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UV-CURED PDMS FOR OIL REMOVAL FROM WASTEWATER

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Keywords UV-curing, PDMS, wastewater treatment, oil-water separation

The removal of oil from water is a worldwide challenge that must be faced to avoid irreversible marine habitat destruction. A novel fast and simple technique to obtain polydimethylsiloxane (PDMS) membranes is developed using the photopolymerization technique. The high reactivity of the acrylated PDMS formulation towards photo-induced free radical polymerization is assessed *via* the Differential Scanning Photo-Calorimetry (photo-DSC) technique. Two different membranes dense or porous are developed and investigated. Porous membranes, having 100-200 μm as pore size, were obtained using a low-cost environmentally friendly sodium chloride template. Thanks to the hydrophobic/oleophilic intrinsic characteristic of PDMS, the UV-cured membranes can selectively remove dodecane, selected as the target oil, from water. The dodecane sorption capability of both membranes is investigated and compared. Moreover, the membranes can be easily reused since the adsorbed oil can be recovered by simply compressing the membrane. Those PDMS sorbents show high mechanical stability after five adsorption/desorption cycles.

1. Introduction

A critical challenge of the 21st century is the availability of clean water. This is particularly important taking into account the recent drought problems coupled with pollutants spoiling water resources.

As the development of both marine and petrochemical industries speeds up, industrial oily wastewater and accidental oil spillage have become a global issue that threats both the environment and the economy. For this reason, different strategies have been investigated in the literature to address this serious problem. [1]

A variety of methods were proposed to clean water from oil pollutants such as filtration, in situ burning [2], bioremediation [3,4], chemical treatments [5], and sorbent materials. [6–9] Among these techniques, the sorption process can be considered the most environmentally friendly since it does not generate secondary pollution. [10]

The most traditional sorbent materials are silica, zeolite, and activated carbon but they are generally difficult to recycle and possess poor selectivity and sorption capacity. [11]

Therefore, the research interest has been driven toward the development of new types of sorbent materials like sponges [12,13], aerogels [14], and particles [15] with enhanced water-oil separation.

In particular, the use of polydimethylsiloxane (PDMS) as a sorbent material has recently attracted increasing interest since it possesses a mixture of unique properties; it is flexible, biocompatible, easily molded, mechanically and chemically stable. [16] Moreover, PDMS with its Si-O-Si polymeric structure possesses a high hydrophobic as well as high oleophilic nature, which allows the selective oil sorption from water. [17–23]

So far, several strategies have been proposed to produce PDMS sorbents that can be classified into different categories: sol-gel [24], foaming agent [25], emulsion [26], and particle templating. [27] Choi et. al. [10] and later Zhang et. al. [28] developed PDMS sponges using sugar particles as an easy-removal template with high oil mass adsorption. Later Shin et al. investigate the possibility to use 3D printed polycaprolactone as a sacrificial template for the PDMS sponge fabrication [29]. More recently, Zhou et al. propose microstructured PDMS meshes realized via an aluminum sheet template with high water-oil separation efficiency. [19]

Jiang et. Al. successfully prepared porous PDMS using suspension polymerization with surfactant gelation [30] while Wang et. al. described a one-pot method to generate pores within the PDMS matrix by reaction of NaHCO3 and HCl. [31]

However, all the previously reported methods possess a long preparation time making those sorbents difficult to scale up at the industrial level. [32]

More recently, new attempts to obtain silicon-based sorbents have been made using photopolymerization processes. The photopolymerization mechanism generally allows a striking reduction of the processing time, is solvent-free, and has no Volatile Organic Compound (VOC) emissions, and has low energy consumption. [33,34] Ozmen e at. developed silicon-based cryogels using a photoinduced thiol-ene reaction [32] which was later optimized by Cao et al. [35] Nonetheless, these processes involved the use of cyclohexane which is very toxic for aquatic organisms, and the use of energy to freeze the solvent to obtain the desired porosity.

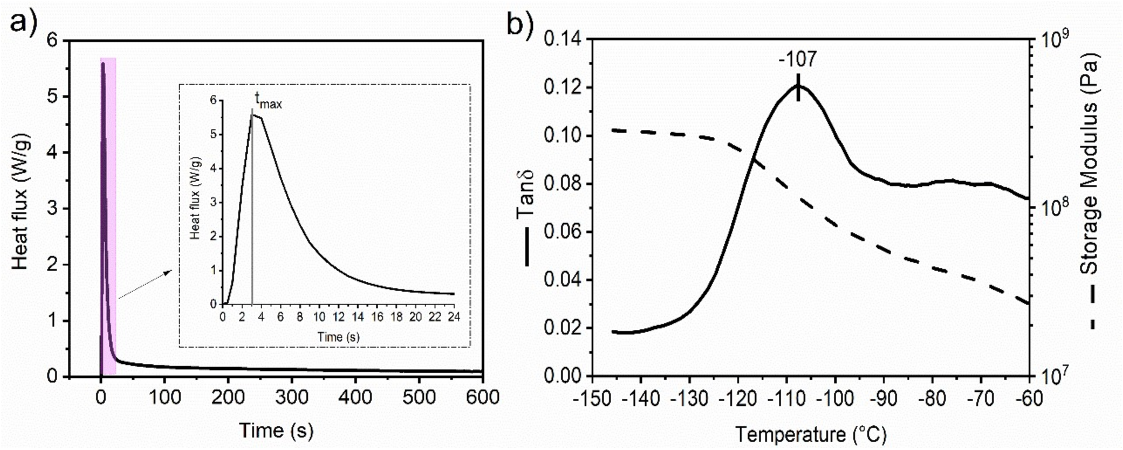
To minimize the energy consumption and to ease its scalability for a high production level, herein, we exploited the photocuring of an acrylated PDMS to obtain either dense or porous membranes. The interconnected porous structures were obtained using NaCl salt, which was chosen as a low-cost and eco-friendly template. The photocuring process of the PDMS was evaluated using a Photo-DSC test and the properties of the UV-Cured PDMS samples were fully investigated *via* DMTA and contact angle analysis. The sorption properties of the PDMS were studied using dodecane as a target oil. Furthermore, the efficiency of oil removal of the dense and porous PDMS membranes was evaluated and compared.

3. Results and Discussion

UV-Cured PDMS membranes were selected, in this work, as a good candidate for oil remediation from wastewater because of high hydrophobic and oleophilic properties. The acrylated PDMS (TEGORAD) formulations were photocrossliked in the presence of a radical photoinitiator at 2 phr. In Figure 1,a the photo-DSC curve of the UV-curable silicone is reported to show its high reactivity towards photopolymerization reaction. As can be observed from the graph, the reaction starts immediately (t_{onset} negligible) and it reaches the t_{max} after 3 seconds of irradiation with a very high exothermicity, showing the good reactivity of the silicone precursors in free-radical chain-growth polymerization.

The dynamic thermal-mechanical properties of the UV-cured PDMS sample were subsequently investigated by DMTA analysis. As it can be observed in Figure 1,b, the result demonstrates the high network flexibility proved by its low glass transition temperature (Tg = -107 °C) measured as the maximum of the tanδ plot. Moreover, in Figure F1,b it can be also observed a storge modulus decrease in the so-called glass transition region stating the passage of the thermoset from a plastic to a rubber behaviour.

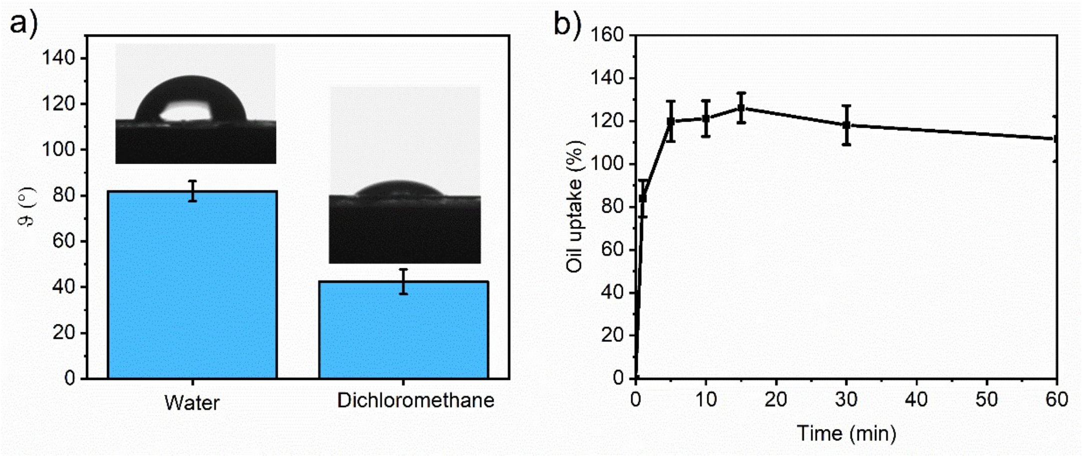
Figure 1. a) Photo-DSC curve of TEGORAD 2800 in the presence of 2 phr of the radical photoinitiator, b) Tanδ and storage modulus of TEGORAD 2800.



The contact angle measurements on UV-cured PDMS membranes reported in Figure 2,a showed values of about 85° with water and 40° with diiodomethane with a surface tension of 39.7 mN m^{-1} confirming the high hydrophobicity and good oleophilicity of the crosslinked silicone material.

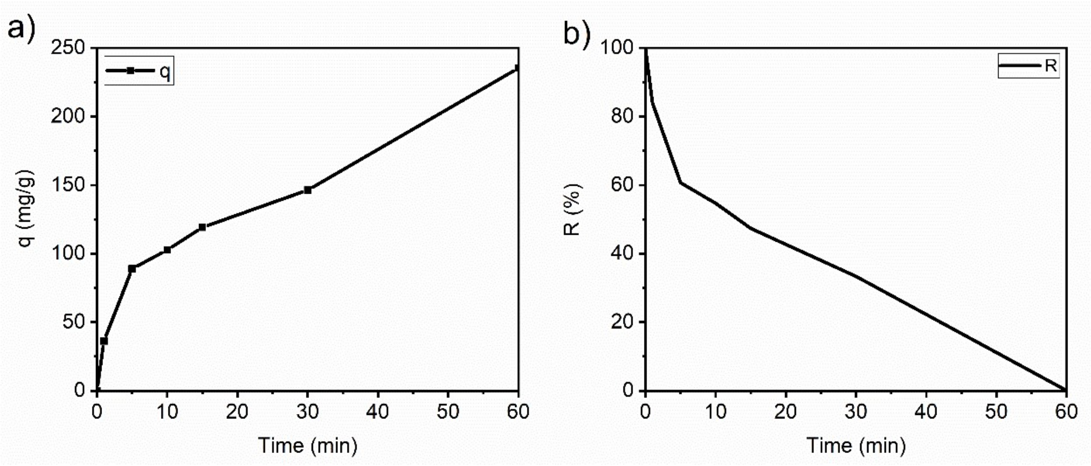
The adsorption efficiency of the UV-Cured silicone membranes was evaluated gravimetrically using dodecane as a target oil. The weight upload as a function of time is reported in Figure 2,b. The oil uptake is very fast reaching a plateau of about 126% after 5 minutes of immersion. The same gravimetric analysis was performed by immersing the UV-Cured silicone in water and it did not show any water uptake, suggesting the selectivity of oil adsorption in the case of the water-oil mixture.

Figure 2. a) Contact angle with water and dodecane of the UV-Cured TEGORAD 2800 membrane and b) Oil uptake (%) as a function of time of the dense membranes immersed into pure dodecane.



The next step was the evaluation of oil uptake of the UV-cured silicone membrane immersed in a water solution containing 500 ppm of dodecane. Taking into consideration the absence of water uptake from the crosslinked membrane, the oil adsorption capacity over time (q_t) value was evaluated by using equation 3 and the removal efficiency (R%) by using equation 4. The adsorption capacity (q vs time) and the removal efficiency (R% vs time) are reported in Figure 3, when the crosslinked silicone membrane was immersed in water containing 500 ppm of dodecane as an oil target molecule. Noteworthy, the removal capacity gradually increases over time leading to complete removal of the oil from the water solution after only 1 hour of immersion time.

Figure 3. a) Adsorption capacity (q) and b) removal efficiency R as a function of time of UV-Cured TEGORAD 2800 membranes immersed into a water solution containing 500 ppm of dodecane.



To enhance the efficiency of oil uptake from water, porous UV-Cured silicone membranes were fabricated using NaCl particles as templates. The random porous structures with averaged pore dimensions of 100-200 μm were achieved as can be observed from the SEM images reported in Figure 4.

Figure 4. SEM images of the porous silicon membrane.

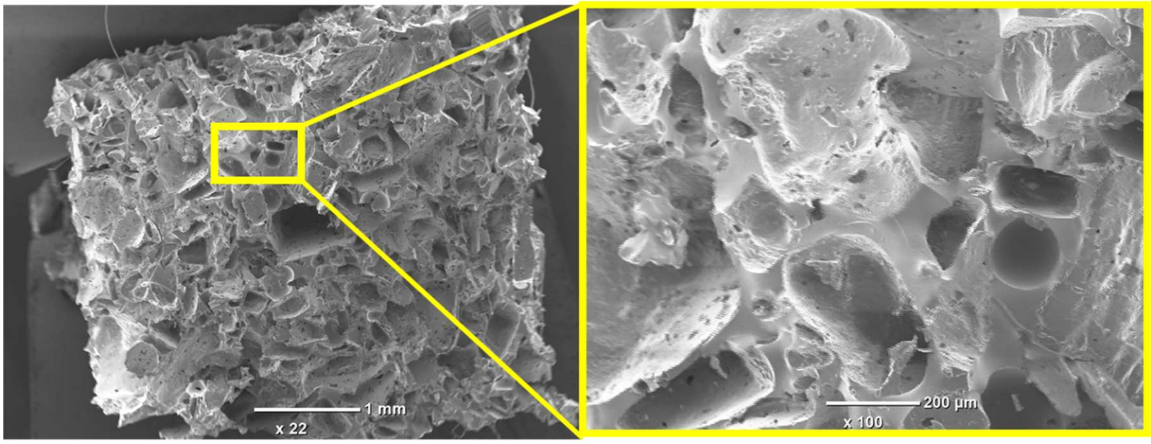
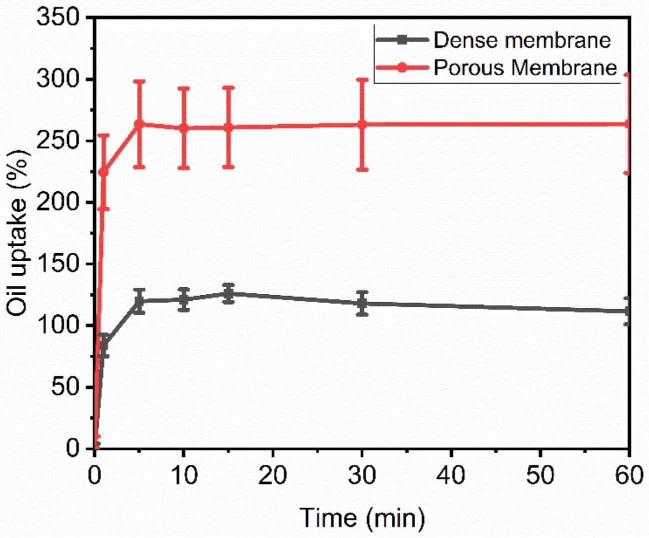


Figure 5 reports a comparison of the oil uptake as a function of time for the dense and porous silicone membranes immersed in dodecane. From this graph, a strong enhancement of oil uptake achieved by the porous membranes can be observed with respect to the dense ones. In fact, dense membranes showed an oil removal of 126% while the porous ones reached up to 264%. This result can be attributed to the increased surface area which has induced the increase in adsorption capability. The achieved oil uptake % of the porous membranes is higher than the ones obtained by the PDMS sponges obtained using a 3D printed PCL template (~90%) with comparable pore size. [29]

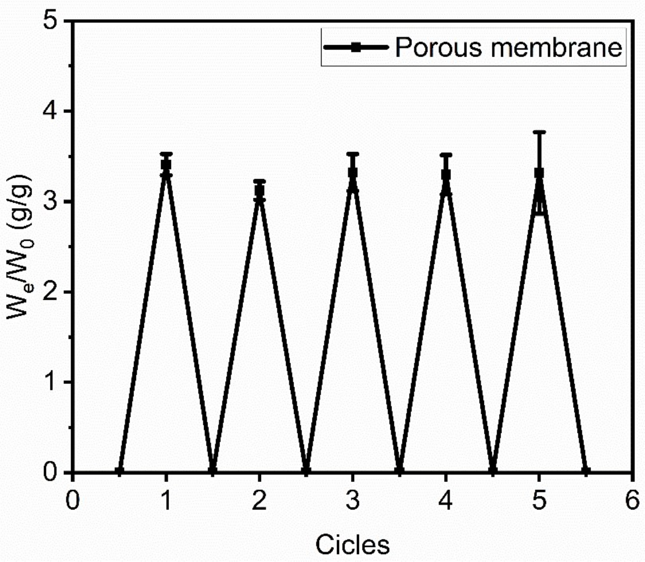
Figure 5. comparison of oil uptake as a function of time for the UV-Cured TEGORAD 2800 dense and porous membranes immersed into dodecane.



The recyclability of the PDMS porous membranes was tested by performing five different adsorption/desorption cycles. The results are reported in Figure 6. After the adsorption, the oil can be recovered from the membrane by performing a simple manual squeezing. After the squeezing, the same membrane was placed again in the dodecane solvent and the adsorption test was repeated.

As can be seen from the graph, no significant change in oil absorption capacity and in the porous membrane weight was observed after the 5 absorbing/desorbing cycles.

Figure 6. Normalized porous membrane weight at different adsorption/desorption cycles in dodecane.



4. Conclusions

In conclusion, in this work, it was developed a new type of low-cost and environmentally friendly PDMS adsorbents with high adsorption and excellent reusability. These membranes can be directly obtained by mixing the acrylated PDMS with 2wt% of radical photoinitiator followed by 1 minute of irradiation. It was possible to achieve both dense and porous membranes by simply adding NaCl salt as a template into the initial formulation. The choice of NaCl powder as an economic template and the very fast UV-curing reaction made this process feasible for large-scale manufacturing. The UV-cured membranes showed low glass transition temperature which gives them high flexibility.

The PDMS membranes possess excellent sorption capability and selectivity towards dodecane in both pure solvent tests and in real water/oil mixtures. Moreover, those membranes possess high stability and recycling capability as shown by the results of five adsorption/desorption cycles. Therefore, the UV-cured PDMS membranes are expected to have promising applicability in the water/oil separation treatment at the industrial level.

2. Experimental

2.1. Materials

The acrylated PDMS resin "TEGORAD 2800" was gently given by Evonik. The radical photoinitiator 2-Hydroxy-2-methylpropiophenone, and the solvent dodecane were purchased from Sigma Aldrich, Milano, Italy**.**

2.2 UV-Curing of silicone membranes

The silicone resin TEGORAD2800 was mixed with 2 phr of the radical photoinitiator and then poured on a glass slide forming a film of 1 cm length, 0.5 cm width, and 400 μm thickness. The film was irradiated with the static Dymax UV lamp with a light intensity of 165 mW cm^{-2}, under nitrogen for 1 minute. The obtained crosslinked membranes were used for the dodecane adsorption tests without further modifications.

The porous membranes were obtained by filling a silicone mold with NaCl, used as a template, and subsequently pouring on top of it, the photocurable silicone formulation, with a weight ratio of template/silicone precursor 5:1. The formulation was kept under vacuum for 10 minutes, to assure a complete wettability of the viscous formulation and UV-irradiated for 2-3 minutes under nitrogen. The fabricated crosslinked material was kept under stirring in water at 90 °C for 12 hours, to assure the complete NaCl solubilization.

2.3 Characterization

2.3.1 Photo-differential scanning calorimetry (Photo-DSC)

The photo-DSC measurements were conducted with a Mettler-Toledo DSC instrument. The light source consists of a Hamamatsu LC8 lamp with a light intensity of 100 mW cm^{-2} equipped with an 8 mm light guide. Samples having masses of approximately 10 mg were inserted in 100 μL aluminum pans and tested at 25ºC under a nitrogen atmosphere. The exothermicity of the photocuring reaction was studied using the following method: 1) isothermal of 120 s with no light source, 2) isotherm of 600 s with irradiation, 3) isotherm with no irradiation and 4) isotherm of 600 s with irradiation. Then the curve of the second irradiation was subtracted from the first irradiation and plotted. This step was conducted in order to eliminate the heat component deriving from the light dissipation. From the Photo-DSC curve, it was possible to calculate the time to start the polymerization (t_{onset}) and the time to reach the maximum heat flux (t_{max}).

2.3.2. Dynamic Thermal Mechanical Analysis (DMTA)

Dynamic thermal-mechanical analysis was performed using a Triton Technology instrument. PDMS samples (10 x 5 x 0.2 mm) were tested with uniaxial stretching with the frequency fixed at 1 Hz and strain at 0.02%. The heating rate was set as 3 °C min^{-1}. The storage modulus (*E*') and the loss factor (tanδ) were recorded as a function of temperature.

2.3.3 Contact angle measurements

Contact angle measurements were performed using a Kruss DSA10 instrument, equipped with a video camera. Analyses were performed at room temperature using a sessile drop technique. Six measurements were performed on each sample. The surface free energy was determined using the Owens-Wendt-Rabel-Kaelble (WORK) method. [36] Double distilled water (γ = 72.8 mN m^{-1}) and diiodomethane (γ = 50.8 mN m^{-1}) were used as measuring liquids.

2.3.4 Scanning Electron Microscopy (SEM)

The morphological characterization of the porous crosslinked membranes was performed by using SEM (JCM-6000PLUS, JEOL) instrument. All the samples were coated with a thin layer of platinum.

2.3.5 Adsorption experiments

The oil removal efficiency of the dense and porous membranes was tested by immersing the samples either in pristine dodecane or in a water solution containing 500 ppm of dodecane.

The oil uptake percentage over time and oil uptake percentage at equilibrium of the membranes were measured using the following equations:

$$Oil\ utake\ (\%) = \frac{(W_t - W_0)}{W_0} \qquad (1)$$

$$Oil\ utake_{eq} = \frac{(W_e - W_0)}{W_0} \qquad (2)$$

were W_t is the weight of the sample at time t,W_0 is the initial weight of the sample and W_e is the weight of the sample at the equilibrium.

The adsorbent capacity at time t (q_t [mg g^{-1}]), and the removal efficiency (R%) were calculated according to Equations 3 and 4, respectively [37,38].

$$q_t = \frac{(C_0 - C_t) * V}{W} \quad (3)$$

$$R(\%) = \left(\frac{C_0 - C_e}{C_0}\right) * 100 \quad (4)$$

where C_0 (mg/L) is the initial dodecane concentration, while C_t (mg L^{-1}) is the dodecane concentration at time t. V (mL) is the volume of the dodecane solution, and W (g) is the mass of the crosslinked silicone membrane.

2.3.6 Recyclability test

The dodecane adsorption and desorption test were repeated five times to evaluate the reusability of the PDMS porous membranes.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

A.G. performed all the experimental part, C.N., G.R. and M.S., wrote the manuscript and give suggestion on the design of the experiments. All authors reviewed the manuscript.

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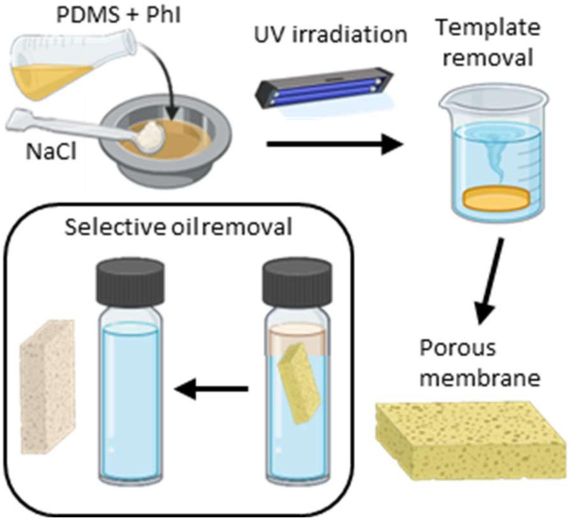
UV-CURED PDMS FOR OIL REMOVAL FROM WASTEWATER

Antonio Grieco, Camilla Noè, Giancarlo Rizza, Marco Sangermano *

UV-Cured PDMS membrane is obtained either as dense or porous membrane and investigated for oil removal from wastewater.



Dimensions 55 x 50 mm