Marshmallow-like macroporous silicone monoliths as reflective standards and high solar-reflective materials

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Abstract
A surfactant-free acetate-triethanolamine two-step catalytic sol-gel process with varying solvent content prepared marshmallow-like macroporous silicone monoliths. The resulting gels had fewer bubbles and other defects than conventional preparation methods. These materials exhibited high total reflectance of over 95.0 % in the visible light region. Samples with optimized solvent-to-precursor ratios show absolute reflectance greater than 97.5 % at 400–1100 nm and can be used in place of reflectance standards. Unlike existing reflectors, macroporous silicon monoliths are bulk materials that can be fabricated in a single reaction, allowing them to be large-area and arbitrarily shaped. These materials can be used not only for indoor measurements but also for outdoor telemetry applications such as drones and robots. They also exhibit excellent solar reflectance and significant absorption suppression over the entire wavelength range of sunlight. Their water repellency, UV resistance, low thermal conductivity, and efficient radiative cooling properties make them an ideal material for outdoor thermal management. The results of this study suggest that macroporous silicon monoliths have potential for use as a highly solar-reflective material that can successfully control surface temperature rise while contributing to environmental concerns.

Keywords macroporous monoliths, silicone, thermal management, reflective materials

1. Introduction
In the spectroscopic measurements and colorimetry of material surfaces, materials with known
reflectance are indispensable as calibration standards for quantitative optical measurements. Correct calibration of measuring instruments using standard materials provides accurate and reproducible results in the comparative evaluation of optical properties and color, as well as in the normalization of data. Typical materials used as reflective standards include porous barium sulfate and polytetrafluoroethylene (PTFE).\textsuperscript{1–3} In recent years, drones and robots have been increasingly used to perform remote measurements.\textsuperscript{4} Thus, the demand for reflective materials for outdoor use has increased. The white plates that are used in fields must be weather resistant and have large areas.\textsuperscript{5} High weather resistance ensures that the material will not degrade over time, maintaining the reliability of measurement results and reducing the cost of administration. Since telemetry using drones and robots typically involves measuring at high elevations and over large areas, the use of large-area white plates allows for a wider range of measurement targets and more accurate data collection. However, existing reflectors require advanced manufacturing techniques, and high-precision standard materials for outdoor use are generally expensive. Compared to powder sintering and powder coating, which are commonly employed for fabricating highly reflective porous structures, the sol-gel method offers a straightforward and efficient approach to creating porous materials.\textsuperscript{6,7} This technique enables precise control of uniformity at the molecular level and fine structure adjustments. Additionally, the sol-gel process can be completed at low temperatures, thereby eliminating the requirement for specialized equipment. Furthermore, the versatility of this method allows for the fabrication of certain materials directly at the measurement site.

Recently, we discovered the potential of macroporous silicon monoliths prepared by a sol-gel process with time evolution of phase separation as simple reflective materials. Our group has studied flexible white silicone monoliths, which we call marshmallow-like gels (MGs), from the copolymerization of mono-, bi- and tri-functional organosilicon alkoxides in aqueous systems.\textsuperscript{8,9} Owing to their high porosity, low bulk density, excellent thermal insulation properties, outstanding water repellency, and chemical resistance, these highly flexible and porous materials have been successfully applied in various fields. Consequently, we have reported their utilization in diverse applications, such as thermal insulators,\textsuperscript{10} separation media,\textsuperscript{9,11} liquid-repellent materials,\textsuperscript{12,13} liquid nitrogen retention materials,\textsuperscript{10} and giant vesicle formation tools.\textsuperscript{11,14,15} In recent applied research, our group has developed an optical tactile sensor that utilizes the intensity change of multiple Mie scattering by a skeleton with a few micrometers in diameter inside the
MGs.\textsuperscript{16} The silicone framework of MG effectively scatters a wide range of wavelengths in the visible and near-infrared spectrum due to its size. Despite employing a highly porous silicone material as the optical component, the sensor can be made as thin as 1 mm owing to its low external light penetration. We have already reported that the reason for this property is the high reflectivity of the MG surface. However, the details had not yet been investigated. Silicone materials have been industrialized as a highly reflective material for surface coatings and LEDs,\textsuperscript{17} and MGs with viscoelastic phase-separation structures\textsuperscript{18} have the potential for similar applications because of their propensity for effective light scattering. Unlike particle aggregates or their composites, MG is a bulk material with the advantages of a large homogeneous area and the ability to be processed into arbitrary shapes. These properties are considered advantageous for the fabrication of easy-to-handle reflective materials. To fabricate MGs specializing in optical properties, a surfactant-free fabrication method with a stable surface morphology was developed, and the relationship between the starting composition and the reflective properties was investigated. In addition, their applicability as high solar-reflective materials for outdoor thermal management is discussed, as this has recently attracted attention owing to environmental concerns.\textsuperscript{19–21} Thermal management materials with high solar reflectance tend to require more complex processes in return for their performance. Achieving high reflectance often requires precise control of the material's composition, structure, and properties, which may require multiple steps, specialized equipment for uniform deposition and coating, or advanced techniques. I demonstrate the potential of MG as a bulk optical material that can be reproducibly fabricated by a simple sol-gel process.

This study raises the possibility that MGs produced by an improved sol-gel process could be widely used in outdoor light reflection applications. It is expected to serve as a reliable, high-performance, and cost-effective alternative to existing reflective materials in a variety of situations.

2. Experimental materials and methods

2.1 Materials

Tetramethoxysilane (TMOS; Si(OCH\textsubscript{3})\textsubscript{4}), methyltrimethoxysilane (MTMS; CH\textsubscript{3}Si(OCH\textsubscript{3})\textsubscript{3}), dimethyldimethoxysilane (DMDMS; (CH\textsubscript{3})\textsubscript{2}Si(OCH\textsubscript{3})\textsubscript{2}), and triethanolamine (TMA) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Acetic acid, methanol, and 2-
propanol were purchased from Kanto Chemical Co., Inc. (Japan). All the reagents were used as received.

2.2 Sample preparation

TMOS (10 mL), MTMS (25 mL), and DMDMS (15 mL) were added to \( x \) mL of a 5 mM aqueous acetic acid solution. The mixture was stirred for 10 min to hydrolyze the silicon alkoxides. A 1 M TMA aqueous solution (0.020 \( \cdot \) \( x \) mL) was added to the resulting sol. The mixture was stirred for 3 min and then rapidly transferred to a sealed mold and placed in an 80 °C oven for 12 h. The resulting wet gels were solvent exchanged with methanol followed by 2-propanol and subjected to evaporative drying. The resulting xerogel was designated as MG\( x \). The samples were machined on a CNC milling machine (Kitmill CL200, ORIGINALMIND Inc., Japan) as required. The flowchart of the experimental procedure and a photograph of the CNC machining process are shown in Figure 1.
2.3 Characterization

The bulk density was calculated within 5% error on the basis of the weight and volume. Porosity was calculated using the true density obtained via helium pycnometry. Scanning electron microscopy (SEM; TM3000, Hitachi High-Tech Corp., Japan) was used for microstructural observations. The total reflectance was measured using a V-770 ultraviolet–visible–near-infrared (UV–Vis–NIR) spectrometer with an integrating sphere ISN-923 (JASCO Corp., Japan). The absolute reflectance was determined from the relative reflectance using the diffuse reflectance standard (Spectralon SRS-99-010, Labsphere, Inc., USA) with the calibration certificate of the National Institute of Standards and Technology (NIST, USA) as the reference material. Note that this diffuse reflectance standard is not a strict reference because the data obtained using ISN-923 includes a specular reflectance component. However, it was used in the calculation for convenience, as no significant errors occurred. An outdoor solar radiation test was conducted on October 29, 2022, on the lawn of the National Institute for Materials Science (140.13310° E longitude, 36.06948° N latitude). An MG180 sample with dimensions of 110 mm × 110 mm × 10 mm, half of which was covered with aluminum foil, was placed on a perforated stainless-steel plate ~25 cm above the ground. K-type thermocouples were fixed to the surface using Kapton (polyimide) tape. The weather was clear, and the sunshine duration was 100% during the measurements. Neighborhood weather information was obtained from the Automated Meteorological Data Acquisition System (AMeDAS) on the day of the measurement. This information is provided in Supporting information, and it can be found on the Japan Meteorological Agency website. The temperature was allowed to stabilize for 1 h in a well-ventilated shade. Thereafter, the sample panel was exposed to sunlight at the beginning of the measurement. K-type thermocouples were used to measure the sample surface temperature, and a data logger (AD-5695DL A&D Co., Ltd., Japan) was used to measure the ambient air temperature. Thermal conductivity was measured using a heat flow meter (HFM; HFM 446 Lambda Small, Netzsch GmbH, Germany) using a panel with a size of approximately 110 mm × 110 mm × 10 mm. The temperature difference between the upper and lower hot plates was set as 10°C, and measurements were obtained at an average temperature of 15–60°C. The measurement error for each sample was around 3%. Fourier transform infrared (FTIR) spectra were recorded.
using IRSpirit-L (Shimadzu Corp., Japan) equipped with an attenuated total reflection (ATR) attachment (QATR-S, Shimadzu Corp., Japan). A total of 100 scans of the sample were recorded at a resolution of 4 cm$^{-1}$. Uniaxial compression tests were performed using a universal tensile testing machine (EZ-SX, Shimadzu Corp., Japan) and a 500 N pressure gauge. The samples were cut into rectangular pieces with dimensions of 15 mm × 15 mm × 8 mm and used for the measurements. Young's modulus was calculated from the change in stress at a compressive strain of 2.5–5.0%.

3. Results and Discussion

3.1 Yieldable fabrication process using triethanolamine and reflectance measurement

It is essential to eliminate the inhomogeneity caused by the presence of bubbles in the fabrication of highly reflective monolithic porous materials. First, I improved the sol-gel process to prevent air bubbles from remaining in the monolith. In a previous report, urea was used as a base generator in an acid–base two-step sol–gel reaction to prepare MGs. Urea provided the advantage that it gradually decomposes and releases ammonia through hydrolysis, resulting in a homogeneous increase in pH throughout the sol and a high yield. However, carbon dioxide, a by-product of hydrolysis, tends to remain in the gel as bubbles. The continuous application of gentle vibration to the sol or pressure using an airtight seal effectively prevented the inclusion of bubbles. Nevertheless, bubbles could not be eliminated in large-volume synthesis. When dilute ammonia water was added to the reaction sol instead of urea, the gel was prone to inhomogenization due to abrupt pH changes, and the skeleton (solid phase) tended to freeze without fully developing the phase-separated structure (Figure S1, Supporting information). As a result, the yield was greatly reduced. However, it was found experimentally that the addition of a weaker base facilitated the formation of a homogeneous gel. Monolithic gels were efficiently obtained when TMA (p$K_b$ = 6.20) was used instead of ammonia water (p$K_b$ = 4.75) with a slight difference in reaction (Figure S2, Supporting information). I could obtain MGs by optimizing the TMA concentration even when the composition ratio of the silicone precursors was changed somewhat. However, the conditions were complex. Therefore, I prepared samples with fixed mixing ratios of organic silicone alkoxides in this study.

In general, the physical properties of monolithic porous materials produced using the sol–gel method can be adjusted by altering the amount of solvent used in the starting process. In
the MGx system, xerogels were stably produced using a variable (x) acetic acid solution volume (90–210 mL). Table 1 lists the prepared samples, and Figure 2 shows the SEM images of the samples. The obtained gels were similar to the MGs obtained using the previously reported urea method. The gels were flexible white monoliths consisting of a continuous skeleton with a diameter of approximately 3 μm (Figure S3, Supporting information). When the amount of solvent was changed, the density and porosity varied, the skeleton diameter varied negligibly. The total reflectance of each sample (approximately 5 mm thick) was measured using an integrating sphere. All gels showed a high reflectance of over 95.0 % in the visible light range (400–800 nm) (Figure 3a). The reflectance of MG90 and MG210 was slightly lower than that of the other samples. This indicated that there was an optimum range for the amount of solvent in the starting composition. The absolute reflectance of MG120-180 was 97.5 % or higher at all wavelengths in the main detection range of silicon diodes (400–1100 nm). Almost no degradation was caused by water vapor absorption owing to the nature of silicone. Furthermore, a self-cleaning effect on the surface was expected owing to its superhydrophobic properties (Figure S4, Supporting information). These properties make the MG suitable for a wide range of optical applications, such as a standard white plate for spectroscopic measurements, material for the inner wall of integrating spheres, and target for outdoor measurements (Figure 3b). Near-infrared and near-UV reflectance can be used to create simple UV and IR sensor cards with dyes soaked in the porous structure of MGs (Figure S5, Supporting information).

Table 1. Physical properties of MGx.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density [g cm(^{-3})]</th>
<th>Porosity [%]</th>
<th>Reflectance at a wavelength of 550 nm [%]</th>
<th>Thermal conductivity at 20 °C [W m(^{-1}) K(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG90</td>
<td>0.167</td>
<td>88.1</td>
<td>97.0</td>
<td>0.0355</td>
</tr>
<tr>
<td>MG120</td>
<td>0.135</td>
<td>90.4</td>
<td>98.0</td>
<td>0.0348</td>
</tr>
<tr>
<td>MG150</td>
<td>0.122</td>
<td>91.3</td>
<td>98.2</td>
<td>0.0341</td>
</tr>
<tr>
<td>MG180</td>
<td>0.112</td>
<td>92.0</td>
<td>98.2</td>
<td>0.0318</td>
</tr>
<tr>
<td>MG210</td>
<td>0.112</td>
<td>92.0</td>
<td>97.5</td>
<td>0.0356</td>
</tr>
</tbody>
</table>
**Figure 2.** Scanning electron microscope (SEM) images of (a) MG90, (b) MG120, (c) MG150, (d) MG180, and (e) MG210.

**Figure 3.** (a) Total light reflectance of MGs. (b) Photograph of Spectralon white reflectance standard and CNC-machined cylindrical MG180.
3.2 Marshmallow-like gel as a high solar-reflective material

Previous studies showed that MGs exhibited low thermal conductivity and that their thermal insulating properties did not decrease with deformation. As silicone is commonly used in practical applications as a solar-reflective paint, it can be used to create a multifunctional thermal management material by adding solar-reflective properties to the thermal insulating properties. Experiments were performed to assess the reflectivity under visible light irradiation using MG180, which displayed the lowest thermal conductivity among all samples due to the balance between bulk density and pore size, factors that influence thermal conductivity in both solid and gas phases.23

The total reflectance of MG180 was measured using a spectrophotometer with an integrating sphere at wavelengths of 250–2500 nm (radiation wavelength range of sunlight). Glossy aluminum foil was used as the reference sample owing to the ease of availability and reproducibility. Figure 4a shows that the reflectance of MG180 was better than that of aluminum in the near-UV to NIR range. The optical absorption per unit area on the surfaces of both samples was calculated using the reflectance of MG180 and aluminum foil and the spectral emission intensity of Air Mass 1.5 (AM1.5, the solar spectrum on the surface of Japan), and the values were significantly different (Figure 4b). This indicated that unlike aluminum, MG180 absorbed negligible sunlight over the entire wavelength range of light that reached the ground. MG180 showed a few absorption peaks in the NIR reflectance measurements. However, there were no significant peaks for sunlight absorption compared with the visible light region, where the reflectance was higher.
Figure 4. (a) Total light reflectance spectra of MG180 and Al, and AM1.5 (solar radiation).\textsuperscript{24,25} (b) Calculated solar absorption spectra of MG180 and Al.

An experiment was conducted by exposing the MG180 to sunny conditions to demonstrate that the increase in surface temperature under solar radiation was significantly suppressed. MG180 panels with dimensions of 12 cm × 12 cm × 1 cm were prepared. Half of the panels were wrapped with aluminum foil, and thermocouples were placed in each area. Figure 5 shows the change in temperature recorded during 1 h of daylight in a well-ventilated area (see the experimental method section for detailed conditions such as the date, time, location, and weather). The temperature of the aluminum surface increased rapidly when exposed to sunlight but that of MG180 did not change significantly. The thermal conductivity of MG180 measured using the HFM method was 33.0 mW m\(^{-1}\) K\(^{-1}\) at a central temperature of 30 °C, indicating high thermal insulation properties (Figure 6). Therefore, MG180 can be used as a thermal management material for outdoor equipment exposed to direct sunlight, such as the outdoor units of air conditioners and cooling pipes.
Radiative cooling is a material property that is gaining attention in the context of reducing the heat island effect and global warming.\textsuperscript{23} Materials that cause radiative cooling have an infrared radiation spectrum in the "atmospheric window" at 8–13 $\mu$m.\textsuperscript{26} This property has been known for more than 50 years,\textsuperscript{27–30} and it has been increasingly reported for silicone-based
materials in recent years.\textsuperscript{31–35} MG180 exhibits an absorption spectrum at a wavelength corresponding to the infrared atmospheric window (Figure 7). Kirchhoff's law states that the absorption and emission spectra coincide.\textsuperscript{36} Thus, thermal management materials with MG180 are expected to exhibit radiative cooling after solar-heat absorption. Although there have been few reports of heat insulators with passive cooling capabilities,\textsuperscript{37} continued improvement of porous silicone materials is expected to lead to further application development. The practicality of macroporous materials, which include but are not limited to current MGs, is limited owing to strength issues such as abrasion resistance. Nevertheless, their performance can be demonstrated in conditions where pressure and force are not applied. The mechanical strength of these materials can be improved by creating composites with other materials. Hence, I expect MGs to be used in the outdoor applications that utilize the environmental resistance of organosiloxanes, such as UV resistance and water repellency.

![Figure 7. (a) Fourier transform infrared (FTIR) of MG180. (b) Absorption spectra of MG180 (approximately equal to the radiation spectrum) and the infrared atmospheric window spectrum.\textsuperscript{38}](image)

4. Conclusion
Highly reflective silicone monolithic porous materials with smooth surfaces were prepared using
a surfactant-free process. The process was modified using TMA instead of urea in an acid–base two-step sol–gel reaction so that no bubbles remained in the monolith. Monolithic macroporous materials were prepared by varying the amount of solvent used in the starting process, and their physical properties were measured. All the samples exhibited a high total reflectance of more than 95.0 % in the visible-light range, but there was an optimum range for the amount of solvent. The MG180 sample exhibited excellent solar reflectance and significant absorption suppression in all wavelength ranges of sunlight, resulting in a well-controlled increase in the surface temperature. Moreover, it exhibited low thermal conductivity as low as ~0.032 W m⁻¹ K⁻¹ around room temperature. Similar to previously known silicone materials, MG180 showed radiative cooling properties and efficiently radiated heat in the 8–13 μm atmospheric window. Macroporous silicone monoliths are expected to be useful for outdoor thermal management owing to their water repellency and UV resistance.

**Note**
The author declares no conflict of interest.

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