

Short communication

Continuous fabrication of polymer microfiber bundles with interconnected microchannels for oil/water separation

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ABSTRACT

Recently, the development of methods for the cleanup of large-scale oil spills or organic pollutants from water has been attracting global attention. However, traditional techniques suffer from the limits of low efficiency and high operation cost. Herein, we propose a high efficiency, large-scale and easy operation approach to fabricate a hydrophobic and oleophilic high density polyethylene microfiber bundles with interconnected microchannels for oil/water separation. The microfiber bundles with high porosity, excellent absorption capacity and large water contact angle are continuously fabricated by a melt extrusion and leaching technique. More importantly, they are readily cleaned by centrifugation and exhibit excellent shape-recoverable property, which are very promising for the cleanup of large-scale oil spills. This study provides a great promising way to fabricate multifunctional polymer materials by using common polymer molding method.

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1. Introduction

Recently, water pollution caused by oils spills and chemical-reagent leakage has become an urgent global environmental issue, which needs to quick clean up in case of accidents and emergencies [1–3]. A variety of approaches have been developed to solve this problem including combustion, oil containment booms, filtration, and absorption [4–6]. Among these methods, physical absorption via absorbent materials is the most promising way, because it will not generate byproducts and secondary pollution [7–9]. Various absorption materials made from organogels, structure-assembled fibers and porous materials have been reported [10–16]. However, these materials usually suffer from shortcomings such as complicated and time-consuming fabrication procedures, high production cost, environmental incompatibility. Therefore, some more affordable and feasible innovations are still urgently demanded.

As well known, polyethylene (PE) is one of the most abundantly produced plastics worldwide (more than 70 million metric tons per year), showing excellent comprehensive performances like non-toxicity, easy processing, good chemical stability and low price

[17,18]. PE products, such as utensils, films, bottles, pipe, wire, cable insulations and processing equipment, are widely used in commodities, automobiles, construction industry and so on [17]. On the other hand, common melt extrusion molding is widely employed in plastics industry due to its simple operation, continuous production with low-cost and automatization capacity [19,20]. More importantly, it is a solvent-free processing and environmentally friendly method to prepare polymer skeletons. In view of this, it will be a very interesting work if raw PE can be endowed with functional structure during the “structuring” process of the common polymer molding method [21,22].

In this study, we have developed an efficient, low-cost, and environmentally friendly method of continuous producing high-density polyethylene (HDPE) microfiber bundles (PMBs) with interconnected microchannels, and such as-prepared PMBs show various hydrophobicity and oleophilicity with controllable draw ratios. Moreover, the absorption capacity of PMBs is not reduced even after 100 absorption/centrifugation cycles. Moreover, a bench-scale oil collection apparatus was built to achieve continuous oil/water separation by pumping. Therefore, such materials can be considered as a promising candidate in cleaning up large-scale oil spills. This study shows great potential in fabrication multifunctional polymer materials by melt “structuring” process of conventional polymer molding method.

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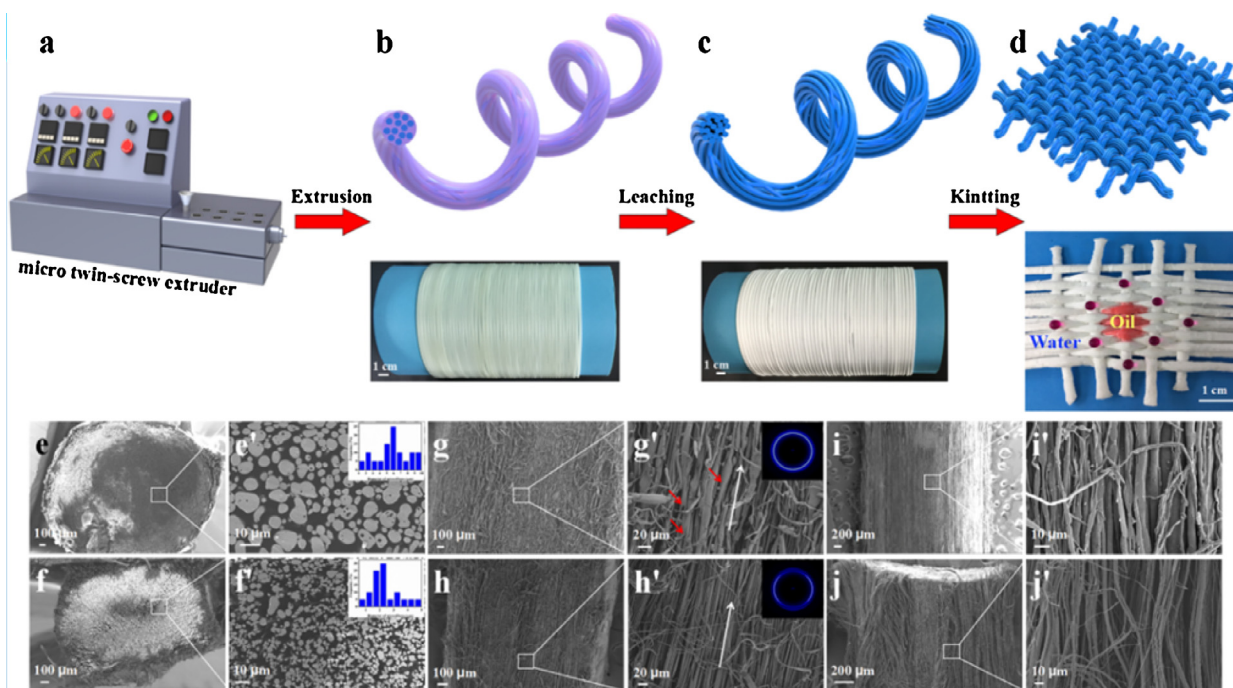


Fig. 1. Fabrication procedure and SEM micrographs of HDPE microfiber bundles (PMBs). (a) Schematic of the micro twin-screw extruder. Schematics and images of (b) HDPE/PEO fibers, (c) PMBs and (d) textile by knitted PMBs and wettability properties of the textile surface. SEM micrographs of (e, e', f, f') cross section, (g, g', h, h') longitudinal section and (i, i', j, j') surface of PMBs with draw ratio of (e, e', g, g', i, i') 1 (PMBs1) and (f, f', h, h', j, j') 4 (PMBs4), and inset in (e', f') is the diameter distribution of microfibers, inset in (g', h') is the 2D-WAXD patterns, the red arrows show the interconnected fibers and white arrows is the extrusion direction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2. Results and discussion

The fabrication process of PMBs is schematically shown in Fig. 1a–c. It consists of three processes: melt mixing, extruding and leaching. First, HDPE and polyethylene oxide (PEO) granules (50/50 wt.%) were melt mixed in a micro twin-screw extruder (Fig. 1a). Secondly, the HDPE/PEO extrudates were hot-drawn at the die exit by a take-up device with a given draw ratio, then air-cooled and taken up by a winder (Fig. 1b). Finally, PMBs containing interconnected microchannels were obtained by aqueous dissolution of PEO into water (Fig. 1). Note that PEO can be completely removed by leaching confirmed by 1D-WAXD results (Fig. S2) and it also can be subsequently recycled from the leached solution by evaporating the water. The obtained PMBs are very soft and can be knitted as shown in Fig. 1d.

Fig. 1e–h shows the morphology of cross- and longitudinal section of PMBs. Clearly, the island-like morphology in cross-section is obtained (Fig. 1e' and f'), indicating that the formation of microfiber in the bundle (Fig. 1g' and h'). Interestingly, some of the microfibers are connected with each other (Fig. 1g', as indicated by the red arrows), indicating that the formation of interconnected microfibers networks in the bundle. Compared with PMBs1, the microfibers in PMBs4 become finer, which can be confirmed by the diameter distribution (insert in Fig. 1e' and f') and the concentrated arc-like diffractions of 2D-WAXD patterns (insert in Fig. 1g' and h'). This is attributed to the synergistic effect of the intense stretching field in die during extrusion and further hot drawing [23,24]. The surface morphology of PMBs in Fig. 1i, i', j and j' also exhibits the fibrous structures with many pores and gaps between microfibers. Accordingly, the entire structure of PMBs is composed of microfibers which align along extrusion direction, and interconnected microchannels are throughout PMBs. However, because the diameter of PMBs4 is too small to be macroscopically observed, therefore, PMBs1 as an example is used to test wettability in the following study.

The water droplets retain hemisphere on the surface of as-extruded HDPE/PEO fibers, while cyclohexane droplets are spread out (Fig. 2a). The contact angle (CA) of water and cyclohexane is 81° and 15° , respectively. Interestingly, cyclohexane droplets spread and penetrated into the 3D interconnected structure of PMBs1, but the water droplets show a nearly sphere with a CA of 134° (Fig. 2a', CA of PMBs4 can reach 141° in Fig. S3). Similar phenomena are observed in the cross-section of as-extruded HDPE/PEO fibers (Fig. 2b) and PMBs1 (Fig. 2b'). Moreover, such hydrophobic and oleophilic properties can be also found in the textile knitted by PMBs1 (Fig. 1d). The hydrophobicity and oleophilicity of PMBs are attributed to the low surface free energy of HDPE material and their interconnected microchannels [25–27]. As well documented [25], HDPE has a low surface free energy of 35.7 mN/m and its smooth surface shows an intrinsic hydrophobicity with a water CA of 101° (Fig. S4). Additionally, the interconnected microchannels of PMBs increase surface roughness, and surface roughness contributes significantly to enhancing liquid repellence [26,27]. Accordingly, the prepared PMBs have a higher water CA than raw HDPE extrudate (Fig. S5).

The microfiber surface of PMBs1 has many edge-on lamellae (Fig. 2c and c'). The formation of these lamellae can be explained as follows: the crystallization temperature of HDPE is higher than the melting point of PEO (Fig. S6). When HDPE began to crystallize after leaving the die exit of extruder, PEO was still in molten state. In this non-confined crystallization process, the surface of microfibers formed some large and clear lamellae. Because of these random lamellae, multiscale roughness is reasonably introduced on surface of PMBs1. According to the Wenzel and Cassie-Baxter model, the introduction of an appropriate multiscale roughness could improve the hydrophobicity [26,27]. Therefore, it is logical that the water CA of PMBs1 surface (134°) is larger than its cross-section (124°).

Because of the interconnected structure and highly hydrophobic surface, the PMBs should exhibit excellent absorbency for oils/organic pollutants. Fig. 3 shows an example of oil/water separa-

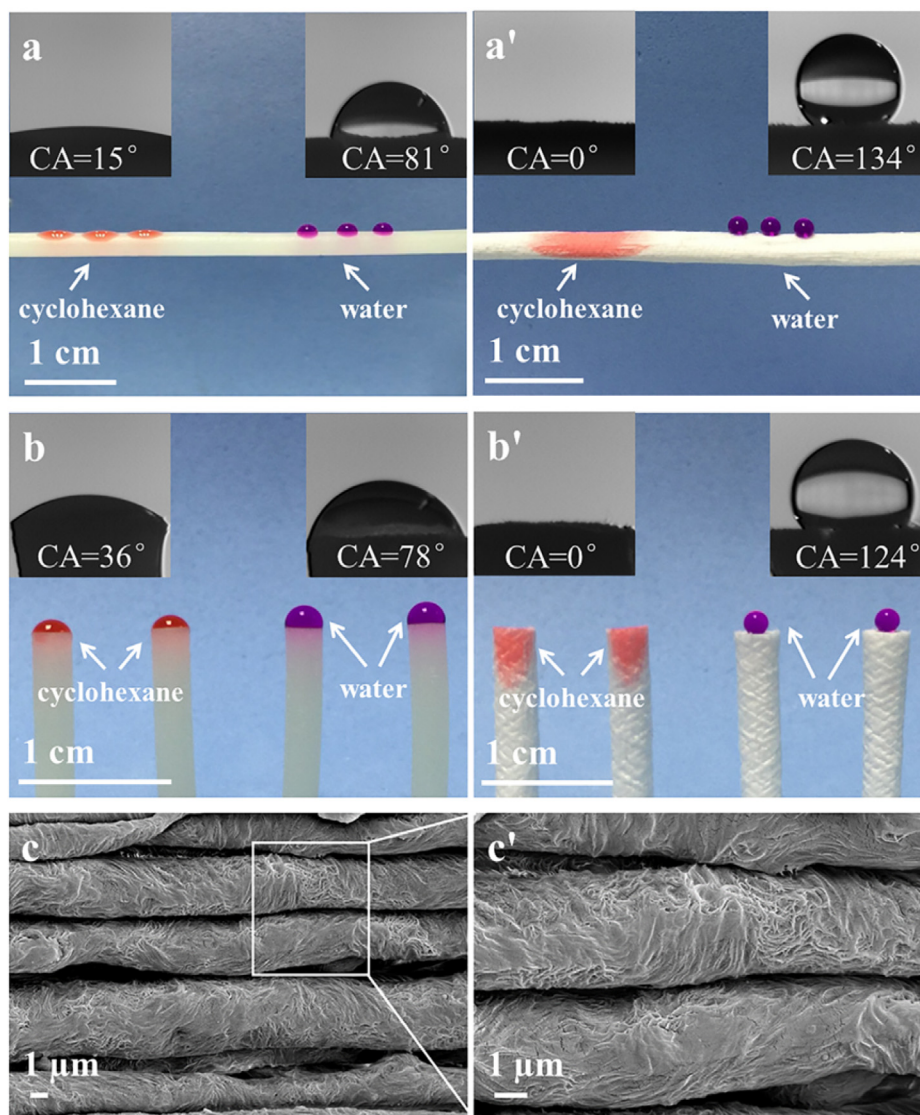


Fig. 2. Contact angle and SEM micrographs of the microfibers in PMBs. Contact angle images of water (dyed with potassium permanganate) and cyclohexane (dyed with Sudan III) droplets on the (a, a') surface and (b, b') cross-section of (a, b) HDPE/PEO extrudate and (a', b') PMBs1, inset images show the contact angle. (c, c') SEM micrographs of the microfiber surface of PMBs1.

tion and absorption capacity of PMBs. When PMBs1 was placed on a cyclohexane–water mixture, cyclohexane was quickly and selectively absorbed from water surface in several seconds (Fig. 3a and Movie S1). The underwater chloroform was also absorbed quickly by PMBs1 (Fig. 3b and Movie S2). Furthermore, we also performed the collection of soybean oil from water surface. The result shows that the soybean oil can be completely collected (Fig. S7), further demonstrating the excellent selective absorption of PMBs1 for oils/organic pollutants. The oil absorption mechanism of PBMs is attributed to the capillary force, via which the oil can be absorbed into the interconnected microchannels in PMBs and replaces the air within microchannels [28,29].

Absorption capacity is an important index of a promising oil/water separation material [30,31]. The absorption capacity Q is calculated by Eq. (1) [32]:

$$Q (\%) = \frac{(m_e - m_0)}{m_0} \times 100 \quad (1)$$

where m_0 and m_e are the absorbent material weights before and after absorption test, respectively. Fig. 3c shows the absorbent capacity of PMBs for various kinds of oils and organic solvents.

PMBs1 shows absorption capacities in the range from 205 wt.% to 453 wt.% for various oils and organic solvents, and PMBs4 is in the range from 343 wt.% to 700 wt.% with the maximum absorption capacity up to 7 times its weight. The absorption capacity of PMBs4 is higher than PMBs1 due to the higher porosity (Fig. S8).

The recyclability and recoverability of absorption materials are key criteria for oil/chemical cleanup applications [30–32]. Fig. 3d and e, respectively, shows the recyclability and recovery process of PMBs1. The materials were alternately immersed in soybean oil for absorption and then centrifuged to release oil (inset in Fig. 3d). No apparent deterioration in absorbency is observed over 100 cycles, and nearly 90% of the absorbed oil is centrifuged during each cycle (Table S1), indicating the excellent recyclability of PMBs. After centrifugation, the shape of PMBs1 undergoes large deformation (Fig. 3e3). Surprisingly, after oil absorption to saturation, PMBs1 are able to recover its original shape (Fig. 3e4). Obviously, the oil absorption performance of PBMs will not be damaged, and therefore it is a potential absorbent for dealing with oil spills or oil/water separation.

As well documented [33–35], pumping technique can lead to continuous oil–water separation or oil collection. As a result, the

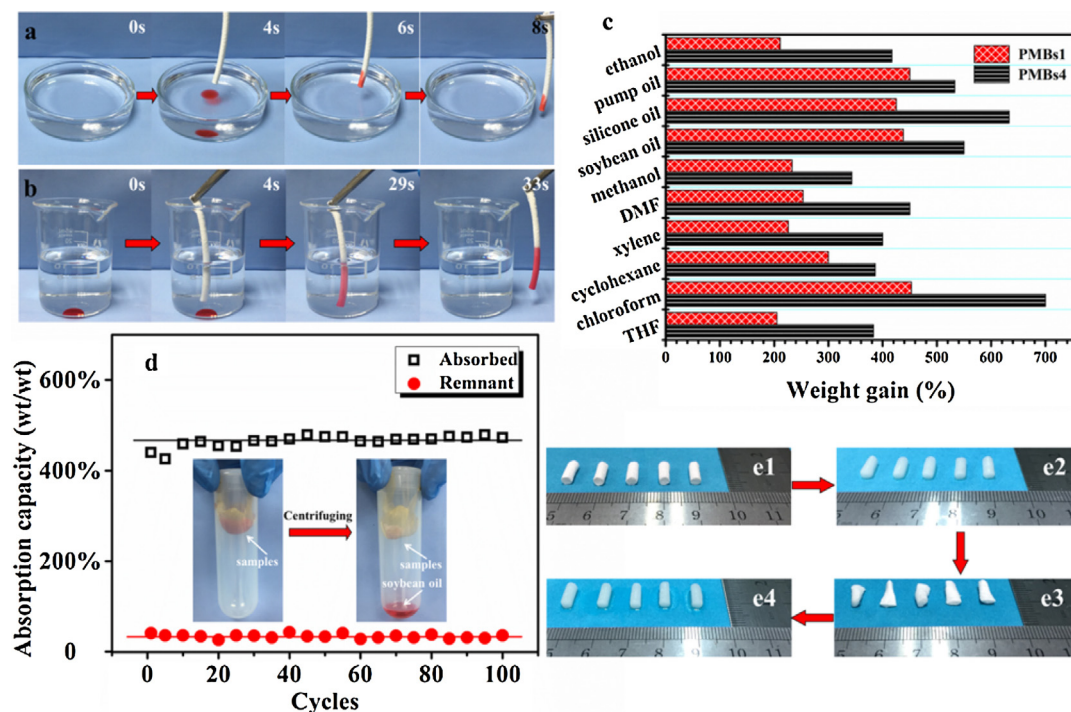


Fig. 3. Oil/water separation and absorption capacity of PMBs. Snapshots of removal process of (a) cyclohexane floating on water and (b) chloroform sinking underwater. (c) Mass absorption capacities of the PMBs1 and PMBs4 for various organic solvents and oils. (d) Oil-absorption capacity of PMBs1 with different absorption/centrifugation cycles, inset shows the oil recovery process by centrifugation. (e) The shape change of PMBs1 during absorption and centrifugation process.

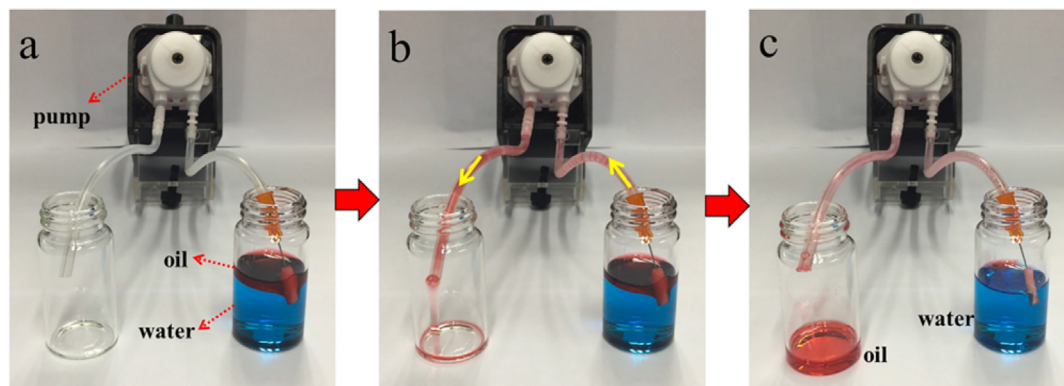


Fig. 4. Photographs of continuous pumping collection of cyclohexane from water with PMBs1. Cyclohexane and water were respectively dyed with Sudan III and methylene blue for clear observation.

oil absorption capacity is no longer limited to the volume or weight of the absorption materials. Naturally, it will bring the absorption materials closer to practical application in oil spill remediation. Based on the different wettability of PMBs1 for oil and water, we built up an oil continuous pumping collection apparatus (Fig. 4a). Cyclohexane is selectively absorbed into PMBs1 by immersing PMBs1 into the cyclohexane/water mixture. After turning on the pump, cyclohexane around PMBs1 can be consecutively absorbed into PMBs1. Subsequently, the cyclohexane absorbed by PMBs1 is pumped to the collecting bottle (Fig. 4b). When the adsorption process is completed, PMBs1 is nearly reverted to the original color and no water can be observed in the collecting bottle (Fig. 4c and Movie S3). This result demonstrates the promising potential of PMBs for continuous oil–water separation.

In summary, PMBs with high absorption capacity and excellent reusability have been developed by combining melt extrusion molding and leaching technique. The results demonstrate that PMBs possess 3D interconnected structures, and can selectively col-

lect oils and organic solvents from water. The absorbed oils and organic solvents can be removed by a simple treatment of centrifugation, but the absorption capacity is not reduced even after 100 absorption/centrifugation cycles. In addition, PMBs can achieve continuous oil–water separation, thus breaking the limit of the absorption capacity of sorption materials. Due to the continuous and solvent-free preparation, good commercial availability of raw materials, excellent reusability, great potential for practical application, PMBs reported here might be a promising candidate to clean up oil spills and chemicals leaks.

3. Materials and methods

3.1. Preparation of PMBs

The commercial HDPE granules (5000S) with a weight-average molecular weight of 5.28×10^5 g/mol were purchased from Daqing Petroleum Chemical Co., China. PEO (Polyox N10) with a weight-

average molecular weight of 1×10^5 g/mol was provided by the Dow Chemical Company.

HDPE/PEO blends (50/50 wt.%) were melt mixing in a mini co-rotating twin-screw extruder (SJSZ-10A, Wuhan Ruiming Plastic and Mechanical Co., Ltd.) with a length-to-diameter ratio (L/D) of 16 and a die diameter of 3.0 mm. The extrudates were hot-drawn at the die exit by a take-up device keeping a draw ratio, then air-cooled and taken up by a winder. The draw ratio of 1 is without hot drawing. Then, the raw HDPE/PEO extrudates were placed in an ultrasonic cleaner (PS-20A, Dongguan Jiekang Ultrasonic Equipment Co., Ltd.) filled with deionized water to dissolve PEO. After prolonged immersion and thorough drying, the PEO was removed and HDPE microfibril bundles (PMBs) were obtained.

3.2. Characterization

SEM (Zeiss MERLIN Compact) was used at an accelerating voltage of 5 kV to study the morphology of PMBs. 2D-WAXD measurement was conducted on a Bruker D8 Discover X-ray diffractometer to characterize whether PEO was completely removed by leaching and the molecular chains orientation level. The hydrophobicity and oleophilicity were estimated on a contact angle measurement apparatus (JC2000C1, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd.) using a droplet of water or cyclohexane at room temperature. Average value of contact angle was obtained from five measurements. In oil–water separation test, cyclohexane and chloroform were used as sample oils to investigate the separation of oil from water. Both cyclohexane and chloroform were dyed with Sudan III. The absorption capacity of oil-absorbent for different kinds of oils and organic solvents was measured, including cyclohexane, xylene, chloroform, ethanol, DMF, pump oil, silicon oil, THF, methanol and soybean oil. PMBs were immersed in organic solvents and oils for 2 h in a chemical hood and then taken out for weight measurement. Desorption test was performed in a centrifuge (TG16-WS, Hunan Xiangyi Centrifuge Instrument Co., Ltd.). Briefly, in absorption/centrifugation cycles, these oil-absorbed PMBs1 were regenerated by centrifuge treatment at a rotating speed of 6000 rpm for 5 min, and then the samples were used in further cycles. The weights of PMBs1 were recorded before and after each cycle to determine the absorption capacity. In the process of collecting oil in situ, PMBs1 (length of 1 cm) connected pipes and pump was used as a continuous oil collection system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apmt.2017.05.007>.

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