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Preparation of water-in-oil emulsions using a hydrophobic polymer membrane with 3D bicontinuous skeleton structure



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ABSTRACT

Epoxy-based polymer (EP) membrane with 3D bicontinuous skeleton structure was firstly processed into tubular membrane and used in membrane emulsification for water-in-oil (W/O) microspheres. Since uniform W/O microspheres have not been obtained using shirasu porous glass (SPG) membrane unless SPG membrane was rendered hydrophobic by treatment with silanes, it is desired to find a hydrophobic polymer membrane which is capable of providing uniform W/O microspheres. To testify the feasibility of EP membrane in membrane emulsification, uniform agarose (coefficient variation (CV)=11.8%) and Ca-alginate (CV=11.4%) microspheres were achieved with EP membrane by direct and premix membrane emulsification, respectively. In comparison with SPG membrane, EP membrane showed good performance in whether direct or premix membrane emulsification in terms of the droplets size distribution and stability of membranes due to its narrow pore size distribution and uniform hydrophobic surface. SPG membrane is chemically unstable and dissolves under basic aqueous condition. However, it was found that EP membrane could tolerate 1 M NaOH aqueous solution for at least one week and keep its stable hydrophobic surface. Hence, EP membrane could be used in alkali condition, which enables to extend the range of applications in membrane emulsification. So EP membrane had huge potential in further preparation of W/O emulsions.

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1. Introduction

Membrane emulsification technology [1], as a simple emulsion preparation method, has received increasing attention over the last 10 years with potential applications in many fields, such as foods, cosmetics and medicines [2]. This method can be simply described as that the dispersed phase is pressed through a membrane with uniform pore-size distribution into a flowing continuous phase under suitable conditions. The resulting emulsion size and size distribution are controlled primarily by the choice of membrane [3]. Membrane parameters including pore shape [4], pore size and size distribution [5], porosity [6] and surface properties [7] play very important roles in the formation of emulsions.

Shirasu porous glass (SPG) membranes with cylindrical, interconnected, uniform microspores, which are synthesized from CaO–Al₂O₃–B₂O₃–SiO₂ type glass, are the most suitable membrane

presently available for a membrane emulsification medium [8]. Generally, the membrane must be capable of being wetted by the continuous phase, but not by the dispersed phase in membrane emulsification, which means that hydrophilic membranes are available for preparing oil-in-water (O/W) emulsions and hydrophobic ones for water-in-oil (W/O) emulsions [9]. SPG membrane is hydrophilic in nature due to a great amount of Si–OH groups on its surface [10], therefore it is more adequate to producing O/W emulsions. The hydrophobic modification of SPG membrane must be performed for the preparation of W/O emulsions. Chemical modification or physical adsorption method was usually used to increase the hydrophobicity of SPG membrane. The physical adsorption method was pre-soaking the membrane in oil phase to improve its hydrophobicity, but the absorbed layer was easily desorbed in emulsification process [11]. In chemical modification, hydrophobic silane coupling agent or silicone resin [10,12] was used to react with hydrophilic silanols on the surface of SPG membrane by forming the silicon–ether bonds to make it bear strong hydrophobic group [13–15]. Due to the steric hindrance, it is difficult for modified layer to homogeneously cover the membrane surface. This method may cause problems in certain

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circumstances where silane coupling agents are banned, such as foods and medicines. It may also be necessary to repeat the surface treatment after each cleaning cycle. In addition, since these silicon ether bonds were non-resistant to alkali, the hydrophobic layer came off easily in alkali environment [16], which restricted the applications of membrane emulsification technology. For example, Konjac glucomannan, a polysaccharide extracted from the Konjac

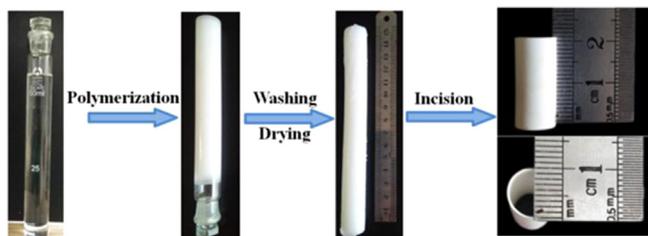


Fig. 1. Preparation process of EP membrane.

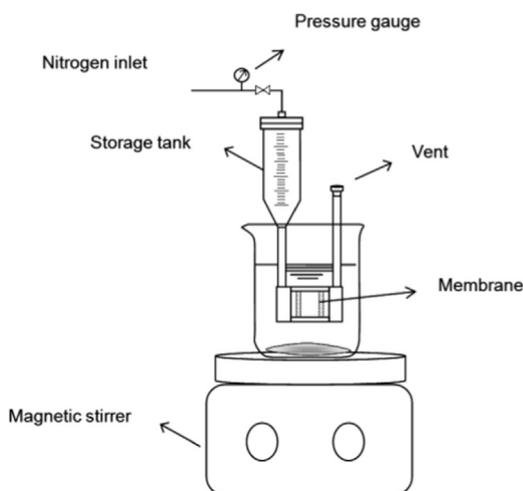


Fig. 2. Schematic diagram of direct membrane emulsification.

plant, shows promise in the pharmaceutical, food, chemical engineering and environmental protection aspects. The gel of Konjac glucomannan is made by heating konjac flour in the presence of alkali, which requires the membrane must have a hydrophobic layer resistant to alkali [17].

To avoid those problems, hydrophobic polymer membrane was applied in membrane emulsification as an alteration, which has been paid increasing attention by many investigators. In our previous reports, polytetrafluoroethylene (PTFE) membrane was used to prepare W/O emulsification. But droplets coalescence occurs on membrane surface in the emulsification process due to its high porosity which makes droplets formed on its surface be very close to each other [18], and badly reduces the emulsions uniformity [19,20]. Polyethylene (PE) membrane has also been used in membrane emulsification in our group. Wide droplets size distribution was obtained in direct membrane emulsification due to the wide pore size distribution of PE membrane [21]. Therefore the membrane for emulsification technology should have appropriate porosity and pore size distribution, as well as special pore structure [22]. In previous study [23], we have successfully obtained different pore size of porous monolithic materials with 3D bicontinuous structure. In present study, the porous monolithic materials were processed into tubular membrane for emulsification technology. Uniform agarose and Ca-alginate microspheres were successfully prepared with EP membrane by direct and premix membrane emulsification, respectively. EP membrane with narrow and controllable pore size distribution, 3D bicontinuous skeleton structure and hydrophobic surface has huge potential in the preparation of uniform W/O emulsions. In addition, EP membrane shows high resistance to alkalis, which enables to extend the range of applications in membrane emulsification.

2. Experimental section

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, epoxy equivalent weight, EEW 196), provided by Wuxi Resin Factory of Blue Star

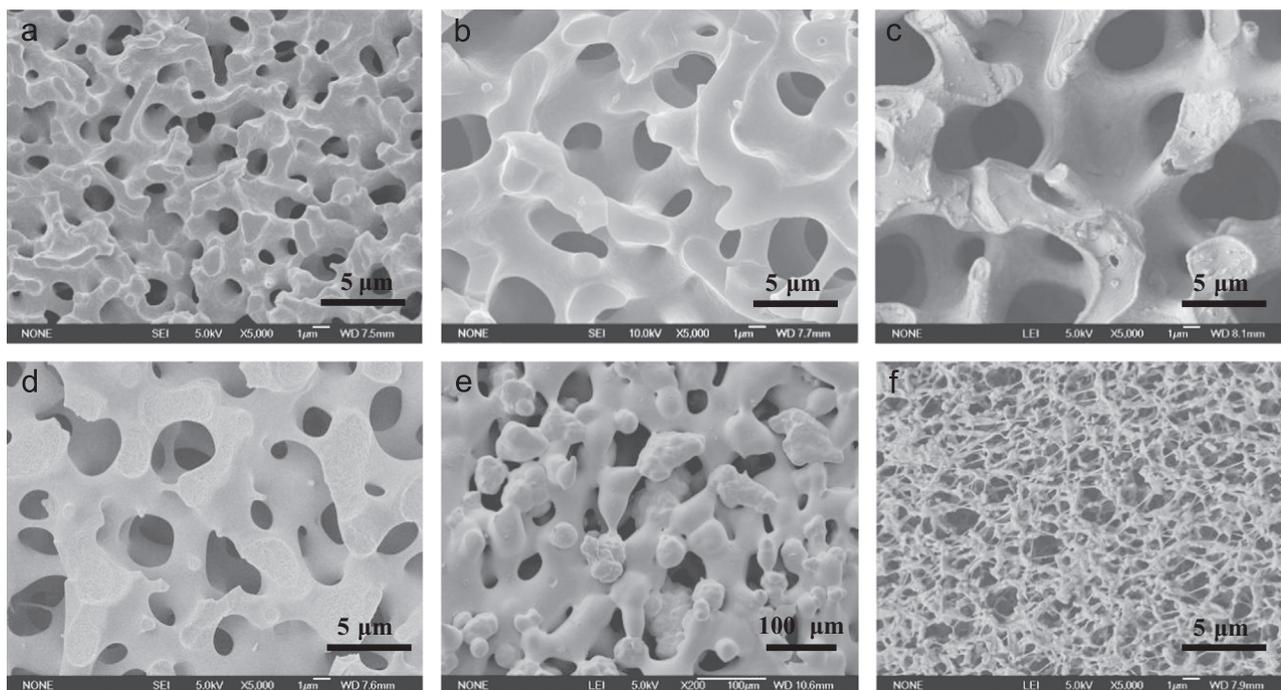


Fig. 3. SEM photographs of membranes: (a), 1.22 μm EP membrane ($\alpha=0.180$, $\beta=0.750$, $\gamma=1.250$); (b), 2.77 μm EP membrane ($\alpha=0.175$, $\beta=0.750$, $\gamma=1.250$); (c), 4.67 μm EP membrane ($\alpha=0.160$, $\beta=0.750$, $\gamma=1.250$); (d), 2.39 μm SPG membrane; (e), 25.60 μm PE membrane; (f), 0.22 μm PTFE membrane.

New Chemical Materials Co. (China), with a commercial code of E-51, was used as base resins of epoxy-based monoliths. 4, 4'-diaminodicyclohexylmethane (DDCM) obtained from Sinopharm Chemical Reagent Co., Ltd., was used as curing agent. Sodium alga acid (AR, 450–550 kDa) purchased from Acros Organics (New Jersey USA) and agarose (AR, MW=120,000) purchased from Promega (USA) was used in the preparation of microspheres. Hexaglycerin penta ester (PO-5s) purchased from sakamoto yakuhin kogya Co., Ltd. (Japan) was used as emulsifier. KP-18C (a silane coupling agent with a C₁₈ hydrophobic chain) was obtained from Shin-Etsu Chemical Co., Ltd. (Japan). Polyethylene glycol 200 (PEG₂₀₀) and dimethyl sulfoxide (DMSO) used as porogen, petroleum ether (boiling range 90–120 °C) and liquid paraffin used as oil phase and calcium chloride used as curing agent were of analytical grade and bought from Beijing Chemical Factory (Beijing, China).

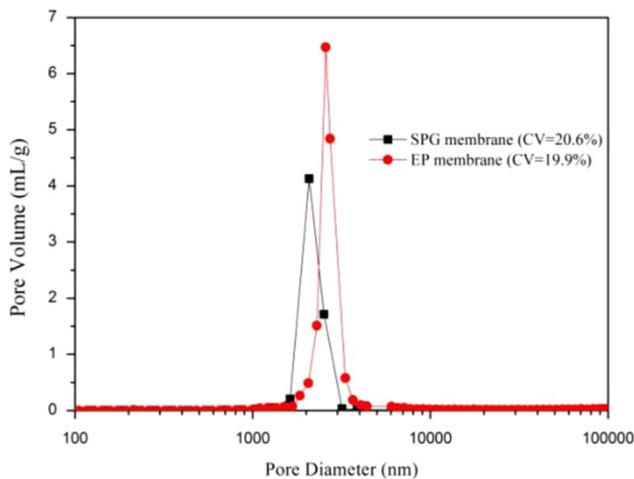


Fig. 4. Pore size distributions of SPG membrane and EP membrane: the CV values of SPG and EP membranes were 20.6% and 19.9%, respectively.

Table 1
Characteristic parameters^a of EP and SPG membranes.

Species	Mean pore diameter ^b /nm	Porosity/%(V/V)
EP membrane	2768.8 ± 2.5	57.9 ± 0.5
SPG membrane	2391.6 ± 2.5	60.6 ± 0.5

^a All of data were the average values from three determinations.

^b Mean pore diameter was the volume mean diameter.

2.2. Preparation of EP membrane

The synthesis of epoxy based polymer materials with 3D bicontinuous skeleton structure was developed in our group [23]. As shown in Fig. 1, a given amount of monomer (DGEBA), curing agent (DDCM) and porogens (DMSO and PEG₂₀₀) were mixed to form a homogeneous solution. Here we use α to represent the weight ratio of good solvent to poor solvent, β to stand for the weight ratio of porogens (DMSO and PEG₂₀₀) in the solution, and γ to behalf the ratio of curing agent to the stoichiometric amount of curing agent for the epoxy resin. The pore size of the resulted membrane can be adjusted by changing the above three parameters. The bubbles in the reactive solution were removed by ultrasonic, and then this solution was poured into a sealed mold and cured at 70 °C for 24 h. The porogens in monolith were removed by extracting with ethanol for 24 h. Finally, the samples were dried in vacuum at a room temperature for 24 h and then lathed into tubular membrane. The resulted EP membrane has inside diameter of 0.8 cm, outside diameter of 1.0 cm and length of 2.0 cm.

2.3. Modification of SPG membrane

Hydrophobic modification of SPG membrane was carried out according to the previous report [24], the detailed procedure was as following: SPG membrane was firstly fired at 500 °C for 2 h and cleaned under ultrasonic cleaner in deionized water for 0.5 h. After that, SPG membrane was soaked in 3% (V/V) KP-18C solution for 2 h under ultrasonic and vacuum (−0.07 MPa). Finally SPG membrane was heated for 4 h at 120 °C.

2.4. Characterization of EP and SPG membranes

The pore size distribution and porosity of membranes including EP and SPG were measured with a mercury porosimeter (AutoPore IV 9500 V1.09, Micromeritics Co., Ltd., USA). The coefficient variation (CV) value was obtained by the data of pore size distributions according to the following equations:

$$C.V. = \left(\sum_{i=1}^n \frac{(d_i - \bar{d})^2}{N} \right)^{1/2} / \bar{d}$$

$$\bar{d} = \sum_{i=1}^n d_i / N$$

where, d_i is the diameter of the i th membrane pore. \bar{d} is the arithmetic mean of the statistical membrane pores and N is the measured number of pores.

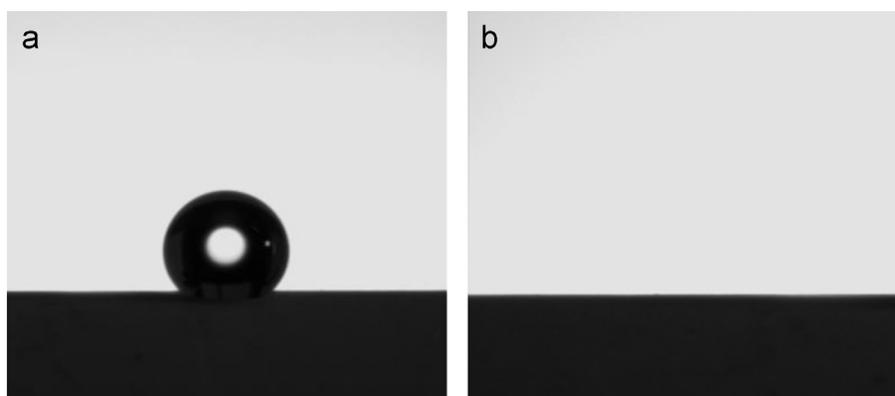


Fig. 5. Photographs of contact angles of the water droplets on the surface of membranes: (a), EP membrane (CA=130°); (b), SPG membrane (CA=0°).

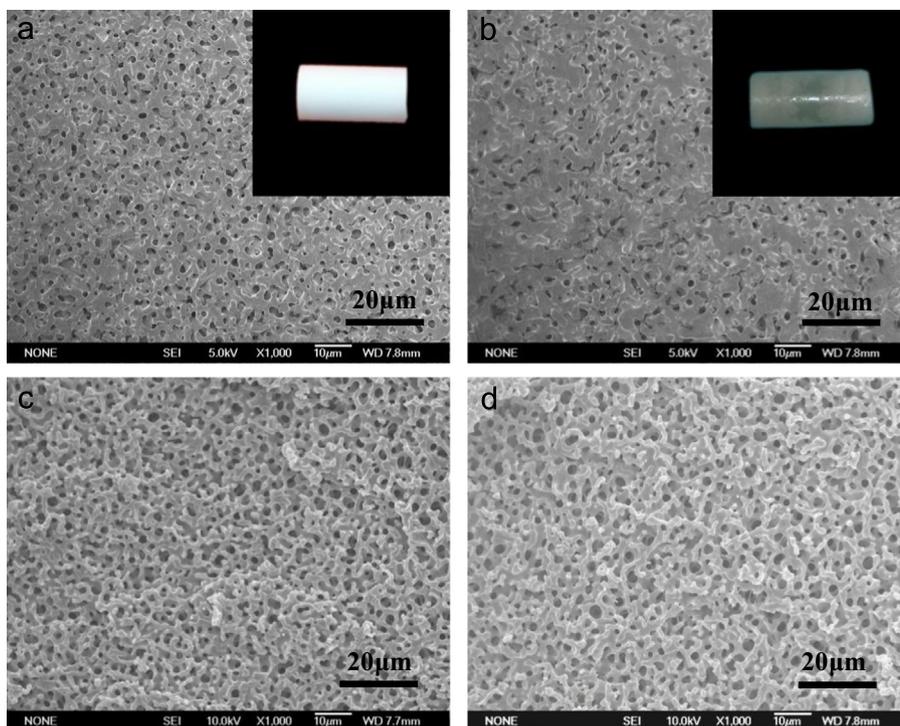


Fig. 6. SEM photographs and pictures of membranes: (a), SEM photograph and picture of SPG membrane with hydrophobic layer before being treated with alkali solution; (b), SEM photograph and picture of SPG membrane with hydrophobic layer after being treated with alkali solution for 65 h; (c), SEM photograph of EP membrane before being treated with alkali solution; (d), SEM photograph of EP membrane after being treated with alkali solution.

Table 2

The contact angle changes of hydrophobically modified SPG and EP membranes before and after being soaked in 1 M NaOH.

	Contact angle with water		
	Before soak	After soak for 6 h	After soak for 65 h
SPG membrane	132.4° ± 1.0°	^a	0°
EP membrane	131.2° ± 1.0°	128.7° ± 1.0°	

^a The contact angle varies from 0° to 130° which means some locals of membrane have been hydrophilic for the completely loss of hydrophobic layer and the other locals keep varying degrees of hydrophobicity for the different remaining degree of hydrophobic layer.

Scanning electron microscopy (SEM, JSM-6400, JEOL Lim. Co., Japan) was used to observe the microstructures of the samples. The hydrophobicity of membrane was evaluated by the value of average contact angle of the water droplet on membrane surface using a contact angle meter (DatePhysics Instrument GmbH, Germany).

2.5. Preparation of the agarose microspheres by direct membrane emulsification

The apparatus in Fig. 2 was used in direct membrane emulsification [25]. Before emulsification, membrane should be immersed in oil phase for at least 24 h to allow continuous phase to permeate into the membrane. Agarose powder (0.95 g) was dissolved in boiling water (15 g), and the solution was pressed into oil phase to form uniform droplets at 65 °C with the device in Fig. 2. The continuous phase was composed of emulsifier (PO-5S, 3.57 g), liquid paraffin (79.26 mL) and petroleum ether (6.53 mL), which was preheated to 65 °C. The operation pressure was critical pressure [26] (15 kPa for 4.50 μm SPG membrane and 12 kPa for 9.45 μm EP membrane) and the stirring rate in the continuous phase was 300 rpm. The obtained emulsion was allowed to slowly cool to room temperature and formed solid

microspheres with gentle stirring. Finally, the agarose microsphere suspension was centrifuged and washed successively with petroleum ether, ethanol and distilled water to remove the oil phase.

2.6. Preparation of Ca-alginate microspheres by premix membrane emulsification

Ca-alginate microspheres were prepared by premix membrane emulsification. The oil phase is a mixture of liquid paraffin and petroleum ether (volume ratio 2:1) with an emulsifier PO-5s (4 wt%). Aqueous phase of alginate solution (1.0 wt%, 2 mL) and oil phase (60 mL) were emulsified by homogenizer (3600 rpm, 1 min) to form coarse emulsion. Then the coarse emulsion was poured into storage tank and pressed through membrane for 5 times under nitrogen pressure (200 kPa) to achieve uniform emulsions. CaCl₂ solution (5 mol/L, 12 mL) as curing agent was dispersed into oil phase (24 mL) by ultrasonic processor (120 W, 1 min) to form mini-emulsion. The CaCl₂ mini-emulsion and the uniform-sized alginate emulsion prepared above were mixed together in water bath (37 °C, 5 h) to obtain colloidal particles. After that, the Ca-alginate microspheres were collected by washing them with petroleum, ethanol and water, respectively.

2.7. Determination of size and size distribution of agarose and Ca-alginate microspheres

The size and size distribution of agarose and Ca-alginate microspheres were measured using a laser particle size analyzer. The CV value was obtained from the data of microspheres size distribution by the following equations:

$$C.V. = \left(\sum_{i=1}^n \frac{(d_i - \bar{d})^2}{N} \right)^{1/2} / \bar{d}$$

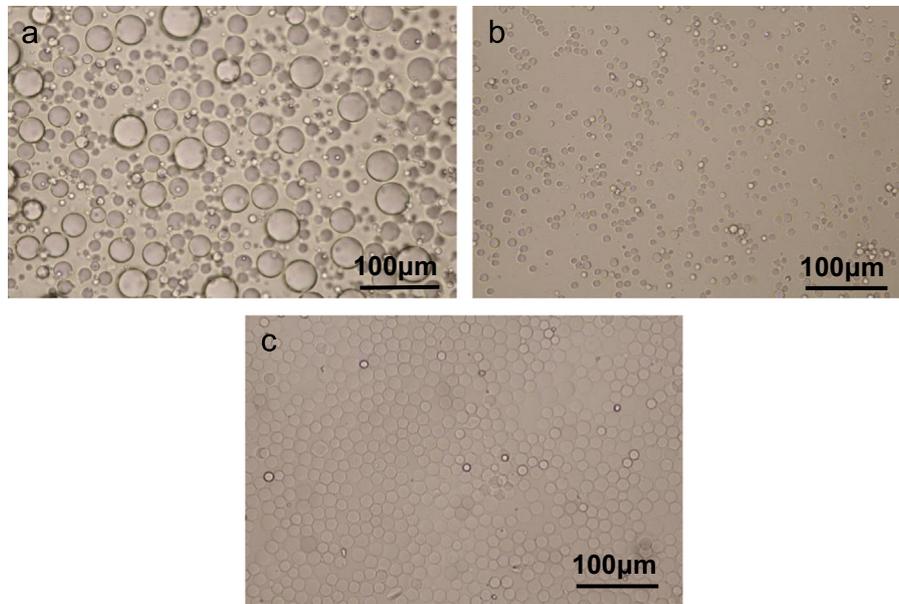


Fig. 7. Optical micrographs of agarose microspheres prepared by direct emulsification technology: (a), 37.56 μm agarose microspheres prepared by 4.50 μm SPG membrane; (b), 10.19 μm agarose microspheres prepared by 4.50 μm SPG membrane with hydrophobic modification; (c), 16.53 μm agarose microspheres prepared by 9.45 μm EP membrane. The diameter of agarose microspheres was the volume mean diameter.

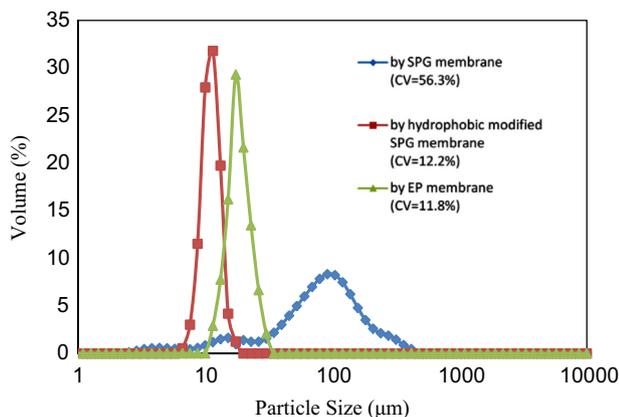


Fig. 8. Particle size distribution of agarose microspheres prepared by direct emulsification: the CV values of agarose microspheres prepared by SPG membrane without modification, SPG membrane with hydrophobic modification and EP membrane were 56.3%, 12.2% and 11.8% respectively.

$$\bar{d} = \sum_{i=1}^n d_i / N$$

wherein, d_i is the diameter of i th microsphere. \bar{d} is the arithmetic mean of the statistical microspheres and N is the measured number of microspheres.

3. Results and discussion

3.1. Preparation result of EP membrane

A macroporous membrane with 3D bicontinuous skeletons was designed based on a copolymer of DGEBA and DDCM, and the pore size of which can be controlled from 0.5 μm to 25 μm [23]. Fig. 3(a, b, c) showed the EP membranes with different pore sizes and indicated the controllability of the pore size. EP membranes prepared in this paper, which were similar with SPG membrane (Fig. 3d), had 3D bicontinuous skeleton structure and approximately elliptical pores. This special structure contributed to the formation and detachment of the droplets from the surface of

membrane in the process of membrane emulsification [4,22,27]. Fig. 3(e, f) was the SEM images of some commercial membranes including PE (Fig. 3e) and PTFE (Fig. 3f) membrane. The pores of PE membrane had irregular shape and wide size distribution, which directly affected the uniformity of emulsions prepared in direct membrane emulsification [21]. PTFE membrane showed a net structure with high porosity, which resulted in the droplets coalescence on its surface [19,20]. Therefore, with 3D bicontinuous skeleton structure, approximately elliptical pores and controllable pore size, EP membrane showed huge potential for emulsification technology.

3.2. Characterization of EP membrane

In addition to the microstructure, membrane pore size and size distribution, porosity and surface properties play an important role in membrane emulsification technology. Here, EP membrane (Fig. 3b) was evaluated in terms of its pore size and size distribution, porosity and surface properties. As a comparison, SPG membrane (Fig. 3d) was also characterized. It can be seen from Fig. 4 that both EP and SPG membranes had a nice pore size distribution which was in favor of the formation of uniform emulsions. Table 1 showed the mean pore diameter and porosity of EP and SPG membranes. Compared with SPG membrane, EP membrane has a slightly higher porosity, which may be related to the different membrane pore size.

In Fig. 5, it can be seen that the contact angles of the water droplets on the surface of EP and SPG membranes were 130° and 0°, respectively, which means that EP membrane shows strongly hydrophobic, and in contrast, SPG membrane is extremely hydrophilic. In emulsification technology, membrane should be wetted by continuous phase, which means that hydrophilic membranes are available for the preparation of O/W emulsions and hydrophobic ones for W/O emulsions. SPG membrane is inherently hydrophilic owing to the presence of silanol groups on its surface. Therefore, it is necessary for SPG membrane to be rendered hydrophobic when it was used in W/O emulsions preparation. This may cause many problems: (1) the modified layer is non-resistant to alkali; (2) silane coupling agents are banned in some fields such as foods and medicines; (3) homogeneously modifying the membrane surface is difficult due to the

steric hindrance; (4) repeated modification is indispensable after each cleaning cycle. With the hydrophobic surface, EP membrane can be directly used in membrane emulsification to prepare W/O emulsions, which successfully avoids the above problems.

Some hydrophilic microspheres such as konjac glucomannan microspheres were prepared in alkali condition, which requires the membrane must tolerate this alkali solution. In order to test the alkali-resistance of membranes, the following experiences were carried out. Under the condition of ultrasound, EP membrane and SPG membrane were soaked in liquid paraffin for 48 h in accordance with the membrane pretreatment of membrane emulsification, and then soaked in 1 M NaOH aqueous solution. It was found that after being soaked in 1 M NaOH solution for one week, EP membrane had no obvious change in terms of its microstructure (Fig. 6d) and hydrophobicity (Table 2). However, the hydrophobic layer of SPG membrane was badly damaged after being treatment with 1 M NaOH for 6 h and was completely damaged after 65 h (Table 2). In addition, some local areas on the surface of SPG membrane tended to be semitransparent and a lot of pores have been locked up or wrecked (Fig. 6b) after 65 h, which meant the membrane bulk was destroyed badly. These blocked pores will lead to obvious increase of critical pressure and bad emulsion results in membrane emulsification technology.

3.3. Preparation of agarose microspheres by direct membrane emulsification

Agarose microspheres, which are widely applied in chromatographic separation [28], cell encapsulation [29] and so on, have been attached large attention from many investigators working in these fields. In this paper, EP membrane was firstly used to prepare agarose microspheres. The photographs of agarose microspheres prepared by SPG and EP membranes were shown in Fig. 7, respectively. It can be seen that uniform agarose microspheres can not be obtained by the SPG membrane (Fig. 7a) unless it was rendered hydrophobic by treatment with silanes coupling agent

(Fig. 7b). However, monodispersed droplets were obtained with EP membrane (Fig. 7c). The corresponding size distribution of these agarose microspheres was shown in Fig. 8. The CV value of these agarose microspheres prepared by EP membrane (CV=11.8%) was much less than those prepared by SPG membrane (CV=56.3%), and even SPG membrane was hydrophobically modified (CV=12.2%). This indicated that EP membrane without modification can be directly used to prepare uniform agarose microspheres, which successfully avoided many problems caused by the modification of SPG membrane.

After membrane emulsification, membrane should be washed for the next use. In order to remove the agarose gel adhered to the walls of the membrane pores, the membrane needs to be washed in boiling water for at least 2 h. As shown in Table 3, EP membrane with a stable surface can remain hydrophobic after more than five times using and washing. As a comparison, it was found that the hydrophobically modified SPG membrane surface turned to be completely hydrophilic after cleaning which means that the hydrophobic layer has been completely destroyed.

3.4. Preparation of Ca-alginate microspheres by premix membrane emulsification

With the characteristics of biocompatibility and biodegradability, Ca-alginate microspheres prepared by emulsification method [30] have been applied in biomedical fields [31]. Here, Ca-alginate microspheres were prepared with EP membrane by premix membrane emulsification. Fig. 9 was the comparison images of the calcium alginate microspheres prepared by hydrophobically modified SPG membrane and EP membrane respectively. It can be seen that the microspheres prepared by EP membrane were as uniform as those prepared by SPG membrane. Meanwhile, EP membrane got lower value of CV (11.4%) than that on the modified SPG membrane (14.3%). This implied that EP membrane also had a potential to be used in premix membrane emulsification.

Table 3
The contact angle changes of SPG and EP membranes before and after using and washing.

	Contact angle with water Before modification	After modification	After the first using ^a and washing ^b
SPG membrane	0°	131.7° ± 1.0°	0°
EP membrane	130.4° ± 1.0°	129.8° ± 1.0°	After more than five times of using and washing 130.1° ± 1.0°

^a Membranes were used to prepare agarose microspheres.

^b After being used, membranes should be immersed into boiling water for at least two hours to remove agarose gel adhered on the membrane wall.

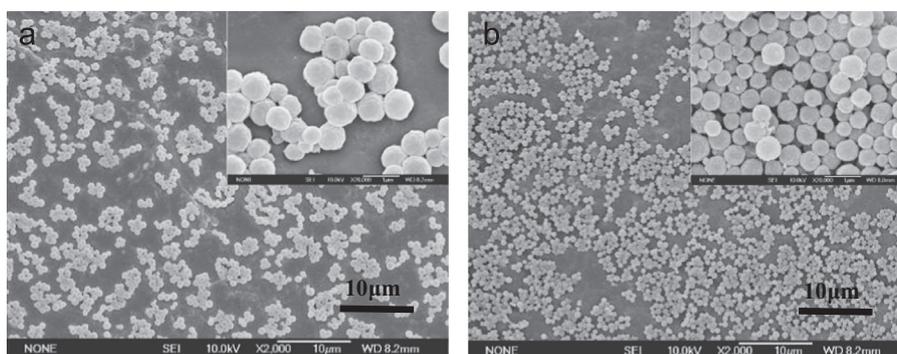


Fig. 9. SEM photographs of Ca-alginate microspheres prepared by premix membrane emulsification: a, 0.78 μm Ca-alginate microspheres (CV=14.3%) prepared by 5.30 μm SPG membrane with hydrophobic modification; (b), 0.56 μm Ca-alginate microspheres (CV=11.4%) prepared by 4.67 μm EP membrane. The diameter of Ca-alginate microspheres was the volume mean diameter.

4. Conclusions

Uniform microspheres of agarose (CV=11.8%) and Ca-alginate (CV=11.4%) were successfully prepared by EP membrane in this paper. With hydrophobic surface, special pore structure and narrow size distribution, EP membrane showed good performance in whether premix or direct membrane emulsification in terms of the droplets size distribution and stability of emulsions. The successful application of EP membrane in W/O emulsions preparation contributes to avoiding those problems caused by the hydrophobic modification of SPG membrane. Besides, EP membrane could tolerate 1 M NaOH aqueous solution for a week and keep its stable hydrophobic surface. Hence it could be used in alkali condition, which extended the range of applications in membrane emulsification. There is a huge potential for EP membrane in membrane emulsification and some detailed researches about the effects of EP membrane parameters need to be done in future study.

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