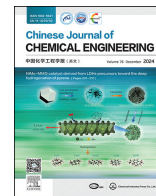




Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: [www.elsevier.com/locate/CJChE](http://www.elsevier.com/locate/CJChE)

## Full Length Article

## The robust design of PMIA braided tube reinforced PFA hollow fiber membranes with graphene doping for water-in-oil separation

Wei Zhao<sup>1</sup>, Xin Jin<sup>1,\*</sup>, Kaikai Chen<sup>1,\*</sup>, Haoyang Ling<sup>3</sup>, Hailiang Liu<sup>1</sup>, Changfa Xiao<sup>1,2</sup><sup>1</sup> School of Materials Science and Engineering, and State Key Laboratory of Separation Membranes and Membrane Processes, Tiangong University, Tianjin 300387, China<sup>2</sup> Fiber Materials Research Center, School of Textiles and Fashion, Shanghai University of Engineering Science, Shanghai 201620, China<sup>3</sup> CAS Key Laboratory of Bio-inspired Materials and Interfacial Science, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

## ARTICLE INFO

## Article history:

Received 22 February 2024

Received in revised form

21 July 2024

Accepted 30 July 2024

Available online 28 August 2024

## Keywords:

Poly(tetrafluoroethylene-co-vinylether)

Graphene

PMIA braided tube

Hollow fiber membrane

Oil-water separation

## ABSTRACT

In order to solve the problem of oily wastewater, the poly(*m*-phenyleneisophthalamide) (PMIA) braided tube reinforced (PBR) poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA) hollow fiber membrane with thermal and solvent resistant property was prepared via no-solvent green method. The membrane surface and pore structure was optimized by changing the sintering temperature and graphene (GE) content. The morphologies showed that the spherical surface with good lipophilicity was formed, and the excellent mechanical strength with a favorable interface bonding state could be obtained due to the PFA melts permeating into the supporting layer. The doping of GE produced synergistic effects with the sintering temperature owing to its good thermal conductivity and pore formation. The PBR-PFA/GE hollow fiber membrane exhibited good hydrophobicity and lipophilicity with more than 97% separation efficiency for different oil products at  $-0.02$  MPa. With the addition of GE, the average pore size first increases and then decreases, and the porosity gradually decreases. In addition, the hollow fiber membrane showed high separation ability to the water-in-oil emulsion, and maintained a stable flux recovery rate after recycling, making it possible to apply in the field of oily wastewater treatment.

© 2024 The Chemical Industry and Engineering Society of China, and Chemical Industry Press Co., Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

## 1. Introduction

With the rapid development of industry, environmental and energy issues have become increasingly prominent. Oil spills, oil pollution, and difficulty in oil recovery pose a threat to human health and ecosystem stability [1–3]. Currently, oil-water separation technology can effectively solve the problem of oily wastewater and plays an important role in sustainable development [4,5]. Compared with traditional oil-water separation technologies, membrane separation technology as an effective method for treating oily wastewater, has advantages such as low energy consumption, simple operation, high separation efficiency, etc. [6–8]. Up to now, the hollow fiber membrane with self-supporting structures, high packing density, large specific surface area, etc.

demonstrated better performance and potential than other types of membranes such as the flat-sheet membranes, and tubular membranes [9,10]. However, the hydrophobic and oleophilic hollow fiber membranes have problems such as membrane surface fouling and pore blockage by oily pollutant [11].

Fluoropolymers exhibit good hydrophobic properties, such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF), which have received widespread attention and application [12–14]. However, the PTFE is difficult to melt processing, and PVDF requires a large number of harmful solvents. PFA was first introduced in the mid-1970s, synthesized from an amount of perfluoropropylvinyl ether, which overcomes the “insoluble and infusible” nature of PTFE and allows for melt processing, giving it great application prospects [15]. Up to now, most works focused on the construction of PFA coating, reducing wear rate, and grafting other polymers to achieve certain functions. For example, Wang *et al.* [16] prepared a super-hydrophobic coating by doped carbon nanotubes with PFA in order to obtain an adjustable lamellar structure. The results indicated that the water contact angle (WCA) of  $153^\circ$  and a rolling angle of

\* Corresponding authors.

E-mail addresses: [jinxin@tiangong.edu.cn](mailto:jinxin@tiangong.edu.cn) (X. Jin), [chenkaikai@tiangong.edu.cn](mailto:chenkaikai@tiangong.edu.cn) (K. Chen).

less than 5° under high pressure and strong acid conditions. Zhai *et al.* [17] prepared a PFA/Ag coating with good antifouling and antibacterial properties. Sidebottom *et al.* [18] prepared a PFA/ $\alpha$ -alumina plate by blending method in order to obtain the ultra-low wear rate of material (reducing the wear rate from  $1.4 \times 10^{-4}$  to  $4.0 \times 10^{-8} \text{ mm}^3 \cdot \text{N} \cdot \text{m}^{-1}$ ). In addition, some works have improved the ion transport function by modifying PFA to prepare ion exchange membranes for batteries [19–21].

Graphene has attracted widespread attention due to its two-dimensional lamellar structure and excellent properties. Leenaerts *et al.* [22] found that the binding energy between water molecules is much greater than the adsorption energy on graphene, and water molecules tend to form clusters on the surface of graphene. In addition, the surface energy of graphene is lower than that of water [23], making it more easily wetted by oily substances and exhibiting hydrophobic and oleophilic properties. In recent years, graphene-based oil-absorbing materials have developed rapidly, such as nanoporous graphene sponges prepared by Bi and Nguyen *et al.* [24,25], which have a sorption capacity for trichloromethane up to 86 times and 165 times than own weight, respectively. In the same way, the doping of graphene in membrane matrix could improve the hydrophobic and oleophilic properties of hollow fiber membranes. For instance, Wu *et al.* [26] prepared a PU/graphene hollow fiber membrane with oil-water separation efficiency and oil flux recovery rate both exceeding 90%, and Hao *et al.* [27] prepared a PVDF/graphene hollow fiber membrane with a separation efficiency of 99.37% when 0.5% graphene was added. In brief, graphene shows great potential in the field of membrane treatment of oily wastewater.

With the continuous expansion of membrane separation applications, high-performance and high-strength hollow fiber membranes have gradually been studied by researchers. As a supporting material, braided tubes can increase the mechanical strength of hollow fiber membranes, combined with the high separation accuracy of the membrane [28–30], making it possible for hollow fiber membranes to be used in harsh environments. Xiao *et al.* [30] demonstrated that the method of coating a separation layer on a high-strength hollow tubular braid is effective in improving the mechanical properties of hollow-fiber membranes. Kolon Industries Inc. developed a braid-reinforced hollow-fiber membrane that comprised a reinforced material of tubular braids and a resinous thin film coated on the surface of the reinforced material. Chen *et al.* [31] prepared poly(ethylene terephthalate) fiber tubular braids/PVDF composite hollow-fiber membrane by a PVDF separation layer coating on the PET fiber tubular braids by a dry-jet spinning method. The membranes as prepared showed good properties, including high flux, high strength, and high rejection. Poly(*m*-phenyleneisophthalamide) (PMIA) is an important aromatic polyamide compound, and the phenylamide bond endows it with excellent thermal stability and mechanical properties. Chen *et al.* [31] utilized interfacial polymerization to prepare PMIA nanofiltration membranes, which exhibit good thermal stability.

Based on the current work of hollow fiber membrane in oil-water separation field, the thermal- and solvent-resistant PBR-PFA/GE hollow fiber membranes with good oil-water separation performance were prepared by the non-solvent green method. The membrane morphologies and performance were researched by the effect of sintering temperature and GE content. The increased separation efficiency and operation stability for oil-in-water emulsions could be obtained by the adjusted pore size and hydrophobic and oleophilic properties. Consequently, the PBR-PFA/GE hollow fiber membranes are expected to be used in oily wastewater treatment processes.

## 2. Experimental

### 2.1. Materials

PFA emulsion (PFA D 335D, Dongguan Jinyunlai Plastic Raw Materials Co., Ltd., China), polyvinyl alcohol (PVA1799, Shanghai McLean Biochemical Reagent Co., Ltd., China), graphene (KNG-G5, Xiamen Kaner Graphene Technology Co., Ltd.), sodium hydroxide (NaOH, analytical pure) and Span-80 (analytical pure) were purchased from Tianjin Fengchuang Chemical Reagent Technology Co., Ltd., China. Anhydrous ethanol (analytical pure, Tianjin Fengchuang Chemical Reagent Technology Co., Ltd., China), Congo red (indicator), cyclohexane (analytical pure), hexane (analytical pure) were purchased from Tianjin Kemio Chemical Reagent Co., Ltd., China, and kerosene and diesel were purchased from Tianjin Rongshunt Petrochemical Co., Ltd. PMIA fiber was self-made in the laboratory by melt spinning method. The solid content of PFA emulsion is 60%, the average particle size is 200 nm and the melting temperature is 305° C. The information on used PFA is shown in Table 1.

### 2.2. Preparation of PBR-PFA/GE hollow fiber membrane

Firstly, PMIA filament was manufactured into braided tube on a two-dimensional braiding machine. Then, the braided tube was immersed in 3% NaOH solution for 2 h to remove oil dirt or stains on the surface of fibers. After that, it was washed with deionized water for 30 min and dried in an oven at 50 °C for 30 min. Secondly, a certain amount of PFA emulsion, GE, and distilled water were added to a three-neck flask. Then, PVA was added at room temperature while stirring to fully disperse. After stirring for 30 min, the water bath was heated to 90 °C and stirred for 2.5 h. After cooling to room temperature, it was placed to defoam treatment in a vacuum drying oven for 2 h, and finally obtain the homogenous casting solution. The casting solution was sonicated for 30 min and then uniformly coated (5 min) on the surface of the braided tube by immersion method. It was placed in the air until the surface dried and then moved into a muffle furnace. The temperature was increased from 20 °C to 340 °C, 360 °C, 380 °C, and 400 °C at a rate of 5 °C·min<sup>-1</sup>, respectively, and maintained for 5 min before naturally cooling down to obtain the final PBR-PFA/GE hollow fiber membrane (HFMs). The schematic diagram and compositions of PBR-PFA/GE HFMs were exhibited in Fig. 1 and Table 2.

### 2.3. Characterization

#### 2.3.1. Morphologies

The morphology of the membrane surface and cross-section was observed by scanning electron microscopy (SEM) with Phenom XL (Phenom-World, Netherlands) and TM3030 (Hitachi, Japan). The samples were sputter-coated with gold before observation.

The surface roughness of the membranes was measured using a CSM700 confocal scanning microscope (ZEISS, Germany). The membrane samples were fixed on glass slides and then placed on the sample stage for testing.

#### 2.3.2. Thermal analysis

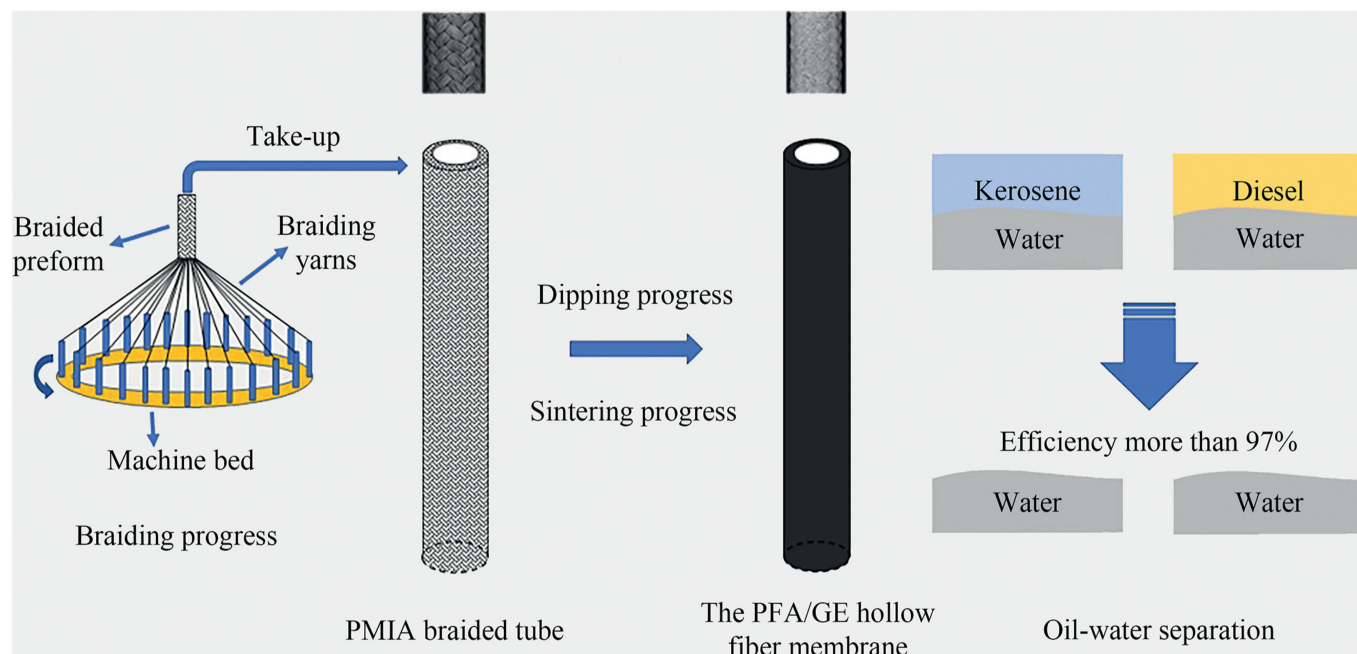
The TG curve of the membrane samples was determined by STA449F3 thermogravimetric analyzer (Netzsch, Germany). The temperature setting range was 20–800 °C and the heating rate was 10 °C·min<sup>-1</sup> under the N<sub>2</sub> atmosphere.

#### 2.3.3. Functional group analysis

The functional group composition of the membrane samples was measured by Nicolet iS50 Fourier infrared spectrometer

**Table 1**  
The parameters of PFA aqueous dispersion

| Characteristic | Solid Content/% (mass) | pH | Density/g·cm <sup>-3</sup> | Average particle size/nm |
|----------------|------------------------|----|----------------------------|--------------------------|
| Value          | 60                     | 10 | 1.5                        | 200                      |



**Fig. 1.** Schematic diagram of PBR-PFA/GE HFMs preparation process.

(Thermo Fisher Scientific, USA) under the test conditions: attenuated total reflection mode, resolution of 4 cm<sup>-1</sup>, and scanning range of 4000–400 cm<sup>-1</sup>.

#### 2.3.4. Mechanical properties

The mechanical properties (breaking strength and elongation at break) of the membrane samples were measured by an electronic single yarn tensile tester (YG061, China) with the gripping range and tensile rate of 100 mm and 2 mm·min<sup>-1</sup> at 25 °C, respectively. Average value of three membrane samples was selected.

#### 2.3.5. Pore size and porosity measurement

The pore size and distribution of the membrane samples were measured by a 3H–2000 PB bubble point method membrane porometer (Beishide Instrument Beijing Co., Ltd.). A pressure difference was applied to both sides of the membrane sample to overcome the surface tension of the impregnating liquid in the membrane pore and drive the impregnating liquid through the pore channel, thereby obtaining the pore size and distribution of the membrane. Besides, the gravimetric method was carried out for assessing the membrane porosity with *n*-butyl alcohol as the wetting liquid. The porosity ( $\varepsilon$ ) was calculated as the following Eq. (1):

$$\varepsilon = \frac{M_1 - M_2}{(\pi/4)(D^2 - d^2)\rho l} \times 100\% \quad (1)$$

where  $M_1$  is the mass of the wet membrane (g).  $M_2$  is the mass of the dry membrane (g).  $D$  is the outer diameter (mm).  $d$  is the inner diameter (mm).  $l$  is the length of the sample membrane (mm).  $\rho$  is the *n*-butyl alcohol density ( $\rho = 0.811 \text{ g}\cdot\text{ml}^{-1}$ ).

#### 2.3.6. Wettability measurement

The static WCA of the membrane samples was measured by a DSA100 contact angle measuring instrument (German KRUSSA Company). The dried membrane was fixed on a glass slide, and 0.2  $\mu\text{l}$  of water droplets were dropped on the surface of the membrane at room temperature. After 30 s, the surface of the membrane was photographed and the contact angle was measured. Each group of samples was measured five times and the average value was taken.

#### 2.4. Permeability experiment

The membrane was tested by negative pressure dead-end filtration using a self-made oil-water separation device in the laboratory, as shown in Fig. 2. The membrane module was placed in a graduated cylinder so that the center position was exactly at the oil-water interface, and the entire device was in a sealed state. When the vacuum pump was turned on, the oil was continuously pumped out and collected under negative pressure, while the water was intercepted to achieve effective oil-water separation. The oil flux  $J$  (L·m<sup>-2</sup>·h<sup>-1</sup>) and oil-water separation efficiency  $\eta$  (%) were measured at -0.02 MPa negative pressure. The volume ratio of oil

**Table 2**  
The composition of hollow fiber membranes

| Samples | GE/% (mass) | PVA/% (mass) | PFA/% (mass) | Viscosity (30 °C)/mPa·s |
|---------|-------------|--------------|--------------|-------------------------|
| M-1     | 0           | 7.5          | 15           | 1620                    |
| M-2     | 0.1         | 7.5          | 15           | 1654                    |
| M-3     | 0.2         | 7.5          | 15           | 1695                    |
| M-4     | 0.3         | 7.5          | 15           | 1747                    |

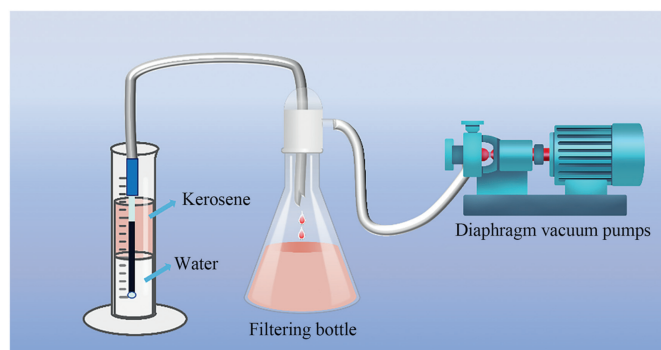


Fig. 2. Schematic diagram of oil-water separation.

to water was 1:1, and the test was performed every 5 min for 10 times. The oil flux  $J$  was calculated according to Eq. (2), and the oil-water separation efficiency  $\eta$  was calculated according to Eq. (3):

$$J = \frac{V}{A \cdot t} \quad (2)$$

where  $V$  is the permeable liquid volume (L).  $A$  is the membrane effective area ( $\text{m}^2$ ).  $t$  is the experiment time (h).

$$\eta = \frac{V_t - V_w}{V_t} \times 100\% \quad (3)$$

where  $V_t$  is the total volume of oil and water collected in one cycle of filtration (L);  $V_w$  is the volume of water collected in one cycle of filtration (L).

In addition, 0.1 g of Span-80 was added to 100 g of oil (kerosene and diesel) and stirred for 30 min, then 1 g of water was slowly added and stirred vigorously for 3 h to prepare a stable W/O emulsion. The water content in the W/O emulsion and the filtrate was determined by a fully automatic micro moisture analyzer, with five tests performed for each sample and the average taken. The emulsion separation efficiency  $k$  (%) of the membrane was calculated according to Eq. (4):

$$k = \frac{C_0 - C_1}{C_0} \times 100\% \quad (4)$$

where  $C_0$  is the water content of the W/O emulsion ( $\text{g} \cdot \text{L}^{-1}$ ), and  $C_1$  is the water content of the permeate ( $\text{g} \cdot \text{L}^{-1}$ ).

The membranes that had undergone the oil-water separation test were soaked in ethanol for 1 h with continuous ultrasound to remove the oil stains on and inside the membrane, dried to constant mass, and then the oil-water separation process was repeated. The flux recovery rate  $r$  (%) was calculated according to Eq. (5):

$$r = \frac{F_i}{F_1} \times 100\% \quad (5)$$

where  $F_i$  ( $i = 2, 3, 4$ ) is the initial kerosene flux in the repetition test ( $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ), and  $F_1$  is the initial kerosene flux in the first test ( $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ).

### 3. Results and Discussion

#### 3.1. Membrane morphology and structure

The surface and cross-sectional morphology of M-1 before and after sintering at  $360^\circ\text{C}$  are shown in Fig. 3. It can be seen from the figure that the membrane exhibits a relatively thin separation layer,

only about  $2 \mu\text{m}$ , and the braid tube texture on the surface of the membrane can be observed before and after sintering. After sintering, the surface texture becomes shallower than that before sintering, which is due to the fact that PFA melts and spreads on the surface of the braided tube. From the enlarged morphology of the cross-section, it can be seen that molten PFA penetrates into the interior of the braid tube. Although the membrane is heterogeneously reinforced, the PFA melt extends into the interior of the supporting layer, and the favorable bonding strength between the surface separation layer and the interface of the braided tube supporting layer can be obtained. This may be suitable for the stable operation of the membrane.

#### 3.2. Thermal properties of membrane

TG curves of M-1 before and after sintering, as well as PVA and PMIA braided tubes at a sintering temperature of  $360^\circ\text{C}$  are shown in Fig. 4. Before sintering, M-1 appears on two kinds of weight loss peaks, corresponding to the decomposition processes of PVA and PFA. Around  $230^\circ\text{C}$ , PVA starts to decompose, which is consistent with the TG results of pure PVA. By  $360^\circ\text{C}$ , the mass loss rate is about 30%, and near  $450^\circ\text{C}$ , PFA decomposes. The sintering temperature of  $360^\circ\text{C}$  is between the decomposition temperatures of PVA and PFA. During sintering, PVA is removed while PFA melts and penetrates into the interior of the braided tube, resulting in a favorable bonding strength between the surface separation and the supporting layer. There is almost no mass loss before  $300^\circ\text{C}$ , and the mass loss rate is only 3.03% at  $360^\circ\text{C}$ , indicating that most of the PVA has been removed during the sintering process. The remaining small amount may be due to the large content of PVA in the matrix before sintering (33%), resulting in incomplete decomposition of PVA during the sintering process [32]. After  $450^\circ\text{C}$ , it still corresponds to the decomposition process of PFA. The high decomposition temperature of PFA is due to its strong thermal stability with large bond energy C–F functional groups. In addition, the TG curve of the PMIA braided tube shows excellent thermal resistance. The initial decomposition temperature ( $406^\circ\text{C}$ ) of PMIA is higher than the sintering temperature, and hence it does not undergo deformation or decomposition during the sintering process, making it suitable as a supporting layer for providing mechanical properties to the PBR-PFA/GE hollow fiber membranes.

#### 3.3. FTIR analysis of membrane

The FTIR of M-1 before and after sintering at  $360^\circ\text{C}$  are shown in Fig. 5. As can be seen from the figure, the typical absorption peaks of PVA at  $3290 \text{ cm}^{-1}$  (—OH),  $2930 \text{ cm}^{-1}$  (—CH),  $1420 \text{ cm}^{-1}$  (—CH<sub>2</sub>) and  $917 \text{ cm}^{-1}$  (—CO) all disappear after sintering, while the absorption peaks corresponding to PFA at  $505 \text{ cm}^{-1}$  (—CF<sub>2</sub>) and  $626 \text{ cm}^{-1}$  (—CF<sub>3</sub>) are no significant change after sintering. In particular, the absorption peaks at  $1146 \text{ cm}^{-1}$  and  $1200 \text{ cm}^{-1}$  correspond to —O— become strong after sintering [32]. This is attributed to the oxygen-containing functional groups on PVA that gradually disappear during the sintering process, and the main components of the membrane after sintering are PFA. The changes in absorption peaks before and after sintering prove that PVA has been removed during the sintering process, and PFA has not decomposed but melted into a membrane.

#### 3.4. The effect of surface morphologies by sintering temperature

The surface morphology of M-1 at different sintering temperatures is shown in Fig. 6. As can be seen from the figure, the PFA particles are relatively independent of each other and only partially melt at  $340^\circ\text{C}$ . As the sintering temperature increases, the more PFA particles melt and the less number of microspherical particles



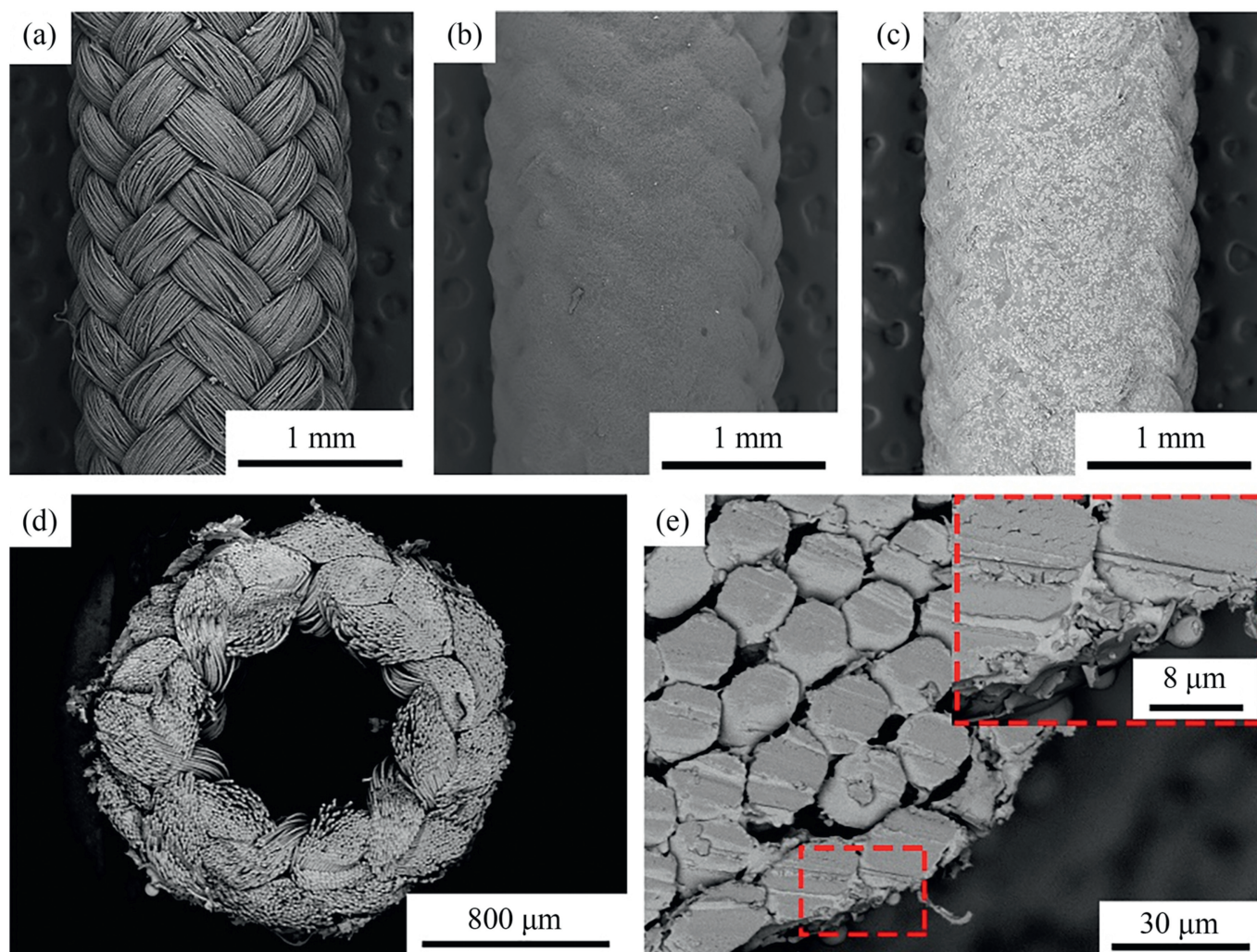


Fig. 3. SEM images: (a) PMIA braided tube, (b) M-1 before sintered, (c) M-1 after sintered, (d) the whole sintered cross-section, (e) the sintered cross-section  $\times 2000$ , inset  $\times 10000$ .

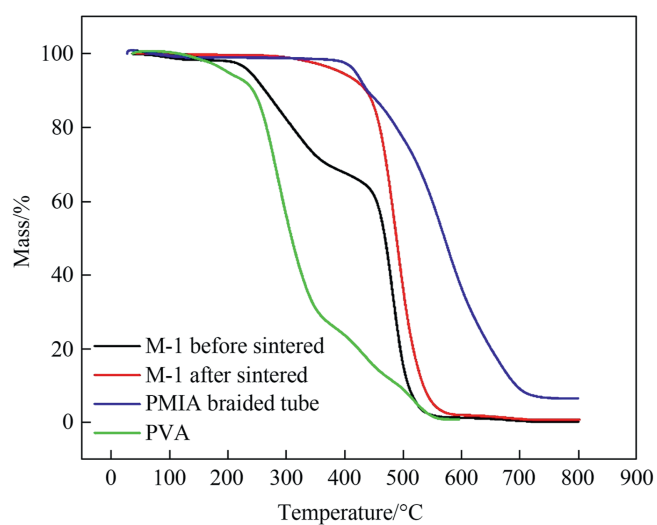


Fig. 4. TG of M-1, PMIA braided tube, and PVA.

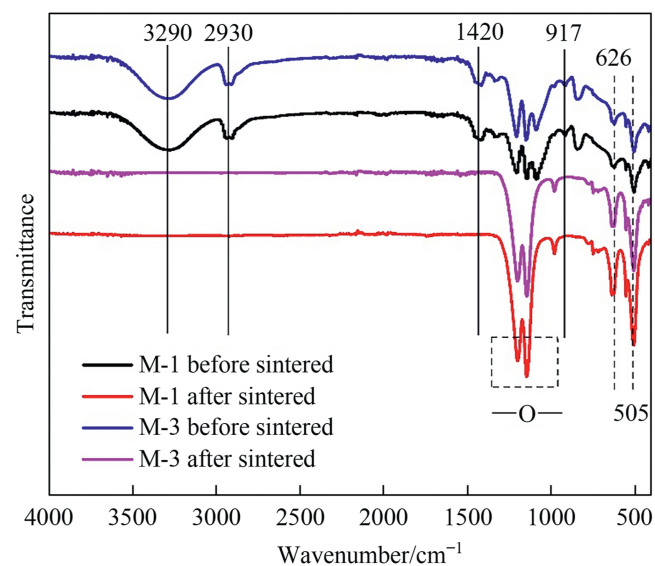


Fig. 5. FTIR of M-1 and M-3 before and after sintering.



obtain. When the sintering temperature increases to 380 °C and 400 °C, the melted shape of PFA particles becomes flat and the number of microspherical particles basically disappears. The increase in sintering temperature accelerates the thermal motion of PFA polymer chains and enhances the distance between molecules, resulting in a decrease in melt viscosity. In other words, the thorough melting process produces (the flatter and flatter shape of the PFA particles) with the increased sintering temperatures.

### 3.5. The effect of surface morphologies by GE content

According to the previous discussion on the influence of sintering temperature on membrane structure, the effect of GE

content on membrane structure was investigated at the sintering temperature of 360 °C. The surface morphologies of M-1, M-2, M-3, and M-4 before and after sintering are shown in Fig. 7. As can be seen from Fig. 7(a), the membrane morphology changed significantly with the addition of GE before sintering. Without GE addition, PFA particles were evenly distributed on the surface of the membrane, however, as the content of GE increased, the dispersion of PFA particles on the surface of the membrane decreased and aggregation occurred. This is due to the change in viscosity of the casting solution caused by the addition of GE. According to Table 2, the viscosity of the casting solution also increases as the content of GE increases. This is because GE possesses a high Young's modulus ( $1.1 \times 10^3$  GPa), and the presence of rigid GE increases the flow

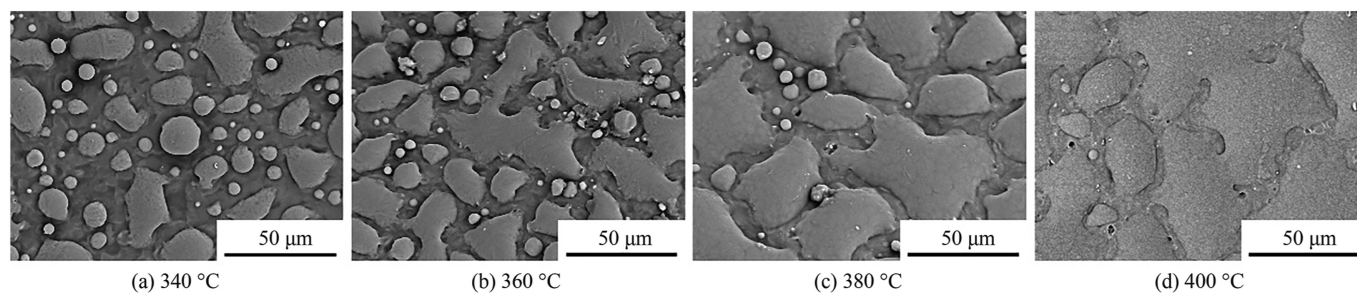


Fig. 6. Effect of temperature on PBR-PFA/GE hollow fiber membranes: (a) 340 °C, (b) 360 °C, (c) 380 °C, (d) 400 °C.

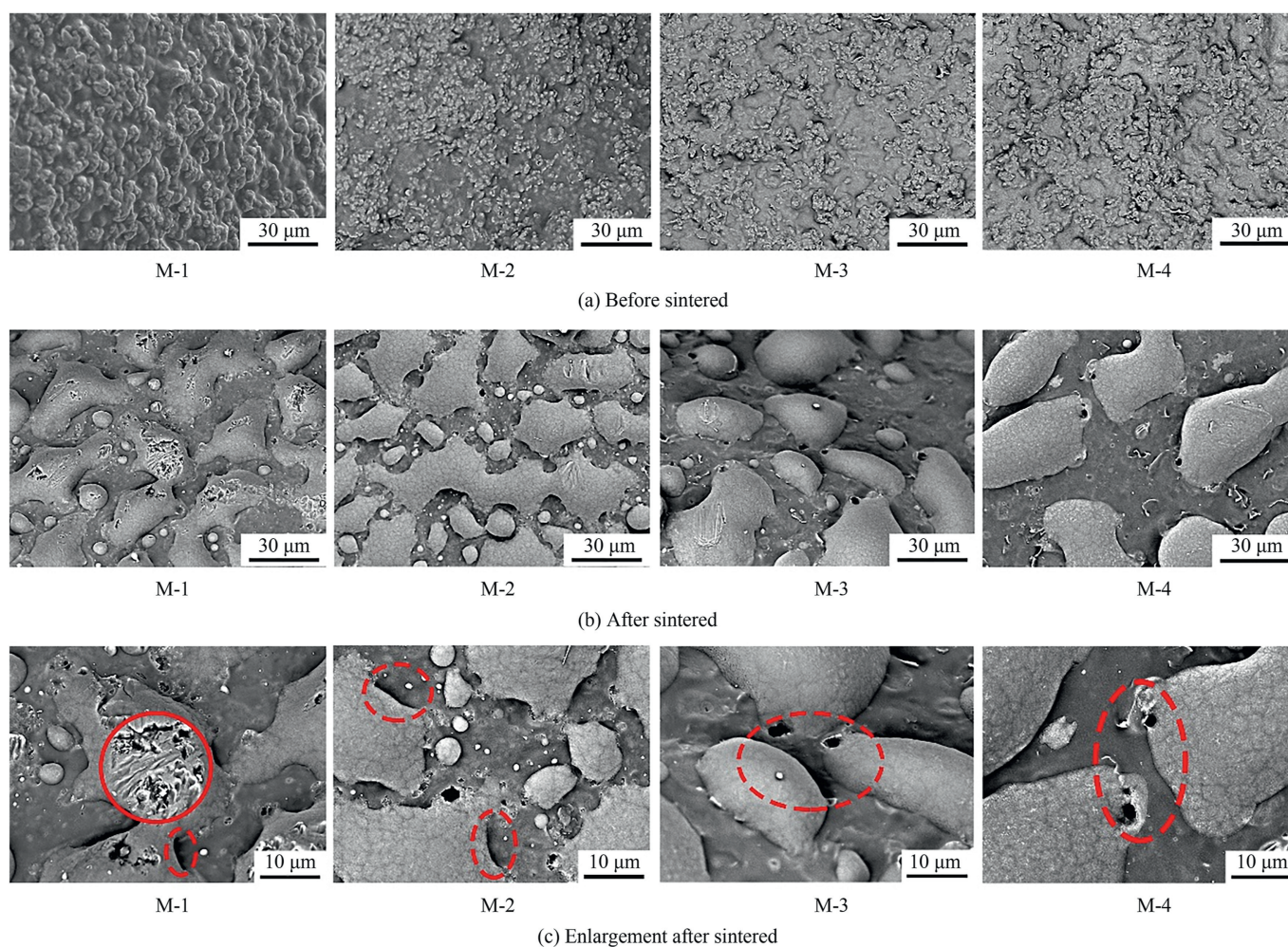


Fig. 7. Effect of GE content on PBR-PFA/GE hollow fiber membranes: (a) before sintered, (b) after sintered, (c) enlargement after sintered.



resistance of the casting solution, leading to an increase in viscosity and thus poor dispersion of PFA particles.

After sintering, the PFA particles were all bonded to each other with a size range of 10–30  $\mu\text{m}$ . With the increase in GE content, the number of microspherical PFA particles gradually decreased, which is similar to the results obtained by increasing the sintering temperature. As shown in Fig. 7(c), the interface pores are observed around the melted PFA (as indicated by the dashed lines), and “grainy” patterns were observed on the surface of the melted PFA. Further observation revealed that M-1 also exhibited pores on the surface of the melted PFA (as indicated by the solid lines). This is due to the poor heat transfer efficiency of PFA, which has a low thermal conductivity and causes uneven melting with inconsistent volatilization of PVA decomposition. Some reports have suggested that GE can significantly improve the thermal conductivity of PFA [33,34]. After adding GE, the thermal conductivity of PFA improved by enhancing heat transfer during the melting process. This caused fast bonding between PFA particles with the increased temperature, and prevented PVA decomposition substances from escaping through the surface of the melted PFA, leading to the different shapes of interface pores. The presence of these two different types of pore structures on the membrane surface not only demonstrates the decomposition process of PVA but also confirms the promoting effect of GE on the melting of PFA.

### 3.6. Roughness and pore size distribution

The surface roughness of M-1, M-2, M-3, and M-4 at a sintering temperature of 360 °C is shown in Fig. 8(a). It can be seen from the figure that the roughness gradually decreases with the addition of GE. The GE improves the heat conduction ability of the membrane and reduces the melt viscosity, which increases the flow rate and causes the complete spreading of molten PFA on the membrane surface for a decrease in roughness.

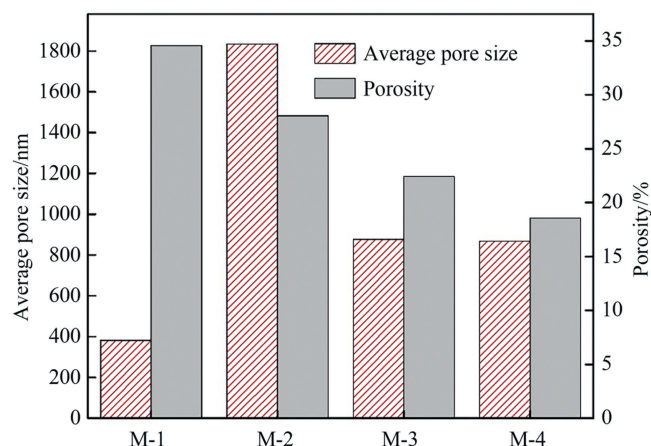


Fig. 9. The average pore size and porosity of PBR-PFA/GE hollow fiber membranes.

The pore size distribution, average pore size, and porosity of PBR-PFA/GE hollow fiber membranes at a sintering temperature of 360 °C are shown in Figs. 8(b) and 9. It can be seen that M-2 exhibits a wide pore size distribution. With the addition of GE, the average pore size first increases and then decreases, and the porosity gradually decreases. The change in average pore size is caused by the distribution of PFA particles on the surface of the membrane before sintering and their melting after sintering. In addition, PFA particles become flat and thin during the melting process due to the promotion of GE on the melting of PFA. As mentioned above, the PFA melt can be spread out fast on the surface of the membrane with the increased GE content, and make the surface of the membrane more and more dense. Therefore, the porosity gradually decreases with the addition of GE.

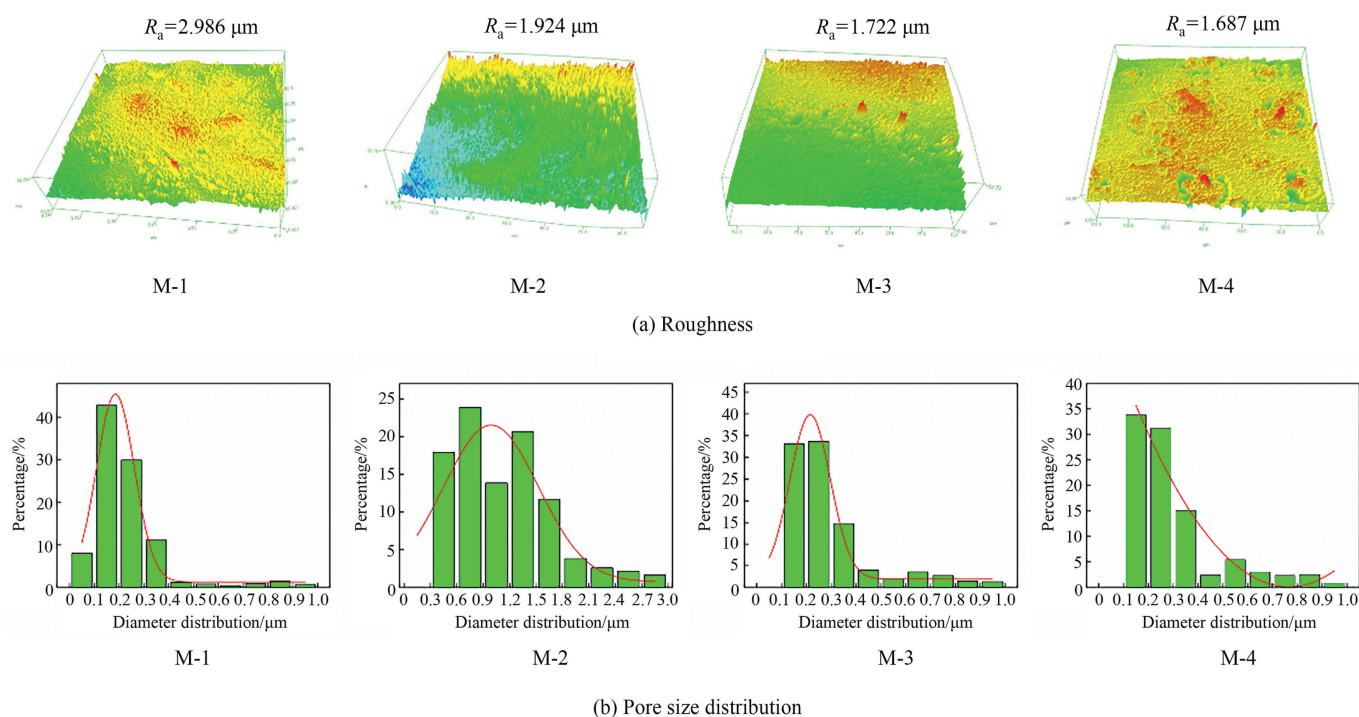


Fig. 8. The roughness (a) and pore size distribution (b) of PBR-PFA/GE hollow fiber membranes.

### 3.7. Surface wettability

The hydrophobicity of the material surface is a key factor affecting its oil-water separation performance [35]. The WCA changes of M-3 membranes at different sintering temperatures and GE contents at 360 °C are shown in Fig. 10(a) and (b). As can be seen from the figures, the WCA gradually decreases with increasing sintering temperature and GE content. Wenzel's theory reveals the relationship between wettability and roughness for the rougher surface of hydrophilic membrane, the rougher surface of hydrophobic membrane, the better the hydrophobicity [36,37]. Increasing the sintering temperature and adding GE promote the melting of PFA result in a decrease in surface roughness, so the WCA shows a decreasing trend. The hydrophobicity of the membrane was also improved due to hydrophobic and lipophilic properties of GE and the irregular stacking and folding on the membrane surface. Therefore, the WCA of PBR-PFA/GE hollow fiber membranes remains around 120°, indicating strong hydrophobicity.

As shown in Fig. 10(c) and (d), the contact angle of M-3 membrane with kerosene and the WCA under kerosene were measured. It can be seen that the kerosene immediately spreads out and penetrates into the membrane within only 1668 ms, with a contact angle of 0° as soon as it contacts the surface of the membrane, showing excellent lipophilicity. In addition, when the water droplet comes into contact with the membrane, the membrane completely repels water, showing strong hydrophobicity under the environment of the membrane soaking in kerosene. The results of the oil contact angle (OCA) and oil-water contact angle show that PBR-PFA/GE hollow fiber membrane has good hydrophobic and lipophilic properties and can be used for oil-water separation.

### 3.8. Mechanical properties of membranes

Fig. 11 shows the stress-strain curves of the original PMIA braided tube, the unsintered M-1, and the sintered M-1. The membrane's tensile strength exceeds 200 MPa, indicating excellent mechanical properties, which contribute to the high-strength

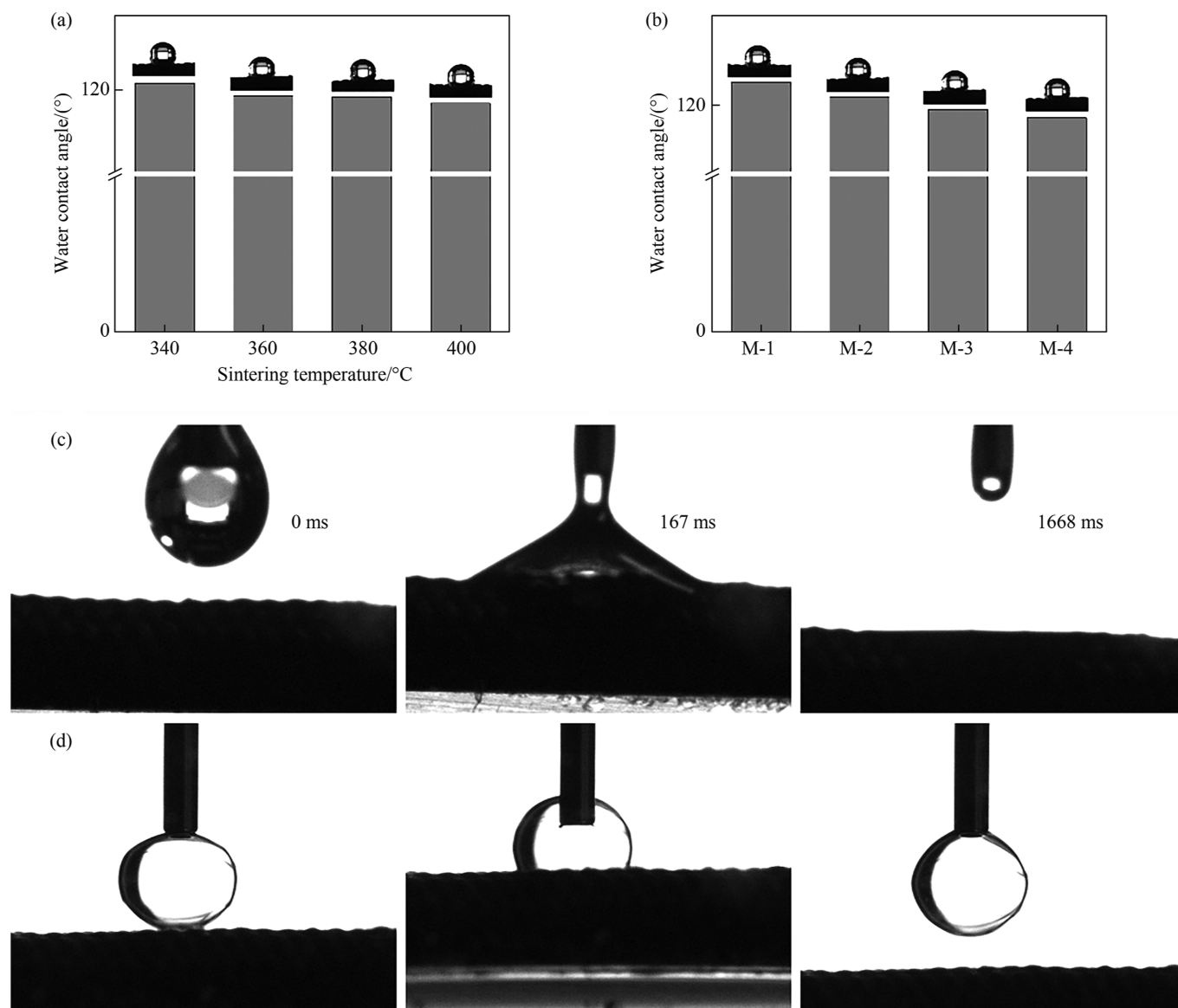


Fig. 10. Effect of (a) sintering temperature and (b) GE content on the WCA of PBR-PFA/GE hollow fiber membranes; (c) in-air kerosene contact angle; (d) under-kerosene WCA.



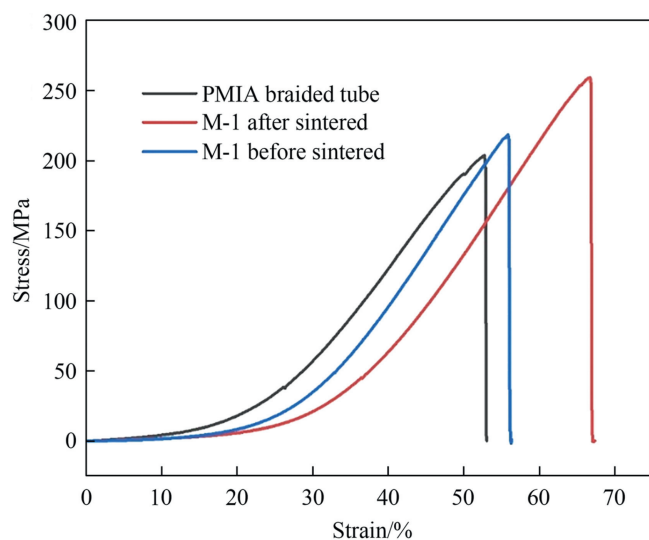


Fig. 11. The stress-strain curves of the original PMIA braided tube, the unsintered M-1, and the sintered M-1.

aramid braided tube as a reinforcing material. The casting solution can fill the surface micropores and irregular structures of the braided tube, making the surface smoother and more robust. This enhances the structural stability and strength of the braided tube,

reducing deformation or damage from external forces. In the unsintered membrane, PFA particles are randomly arranged, resulting in only marginal improvement in mechanical performance. After sintering, thermal shrinkage of the coating on the braided tube and the infiltration of melted PFA into the braided layer also affect its mechanical properties. Moreover, melted PFA particles bond to form a continuous phase, hence maximizing the mechanical strength of the sintered membrane.

### 3.9. Oil-water separation performance

When investigating the effect of sintering temperature on the oil-water separation performance of the membrane, M-1 without GE was tested in order to eliminate the possible effect by GE. The kerosene flux and oil-water separation efficiency of M-1 at different sintering temperatures are shown in Fig. 12(a). The stable kerosene fluxes were  $49.7 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ,  $45.79 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ,  $37.97 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ , and  $32.95 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ , respectively, with corresponding separation efficiencies of 97.2%, 97.9%, 99%, and 99%. As can be seen from the figure, the kerosene flux decreases and the oil-water separation efficiency increases with increasing sintering temperature. The reason can be attributed to the decrease in porosity and an increase in the adhesion of kerosene to the surface and inner pores, which slows down the flow rate inside the membrane and thus reduces the flux and increases the separation efficiency. It was also found that the kerosene flux of membrane showed a trend of first decreasing and then approaching stability. This is because the

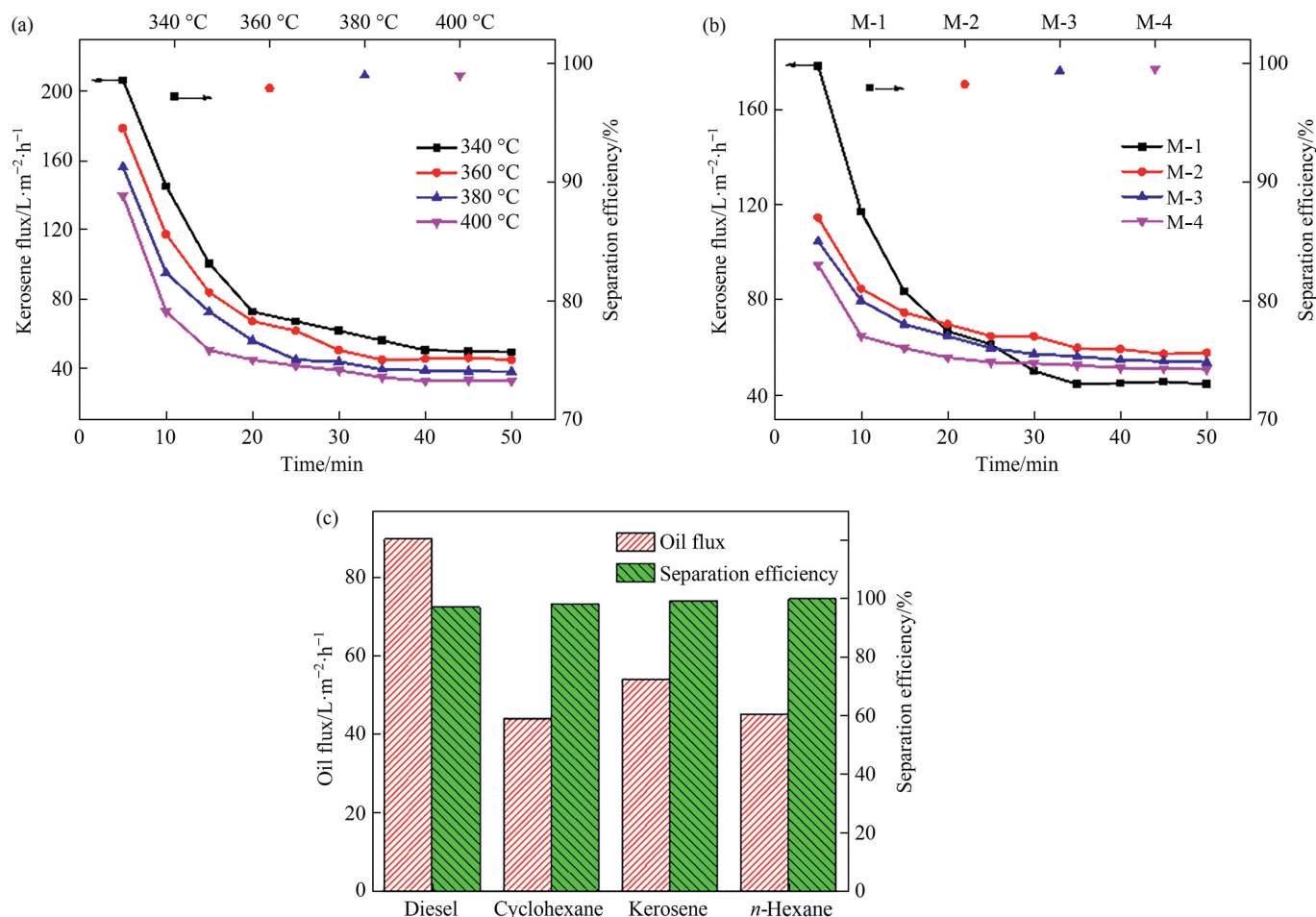


Fig. 12. (a) Effect of sintering temperature, (b) effect of GE content, (c) flux and separation efficiency of different oils of PBR-PFA/GE hollow fiber membranes.

membrane pores were not completely wetted by kerosene in the initial stage of testing. As testing progressed, more and more kerosene adhered to the membrane pores, and prolonged negative pressure operation may cause deformation of the pore with increased fluid resistance, which slowed down the transport speed of kerosene until the steady state.

The kerosene flux and oil-water separation efficiency of M-1, M-2, M-3, and M-4 at a sintering temperature of 360 °C are shown in Fig. 12(b). The stable kerosene fluxes were 45.79 L·m<sup>-2</sup>·h<sup>-1</sup>, 57.42 L·m<sup>-2</sup>·h<sup>-1</sup>, 54.42 L·m<sup>-2</sup>·h<sup>-1</sup>, and 51.43 L·m<sup>-2</sup>·h<sup>-1</sup>, respectively, with corresponding separation efficiencies of 97.9%, 98.2%, 99.3%, and 99.5%. As can be seen from the figure, the membrane kerosene flux decreases, while the oil-water separation efficiency increases with increasing GE content. The kerosene flux of M-1 is relatively higher than M-2, M-3, and M-4 in the initial stage due to its large porosity, but its flux decreases at the fastest rate owing to the compacted pores during operation and the absence of hydrophobic GE on its surface for promoting the nearby kerosene to pass through the membrane pores under negative pressure driving. On the other hand, M-2, M-3, and M-4 all have hydrophobic GE on their surfaces, so the decrease in effective pore size is relatively slow, and the flow rate of kerosene through the membrane pores is faster, resulting in larger stable kerosene flux than M-1. The difference in their kerosene fluxes is mainly affected by their average pore sizes and porosities. Hence, the stable kerosene flux of M-2 is slightly higher than that of M-3 and M-4 due to its large average pore size and porosity.

The stable oil flux and oil-water separation efficiency of M-3 for different oils at a sintering temperature of 360 °C are shown in Fig. 12(c). The stable oil fluxes for diesel, cyclohexane, kerosene, and *n*-hexane were 89.88 L·m<sup>-2</sup>·h<sup>-1</sup>, 45.94 L·m<sup>-2</sup>·h<sup>-1</sup>, 54.42 L·m<sup>-2</sup>·h<sup>-1</sup>, and 45.09 L·m<sup>-2</sup>·h<sup>-1</sup>, respectively, with corresponding separation efficiencies of 97%, 98%, 99.3%, and 99.9%. In addition, the OCAs and surface tensions of different oils are shown in Table 3. All oils quickly spread and penetrated into the membrane surface after contact with an OCA of 0° due to their low surface tension [38,39], which makes them more easily wettable than water and thus the membrane exhibits hydrophobic and lipophilic properties. For M-3, it shows different flux and separation efficiencies for different oils, which is related not only to the properties of the membrane itself but also to the differences in oil density and viscosity. The high separation efficiency exceeding 97%

**Table 3**

The surface tension and WCA of different oils at 25 °C

| Oil products                       | Diesel | Cyclohexane | Kerosene | <i>n</i> -Hexane |
|------------------------------------|--------|-------------|----------|------------------|
| OCA/(°)                            | 0      | 0           | 0        | 0                |
| Surface tension/mN·m <sup>-1</sup> | 28.8   | 24.7        | 28.3     | 17.9             |

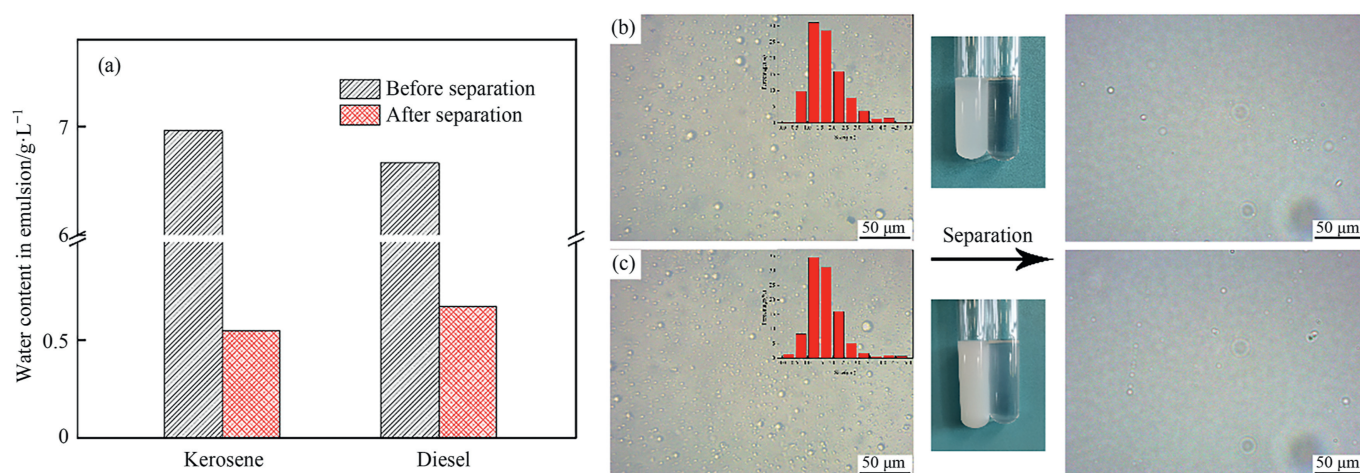
for all oils indicates that M-3 exhibits excellent oil-water selectivity and oil-water separation performance for different oils.

### 3.10. Separation performance of water-in-oil emulsions

The separation performance of the oil-in-water emulsion was tested by using M-3 at a sintering temperature of 360 °C. As shown in Fig. 13(a), the water content in the prepared kerosene emulsion was about 6.96 g·L<sup>-1</sup>, and that after separation was 0.5464 g·L<sup>-1</sup>, with a separation efficiency of 92.15%. The water content in the diesel emulsion was about 6.6646 g·L<sup>-1</sup>, and that after separation was 0.6695 g·L<sup>-1</sup>, with a separation efficiency of 89.95%. The demulsification of the membrane is related to its porous structure and hydrophobicity. The more uniform the porous structure and larger the WCA are, the stronger the demulsification is. As shown in Fig. 13(b) and (c), the average size of water droplets in the kerosene emulsion was 1.84 μm, and that in the diesel emulsion was 1.69 μm. During the separation process, the demulsification process occurs on the hydrophobic membrane surface with oil droplets penetrating through the membrane but the water droplets intercepted on the membrane surface. Only a low fraction of the water droplets with small size passes through the membrane, and condensation occurs during the separation process. Consequently, the filtrate became clear and only a few water droplets could be seen after separation, indicating that M-3 possesses a high demulsification ability. However, the separation efficiency of M-3 still exhibits lower than those reported, which might be attributed to large pore size (0.877 μm) and differences in hydrophobicity.

### 3.11. Operation stability of membrane

The operation stability and recycling performance of M-3 for kerosene and *n*-hexane separation was also evaluated at a sintering temperature of 360 °C. As shown in Fig. 14(a) and (b), the oil flux increased rapidly at the initial stage of each cycle due to the easy



**Fig. 13.** (a) The water content in water-in-oil emulsion before and after separation, Optical microscopy images of M-3 membrane separation results for (b) water-in-kerosene, (c) water-in-diesel emulsions; insets were droplet size distribution.



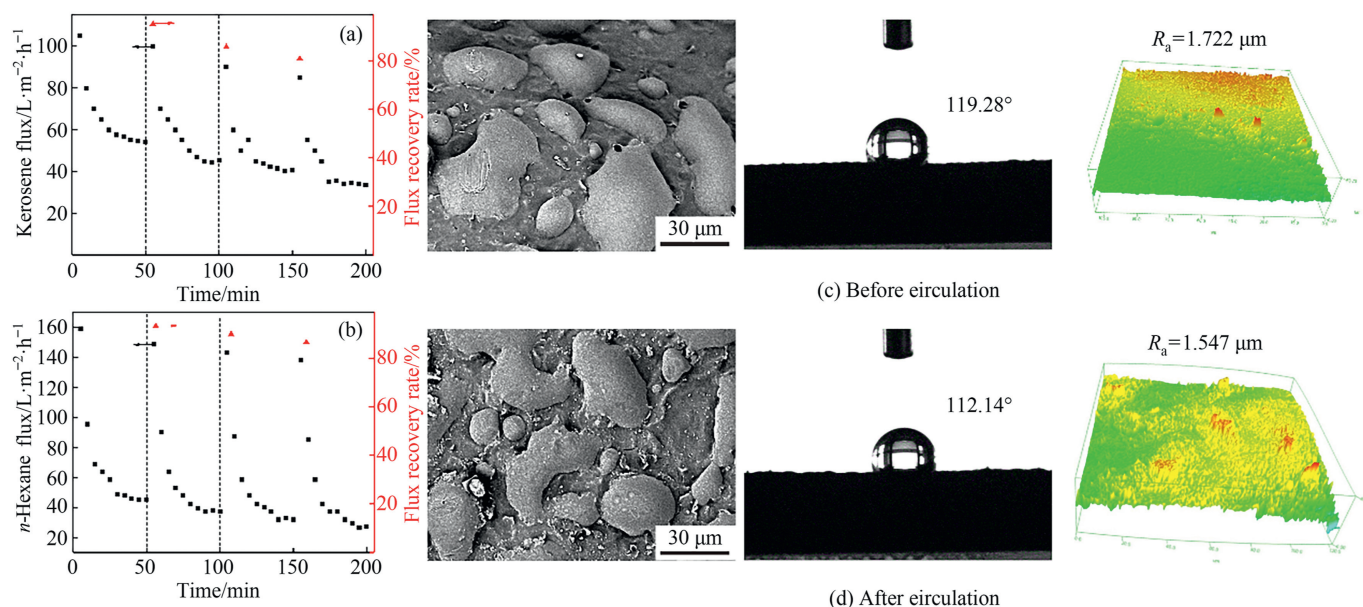


Fig. 14. Reusability and flux recovery rate of PBR-PFA/GE hollow fiber membranes: (a) kerosene; (b) *n*-hexane, and the membrane structure, WCA, and roughness: (c) before circulation; (d) after circulation.

Table 4

The performance comparison of the M-3 membrane and membranes reported in literature

| Membrane  | Flux/ $L \cdot m^{-2} \cdot h^{-1}$ | Separation efficiencies/% | Separation layer thickness/ $\mu m$ | Ref.      |
|-----------|-------------------------------------|---------------------------|-------------------------------------|-----------|
| R-PVDF    | 47.7                                | —                         | 210.0                               | [40]      |
| R-PVDF/GE | 15                                  | 99.3                      | 92.5                                | [27]      |
| R-PVC     | 66.8                                | 99.4                      | 52.0                                | [41]      |
| R-CA      | 5.0                                 | 90.0                      | 102                                 | [42]      |
| R-PAN     | 105.1                               | 92.0                      | 99                                  | [43]      |
| R-PMIA    | 75.8                                | 97.9                      | 102.5                               | [44]      |
| R-PFA/GE  | 54.42                               | 99.3                      | 8.0                                 | This work |

access of oil into the membrane pores. The oil flux gradually decreased until it reached a steady state due to the formation of stable oil absorption layer and pore structure under pressure. The recovery ratio of flux decreased gradually with the increase of cycles. After four consecutive cycles, the recovery ratios of flux for kerosene and *n*-hexane were maintained above 80% and 86%, respectively, which was attributed to the excellent hydrophobic stability of the membrane and demonstrated good reusability.

The changes in the membrane before and after reuse are shown in Fig. 14(c) and (d). As can be seen from the figure, the structural change of the membrane was relatively small, and a few impurities appeared on the surface. The reason could be attributed to the adhesion of impurities in the oil products to the membrane surface. In addition, the WCA on the surface decreased from 119.28° to 112.14° after reuse, indicating a slight decrease in hydrophobicity. The roughness also decreased from 1.722  $\mu m$  to 1.547  $\mu m$ . As analyzed earlier, this may be due to the compaction of the membrane surface caused by long-term negative pressure operation, resulting in a decrease in roughness. The changes in the surface structure and WCA of the membrane before and after reuse demonstrate that the membrane exhibits excellent reusability and can be used for long-term oil-water separation processes.

The comparison of membrane performance including (permeate flux, rejection, etc.) with reported literatures for braid-reinforced hollow fiber membranes was shown in Table 4. For oil-water separation application, the oleophilic/hydrophobic surface

property of PBR-PFA/GE hollow fiber membrane ensured good average permeate flux as well as separation efficiencies of different oils. Although the performance of PBR-PFA/GE hollow fiber membrane is not yet optimal, but none of the studies explored the combined effect of PFA separation layer and GE on the braid-reinforced hollow fiber membranes structure and morphology. This kind of no-solvent green method, coupled with the temperature and solvent resistance of the PFA, may expand the application of hollow fiber membrane oily wastewater filtration.

#### 4. Conclusions

In conclusion, PBR-PFA/GE hollow fiber membranes were successfully prepared by the no-solvent green method. The results showed that with the increase of GE content, the contact angle of water, roughness, and porosity decreased. When the sintering temperature was 360 °C, the pore size of the membrane was between 0.3 and 1.8  $\mu m$ , and the contact angle of water remained around 120°, showing strong hydrophobicity. The oil-water separation tests showed that oil permeability decreased with the increase of sintering temperature, but oil permeability first increased and then decreased with the increase of GE content. At the same time, PBR-PFA/GE hollow fiber membrane with 0.2% (mass) GE exhibits excellent oil-water selectivity for different oils, and a separation efficiency of more than 97%. Moreover, the recovery rate of kerosene and *n*-hexane fluxes remained above 80% and 86%,

respectively. The membrane preparation process uses water as a solvent and is driven by low pressure, which can be called a green and pollution-free process. Consequently, PBR-PFA/GE hollow fiber membranes are expected to be further applied to the field of actual oily wastewater treatment.

### Declaration of Interests

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.

### CRediT Authorship Contribution Statement

Wei Zhao: Writing – original draft, Software, Investigation, Formal analysis, Data curation. Xin jin: Supervision, Resources, Data curation. Kaikai Chen: Writing – review & editing, Supervision, Funding acquisition. Haoyang Ling: Software, Resources, Investigation, Conceptualization. Hailiang Liu: Software, Resources, Investigation, Formal analysis. Changfa Xiao: Supervision, Investigation, Funding acquisition.

### Acknowledgments

The authors gratefully acknowledge the research funding provided by the National Natural Science Foundation of China (52103035, 52173038).

### References

- [1] A. Mazumder, S. Sarkar, D. Sen, C. Bhattacharjee, Environmental effects and human health challenges originated from oily wastewater, in: *Advanced Technologies in Wastewater Treatment*, Elsevier, 2023.
- [2] X.S. Ma, J.G. Xu, J. Pan, J. Yang, P.H. Wu, X.C. Meng, Detection of marine oil spills from radar satellite images for the coastal ecological risk assessment, *J. Environ. Manag.* 325 (Pt B) (2023) 116637.
- [3] P.K. Renjith, C. Sarathchandran, N. Chandramohanakumar, V. Sekkar, Silica aerogel composite with inherent superparamagnetic property: a pragmatic and ecofriendly approach for oil spill clean-up under harsh conditions, *Mater. Today Sustain.* 24 (2023) 100498.
- [4] W.Q. Zhang, Y.T. Liu, F.B. Tao, Y.H. An, Y. Zhong, Z.C. Liu, Z.C. Hu, X.T. Zhang, X. M. Wang, An overview of biomass-based Oil/Water separation materials, *Sep. Purif. Technol.* 316 (2023) 123767.
- [5] Q. Tian, Y.H. Jiang, D.F. Liu, Y.T. Dai, B.C. Zhao, T. Zhang, F.X. Qiu, Recycling waste dredged sludge into bifunctional coating for one-step separation of multitasking dye contaminated oil/water emulsions, *J. Ind. Eng. Chem.* 134 (2024) 448–456.
- [6] A.F.V. da Silva, J. da Silva, R. Vicente, A. Ambrosi, G. Zin, M. Di Luccio, J.V. de Oliveira, Recent advances in surface modification using polydopamine for the development of photocatalytic membranes for oily wastewater treatment, *J. Water Process Eng.* 53 (2023) 103743.
- [7] J.L. Zhang, K.M. Peng, Z.K. Xu, Y.J. Xiong, J. Liu, C. Cai, X.F. Huang, A comprehensive review on the behavior and evolution of oil droplets during oil/water separation by membranes, *Adv. Colloid Interface Sci.* 319 (2023) 102971.
- [8] J. Zhang, W.S. Qu, X.Y. Li, Z.X. Wang, Surface engineering of filter membranes with hydrogels for oil-in-water emulsion separation, *Sep. Purif. Technol.* 304 (2023) 122340.
- [9] M.A. Restrepo, S. Emonds, A. Zhao, F. Karakas, J. Kamp, H. Roth, M. Wessling, Self-supporting biocatalytic polyelectrolyte complex hollow fiber membranes via salt-dilution induced phase separation, *J. Membr. Sci.* 689 (2024) 122157.
- [10] Q.T. Jiang, S.H. Liu, W. Zhao, K.K. Chen, H. Zhu, H.B. Yan, C.F. Xiao, The structure design of poly(tetrafluoroethylene-co-perfluoropropylvinylether) (PFA) hollow fiber membrane with high-temperature and chemical resistance for oil purification, *J. Taiwan Inst. Chem. Eng.* 155 (2024) 105315.
- [11] Y.X. Zhai, Y.H. Li, X.M. Jie, G.D. Kang, Y.M. Cao, X.Y. Fu, Y.F. Hou, H.J. Yu, Poly(tetrafluoroethylene hollow fiber membranes with thru hydrophilic channels for enhancing water transfer and anti-oil-fouling properties, *J. Environ. Chem. Eng.* 12 (1) (2024) 111747.
- [12] G. Zapsas, Y. Patil, Y. Gnanou, B. Ameduri, N. Hadjichristidis, Poly(vinylidene fluoride)-based complex macromolecular architectures: from synthesis to properties and applications, *Prog. Polym. Sci.* 104 (2020) 101231.
- [13] P. Kianfar, R. Bongiovanni, B. Ameduri, A. Vitale, Electrospinning of fluorinated polymers: current state of the art on processes and applications, *Polym. Rev.* 63 (1) (2023) 127–199.
- [14] D. Kalita, P. Konwar, D. Sahu, S. Baruah, S. Barua, Fluoropolymer nanocomposites: introduction, fundamental properties, and high-performance applications, in: *Advanced Fluoropolymer Nanocomposites*, Elsevier, 2023.
- [15] T. Hiyama, *Organofluorine Compounds: Chemistry and Applications*, Springer Science & Business Media, 2013.
- [16] K.W. Wang, N.X. Hu, G. Xu, Y. Qi, Stable superhydrophobic composite coatings made from an aqueous dispersion of carbon nanotubes and a fluoropolymer, *Carbon* 49 (5) (2011) 1769–1774.
- [17] M.J. Zhai, Y.F. Gong, X.Y. Chen, T.H. Xiao, G.P. Zhang, L.H. Xu, H. Li, Mass-producible hydrophobic perfluoroalkoxy/nano-silver coatings by suspension flame spraying for antifouling and drag reduction applications, *Surf. Coat. Technol.* 328 (2017) 115–120.
- [18] M.A. Sidebottom, *Ultralow Wear Fluoropolymer Metal-Oxide Composites: Nanomechanics & Tribochemistry*, PhD Thesis, Lehigh University, USA, 2018.
- [19] K. Yang, X.M. Chu, X.J. Zhang, X.F. Li, J.F. Zheng, S.H. Li, N.W. Li, T.A. Sherazi, S. B. Zhang, The effect of polymer backbones and cation functional groups on properties of anion exchange membranes for fuel cells, *J. Membr. Sci.* 603 (2020) 118025.
- [20] C.R. Peltier, Z. Rhodes, A.J. MacBeth, A. Milam, E. Carroll, G.W. Coates, S.D. Minter, Suppressing crossover in nonaqueous redox flow batteries with polyethylene-based anion-exchange membranes, *ACS Energy Lett.* 7 (11) (2022) 4118–4128.
- [21] R.K. Nagarale, G.S. Gohil, V.K. Shahi, Recent developments on ion-exchange membranes and electro-membrane processes, *Adv. Colloid Interface Sci.* 119 (2–3) (2006) 97–130.
- [22] O. Leenaerts, B. Partoens, F.M. Peeters, Water on graphene: hydrophobicity and dipole moment using density functional theory, *Phys. Rev. B* 79 (23) (2009) 235440.
- [23] N. Ahmmed, L.G. Asirvatham, S. Wongwises, Effect of volume concentration and temperature on viscosity and surface tension of graphene–water nanofluid for heat transfer applications, *J. Therm. Anal. Calorim.* 123 (2) (2016) 1399–1409.
- [24] H. Bi, T.Q. Lin, F. Xu, Y.F. Tang, Z.Q. Liu, F.Q. Huang, New graphene form of nanoporous monolith for excellent energy storage, *Nano Lett.* 16 (1) (2016) 349–354.
- [25] P. Nguyen-Tri, H.N. Tran, C.O. Plamondon, L. Tuduri, D.V.N. Vo, S. Nanda, A. Mishra, H.P. Chao, A.K. Bajpai, Recent progress in the preparation, properties and applications of superhydrophobic nano-based coatings and surfaces: a review, *Prog. Org. Coating* 132 (2019) 235–256.
- [26] Y.J. Wu, C.F. Xiao, H.L. Liu, Q.L. Huang, Fabrication and characterization of novel foaming polyurethane hollow fiber membrane, *Chin. J. Chem. Eng.* 27 (4) (2019) 935–943.
- [27] J.Q. Hao, C.F. Xiao, T. Zhang, J. Zhao, Z.W. Fan, L. Chen, Preparation and performance of PET-braid-reinforced poly(vinylidene fluoride)/graphene hollow-fiber membranes, *Ind. Eng. Chem. Res.* 55 (7) (2016) 2174–2182.
- [28] R.M. Moattari, T. Mohammadi, S. Rajabzadeh, H. Dabiryan, H. Matsuyama, Reinforced hollow fiber membranes: a comprehensive review, *J. aiwan Inst. Chem. Eng.* 122 (2021) 284–310.
- [29] T. El-badawy, M.H.D. Othman, M.R. Adam, R. Kamaludin, A.F. Ismail, M.A. Rahman, J. Jaafar, S. Rajabzadeh, H. Matsuyama, J. Usman, T.A. Kurniawan, Y. O. Raji, S.C. Mamah, H. Abdullah, Braid-reinforced PVDF hollow fiber membranes for high-efficiency separation of oily wastewater, *J. Environ. Chem. Eng.* 10 (2) (2022) 107258.
- [30] Y. Huang, C.F. Xiao, Q.L. Huang, H.L. Liu, J. Zhao, Progress on polymeric hollow fiber membrane preparation technique from the perspective of green and sustainable development, *Chem. Eng. J.* 403 (2021) 126295.
- [31] M.X. Chen, C.F. Xiao, C. Wang, H.L. Liu, N.Z. Huang, Preparation and characterization of a novel thermally stable thin film composite nanofiltration membrane with poly (*m*-phenyleneisophthalamide) (PMIA) substrate, *J. Membr. Sci.* 550 (2018) 36–44.
- [32] K.K. Chen, X. Shu, C.F. Xiao, T. Zhang, H.Y. Ling, Green preparation of thermal and solvent resistant poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) hollow fiber membrane for organic solvent recycling, *J. Appl. Polym. Sci.* 138 (32) (2021) e50798.
- [33] M. Cierpisz, J. McPhedran, Y.L. He, A. Edrisy, Characterization of graphene-filled fluoropolymer coatings for condensing heat exchangers, *J. Compos. Mater.* 55 (29) (2021) 4305–4320.
- [34] L.S. Montagna, A.P.B. da Silva, G.F. de Melo Morgado, B. Ribeiro, F.R. Passador, M. C. Rezende, PFA nanocomposites: the influence of three carbon nanofillers on the mechanical and electromagnetic properties, *J. Polym. Res.* 28 (7) (2021) 253.
- [35] Z.L. Chu, Y.J. Feng, S. Seeger, Oil/water separation with selective super-antiwetting/superwetting surface materials, *Angew. Chem. Int. Ed.* 54 (8) (2015) 2328–2338.
- [36] K. Chen, S.C. Zhao, B.Z. Tian, F.Y. Li, C.C. Miao, D.P. Teng, T.T. Xie, M. Wang, Y.F. Hou, P. Li, Q.J. Niu, Hydrophilic-hydrophobic bilayer interlayer for high performance thin-film composite reverse osmosis membranes, *J. Membr. Sci.* 689 (2024) 122177.
- [37] M.B. Mahmud, S.S. Rahman, M. Fashandi, P.C. Lee, C.B. Park, Hydrophilic-to-hydrophobic conversion of polyamide 6-based mat via polyvinylidene fluoride nanofiber integration with enhanced oil-water separation, *Mater. Today Sustain.* 24 (2023) 100559.
- [38] P. Sudersan, M. Müller, M. Hormozi, S. Li, H.J. Butt, M. Kappl, Method to measure surface tension of microdroplets using standard AFM cantilever tips, *Langmuir* 39 (30) (2023) 10367–10374.
- [39] Q. Zhou, B.X. Feng, L.N. Hao, C. Pan, H.B. Song, H.J. Gai, Q.H. Zhu, M. Xiao, T.T. Huang, Preparation and application of low-cost fibers for efficient adsorption



- of oil from coal pyrolysis wastewater and establishment of quantitative equation for calculating oil contact angle under water, *J. Water Process Eng.* 51 (2023) 103461.
- [40] J. Liu, P.L. Li, Y.D. Li, L.X. Xie, S.C. Wang, Z. Wang, Preparation of PET threads reinforced PVDF hollow fiber membrane, *Desalination* 249 (2) (2009) 453–457.
- [41] Z. Zhou, S. Rajabzadeh, L.F. Fang, T. Miyoshi, Y. Kakihana, H. Matsuyama, Preparation of robust braid-reinforced poly(vinyl chloride) ultrafiltration hollow fiber membrane with antifouling surface and application to filtration of activated sludge solution, *Mater. Sci. Eng., C* 77 (2017) 662–671.
- [42] Z.W. Fan, C.F. Xiao, H.L. Liu, Q.L. Huang, J. Zhao, Structure design and performance study on braid-reinforced cellulose acetate hollow fiber membranes, *J. Membr. Sci.* 486 (2015) 248–256.
- [43] Q. Quan, C. Xiao, H. Liu, Q. Huang, W. Zhao, X. Hu, G. Huan, Preparation and characterization of braided tube reinforced polyacrylonitrile hollow fiber membranes, *J. Appl. Polym. Sci.* 132 (14) (2015) 41795.
- [44] M. Chen, C. Xiao, C. Wang, H. Liu, Study on the structural design and performance of novel braid-reinforced and thermostable poly(*m*-phenylene isophthalamide) hollow fiber membranes, *RSC Adv.* 7 (33) (2017) 20327–20335.