly deformed. The MGs produced in this report are expected to find thermal insulation applications under particular conditions. The MGs fabricated by the new process have almost the same physical properties as the silicone materials we have reported before and may be applied in various ways such as liquid-liquid separation, liquid nitrogen adsorption, and liposome preparation tools. The environmentally friendly fabrication process, which does not require surfactants or organic solvents, has been confirmed to be reproducible on a scale of several liters. In the near future, we plan to research the production and use of MGs on an industrial scale.

Acknowledgement

This work was supported by MEXT Leading Initiative for Excellent Young Researchers Grant.

Supporting Information

SEM images, FTIR spectra, stress–strain curves, and other physical properties of MGs. Movie of removing heptane from water using an MG. This material is available on https://doi.org/10.1246/bcsj.****.

References

1. L. J. Gibson, M. F. Ashby, *Cellular Solids: Structure and Properties*. 2nd Edition ed., Cambridge University Press, Cambridge, UK, **1999**.
2. M. Rubin, C. M. Lampert, *Sol. Energy Mater.* **1983**, *7*, 393.
3. K. Duer, S. Svendsen, *Sol. Energy* **1998**, *63*, 259.
4. D. M. Smith, A. Maskara, U. Boes, *J. Non-Cryst. Solids* **1998**, *225*, 254.
5. R. Baetens, B. P. Jelle, A. Gustavsen, *Energ. Buildings* **2011**, *43*, 761.
6. M. A. B. Meador, E. F. Fabrizio, F. Ilhan, A. Dass, G. Zhang, P. Vassilaras, J. C. Johnston, N. Leventis, *Chem. Mater.* **2005**, *17*, 1085.

7. K. Kanamori, M. Aizawa, K. Nakanishi, T. Hanada, *Adv. Mater.* **2007**, *19*, 1589.
8. M. A. B. Meador, E. J. Malow, R. Silva, S. Wright, D. Quade, S. L. Vivod, H. Guo, J. Guo, M. Cakmak, *ACS Appl. Mater. Interfaces* **2012**, *4*, 536.
9. S. Donthula, C. Mandal, T. Leventis, J. Schisler, A. M. Saeed, C. Sotiriou-Leventis, N. Leventis, *Chem. Mater.* **2017**, *29*, 4461.
10. G. Q. Zu, T. Shimizu, K. Kanamori, Y. Zhu, A. Maeno, H. Kaji, J. Shen, K. Nakanishi, *ACS Nano* **2018**, *12*, 521.
11. J. N. Lee, C. Park, G. M. Whitesides, *Anal. Chem.* **2003**, *75*, 6544.
12. S. J. Choi, T. H. Kwon, H. Im, D. I. Moon, D. J. Baek, M. L. Seol, J. P. Duarte, Y. K. Choi, *ACS Appl. Mater. Interfaces* **2011**, *3*, 4552.
13. J. Gao, J. B. Wang, H. Y. Xu, C. F. Wu, *Mater. Des.* **2013**, *46*, 491.
14. G. Hayase, K. Kanamori, K. Nakanishi, *J. Mater. Chem.* **2011**, *21*, 17077.
15. G. Hayase, K. Kanamori, M. Fukuchi, H. Kaji, K. Nakanishi, *Angew. Chem. Int. Ed.* **2013**, *52*, 1986.
16. G. Hayase, K. Kanamori, G. Hasegawa, A. Maeno, H. Kaji, K. Nakanishi, *Angew. Chem. Int. Ed.* **2013**, *52*, 10788.
17. T. Takei, K. Terazono, K. Araki, Y. Ozuno, G. Hayase, K. Kanamori, K. Nakanishi, M. Yoshida, *Polym. Bull.* **2016**, *73*, 409.
18. G. Hayase, S. M. Nomura, *Langmuir* **2018**, *34*, 11021.
19. G. Hayase, Y. Ohya, *Appl. Mater. Today* **2017**, *9*, 560.
20. G. Hayase, K. Nonomura, K. Kanamori, A. Maeno, H. Kaji, K. Nakanishi, *Chem. Mater.* **2016**, *28*, 3237.
21. G. Hayase, S. Nagayama, K. Nonomura, K. Kanamori, A. Maeno, H. Kaji, K. Nakanishi, *J. Asian Ceram. Soc.* **2017**, *5*, 104.
22. S. H. Tu, M. Chen, L. M. Wu, *J. Colloid Interface Sci.* **2020**, *566*, 338.
23. C. J. Brinker, G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press, San Diego, **1990**.
24. C. A. Schneider, W. S. Rasband, K. W. Eliceiri, *Nat. Methods* **2012**, *9*, 671.
25. Contact Angle. https://imagej.nih.gov/ij/plugins/contact-angle.html (accessed May 6, 2021).
26. G. Lamour, A. Hamraoui, A. Buvailo, Y. J. Xing, S. Keuleyan, V. Prakash, A. Eftekhari-Bafrooei, E. Borguet, *J. Chem. Educ.* **2010**, *87*, 1403.
27. L. L. Hench, J. K. West, *Chem. Rev.* **1990**, *90*, 33.
28. T. M. Tillotson, L. W. Hrubesh, *J. Non-Cryst. Solids* **1992**, *145*.
29. H. Dong, J. D. Brennan, *Chem. Mater.* **2006**, *18*, 4176.
30. A. V. Rao, S. D. Bhagat, H. Hirashima, G. M. Pajonk, *J. Colloid Interface Sci.* **2006**, *300*, 279.
31. G. Hayase, S. M. Nomura., *ACS Appl. Polym. Mater.* **2019**, *1*, 2077.
32. H. Tanaka, *J. Phys. Condens. Matter* **2000**, *12*, R207.
33. K. Kamiya, T. Yoko, K. Tanaka, M. Takeuchi, *J. Non-Cryst. Solids* **1990**, *121*, 182.
34. H. Dong, M. A. Brook, J. D. Brennan, *Chem. Mater.* **2005**, *17*, 2807.
35. L. W. Hrubesh, R. W. Pekala, *J. Mater. Res.* **1994**, *9*, 731.
36. G. Wei, Y. Liu, X. Zhang, F. Yu, X. Du, *Int. J. Heat Mass Transfer* **2011**, *54*, 2355.
37. G. Hayase, K. Kugimiya, M. Ogawa, Y. Kodera, K. Kanamori, K. Nakanishi, *J. Mater. Chem. A* **2014**, *2*, 6525.

Graphical Abstract

<Title>
Surfactant-free Aqueous Fabrication of Macroporous Silicone Monoliths for Flexible Thermal Insulation
<Authors' names>
Gen Hayase
<Summary>
Hydrophobic silicone macroporous monoliths with high flexibility were fabricated in surfactant-free aqueous solution by using three different organosilicon alkoxides as co-precursors. The obtained materials had chemical stability and heat resistance above 300 °C. No significant increase in thermal conductivity was observed when the panel-shaped samples were compressed by 60%.
<Diagram>