Hydrophilic polydimethylsiloxane-based sponges for dewatering applications

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ABSTRACT
Separation of water from non-polar liquid mixtures (dewatering) is a challenging, yet an important problem in such fields as petroleum industry and power coolants. We describe a method of fabrication and properties of a high-capacity hydrophilic sponge based on polydimethylsiloxane (PDMS). The sponge is obtained by addition of 1-octanol and incorporating zinc chloride powder template in the precursor PDMS liquid followed by heat curing at 115 °C with subsequent elution of the template. The produced PDMS sponges have water absorbing capacity reaching approx. 1600%, which is two times higher than typically known for dewatering sorbents. Those high-capacity sponges may find use as dewatering agents for oils, hydrocarbons and other nonpolar liquids.

1. Introduction
Polydimethylsiloxane with open pores (PDMS sponge) is highly attractive material that has a lot of different applications [1] including fabrication of flexible conductors [2,3], sensors [4–6], energy harvesting and storage devices [7–9], catalysis [10–12] to name a few. Due to hydrophobic properties of PDMS, sponges made of it are very effective in absorbing nonpolar organic compounds like oils and other hydrocarbons from water [13–15] allowing applications in water purification.

In certain cases, however, the opposite – removal of water from nonpolar organic substances is necessary. For instance, dewatering of hydrocarbons is necessary in the process of oil reforming and mining of petroleum. Another example is dewatering of transformer oil, where presence of water in oil could lead to electrical insulation breakdown. Physical adsorption [16,17] onto solid materials is one of most promising approaches to the problem due to simplicity and low cost. Sorbent materials capable of dewatering of hydrocarbons, include powders made of silica gel, calcium sulfate, several grades of alumina [18], some polymeric microparticles [17] or mixture of magnet particles based of iron oxide [16]. Great advantage of such materials is that they can be used in many cycles [19]. The main weak point there is the need of filtering the powder from liquid after use. There are also chemical methods based on interaction between water and salts with formation of solid hydrates in the form of sediment that should be later removed [20]. Demulsification based on freeze/thaw is another approach [21] with the main disadvantage being high cost. Smart PDMS sponge with switchable pH-responsive wetting was reported [22] allowing water sorption from non-polar liquids, but only in highly acidic environment. PDMS sponge with superhydrophobic (oleophilic) properties using NaCl microparticles as a hard template was reported in [23].

In the present work we describe preparation and properties of dewatering sponges made from a standard PDMS precursor and modified with common chemicals in a simple 4-step process. The hydrophilic PDMS sponges have water absorbing capacity reaching approx. 1600%, which is two times higher than typically known for dewatering sorbents. Those high-capacity sponges may find use as dewatering agents for oils, hydrocarbons and other nonpolar liquids.

2. Experimental
2.1. Fabrication of hydrophilic PDMS sponge
PDMS was prepared using Sylgard 184 Silicone Elastomer Kit (Dow Corning, USA), consisting of two liquid components: base
and curing agent. The PDMS pre-polymer liquid was obtained by mixing the base, curing agent and 1-octanol. In all cases base to curing agent ratio was 10:1 by mass with the total mass of base and curing agent being 1.5 g. Concentration of 1-octanol was varied in the range from 0% to 20% of the total product mass. Next, ZnCl₂ powder (2.7 g) (See Figure S1 in Supporting Information for SEM image) was dispersed in prepolymer solution by mechanical stirring with ES-8000 stirrer (Ecrosp, Russia). ZnCl₂ remained in PDMS in form of solid particles as a template. Additionally we prepared control samples either without 1-octanol, but containing different concentration of ZnCl₂ (10–60% mass), or without ZnCl₂, but with different concentration of 1-octanol (0–20% mass). The obtained suspension was heat cured at 115 °C for three hours. Solid samples were boiled in distilled water for 48 h to remove ZnCl₂ template. Water was changed three times per day. Obtained sponges were dried at 105 °C for 48 h. Fabrication process is shown schematically in Fig. 1.

2.2. Characterization methods

Porosity of the sponges was studied by BET-method (Thermo Scientific Surfer, USA). Chemical composition was analysed with EDX 8000 Shimadzu (Japan).

2.3. Water sorption test

The produced PDMS sponges were kept in distilled water inside a hermetically sealed plastic flask. Mass and volume of the sponges were monitored during several days until reaching saturation (see Figure S4 in Supporting Information). Water sorption capacity ratio was determined as the ratio of absorbed water mass to sponge mass.

3. Results and discussion

3.1. Properties of the PDMS sponges

Freshly produced dry samples had density of 0.62 ± 0.14 g/ml and surface area of the dry samples reached approx. 0.2 m²/g. EDX analysis indicated the presence of zinc and chlorine.

In the water sorption tests, the amount of water absorbed by PDMS sponges greatly depended on concentration of 1-octanol in PDMS (Fig. 2a). Samples with 1-octanol content exceeding 17% did not cure and were not used for tests. For all 1-octanol concentrations water sorption capacity was higher than that of pristine PDMS (see Table 1 in Supporting Information). The highest

Fig. 1. Hydrophilic PDMS-based sponge. Schematic representation of the fabrication process.

Fig. 2. Testing water sorption of the hydrophilic PDMS sponges. (a) Dependence of water capacity of PDMS sponge on concentration of 1-octanol used in its production. (b) Photograph of swelling of the hydrophilic PDMS sponge (17% 1-octanol recipe), before and after the sorption test, and the ruler in [cm].
sorption capacity (16 g of water per 1 g of sponge, or 1600%) was observed for the sponge produced with 17% of 1-octanol. After the test sponges were dried and experiments were repeated with the same result indicating reusability of the material. Obtained maximal value exceeds the typical 600%-800% reported for dewatering agents in literature [16,17]. The compounds without either 1-octanol or ZnCl₂, exhibited no water absorption. Surprisingly, the same result indicating reusability of the material. Obtained water capacity increased steadily with 1-octanol content (16 g of water per 1 g of sponge, or 1600%) was approx. the same. However for 1-octanol containing sample angle decreased significantly faster, which can be linked to absorption of water (see Figure S2 in Supporting Information).

The low surface area revealed in the porosity test and high water swelling capacity suggest that the sponge has “hidden” porosity with glued channels. Morphology of pores is shown in Supporting Information (Figure S3). The nature of this swelling pressure is fundamentally resemblant of osmotic pressure observed in fluid systems with selective membranes. When the sponge is immersed in water the hidden pores are forced to open due to ionic affinity of the polar layers to water molecules (see Fig. 3). We suppose that Zn²⁺ and Cl⁻ ion pairs could form a small bilayer that increased wettability of the polymer. Based on Fig. 2a, the ability of the Zn²⁺ and Cl⁻ pairs to settle in the PDMS matrix strongly depends on the concentration of 1-octanol. Notably, 1-octanol molecules are highly soluble in PDMS due to their nonpolar organic skeleton, wherein ZnCl₂ is soluble in 1-octanol. After boiling (see Fig. 1, #4), the material could hypothetically contain other alkyl chains, whose presence could not be confirmed in this study, e.g. 1-chlorooctane formed hydrochloric acid mediated reaction from hydrated zinc chloride. We conclude that ZnCl₂ powder itself acts as a template for hidden porosity and polar driver for swelling pressure, whereas 1-octanol serves as an intermediate agent for solubility of ZnCl₂ in PDMS matrix.

4. Conclusions

We demonstrated high-capacity dewatering sponge based on polydimethylsiloxane (PDMS) modified with zinc chloride and 1-octanol. Water capacity increased steadily with 1-octanol content and reached 16 g of water per 1 g of the sponge at the maximum possible 17% of 1-octanol. The obtained water capacity was two times higher than reported for dewatering sorbents previously. According to our understanding, this high hydrophilicity of the sponge was conditioned by polar hydroxy group of 1-octanol dissolved in elastomer matrix and solubility of ZnCl₂ in 1-octanol. The presence of 1-octanol allowed Zn²⁺ and Cl⁻ ion pairs to settle-in and form an internal hydrophilic bilayer. The ZnCl₂ powder acted also as a template-forming agent. The proposed method is attractive for oil mining and reforming applications. It benefits from high efficiency and the fact that the sorbent is in bulk form allowing simple separation from oil without using filters contrary to powder dewatering agents.

**CRediT authorship contribution statement**

**Ilya M. Sosnin:** Conceptualization, Methodology, Supervision, Investigation, Formal analysis, Visualization, Writing - original draft. **Sergei Vlassov:** Funding acquisition, Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **Evgeny G. Akimov:** Investigation. **Vладимир И. Агенков:** Investigation. **Leonid M. Dorogin:** Funding acquisition, Project administration, Supervision, Conceptualization, Methodology, Visualization, Writing - original draft, Writing - review & editing.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2019.127278.

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