Preparation of Marshmallow-like Macroporous Silicone Monoliths in Simple Surfactant-free Aqueous Systems and Their Application to Flexible Thermal Insulation Materials

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Hydrophobic silicone macroporous materials prepared in an aqueous solution by the sol–gel method have been considered for various applications such as oil/water 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 are 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, which recover their original shape even after 80 % uniaxial compression and large bending. The macroporous materials showed water repellency and heat resistance characteristic of silicone, and the thermal conductivity ~0.035 W m^{-1} K^{-1} did not increase even after 60 % uniaxial compression. Those silicone monoliths fabricated by a simple and highly reproducible green process are expected to be used widely.

Keywords: sol-gel; macroporous materials; 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 were used as porous insulators, whereas recently, foamed polymers such as polyurethane, styrene, and phenolic resins, as well as glass wool, have been used instead.[1] The performance of vacuum insulation materials has been recently improved, thereby increasing the energy efficiency of home appliances. These 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. Aerogels, although not widely available in the market, have also been studied for thermal insulation applications.[2-5] Aerogels afford excellent insulation; however, they are brittle and therefore difficult to handle. Although alternative, elastic aerogels have attracted increasing research interest recently,[6-10] their industrial applications remain limited by their cost of production and poor handling.

This study investigates polyorganosiloxane (silicone) monolithic macroporous materials that exhibit excellent weatherability and processability. Silicones are generally characterized by low thermal conductivity, biocompatibility, water repellency, and chemical stability (specifically, they are not degraded by oxygen or water vapor).[11-13] Further, they are flexible even when dense, and their flexibility increases when they are produced with a porous structure such as foam. Foamed silicones are already widely used in cushioning and soundproofing materials and other applications. However, the highly porous silicone materials that can be produced by the sol-gel method have higher application potential. Macroporous silicone monoliths, called marshmallow-like gels (MGs) hereafter, 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. They have a structure with a framework diameter of several micrometers and a pore diameter of several tens of micrometers. Unlike porous silica and silsesquioxane materials, which also contain siloxane bonds produced by a similar reaction, silicones are highly flexible and resistant to compression 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].

Using an aqueous solution system to fabricate hydrophobic macroporous materials such as MGs is disadvantageous because a surfactant must be used in the starting sol. Even though the gels are easy to scale up, the need for surfactant removal as a pretreatment for drying remains a significant problem. The larger the volume of the monolithic material, 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 reaction in a simple aqueous solution system remains desirable.

Previous studies have reported methods to prepare macroporous silicone monoliths without using surfactants such as adding nanomaterials and copolymerizing alkoxides containing ionic groups.[20,21] However, none of these methods could produce a material with high flexibility like MGs. In this light, this study proposes a new method for preparing flexible porous silicones in an entirely aqueous solution system by adding highly hydrophilic tetrafunctional alkoxides. Alkoxides with different organic groups are known to have different hydrolysis rates and undergo different polycondensation reactions.[22] In this study, samples of the order of several hundred milliliters are produced through a homogeneous reaction of multiple alkoxides under appropriate conditions. The microstructure and mechanical properties of these samples are investigated, and their thermal conductivity is measured to evaluate their 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, $(CH_3)_2Si(OCH3)_2$), 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 flowchart of the fabrication process and the combinations of alkoxides tested in this paper.

As a reference,[14] 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 100 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.[23-25] 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}. 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

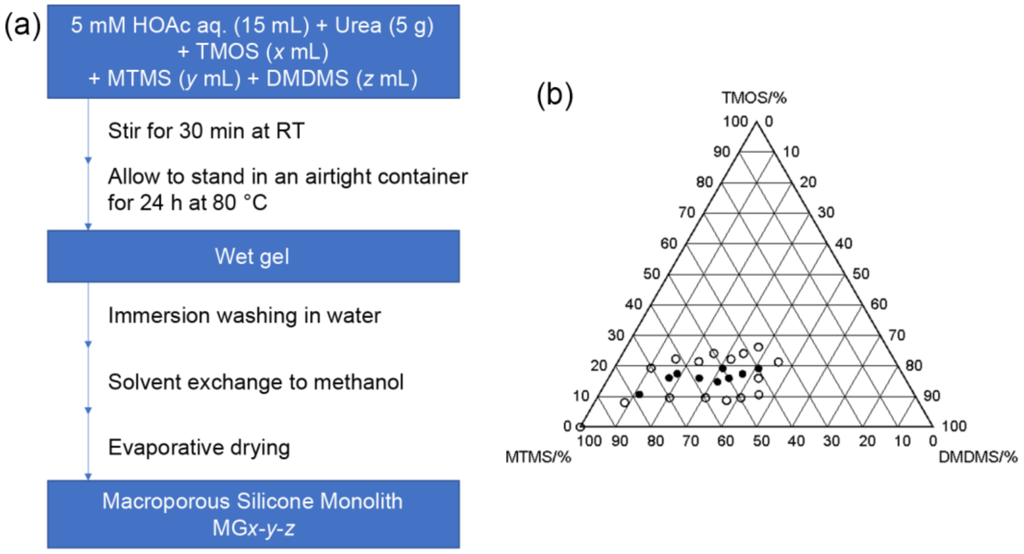

Figure 1. (a) Flowchart of sample preparation. (b) Sample composition of the trial. (a) Flowchart of sample preparation. (b) Sample compositions tested in this paper. The compositions indicated by the black circles yielded MGs with a homogeneous structure and flexibility to recover their original shape 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 group, is added instead of the surfactant to make the oligomer hydrophilic, phase separation will less likely occur before gelation. However, since 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 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.[22,26-29] 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 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 and ammonia water as the acid and base, respectively, in the system with a surfactant.[30] 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[31] similar to MGref and flexibility to return to the original shape 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 samples could not be evaluated using three-point bending measurements because they were deflected by their weight; however, they showed high flexibility against bending. For example, samples with a thickness of 5 mm could be wrapped around a pipe with a diameter of 10 mm. The Young's modulus of MGs was higher with increasing the percentage of tetrafunctional alkoxide TMOS in the coprecursor and lower with tetrafunctional bifunctional alkoxide DMDMS. Although flexibility is a characteristic property of MG, the samples with low Young's modulus showed poor handling of the wet gel before evaporative drying. Highly flexible samples (e.g., MG1.0-2.0-2.0) of several tens of millimeters thick were sometimes collapse under their weight unless immersed in liquid.

Further, the physical properties of an MG1.0-2.5-1.5 sample are described in detail as a representative composition. Figure 2(a) 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 highly hydrophobic silicone surface and diffuses slowly. If the rinsing process were incomplete, the dried sample would shrink or not exhibit its original properties.

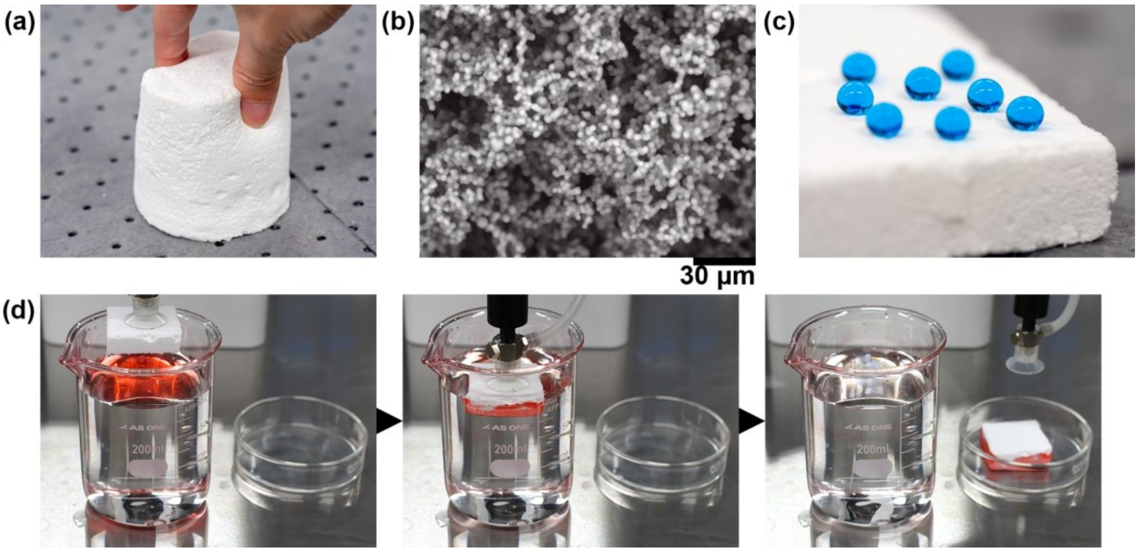

Figure 2. (a) Appearance of MG1.0-2.5-1.5 fabricated at 500 mL scale. (b) SEM image of MG1.0-2.5-1.5. (c) Water repellency of MG1.0-2.5-1.5. Water was stained with methylene blue. (d) Removal of heptane (colored with oil red o) from water utilizing the hydrophobic and lipophilic properties of MGs. The absorbed liquid can be squeezed out and collected. The whole process can be seen in MovieS1.

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 has a viscoelastic phase separation structure similar to that of MGref (Figure 2(b) and S1), and it shows 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 2(c)). At the same time, because of its lipophilicity, the bulk of MG1.0-2.5-1.5 was able to separate oil from water in the same way as previously reported using MGref (Figure 2(d) and Movie S1). However, FTIR measurement results showed unreacted silanol (Si-OH), which has hydrophilicity, at approximately 900 cm^{-1} in all samples prepared using TMOS (Figure 3(a) and S2).[28] Although it is difficult to examine precisely, the silanol on the surface of the microstructure is assumed to have decreased due to aging, with some remaining inside the skeleton.

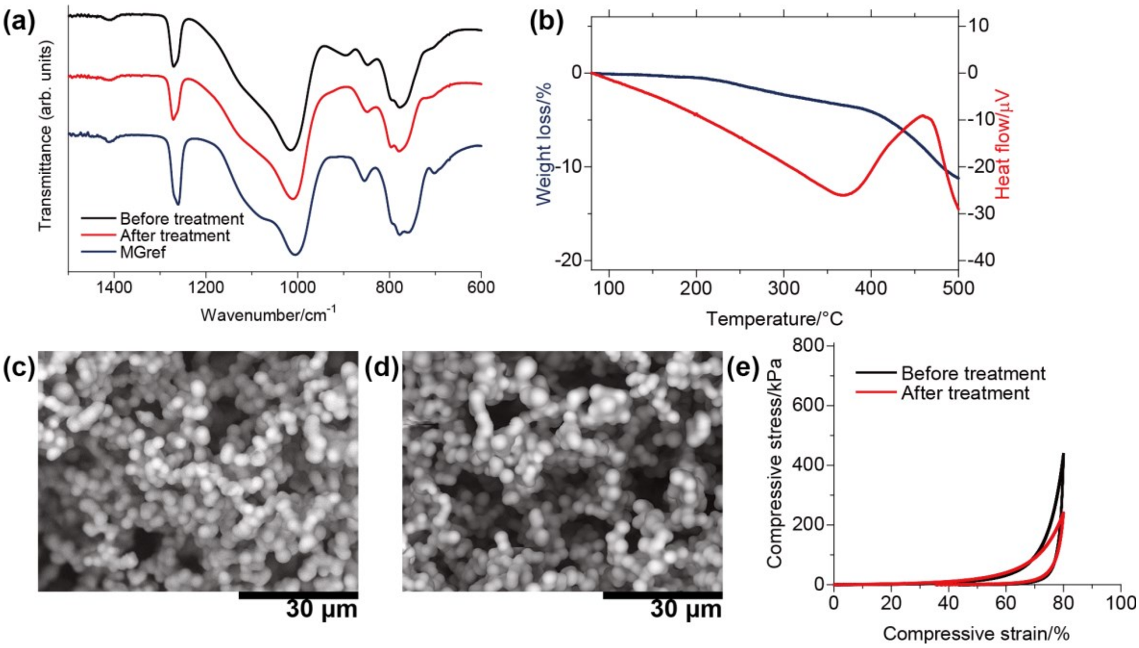

Figure 3. (a) Changes in FTIR spectra before and after heat treatment of MG1.0-2.5-1.5. After treatment, the obeous peak of the silanol group at ~900 cm^{-1} disappears as in MGref. (b) Thermogravimetric–differential thermal analysis (TG–DTA) curve of MG1.0-2.5-1.5. SEM images of MG1.0-2.5-1.5 (c) before and (d) after the heat treatment. There was no obvious 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.[32] Thermogravimetric–differential thermal analysis (TG–DTA) measurements were performed to determine the heat treatment temperature, and a slight dehydration reaction was observed at 200 °C, followed by the oxidation of methyl groups at approximately 360 °C (Figure 3(b)).[28,33] Therefore, heat treatment at 300 °C for 2 h was performed. Subsequently, the Si-OH peak (~900 cm^{-1}) was no longer observed in the FTIR spectrum. SEM observations of the microstructure before and after heat treatment did not reveal any noticeable change; further, no loss of flexibility in bending or compression occurred. Because few unreacted silanol groups existed on the surface, the physical properties such as flexibility did not change much before and after heating. Therefore, MG1.0-2.5-1.5 could be used in applications without any heat treatment. 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 good 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. Silicones have much higher thermal and chemical stability than ordinary organic polymers and glass fibers. Further, they do not degrade over long periods even in environments with rapid temperature changes and high humidity. Marshmallow-like gel, as silicone, is expected to be applied as a superior heat insulator that flexibly fits complex-shaped objects 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 can be applied by the thermal conductivity measurement system 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 (Figure 4(a), S3 and Table S1). As the sample was compressed, the thermal conductivity decreased for a while (Figure 4(b)). 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.[34-36] 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 was larger 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 fact that the thermal conductivity remains almost unchanged even with such a large deformation is expected to be useful for specific applications such as insulation by packing in a narrow space where maintenance is difficult.

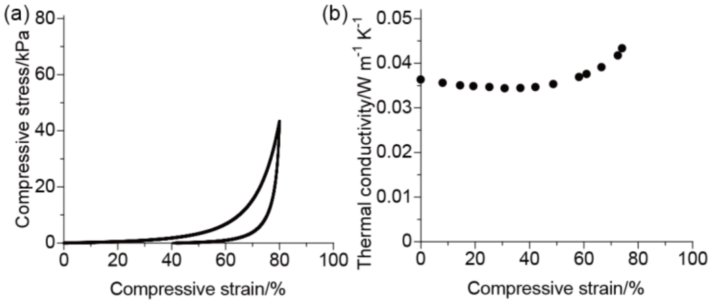

Figure 4. (a) Uniaxial compressive stress–strain curve and (b) thermal conductivity change of the higher flexible MG under uniaxial compression.

4. Conclusions

This study produced macroporous silicone monoliths using the tetra-, tri-, and bifunctional silicon alkoxides TMOS, MTMS, and DMDMS, respectively, as a coprecursor and reacting them in dilute acetic acid and urea aqueous solutions. The obtained porous 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°. 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, where many organic polymers oxidize and lose their physical properties. The material showed a low thermal conductivity of approximately 0.032–0.036 W m^{-1} K^{-1}, even when it was significantly deformed. The MGs produced in this study are expected to find thermal insulation applications as well as a wide range of other applications such as liquid–liquid separation materials, liquid nitrogen adsorption materials, and liposome preparation tools. They are produced at scales of the order of liters using an environmentally friendly aqueous solution process that requires no surfactants or organic solvents. Future studies will be aimed to produce and utilize MGs on an industrial scale.

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