

# A Polydimethylsiloxane (PDMS) Sponge for the Selective Absorption of Oil from Water

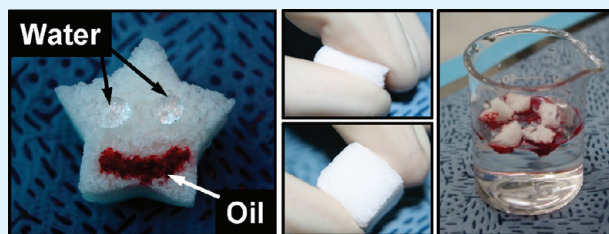
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**S** Supporting Information

**ABSTRACT:** We present a sugar-templated polydimethylsiloxane (PDMS) sponge for the selective absorption of oil from water. The process for fabricating the PDMS sponge does not require any intricate synthesis processes or equipment and it is not environmentally hazardous, thus promoting potential in environmental applications. The proposed PDMS sponge can be elastically deformed into any shape, and it can be compressed repeatedly in air or liquids without collapsing. Therefore, absorbed oils and organic solvents can be readily removed and reused by simply squeezing the PDMS sponge, enabling excellent recyclability. Furthermore, through appropriately combining various sugar particles, the absorption capacity of the PDMS sponge is favorably optimized.

**KEYWORDS:** polydimethylsiloxane, PDMS, sponge, templating, casting, oil spill cleanup, water remediation, hydrophobic, oleophilic



## INTRODUCTION

Cleaning oil spills in a marine environment is a challenging task.<sup>1–3</sup> The methods currently used to clean oil in water can be divided into the following categories: collection of oil from the water surface, mixing of oil with water using dispersing agents to facilitate natural degradation, and in situ burning of oil spills. The collection of oil using materials with both hydrophobic and oleophilic properties is often preferred because it allows for the proper disposal of oil and does not cause secondary pollution. The first example of oil–water separation was reported by Jiang et al. using a mesh coated with hydrophobic and oleophilic materials.<sup>4</sup> Along the same lines, the creation of nanometer- or micrometer-sized porous materials with excellent surface superhydrophobicity has more recently been demonstrated for successful use in the separation and absorption of oils or organic solvents from water. In a representative study, Yuan et al. reported the selective absorption of oil from water by a superwetting nanowire membrane.<sup>5</sup> A similar selective absorption performance has also been reported by Zhang et al. using superhydrophobic nanoporous polydivinylbenzene.<sup>6</sup> Owing to their excellent selective absorption ability, fast absorption kinetics, and large capacity, these materials have significant advantages over traditional absorbent materials such as active carbons.<sup>7,8</sup> To combat global-scale water pollution arising from oil spills and industrial organic pollutants, the development of efficient absorbent materials to separate and remove oils and organic pollutants from water, such as silicas,<sup>9</sup> organic–inorganic hybrids,<sup>10</sup> functionalized polymers and resins,<sup>11</sup> and carbon nanotubes,<sup>12–14</sup> should be of great significance in addressing environmental

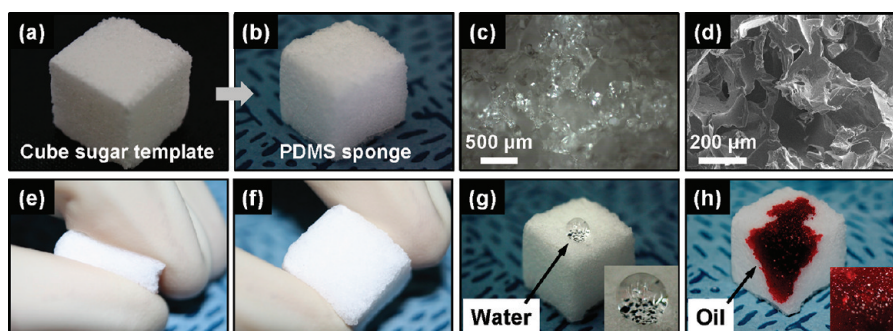
issues.<sup>15</sup> However, only a few experiments have focused on the recyclability of absorbent materials and efficient ways to reuse the absorbed oil.<sup>12,16</sup> Moreover, the complex synthesis processes involved in creating the reported absorbent materials hamper the use of these materials in large-scale applications. Therefore, there is still an urgent need for a low-cost efficient material with considerable absorption capacity, stable performance, and a large-scale template.

Casting, a 6000-year-old process used throughout human history, occurs when a liquid material is poured into a mold containing a hollow cavity with a desired shape and is subsequently allowed to solidify.<sup>17</sup> Casting is frequently used to fabricate complex shapes that are otherwise difficult or uneconomical to implement using other methods. Here we demonstrate the simple templating method to develop an efficient absorbent material for the selective separation of oil and water. Both commercially available cube sugar and handmade sugar are used as the templates, i.e., molds, which can be easily removed through immersion in water.<sup>18,19</sup> This aspect is the most important in an eco-friendly fabrication process. Moreover, the widely used polydimethylsiloxane (PDMS), which is inert, nontoxic, nonflammable, and highly flexible, is employed as the sponge material in the proposed method. The replicated PDMS sponge from the sugar templates does not require intricate synthesis processes or equipment and can be used for the selective

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**Figure 1.** (a) Photograph of a commercially available cube sugar for the templating process. (b) Photograph of the as-replicated PDMS sponge. (c) Optical microscope image of the cross-sectional area of the PDMS sponge. (d) SEM image of the cross-sectional area of the PDMS sponge. (e) Manual compression to over 50% reduction in volume and (f) recovery to the original shape. PDMS sponge wettability showing (g) high hydrophobicity and (h) strong oleophilicity of the surface. Transformer oil was used and colored with Oil red O dye for clarity. (Inset) Magnified view of water and oil droplets on the PDMS sponge.

absorption of oil because of the combination of both hydrophobic and oleophilic properties. Moreover, the PDMS sponge can be elastically deformed into any shape and compressed repeatedly in air or liquids without collapsing. Therefore, the absorbed oils as well as the organic solvents can be readily removed and reused by simply squeezing the PDMS sponge, enabling excellent recyclability. Furthermore, the absorption capacity of the PDMS sponge can be optimized by appropriately combining various sugar particles in the template. Therefore, we believe that the PDMS sponge may be potentially important in remedying chemical accidents and removing organic pollutants from water.

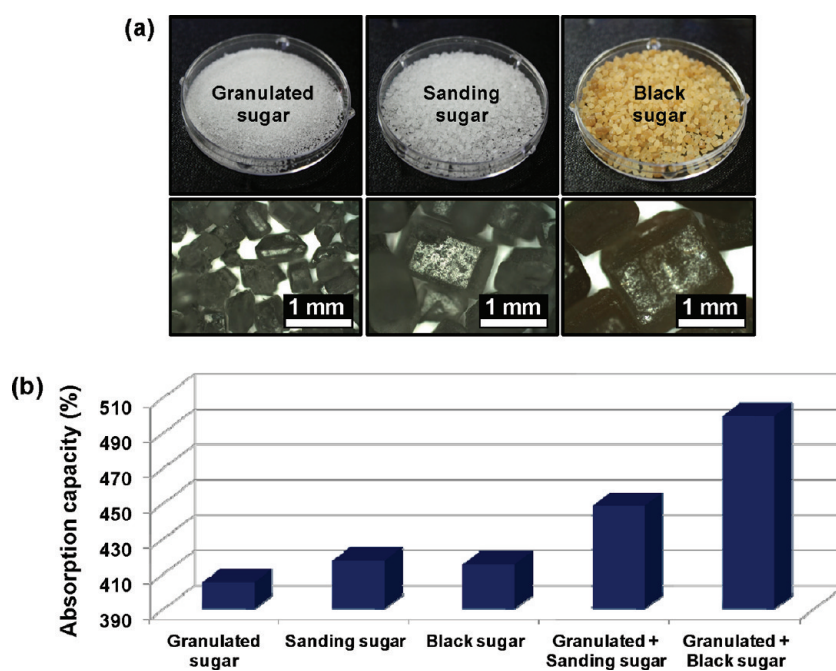
## RESULTS AND DISCUSSION

In a typical experiment using the sugar-templating process, eco-friendly PDMS sponges were replicated from commercially available cube sugars with an approximate particle size of 400 to 500  $\mu\text{m}$  (that is, granulated sugar) (Figure 1a, b); for further details about fabrication, see the Supporting Information, Figure S1. It is noteworthy that the total production time for PDMS sponges is only a few hours, and large-scale production can be readily implemented by virtue of the proposed sugar-templating process. Close-up views from optical microscope (Figure 1c) and scanning electron microscope (SEM; Figure 1d) images show that the proposed PDMS sponges consist of a porous, interconnected three-dimensional framework. No apparent difference in the morphology or distribution is observed from the top surface or the side-walls of the structure. The bulk density of the PDMS sponges ranges from 0.18 to 0.75  $\text{g cm}^{-3}$ , interestingly, depending on the combination of individual sugar particles (i.e., granulated, sanding, and black sugars, to be discussed in detail later) that are used as the template. It is inferred that the porosity of the PDMS sponge strongly depends on the structure of the template and hence can be adjusted to achieve high performance for the separation of oil and water. The fabricated PDMS sponges exhibit a structural flexibility that is rarely observed in other materials with high porosity (e.g., inherently brittle silica aerogels).<sup>20,21</sup> Manual compression involving a volume reduction of over 50% shows that the sponge is remarkably compliant and springy (Figure 1e, f; see the Supporting Information, Movie 1). Moreover, the PDMS sponge can be bent to a large degree without breaking apart and can almost perfectly recover its original shape. The measured elastic modulus of the PDMS

sponge is approximately 0.00002 GPa, which is much lower than that of rubber (0.01–0.1 GPa) and bulk PDMS materials (0.00075 GPa; see the Supporting Information, Figure S2). This structural integrity under significant deformation is due to the three-dimensional isotropic nature of the PDMS material, revealing that its notable springiness can help in recycling absorbed oils and organic liquids. Furthermore, prolonged ultrasonication in various organic solvents did not deteriorate the PDMS sponge.

Importantly, the proposed eco-friendly PDMS sponge has both properties of hydrophobicity and oleophilicity. To demonstrate these properties, we first measured the water contact angle to investigate the surface wettability of the PDMS sponge. When a water droplet is allowed to sit on the surface of the PDMS sponges, the contact angle indicates high hydrophobicity ( $>120\text{--}130^\circ$ ) with neither chemical nor physical surface treatment (Figure 1g); see the Supporting Information, Movie 2). However, the exact value of the water contact angle cannot be precisely estimated due to the highly roughened surface of the PDMS sponge. This highly hydrophobic surface can be attributed to a combination of microporous morphological structures and the PDMS material's hydrophobic chemical properties. Second, the contact angle of the oil droplet was measured. In contrast to its high hydrophobicity, the PDMS sponge shows strong oleophilic properties. For instance, when a transformer oil (0.89  $\text{g cm}^{-3}$ ) labeled with Oil red O dye was placed on the surface of the PDMS sponge, it was quickly absorbed into the sponge, resulting in a contact angle of nearly  $0^\circ$  (Figure 1h; see the Supporting Information, Movie 2). Furthermore, an organic solvent (e.g., ethanol) with relatively low surface tension was immediately absorbed into the PDMS sponge as well (see the Supporting Information, Movie 2). The fast absorption kinetics of the oils and organic solvents can mainly be attributed to the strong oleophilic nature of the PDMS sponge in combination with its microporous features, which can induce capillary action. By taking advantage of hydrophobic and oleophilic properties as well as its microporous features, therefore, the PDMS sponge may be an ideal candidate for use as an absorbent for oil–water separation and the removal of organic solvents from water.

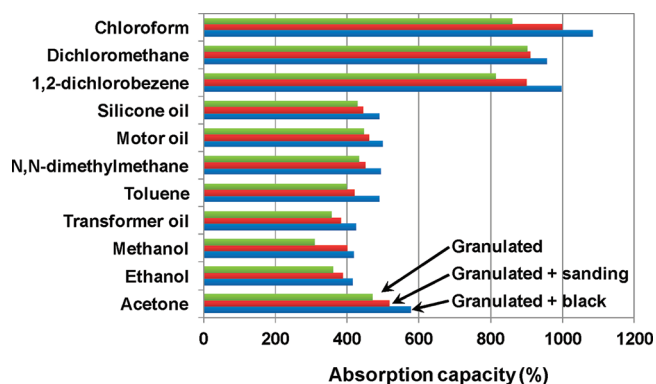
To optimize the sugar template employed in the formation of the PDMS sponge, we prepared three different sugar particle sizes: granulated (400–500  $\mu\text{m}$ ), sanding (1000–1100  $\mu\text{m}$ ), and black (1500–1800  $\mu\text{m}$ ) sugar (Figure 2a). By mixing these sugar particles, we were able to adjust the template of the PDMS sponge to obtain higher absorption capacities. Figure 2b shows



**Figure 2.** (a) Optical microscope images of various sugar particles (i.e., granulated, sanding, and black sugar particles). The size distributions of the granulated, sanding, and black sugar particles at  $400\text{--}500\ \mu\text{m}$ ,  $1000\text{--}1100\ \mu\text{m}$ , and  $1500\text{--}1800\ \mu\text{m}$ , respectively. (b) Absorption capacity of the PDMS sponges replicated from various sugar templates for the transformer oil. For combined sugar templates, two types of sugar particles were mixed in a volume ratio of 1:1.

the absorption capacities of the PDMS sponges measured for transformer oil using different sugar templates: granulated, sanding, black, granulated and sanding, and granulated and black sugar particles. All experiments were conducted at room temperature. By immersing the PDMS sponge replicated from the template of granulated sugar directly into the transformer oil, up to 410 wt % of the original weight was absorbed. Interestingly, even though the size of the sugar particles (i.e., the size of pores) in the templates was notably different, the absorption capacity of the oil did not change significantly, regardless of whether homogeneous sanding or black sugar was used as the template material. In contrast, if the sugar template consisted of heterogeneously mixed sugar particles of different sizes (i.e., templates made from a combination of granulated and sanding or granulated and black sugars), the absorption capacity improved. In this case, the porosity of the sugar template could be further reduced relative to that of uniform sugar case. Consequently, the porosity of the PDMS sponge can be enhanced. That is, the less uniform the sugar particles are, the larger is the absorption capacity of the oil. For the PDMS sponge based on the template with both granulated and black sugar particles, the absorption capacity increased up to 498 wt % of its weight.

To investigate the absorbencies of the PDMS sponge replicated from three kinds of sugar templates (i.e., granulated, granulated and sanding, and granulated and black sugar particles), we employed various organic solvents and oils in this experiment. The PDMS sponge was dipped into the organic solvents and oils for a few seconds. Although longer immersion times were expected to lead to greater absorption, a qualitative visual observation showed that the PDMS sponge was rapidly wetted in the organic solvents and oils, which did not greatly depend on time. Furthermore, the oil-filled PDMS sponge could float on water without the penetration of water into the structure or the release



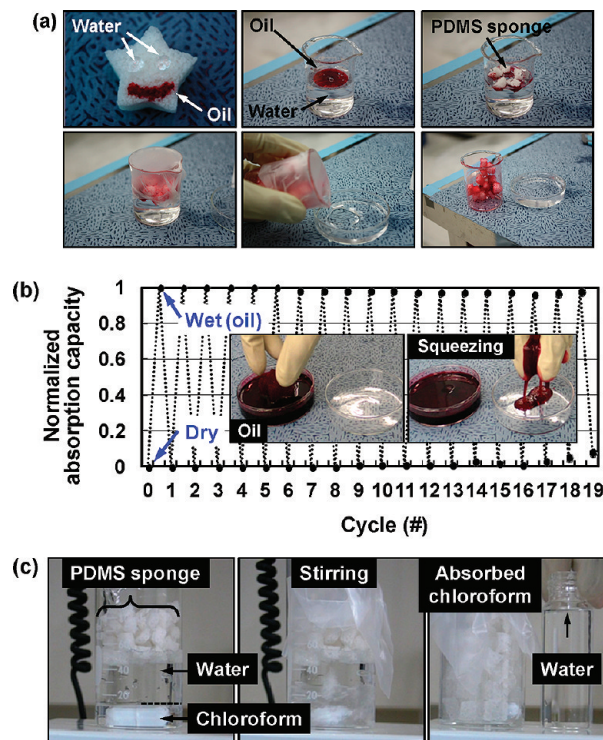
**Figure 3.** Plot of the mass-based absorption capacity for different organic solvents and oils as a function of liquid density.

of the oil; this was verified from the measured weight of the oil-soaked PDMS sponge, which changed by only 6% after 24 h. One important observation was that the absorbed oil was almost completely retained after the PDMS sponge was removed from the water, which was evidenced by the fact that its weight remained within 93% of the wet weight after 24 h. The PDMS sponge approximately showed absorption capacities in the range from 400 wt % to 1100 wt % for various oils and organic solvents, with the maximum absorption capacity reaching up to 10 times its weight (Figure 3). It is important to note that the changes in absorption capacity may predominantly depend on the density of the organic solvents and oils. Furthermore, the PDMS sponge also showed high absorption capacity not only for nonpolar organic solvents but also for polar organic solvents. For instance, the absorption capacity of 1,2-dichlorobenzene (a well-known toxic organic contaminant in water treatment) for the PDMS sponge

based on the template with both granulated and black sugar particles was approximately 1000 wt %. Because the PDMS materials show a relatively excellent chemical inertness, our PDMS sponge may possibly be used for both nonpolar and polar organic solvents, with great potential for the removal of toxic organic contaminants and oil spills from water. Swelling of the PDMS sponge was occasionally observed along with the absorption of organic solvents because the organic solvents can diffuse into the PDMS material. Nevertheless, this swelling did not influence the sponge's absorption properties.

When the PDMS sponge is immersed in water, it does not absorb water, as previously mentioned. However, during the experiment, it seemed as if intermittent water absorption was taking place. This was mainly due to water adhering to the surface of the PDMS sponge, which arises from the pinning effect; we were able to remove the water by gently wiping the surfaces. In contrast, the PDMS sponge can actively absorb and remove oils spreading on the water surface. Transformer oil distributed on the surface of a water bath formed a thin, disk-like shape with a thickness of 2 to 3 mm in the central region. A hexahedral-shaped PDMS sponge was placed in the film and was suspended on top of the distributed oil surface (see the Supporting Information, Figure S3). We observed that the PDMS sponge floated on the water surface and moved freely throughout the oil area. Whenever the PDMS sponge came into contact with the oil, it instantaneously absorbed the oil film, resulting in a local white-colored region that indicated the presence of filtered water. The PDMS sponge tended to drift on the remaining area of the oil film due to its water-repelling and oil-wetting properties, which leads to a unique floating-and-cleaning capability that is particularly useful for cleaning up oil spills. To better verify the sponge's practical applications, Figure 4a illustrates the detailed process of transformer oil absorption by a typical PDMS sponge sample. After cutting the PDMS sponge into small pieces, the pieces of the PDMS sponge were placed in a mixture of oil and water. Then, the samples were briefly vortexed to artificially shake the beaker containing the mixture and the PDMS sponge pieces, mimicking the motion of ocean waves. The obtained results show that all of the oils on the water surface can be completely absorbed into the PDMS sponge within a few seconds (For details on sponge formation, see the Supporting Information, Movie 3). Moreover, when this experiment was performed in seawater, which contains numerous ions such as  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , etc., a similar degree of absorption was observed.

The recyclability of the PDMS sponge and the recoverability of oils and organic solvents address key requirements in practical oil cleanup applications. The absorbed oils and organic solvents in the PDMS sponge can be removed and reused by manually squeezing the PDMS sponge due to the springy nature of the PDMS material (Figure 4b). As such, the proposed PDMS sponge is a desirable material in that it facilitates the recycling of oil-absorbent materials by allowing for the repeated capture and release of oils and organic solvents. To test the recyclability of the PDMS sponge as an absorbent material, we squeezed the PDMS sponge and immediately immersed it in an organic solvent (e.g., ethanol) 20 times after absorbing the transformer oil; the sponge weight was measured before and after drying (Figure 4b). The reason for immersing the oil-absorbed PDMS sponge in ethanol was so to ensure that any oil remaining after squeezing the oil-soaked PDMS sponge would be completely exuded into the ethanol. The results show that the absorption capacity did not deteriorate, and the weight of a dry PDMS



**Figure 4.** Removal of oil by the PDMS sponge in the application of remedying devastated marine environments. (a) By utilizing the PDMS sponge's hydrophobic and oleophilic properties, a layer of oil (dyed with Oil Red O) was removed by adding PDMS sponges to the oil. (b) Demonstration of the recyclability of the PDMS sponge. The absorption capacity of the PDMS sponge after multiple cycles was normalized by the initial weight gain. To completely remove any remaining oil after squeezing the oil-absorbed PDMS sponge, ethanol solvents were used. (c) Absorption process of the PDMS sponge in a mixture of chloroform and water. A vortex stirring process was used to absorb the chloroform submerged underwater.

sponge did not notably change when the PDMS sponge was reused multiple times. When the PDMS sponge was immersed in water after the reusability test, it still did not absorb any water, indicating that hydrophobicity was not lost.

In addition, the absorption of chloroform ( $1.48 \text{ g cm}^{-3}$ ) from water by the PDMS sponge was carried out to verify the use of the sponge with organic contaminants with higher densities than that of water. As shown in Figure 4c, the PDMS sponge was not wetted by water due to its hydrophobicity, and chloroform sunk to the bottom of the water, owing to higher density than water. However, vigorous stirring can overcome this drawback (see the Supporting Information, Movie 4). With this technique, nearly all of the chloroform was fully absorbed into the PDMS sponge within a few seconds.

## CONCLUSIONS

Overall, our precisely controlled and reproducible PDMS sponge enables the separation of oil and water, therefore representing a practical solution for the removal of organics, particularly from marine environments devastated by oil spills. As compared with other previously reported absorbents for the separation of oil and water, our approach utilizes a PDMS sponge replicated by a simple sugar-templating process, and therefore, it requires only a simple as well as eco-friendly preparation process

that is easy to handle for practical use. Importantly, the absorption capacity of the PDMS sponge did not change after repeated cycles, demonstrating the excellent recyclability of the absorbent. Moreover, the absorbed oil can be favorably reused by virtue of the remarkably springy nature of the PDMS sponge. Nevertheless, several drawbacks remain. For example, the capacity could be optimized further, and there are several methods that could increase the capacity. Although materials with densities lower than that of PDMS can increase the absorption capacity, this comes at the expense of sacrificing mechanical durability. Nonetheless, a template with an appropriate combination of sugar particles of different sizes or with a mixture of particles composed of different materials could also enhance the absorption capacity.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Detailed fabrication, characterization, measurement of elastic modulus, and floating and cleaning capability of the PDMS sponge. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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