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# An innovative, fast and facile soft-template approach for the fabrication of porous PDMS for oil–water separation†

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Oil wastewater and spilled oil have caused serious environmental pollution and damage to public health in the past few years. Therefore, considerable efforts are being made to develop sorbent materials that are able to separate oil from water with high selectivity and sorption capacity. However most of them exhibit low reusability, with low volume absorption capacity and poor mechanical properties. Moreover, their synthesis is time-consuming, complex and expensive, limiting their practical application in the case of an emergency. Here we propose an innovative approach for the fabrication of porous PDMS starting from an inverse water-in-silicone procedure able to selectively collect oil from water in a few seconds. The synthesis is dramatically faster than previous approaches, permitting the fabrication of the material in a few minutes independent of the dimensions of the sponges. The porous material possessed a higher volume sorption capacity with respect to other materials already proposed for oil sorption from water and excellent mechanical and reusability properties. This innovative, fast and simple approach can be successful in the case of an emergency, such as an oil spill accident, permitting *in situ* fabrication of porous absorbents.

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## 1. Introduction

Crude oil has been a fundamental part of human life from the beginning of industrial civilization. However, in recent years, oil spill accidents and leakage of organic liquids have caused a huge damage to ecological systems with consequences in health, social and economic fields.<sup>1–3</sup> An example is the oil spill in the Gulf of Mexico in 2010, when an estimated release of 4.9 million barrels of crude oil into the ocean occurred causing a colossal disaster for marine species, with long-term effects still evident today.<sup>4</sup> Therefore, a wide variety of approaches has been developed to separate oil from water, such as physical sorption by sorbent materials, mechanical recovery by oil skimmers,<sup>5,6</sup> *in situ* burning,<sup>7</sup> physical diffusion,<sup>8</sup> filtration membranes,<sup>9,10</sup> centrifugation<sup>11</sup> and biodegradation.<sup>12</sup> However, their practical use still remains problematic due to the low separation efficiency, the use of cumbersome instrumentation and/or the generation of secondary pollutants. To solve these problems, the synthesis of lightweight porous oil absorbents

with high volume absorption capacity is one of the most promising strategies.<sup>13</sup> These materials can separate oil from water and concentrate organic liquids inside their pores, permitting their transport and storage. Practical application also requires easy, fast and cheap fabrication and the ability of the sorbent material to be reusable to cut the costs of oil spill recovery.<sup>14</sup> Different materials have been proposed to achieve this aim, such as carbon nanotubes and/or graphene sponges,<sup>15–20</sup> polystyrene fibers,<sup>21</sup> polyurethane sponges<sup>17,22</sup> and nanocomposite materials.<sup>13</sup> Despite their good performances in water oil separation and mass sorption capacity, most of these materials present drawbacks such as poor durability, complex and time-consuming fabrication and poor volume absorption capacity.

Polydimethylsiloxane (PDMS) is a polymeric material used in many research fields due to its excellent characteristics such as high hydrophobicity and flexibility, oleophilicity, thermal, mechanical and chemical stability and easy fabrication. Recently this material has been proposed in the porous form as a good candidate for water oil separation. The most widely adopted method to obtain this material is the sacrificial hard template approach proposed for the first time by Choi *et al.*<sup>23</sup> in 2011 where the authors fabricated reusable PDMS sponges with fast oil absorption using sugar particles as the template. The synthetic steps included shaping of sugar templates and the use of vacuum apparatus, which complicate the large-scale production of the material. To solve these problems, Zhang *et al.*<sup>24</sup> proposed an innovative synthesis in which a hard

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template was easily added to a PDMS prepolymer diluted in *p*-xylene without the use of expensive equipment. Despite the good oil absorption properties of the sponges the synthesis still requires a long procedure to remove the hard template from the polymeric matrix. Zhao *et al.*<sup>25</sup> synthesized sponges with high oil absorption by diluting a PDMS prepolymer in dimethicone and using sugar particles as the template. Even in this case, the large-scale production of the material was prevented by the required use of centrifuges and long procedure. More recently, to speed up the synthetic procedure, Yu *et al.*<sup>26</sup> tried to substitute sugar particles with citric acid monohydrate (CAM) as the hard template and dissolved them in ethanol. Taking advantage of the superwettability of ethanol to the porous PDMS, CAM could be easily removed from the porous PDMS in a shorter time compared to previous approaches. However at least 6 hours for a small piece of the material is still necessary to remove CAM completely. Moreover, due to the diffusion of the solvent inside the polymeric pores for CAM solubilization, a longer time is needed for bigger sponges. Recently our group proposed an approach in which a PDMS prepolymer was infiltrated between glucose crystals packed in a syringe, applying a positive pressure on their surface. These sponges revealed excellent and improved volume absorption capacity with respect to other oil absorbents without the use of cumbersome instrumentation although the overall process still remains time-consuming.<sup>13</sup> Consequently, all the proposed approaches appear to be time-consuming and require environmentally harmful solvents making difficult their real application in the case of an emergency, where fast material preparation and simple operation are required. Moreover, most of them need the use of cumbersome processes for their preparation, such as centrifugation or vacuum operation, which further complicates sponge production. An attractive route to prepare highly porous and permeable polymeric materials is represented by emulsion templating methods in which a high internal phase emulsion (HIPE) is prepared. The external phase is converted into a polymer and the emulsion droplets are removed yielding a highly interconnected network of micron-sized pores. Recently, a number of different attempts have been made to prepare microporous PDMS by HIPE techniques. In 2015, Tebboth and collaborators<sup>27</sup> produced an elastomeric PDMS containing an aqueous solution of hydrogen carbonate ( $\text{NaHCO}_3$ ). Subsequently, thermal decomposition of  $\text{NaHCO}_3$  caused the release of carbon dioxide into the polymer structure. By subjecting the polymer to reduced pressure, it can be made to expand to many times its original size. Kovalenko *et al.*<sup>28</sup> prepared soft porous PDMS by the UV polymerization of an inverse water-in-silicone PDMS emulsion in the presence of surfactants. The use of different reagents, cumbersome instrumentation, and long synthesis time limited the large-scale synthesis and consequently the application of both materials for water/oil separation. Here we propose an innovative approach for the facile synthesis of highly porous PDMS materials starting from an inverse water-in-silicone procedure similar to a modified emulsion templating technique.<sup>29</sup> However we did not observe the presence of voids and windows inside the pores, characteristic of the emulsion templating

approach.<sup>30</sup> The synthesis is completed in a few minutes and the obtained sponges presented swelling properties and interconnected pores that favour absorption and retention of various organic liquids with a high and fast absorption rate. Without the shaping of the hard template, centrifugation or vacuum operation, the preparation strategy is straightforward and dramatically faster than previous approaches. Moreover, the organic liquids can be easily recovered by simply squeezing the sponges and can thus be reused without loss of efficiency for hundreds of cycles.

## 2. Experimental section

### Chemicals

The PDMS prepolymer (Sylgard 184) and a curing agent were purchased from Dow Corning. Hexane, dichloromethane, chloroform, toluene, tetrahydrofuran, petroleum ether, ether, and glucose were purchased from Sigma Aldrich and used as received. Gasoline was purchased from Kuwait Petroleum Corporation.

### Preparation of PDMS–MWNT sponges

Porous PDMS sponges were prepared according to the following procedure. Unless otherwise indicated a continuous phase consisting of the PDMS prepolymer and the thermal curing agent in a ratio of 10 : 1 by weight were placed into a polypropylene tube, diluted in hexane with a solvent/prepolymer ratio equal to 8 : 2 and intensively stirred for 5 minutes. Then 50% by weight of Milli-Q water was added drop by drop under continuous stirring in the continuous phase. After that, the solution was further mixed for another 20 minutes. After stirring, the solution had the form of a viscous liquid. The tube containing the as-prepared emulsion was then placed in an oven at 120 °C for ten minutes to accomplish the polymerization. Finally, the obtained 3D porous PDMS was removed from the polypropylene tube and used for the experiments. Different PDMS sponges were prepared by changing different parameters such as the concentration of the prepolymer, solvent to dilute the pre-polymer, solvent used as the dispersed phase, and the amount of dispersed phase.

### Oil absorbency and reusability of the PDMS sponges

A piece of sample was immersed in a bath containing only oil at room temperature for 20 minutes. After that, the sample was removed from the oil, wiped with filter paper in order to remove excess oil and weighed. The oil mass sorption capacity ( $M_{\text{abs}}$ ) and volume absorption ( $V_{\text{abs}}$ ) capacity were evaluated by using the following equations:

$$M_{\text{abs}} = (m - m_0)/m_0$$

$$V_{\text{abs}} = (m - m_0)\rho_0/\rho m_0$$

where  $m$  is the weight of the sample after sorption,  $m_0$  is the initial weight of the sample, and  $\rho_0$  and  $\rho$  are density values of the absorbent material and absorbed oil, respectively. Repeated

absorption–desorption cycles of oils were performed to evaluate sponge reusability. For this purpose, the sample was immersed in oil until absorption equilibrium was reached (*i.e.* 20 min) and then weighed to calculate the oil mass sorption capacity. The sample was then squeezed and washed with ethanol three times and dried in an oven at 60 °C. The absorption–desorption procedure was repeated 3 times for each tested oil.

### Characterization of the PDMS sponges

Dynamic and static contact angle measurements were carried out using an OCA 15 Plus instrument (DataPhysics Instruments, Filderstadt, Germany) equipped with a high resolution camera and an automated liquid dispenser. SCA 20 software was employed to obtain additional information on the samples; the software uses an algorithm based on the Young Laplace equation and it allows the correlation of the shape of the drop with its surface tension and the measurement of the contact angle between the liquid and the analyzed surface.

Morphological characterization of the PDMS sponge samples was carried out using a scanning electron microscope (SEM, Carl Zeiss Merlin) using a secondary electrons detector. SEM images were acquired in top view configuration using acceleration voltage of 3 kV and 50× magnification. A Nikon NIS-Elements ND2 software system was used to measure the pore size. Quasi-static hysteresis compression tests were performed on a LLOYD LR50K Plus dynamometer equipped with 50 mm diameter parallel plate tools and a 50 kN load cell. Tests were performed by loading the samples at different strain levels, equal to 60 and 90%. The loading and unloading stages were performed at a rate of deformation of 5 mm min<sup>-1</sup> and 10 mm min<sup>-1</sup> for 60% and 90% strain, respectively.

The porosity ( $\Phi$ ) was measured using a methanol saturation method<sup>24</sup> according to the following equation:

$$\Phi = \gamma_{\text{sat}} - \gamma_{\text{dry}}/\gamma_{\text{meth}}$$

where  $\gamma_{\text{sat}}$ ,  $\gamma_{\text{dry}}$  and  $\gamma_{\text{meth}}$  indicate the densities of saturated PDMS, the dry oil absorbent, and methanol, respectively.

## 3. Results and discussion

### Preparation of the PDMS sponge

The PDMS elastomer was chosen because of its intrinsic properties such as elasticity, mechanical stability and hydrophobicity. PDMS oil absorbents were synthesized starting from an inverse water-in-silicone procedure (Fig. 1a). Compared with conventional sugar-template methods, this approach avoids the use of vacuum operation or centrifugation, the preparation of the shaped salt template beforehand and the long washing procedure necessary for hard template removal. An appropriate amount of water acting as the soft template was added to dilute the prepolymer drop by drop under continuous stirring to produce an emulsion. Then the emulsion was cured in an oven at 120 °C. The emulsion was stable after the formation during all the synthetic steps. No noticeable phase separation was observed during the time needed between emulsion formation and curing of the dissolved silicone. At this temperature, the

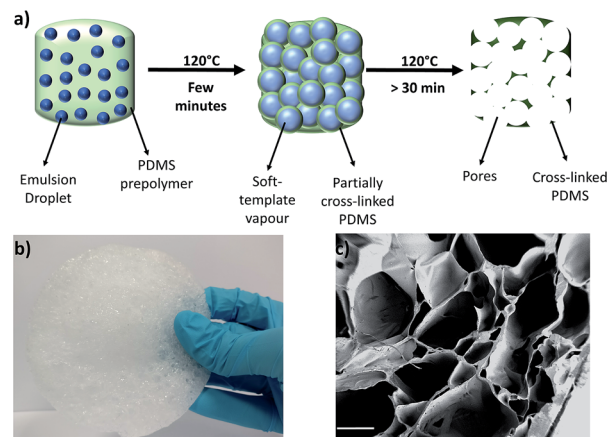


Fig. 1 (a) Schematic illustration of the preparation of the PDMS sponge. (b) Photograph of the freshly prepared PDMS sponge. (c) SEM image of a sponge portion (scale bar = 500  $\mu\text{m}$ ).

PDMS prepolymer quickly forms cross-linking bonding between PDMS prepolymer chains, producing a semi-rigid gel that surrounds the emulsion droplets in a few minutes. As a consequence, closed-pore entrapped soft templates are formed. During evaporation, which naturally occurs at that temperature, the soft templates increase in volume and physically enlarge the closed pores formed by incompletely polymerized PDMS. When the pressure due to evaporation of the soft template inside the formed closed pores becomes high enough, the interconnection between PDMS prepolymer chains could be physically broken causing the explosion of the closed pores, leaving large open cavities inside the polymeric matrices with an average dimension of  $406 \pm 302 \mu\text{m}$ , a minimum pore dimension of  $65.8 \mu\text{m}$  and a maximum of  $1.768 \text{ mm}$  (Fig. 1b and c and S1†).

Therefore, all of the prepolymer was converted into a porous structure with interconnected pores in a few minutes (20 min) independently of the dimensions of the sponge (Fig. 1b).

At the end of the process both the diluting and template solvents are evaporated, leaving a porous PDMS structure ready for use. The simple preparation method adopted here makes sponge fabrication suitable for large-scale production without the need for complex, expensive and cumbersome instrumentation. Moreover, the preparation is faster (few minutes) than other reported methods used for porous PDMS fabrication for which many hours or days are required to produce large amounts of the material.

### Performance of the PDMS sponge for oil absorbency

For an ideal oil absorbent, a highly porous material with 3D interconnected pores is necessary. It is well known that porous PDMS has the ability to absorb oil.<sup>13,23–26</sup>

To select the optimal conditions, an investigation of the most satisfactory oil uptake properties, different solvents and their amounts for both prepolymer solubilization and acting as the soft template has been carried out for the preparation of PDMS sponges.

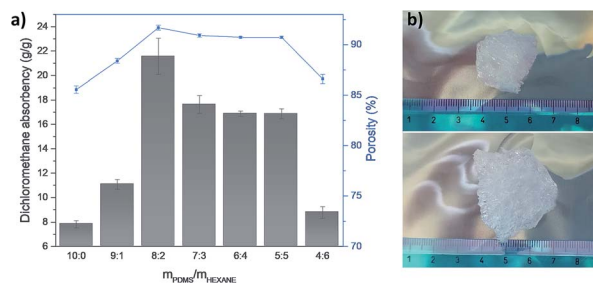


Fig. 2 (a) Dichloromethane mass absorption ( $\text{g g}^{-1}$ ) (columns) and porosity (dots) of the PDMS sponges with different  $m_{\text{PDMS}}/m_{\text{Hexane}}$  ratios. (b) Swelling process of the PDMS sponge before (top) and after (bottom) immersion in oil.

Dichloromethane (DCM) absorption has been used to evaluate the oil uptake properties of different prepared sponges. Fig. 2 shows the porosity and dichloromethane absorbency of the sponges prepared using water as the soft template at 50% by weight with respect to PDMS prepolymer and hexane in different ratios. Once dipped in the organic solvent, all the prepared sponges increased their volume during the absorption process, indicating the occurrence of a swelling process (Fig. 2b). As reported, an oil mass absorption higher than  $21 \text{ g g}^{-1}$  with a swelling ratio of 3.2  $v/v_0$  for dichloromethane was obtained for the PDMS sponges prepared with a ratio of 8 : 2  $m_{\text{PDMS}}/m_{\text{Hexane}}$ . This sponge is characterized by a porosity of about 93%, higher than that of other PDMS porous materials for which a maximum porosity of 84% was observed.<sup>24</sup> Both higher and lower dilutions of the prepolymer in hexane lead to a decrease in porosity and consequently in dichloromethane absorbency. This behaviour could be explained by two different mechanisms. It is well known that the non-diluted prepolymer has a higher cross-linking degree that avoids swelling of the polymer during the oil uptake process, hence decreasing its absorbency.<sup>24,25</sup> If more hexane is used to dilute the prepolymer, the cross-linking degree of the PDMS is lower; therefore, through increasing the hexane amount, more swellable sponges with higher absorption are obtained. Moreover, the non-diluted prepolymer could polymerize faster and with a higher cross-linking degree, preventing pore enlargement during evaporation of the soft template and resulting in lower porosity. However, it is clear that with increasing  $m_{\text{PDMS}}/m_{\text{Hexane}}$  for ratios higher than 8 : 2, a decrease of the absorption capacity occurs. We hypothesized that if the amount of hexane exceeds a certain amount, the cross-linking degree of PDMS sponges decreases dramatically and consequently the skeleton can not support its own weight and collapses.<sup>24</sup> This causes a decrease in the porosity of the sponges and consequently in the absorption capacity. As a further piece of evidence, we observed that for  $m_{\text{PDMS}}/m_{\text{Hexane}}$  ratios lower than 4 : 6, the sponge was completely collapsed and sticky and not suitable for oil absorption.

The impact of the solvent used in PDMS dilution during PDMS sponge formation was evaluated by preparing different sponges with different solvents. We tested hexane, toluene and dichloromethane; the dilution ratio was 2 : 8 solvent/PDMS

prepolymer in the presence of 50% of water with respect to prepolymer and the uptake of dichloromethane was evaluated. The solvent used to dilute the prepolymer has a strong effect on the oil uptake process (Fig. 3); the lower the polarity of the solvent, the higher the dichloromethane absorbency. Arguably, the higher the polarity of the solvent, the greater is its ability to form hydrogen bonds with water. This could cause a decrease in the porosity of the sponges as already reported for systems based on polymerization starting from an emulsion.<sup>31</sup>

In hard template synthesis of PDMS sponges, it has already been demonstrated that different templates could cause different porosities.<sup>13</sup> In the present work, the template namely a soft template is represented by a solvent immiscible with the prepolymer diluted in an appropriate solvent. Sponges with different soft templates at 50% by weight with respect to PDMS prepolymer have been prepared to evaluate their impact on dichloromethane absorption. The  $m_{\text{PDMS}}/m_{\text{Hexane}}$  ratio was kept at 8 : 2. Fig. 4 shows that the soft template has a significant effect on the oil uptake process. We observed that oil absorption increases with increasing boiling point of the soft template. We hypothesized that this could be explained as follows: since polymerization occurs at high temperature, a part of the soft template could evaporate before the formation of prepolymer cross-linking bonding. Consequently, smaller emulsion droplets will be present in the mixture causing the formation of less porous sponges.

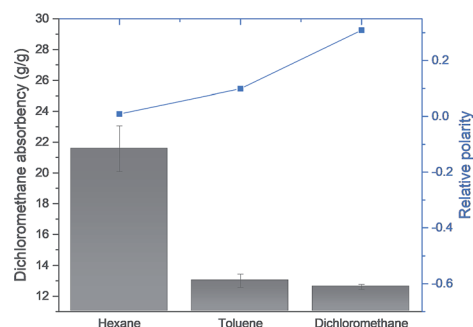


Fig. 3 Variation of mass absorption ( $\text{g g}^{-1}$ ) of the PDMS sponges for dichloromethane with different solvents used to dilute the PDMS prepolymer.

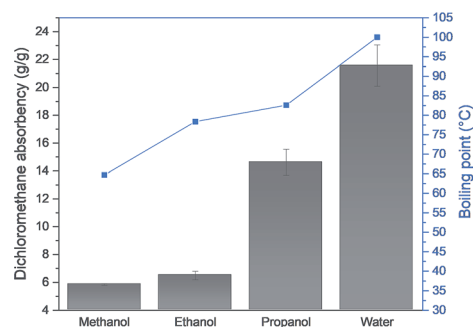


Fig. 4 Variation of mass absorption ( $\text{g g}^{-1}$ ) of the PDMS sponges prepared from different soft templates.

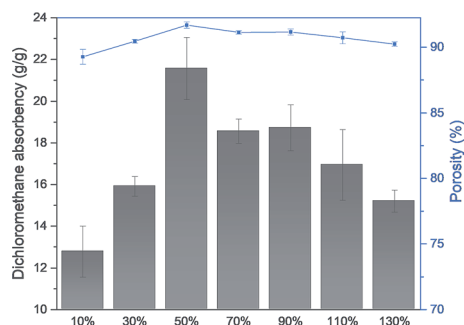


Fig. 5 Dichloromethane mass absorption ( $\text{g g}^{-1}$ ) (columns) and porosity (dots) of the PDMS sponges prepared with different amounts by weight with respect to PDMS prepolymer.

Similarly, a decrease in oil absorbency is observed if a smaller amount of 50% soft template with respect to PDMS prepolymer is used (Fig. 5). However, even increasing the soft template amount to values higher than 50 wt% compared to the prepolymer leads to a decrease in dichloromethane absorbency and porosity. We supposed that the higher the amount of template solvent is, the larger is the distance between the forming polymeric chains, causing a decrease of the cross-linking degree. Consequently, the skeleton collapses on account of its weight, decreasing the porosity.

In Fig. 6, the normalized dichloromethane absorption of the sponges with higher dichloromethane absorbency is plotted as a function of time. The maximum absorbency is observed in less than 30 seconds. The absorption rate is comparable with those of other PDMS based materials<sup>24</sup> and higher with respect to other gel oil absorbents, which took 2 hours or even more to reach equilibrium.<sup>32–34</sup>

Moreover, different sponges produced at different times exhibited similar dichloromethane uptake properties suggesting that the new synthetic route produces materials with reproducible oil uptake properties (RSD = 10%,  $n = 3$ ).

Importantly, the as-obtained PDMS sponges have intrinsic hydrophobicity and oleophilicity, highlighted by a water contact angle (CA) of  $145.5 \pm 1^\circ$  (Fig. 7a). Owing to their lightweight, porous structure and hydrophobic properties, the PDMS sponges float on the water surface, and when immersed in water

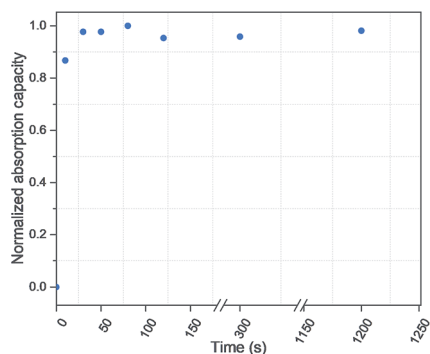


Fig. 6 Oil mass absorption for different contact times of the PDMS sponge.

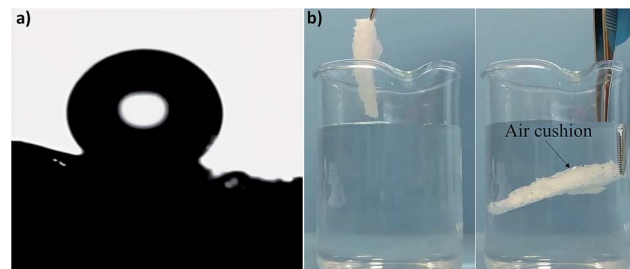


Fig. 7 (a) Digital image of a drop of water deposited on PDMS. (b) The PDMS sponge during immersion in water.

with the help of an external force, an air cushion around the sponge that maintains the sponge dryness is observed (Fig. 7b). This is evident in Movie S1† in which a piece of paper remained dry after a sponge previously submerged in water was placed on its surface. Moreover, the weight of the sponge remains constant before and after immersion in water. The hydrophobicity of the PDMS sponge is maintained even towards corrosive aqueous liquids including 1 M HCl and 2 M NaOH with a water CA of  $\sim 144.7^\circ$  and  $\sim 146.4^\circ$ , respectively. The combined hydrophobicity and oleophilicity of the sponge are commonly attributed to the low surface free energy of the PDMS material and the porous structure. Normally, bulk PDMS shows excellent hydrophobicity with a water contact angle of  $105^\circ$ .<sup>35</sup> It is well known that a porous morphology can increase the water contact angle of a hydrophobic surface due to air entrapment, as described by the Cassie–Baxter wetting model.<sup>36</sup>

The mechanical properties of sorbent materials are important for practical application since in materials with lower mechanical strength the viable stack height of the sorbent after absorption is only a few centimeters.

PDMS is well known for its excellent compression properties in both porous and bulk forms. Fig. 8a presents the stress–strain curve under a loading–unloading compression cycle for the sponge with a higher dichloromethane uptake. The modulus increases slowly until a strain of about 50%, typical of the performance of soft foam. Nevertheless, values higher than 300 kPa at 60% strain for the sponge are recorded, much higher with respect to most of other reported oil-uptake systems, making the material suitable for oil removal.<sup>13</sup> Recyclability of porous materials for water/oil separation is a key point to dramatically cut the costs of production. In Fig. 8b, a PDMS

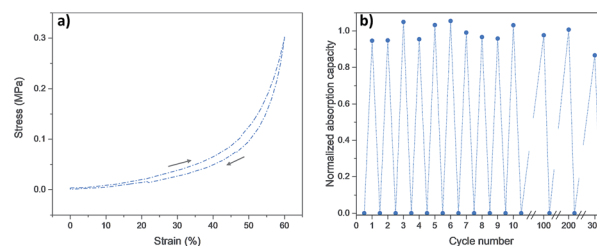


Fig. 8 (a) Compressive stress–strain curve at 60% strain of PDMS. (b) Demonstration of the recyclability of the sponge for dichloromethane absorption.

sponge was pressed until it reached 90% of its original volume at  $10 \text{ mm min}^{-1}$  to mimic the squeezing process necessary to remove entrapped oil in real applications, and the normalized absorption capacity after immersion in dichloromethane was recorded. The results show that the absorption capacity did not significantly deteriorate until 200 cycles and more than 90% of its absorption capacity remained after 300 runs. The decrease in absorption capacity of the PDMS sponges could be ascribed to the small weight changes as deducible from the small decrease of the stress value after successive compression cycles at 90% strain necessary to remove absorbed oil (see Fig. S2†). Importantly, the 3D porous materials preserve their hydrophobicity ( $CA = 145.1 \pm 1^\circ$ ) after 300 usage cycles, evidenced by the fact that dichloromethane is not adsorbed on the pore surface.

### Selective absorption of oils from water

With their hydrophobic/hydrophilic properties, interconnected porous structure and mechanical stability, the PDMS sponges are a good candidate as an oil absorbent for water/oil separation. When left to float on the surface of an oil/water mixture, the sponge absorbed in a short time the oil and all of the water was left (Fig. 9a and Movie S2†), allowing the storage of the collected oil inside the 3D porous structure. Moreover, the PDMS sponge is also able to absorb heavy oil under water if driven by an external force. It is interesting to note that the weight of the sponge after oil uptake is equal to the weight of the

sponge before absorption plus the weight of  $\sim 99\%$  of the oil present in water. Moreover, some air bubbles come out from the sponges during submerged oil absorption, confirming the absence of water inside the absorbents after immersion in water. After oil absorption, the sponge floats on the water surface and can be removed without leakage of oil (Fig. 9b and Movie S3†). This aspect is important in real applications. More importantly, the oil stored in the pores can be easily removed by simple squeezing as shown in Fig. 9c and Movie S4.†

The PDMS oil mass absorption capacity was tested with different oils and organic solvents. As observable in Fig. 10, the oil mass absorption was in the range of  $3.9$  to  $32.3 \text{ g g}^{-1}$  depending on the viscosity, density and surface tension of the organics.

It is well known that PDMS based porous materials have a higher volume absorption capacity compared to other porous oil absorbents (such as polyurethane, carbon soot, aerogel...);<sup>13</sup> this is possible due to the swelling of PDMS after immersion in oil, which significantly increases the available volume for oil storage.

On the other hand, the PDMS porous material evidenced a lower mass-based absorption capacity with respect to other porous oil absorbents due to the higher density of the materials. Consequently, PDMS porous materials with higher mass absorption capacities and volume absorption capacities are in demand for practical application. Moreover, as evidenced before, sorbents with high mechanical strength are in demand for practical application since the viable stack height of the sorbent after absorption is only a few centimeters if this value is low. In Table 1, the PDMS sponges prepared here are compared with other reported sorbents based on PDMS and other materials. It is evident that at 60% strain the material evidences one of the highest mechanical strengths ever reported. As clearly visible, the preparation time is considerably shorter with respect to all the other sorbents. This is very important in the case of an emergency in which timely intervention is required. Due to the lower density of the material and large pores, chloroform and dichloromethane mass absorption evidenced one of the highest values for PDMS based materials. Since mass-based absorption capacity is strongly affected by the density of

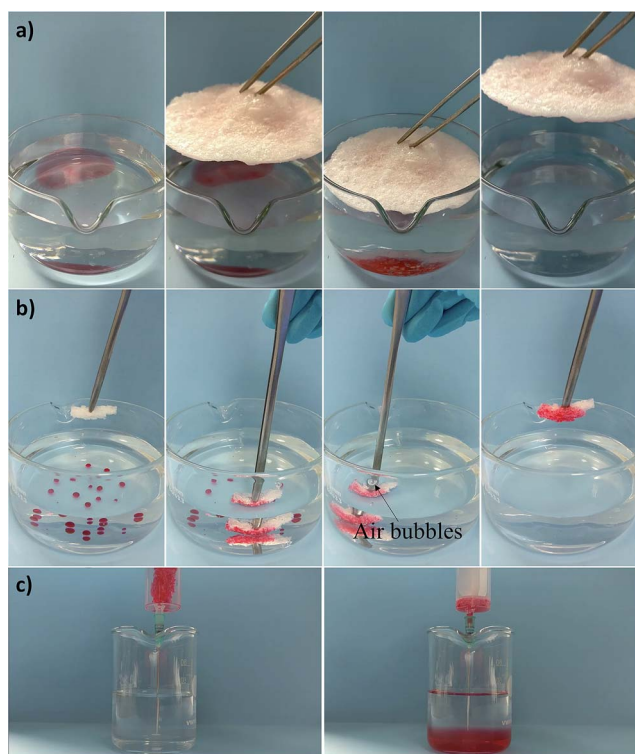


Fig. 9 Removal of (a) oil red O colored hexane from the water surface and (b) oil red O colored chloroform with PDMS sponges. (c) Recovery of absorbed oil red O colored chloroform from the PDMS sponge by squeezing (the transparent solvent is ethanol).

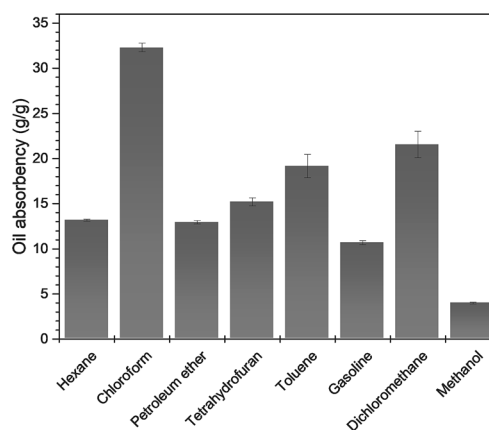


Fig. 10 Different oil absorptions of the PDMS sponge.

Table 1 Comparison of various oil absorbents

| Oil absorbent   | Water contact angle (°) | Estimated time of preparation (h) | Chloroform, $M_{\text{abs}}$ (g g <sup>-1</sup> ) | Chloroform, $V_{\text{abs}}$ (cm <sup>3</sup> cm <sup>-3</sup> ) | Stress at 60% strain (kPa) | Reference |
|---|-------------------------|-----------------------------------|---|--|----------------------------|-----------|
| Swellable porous PDMS sponge prepared by a soft template method | 145                     | ~0.6                              | 32.3, 21.5 (DCM)                                  | 4.33, 3.23 (DCM)   | >300                       | This work |
| Swellable porous PDMS   | 144                     | >12                               | 34  | 4.14   | 5                          | 24        |
| PDMS sponge   | 120–130                 | >5                                | 11  | 1.34   | 12                         | 23        |
| PDMS sponge   | 138.9                   | >8                                | 12 (DCM)  | 1.8 (DCM)  | —                          | 26        |
| PDMS/MWNTs  | 153.4                   | ~40                               | 20.5  | 4.24   | 330                        | 13        |
| Bacterial cellulose aerogel                                     | 146.5                   | >20                               | 185   | 0.84   | ~20                        | 37        |
| Melamine sponge/rGO   | 132                     | Different days                    | 165   | 1.25   | —                          | 38        |
| Nanofibrillated cellulose                                       | 140                     | >24                               | 102   | 0.75   | —                          | 39        |
| Paper waste   | —                       | 15                                | 150   | 0.58   | —                          | 40        |
| rGO/PVDF  | —                       | >18                               | 20  | 0.028  | —                          | 41        |
| Graphene/EDA  | 155                     | 24                                | 180 (DCM)   | 0.84 (DCM)   | 6 (50%)                    | 42        |
| MTMS–DMDMS gels   | 152.6                   | >24                               | 14  | 2.54   | 10                         | 43        |
| 3D graphene framework   | —                       | >15                               | 470   | 0.66   | 4                          | 44        |
| Silanized melamine sponge                                       | 151                     | >1.5                              | 163   | 1.94   | —                          | 45        |

absorbing materials, volume absorption capacity was also taken in account to characterize the absorptive capability of the sponges, as it is not a function of the solvent and absorbent density and better describes the absorption capacity of the material. Interestingly, to the best of our knowledge the best volume absorption capacity for oil absorption has been obtained in the present work making the system valuable for real applications. As described before, this could be due to increased porosity and the presence of larger pores with respect to other PDMS based materials. However, larger pores can favor water penetration inside polymeric matrices. To evaluate the ability of hydrophobic PDMS to retain water we calculated the breakthrough pressure  $P_B$  from  $P_B = \rho g h_{\text{max}}$ , where  $\rho$  is the density of water,  $g$  is gravitational acceleration and  $h_{\text{max}}$  is the maximum height of the water column that the PDMS sponge can support. Experimental results evidenced a  $P_B$  of 1170 Pa. The experimentally measured breakthrough pressures of porous PDMS are compared to theoretical  $P_B$  ( $P_{\text{BT}}$ ) of hydrophobic membranes with cylindrical pores using the Laplace–Young equation:

$$P_{\text{BT}} = \frac{2\gamma|\cos(\theta_w)|}{d}$$

where  $\theta_w$  is the water CA of the porous PDMS surface,  $\gamma = 0.0728 \text{ N m}^{-1}$  is the water surface tension of the water air interface and  $d$  is the average pore diameter. The experimental  $P_B$  is not in good agreement with the theoretical value ( $P_{\text{BT}} = 583 \text{ Pa}$ ). The difference can be attributed to the large variation in pore dimensions inside polymeric matrices and the presence of a higher number of pores smaller than average pore dimensions (<300  $\mu\text{m}$ ) (Fig. S1†).<sup>46</sup> Nevertheless, the experimental  $P_B$  is comparable with  $P_{\text{BT}}$  that can be calculated for other PDMS porous materials for water oil separation with pores more homogeneously distributed for which values between 731 Pa and 1150 Pa can be calculated.<sup>25,26</sup> Moreover, the highest water contact angle was observed for sponges fabricated with only PDMS, probably due to the absence of organic residual

materials on the pore surface that can remain if a hard template technique is used. This confirms that the innovative synthetic procedure proposed here can produce materials with improved properties for water oil separation.

## 4. Conclusions

In conclusion, a new route to fabricate 3D interconnected porous PDMS sponge has been proposed. The proposed fabrication technique is simpler, easier to be scaled up and dramatically faster than other methods reported for porous absorbents. The obtained pores have a dimension range from tens of micrometers to millimeters. Moreover, different sponges prepared at different times evidenced replicable behaviour in dichloromethane absorbency suggesting that the synthetic route results in the fabrication of sponges with the same porosity. Owing to their hydrophobicity and superoleophilicity, the obtained PDMS sponges can selectively collect oils and organic solvents from water in a few seconds. The sponges are able to keep collected oil inside their polymeric structure until a compression is applied and the porous PDMS is readily utilizable for a new cycle of oil collection. The sponges prepared here exhibit improved mechanical properties with respect to other PDMS absorbents. This permits the reuse of the material hundreds of times without loss of function. The volume absorption capacity is higher than those of other porous materials reported for water oil separation and the mass absorption capacity is comparable with the better values recorded for other PDMS oil absorbents. Probably, as previously observed,<sup>23</sup> the heterogeneity in pore dimensions is crucial to obtain materials with high porosity and consequently higher sorption capacity and to prevent water penetration. The achieved volume and mass absorption capacities, improved hydrophobicity and density are fully appropriate for practical applications allowing easy transport and storage.

As an example, for the absorption of 1 ton of petroleum (density  $\sim 0.88 \text{ g cm}^{-3}$ ), only  $\sim 56 \text{ kg}$  of the materials are estimated to be required, which corresponds to a sponge volume of only  $0.28 \text{ m}^3$  (approximately equal to the volume occupied by  $\sim 3.6$  persons), improving on the already good results and decreasing the costs with respect to more complicated systems previously reported based on PDMS and carbon nanotubes.<sup>13</sup>

Moreover, we believe that the simple and dramatically faster preparation strategy can be successful in the case of an emergency permitting *in situ* fabrication and can offer inspiration for researchers to prepare other 3D interconnected porous materials.

## Conflicts of interest

There are no conflicts to declare.

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