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Effect of polytetrafluoroethylene hollow fiber microstructure on formaldehyde carbonylation performance in membrane contactor

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ABSTRACT

Membrane contactor is regarded as a promising method for reaction and process intensification. The feasibility of formaldehyde carbonylation to synthesize glycolic acid using polytetrafluoroethylene (PTFE) membrane contactor has been proved in our previous study. In this paper, the effect of membrane microstructure on process performance was further investigated. Three porous PTFE hollow fibers with different pore sizes and one polydimethylsiloxane (PDMS)/PTFE composite membrane with dense layer were fabricated for comparison. The physical and chemical properties of four membranes, including chemical composition, morphology, contact angle, liquid entry pressure, thermodynamic analysis and gas permeability, were systemically characterized. Experiments of formaldehyde carbonylation under different reaction conditions were conducted. The results indicated that the yield of glycolic acid increased with decreasing pore size for porous membranes, which was due to the improvement of wetting behavior. The dense layer of PDMS in composite hollow fiber could effectively prevent the solvent from entering membrane pores, thus the membrane exhibited the best performance. At reaction temperature of 120 °C and operation pressure of 3.0 MPa, the yield of glycolic acid was always higher than 90% as the mass ratio of trioxane and phosphotungstic acid increased from 0.2:1 to 0.8:1. The highest turnover frequency was up to 26.37 $mol \cdot g^{-1} \cdot h^{-1}$. This study provided a reference for the understanding and optimization of membrane contactors for the synthesis of glycolic acid using solvent with low surface tension.

1. Introduction

Membrane contactor is a membrane system that is employed to "keep in contact" two phases, which has a stable and well-defined interface [1]. To date, membrane contactor has been widely used in gas–liquid processes such as gas absorption [2,3], membrane distillation [4], absorbent regeneration [5], and flow chemistry [6]. Many review articles are published concerning the applications of membrane contactor especially the different types of membrane such as flat-sheet, hollow fiber, *etc.* [7–10]. The high efficiency of membrane contactor is mainly due to its high interface area per unit volume, *i.e.*, generally 1500–3000 $m^2 \cdot m^{-3}$, which is much larger than 100–800 $m^2 \cdot m^{-3}$ of traditional reactors [11]. Another advantage of membrane contactor is that no dispersion occurs between gas–liquid phases [1]. Because the two phases are separated by the membrane, the common issues such as liquid flooding, entrainment and foaming in traditional direct contacting reactors can be effectively avoided [12]. In addition, membrane contactors are flexible, easy in the scale-up and control. Therefore, it is regarded as a promising reactor for process intensification in both fundamental research and industrial implementation.

Porous hollow fiber is a commonly used membrane type in membrane contactors. Since the mass transfer coefficient in gas phase is much higher than that in liquid phase, the membrane pores are expected to be filled with gas phase. The partial or complete occupying of porous membrane pores by liquid phase, *i.e.*, membrane wetting, will result in obvious performance decline due to the increase of mass transfer resistance [13,14]. Some parameters are usually employed to evaluate the antiwetting property of membrane contactor system, including the liquid entry pressure (LEP), contact angle (CA), pore size and solvent surface tension [15,16]. Generally, higher LEP, CA and solvent surface tension, and smaller pore size are advantageous to prevent membrane wetting and improve operation stability of membrane contactor process. For example, Li *et al.* [17] modified polytetrafluo-

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roethylene (PTFE) hollow fiber by spraying silica nanoparticles on membrane surface to increase water CA from 118° to 157°, and the superhydrophobic modification showed great potential to avoid membrane wetting during biogas purification by membrane contactor under pressurized conditions. Ju *et al.* [18] used electrospinning to prepare PTFE/POSS (polyhedral oligosilicone) nanofibrous composite membrane, which had three-dimensional superhydrophobic property with a water contact angle of 151° ± 4°. The developed membrane possessed an excellent long-term stability in a 200 h continuous direct contact membrane distillation operation. Rajabzadeh *et al.* [19] prepared polyvinylidene fluoride (PVDF) hollow fiber membranes by thermally induced phase separation and found that the membrane with low porosity and pore size showed better stability in the CO_2 membrane absorption experiments. Analogously, Chen *et al.* [20] treated PTFE membrane by asymmetric heating to obtain different pore sizes on both sides. The tests indicated that the absorption efficiency of CO_2 was higher when the side with smaller pore size contacted the absorbent due to the less wetting. Apart from the microstructure of membrane, the selection of solvent with higher surface tension was also beneficial to reduce the wetting phenomenon [21].

The use of dense membrane or composite membrane with a dense layer is also an effective way to prevent membrane wetting in membrane contactors. Meanwhile, however, it will increase the mass transfer resistance of membrane phase. Therefore, the material selection of the dense layer is very important. The materials for dense layer reported in literatures are mostly macromolecules with high free volume, such as polydimethylsiloxane (PDMS) [22], poly(trimethylsilyl)propyne (PTMSP) and Teflon AF2400 [19]. For instance, Nguyen *et al.* [23] used two composite hollow fibers with a thin skin of Teflon AF2400 and PTMSP coated on a porous polypropylene (PP) support for post-combustion CO_2 capture from flue gases using chemical solvent. It was found that the dense skin could provide a wetting protection effect without affecting the overall mass transfer coefficient. Kerber *et al.* [22] investigated the mass transfer and selectivity analysis of PDMS and Teflon AF coated composite membrane for upgrading biogas, and both membranes did not exhibit wetting. The coating materials should have high gas permeability to reduce the membrane phase resistance. Moreover, dense membrane or composite membrane is only suitable for the processes where the mass transfer resistance of membrane contactor is mainly controlled by liquid phase but not by membrane, for example, physical absorption of CO_2.

The carbonylation of formaldehyde to synthesize glycolic acid is also a gas–liquid reaction system [24]. So far, sulfolane has been proven to be a suitable solvent for this reaction due to its characteristic to stabilize the intermediate [25,26]. Since the solubility of CO in sulfolane is low, the reaction is usually conducted at high pressures [27]. In our previous studies, the feasibility of carbonylation of formaldehyde in PTFE hollow fiber membrane contactor for process intensification has been proven [28,29]. The preliminary results showed that membrane contactor was more efficient than the conventional stirred reactor, and the yield of glycolic acid could be significantly enhanced at low operation pressures. Moreover, PTFE hollow fibers with smaller size exhibited better process performance. However, the influence of membrane wetting was not investigated. In fact, the surface tension of sulfolane was relatively low, which would easily cause membrane wetting in operation. Therefore, the effect of membrane microstructure on membrane wetting behavior in formaldehyde carbonylation process using membrane contactors was discussed in this paper. Three porous PTFE hollow fiber membranes with different pore sizes and one PDMS/PTFE composite hollow fiber membrane with dense layer were fabricated and employed. The physical and chemical properties of four types of membranes were systemically characterized. The yields of glycolic acid under different experimental conditions were analyzed to investigate the relationship between membrane structure and process performance. This study could provide a reference for the understanding and optimization of membrane microstructurein the synthesis of glycolic acid using membrane contactors.

2. Experimental

2.1. Materials and reagents

PTFE hollow fibers and membrane modules were self-made in our laboratory. All reagents were commercially available and used without further purification. Phosphotungstic acid (HPW, analytical reagent) and sulfolane (analytical reagent) were purchased from Shanghai Macklin Biochemical Co., Ltd. (China). Trioxane (TOX, purity of 99.5%) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China). CO gas (purity > 99.9%) was supplied by Dalian Special Gases Co., Ltd. (China). Sylgard 184 PDMS and curing agent was obtained from Dow Chemical (China) Co., Ltd.

2.2. Membrane preparation

Three porous PTFE hollow fiber membranes (M1, M2 and M3) were prepared by extrusion–stretching–sintering method [30]. The pore sizes were adjusted by varying the stretching ratio and the details were listed in Table 1. PDMS/PTFE composite hollow fiber membrane was prepared *via* penetration coating method as shown in Fig. 1. PDMS solution (the mass ratio of PDMS, curing agent and *n*-hexane was 10:1:11) was injected into the lumen of PTFE hollow fiber (M1) from one end using a syringe. Another end of hollow fiber was sealed to force the solution penetrating the membrane pores until whole fiber was completely wetted. Subsequently, the residual PDMS solution in lumen of PTFE hollow fiber was blow out with air to prevent blocking. The operation above was repeated. After natural drying at room temperature for 12 h and heating at 120 °C for 2 h, the PDMS/PTFE composite hollow fiber membrane (M4) was obtained.

2.3. Membrane characterization

The chemical composition of membranes was analyzed by attenuated total reflectance infrared spectroscopy (ATR-IR, Thermo Fisher Nicolet iS5, USA). The wave number ranged from 500 to 4000 cm^{-1}. Field-emission scanning electron microscope (FE-SEM, Zeiss Supra 55, Germany) was employed to observe the surface morphology and cross-section structures of various PTFE hollow fibers. The contact angle (CA) of membrane surface was measured by contact angle tester (JC-2000D, Powereach, China) using the reaction solution. At least six tests were performed for each sample and the average was used. The thermos gravimetric analysis (TG) was conducted (Setsys16/18, Setaram, France) in the nitrogen atmosphere. The heating rate was 10 °C·min^{-1} and the test temperature ranged from 50 to 800 °C. Moreover, the gas flux and LEP of four types of membranes were also investigated. During CO permeability test, the stainless-steel high-pressure module containing four hollow fibers (effective length of 10 cm) was prepared. CO gas passed through the shell side of the module, and the gas flow in tube side was measured at different pressures using soap bubble flowmeter. Three modules were prepared for each type of membrane and testing results were averaged.

Table 1
Detailed parameters of PTFE hollow fiber membranes

Membrane No.	Stretching ratio/%	Outer diameter/mm	Inner diameter/mm	Mean pore radius/nm	Max pore radius/nm
M1	65	0.9	0.4	73	258
M2	30	0.9	0.4	40	141
M3	10	0.9	0.4	8	80
M4	65	0.9	0.4	/	/

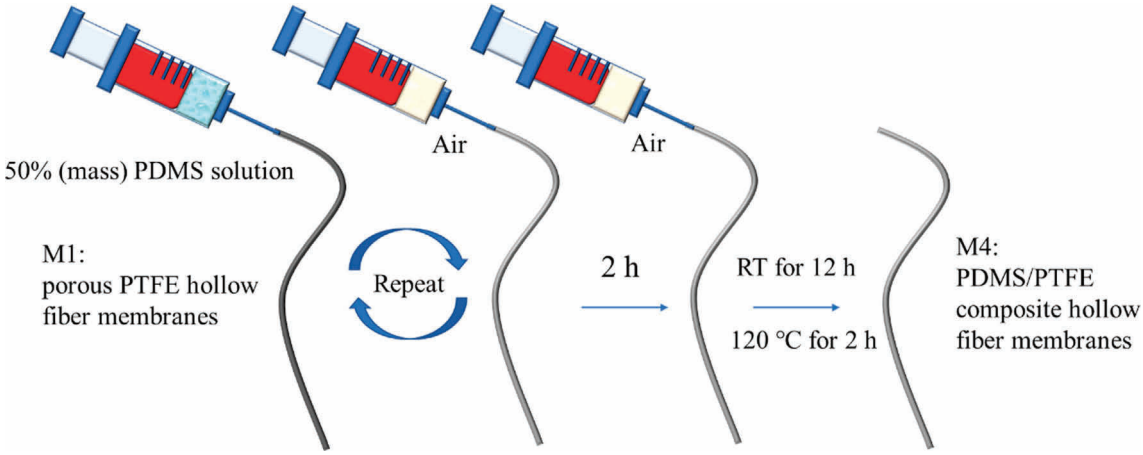

Fig. 1. Schematic diagram of penetration coating method for preparing PDMS/PTFE composite hollow fiber membranes.

2.4. Formaldehyde carbonylation in membrane contactors

Four types of PTFE hollow fiber membranes were used to prepare membrane modules. A series of formaldehyde carbonylation experiments were also conducted to discuss the effect of membrane microstructure on reaction efficiency. The construction of membrane modules, the experimental methods of formaldehyde carbonylation in continuous operation as well as product analysis were described in our previous studies [28,29]. In experiments, the number of hollow fibers packed into all membrane contactors was 143 for each type of membrane.

3. Results and Discussion

3.1. Membrane characterizations

3.1.1. IR

The chemical composition of inner surface of PTFE hollow fiber membranes was investigated by IR spectroscopy. According to the results shown in Fig. 2, the spectra of M1, M2 and M3 were uniform. Only the characteristic peaks of PTFE around 1220, 1150 and 640 cm^{-1} could be observed, which could be attributed to the asymmetric stretching and symmetric stretching of $-CF_2-$, and the wagging stretching of $-CF_2-$, respectively [31]. The adjustment of pore size is a physical behavior, and the chemical composition of membranes will not be affected. For M4 after coating PDMS, the characteristic peaks above disappearred. The spectrum was almost same to that of PDMS, implying the complete coverage of PTFE substrate by coating layer. The absorption peaks at 788 cm^{-1} and 1020–1087 cm^{-1} were corresponding to the stretching vibration of $Si-CH_3$ and the symmetric stretching vibration of Si—O—Si [32]. The small peak at 2963 cm^{-1} could be attributed to the stretching vibration of C—H in $-CH_3$. The IR results preliminarily indicated that PDMS was successfully coated on the surface of PTFE hollow fiber.

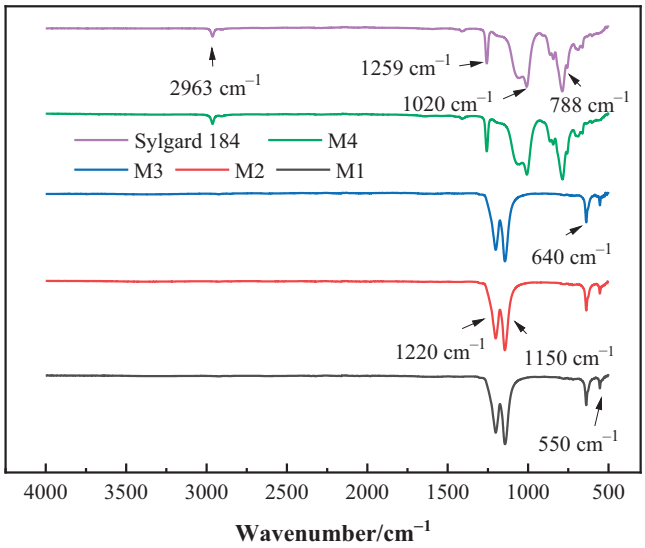

Fig. 2. IR spectra of four PTFE hollow fiber membranes.

3.1.2. SEM

The morphologies of outer surface, inner surface and cross section of four PTFE hollow fiber membranes were further characterized by SEM. The images were shown in Fig. 3. It could be seen that a characteristic fibril-node morphology of porous PTFE hollow fibers was observed for M1. Two regions including the node (*i.e.*, agglomerates of PTFE particles) and the fibrils (*i.e.*, fine threads) were distinguished. Adjoining nodes were bridged by fibrils, and the voids between the fibrils provided gas diffusion channels in gas–liquid membrane contactor process [33]. As the stretching ratio decreased, the pore size was reduced accordingly. The characteristic fibril-node morphology became gradually indistinct for M2 and M3. However, the porous microstructure could be still clearly

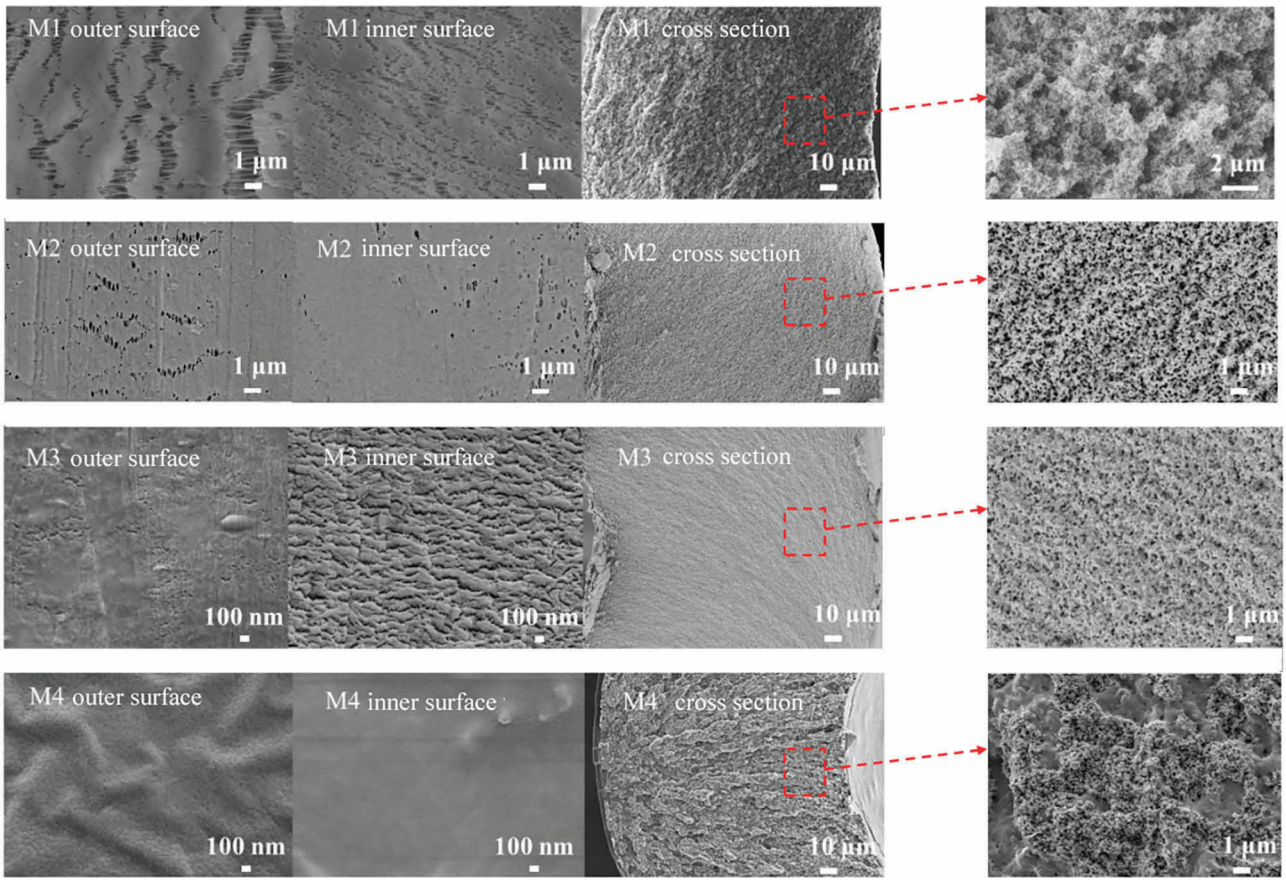

Fig. 3. SEM images of four PTFE hollow fiber membranes.

observed from cross section images at high magnifications. For the PDMS/PTFE composite hollow fiber membrane (*i.e.*, M4), all micropores on the inner and outer surfaces were covered by PDMS. A thin layer of PDMS was formed, which was consistent with the analysis of IR results. The thickness of PDMS layer on outer and inner surfaces was about 6.5 and 3.5 μm, respectively. Moreover, the different morphology of PDMS (*i.e.*, wrinkled structure on the outer surface and smooth structure on the inner surface) was formed due to the different volatilization rate of solvent. In addition, some pores inside the wall were also filled with PDMS according to the SEM images of cross section. Overall, the PDMS/PTFE composite hollow fiber membranes exhibited a sandwich structure. The thin dense layer of PDMS was expected to prevent the reaction solvent entering membrane pores, thus enhancing the antiwetting property of membrane in formaldehyde carbonylation operations.

3.1.3. CA and LEP

The static CA values of reaction solution (mass ratio of 25:1:0.2 for sulfoxide, HPW and TOX) on the surface of four PTFE hollow fiber membranes were tested and shown in Fig. 4. It can be seen that the CA values for M1, M2 and M3 were around 85°, which was much lower than the water CA of about 110° [33]. The surface tension of sulfolane and water was about 36×10^{-3} and 72×10^{-3} $N \cdot m^{-1}$ at 20 °C, respectively. According to the classic surface free energy (SFE) theory, the lower the surface tension of the liquid is, the lower the CA value will be [34]. Moreover, the surface tension of sulfolane would be lower at the reaction temperature of 120 °C, increasing the risk of membrane wetting.

Based on the classic Young-Laplace model, the LEP of membrane could be calculated by $\Delta P = (-2\gamma/r)\cos\theta$, where ΔP is LEP,

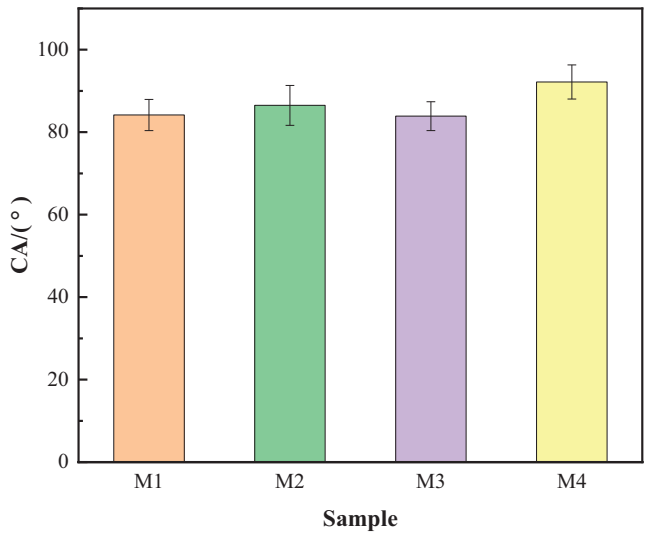

Fig. 4. CA values between the reaction solution and membrane surface (the reaction solution containing sulfoxide, HPW and TOX with a mass ratio of 25:1:0.2).

γ is the surface tension of the liquid, r is pore radius, and θ is the CA between the liquid and the membrane material, which predicts LEP less than zero for all values of θ less than 90° [35]. However, the spontaneous wetting of PTFE hollow fiber membranes by the reaction solution was not observed in experiments. Servi *et al.* [35] reported the similar phenomenon and proposed to use the modified Purcell model to describe the relationship between LEP and CA for the condition when CA was less than 90°. We also tested

the LEP of M1, M2 and M3 with reaction solution containing different reactant concentrations as shown in Fig. 5. When the mass ratio of TOX and HPW was 0.2, the LEP of M1, M2 and M3 was 0.25, 0.61 and 1.57 MPa, respectively. In experiments, the pressure difference between the liquid phase and gas phase was controlled within 0.1 MPa. The penetration of reaction solution through membrane to the gas phase was not observed. However, since the CA values on M1, M2 and M3 was less than 90°, a convex meniscus would form at the gas–liquid interface. The partial occupying of membrane pores by liquid possibly occurred and influenced the mass transfer in membrane contactor operation, which will be discussed in Section 3.3. On the contrary, the dense layer of PDMS on composite membrane M4 would absolutely prevent the risk of membrane wetting.

3.1.4. TG analysis

The reaction temperature for carbonylation of formaldehyde is 120 °C. Therefore, the thermal stability of four membranes was characterized by TG analysis. The results were shown in Fig. 6. It could be seen that the decomposition temperature of M1, M2 and M3 prepared from pure PTFE was up to 500 °C due to the spiral chain structure, high crystallinity and high carbon–fluorine bond (500 kJ·mol^{-1}) of PTFE. The decomposition temperature of M4 composed of PDMS and PTFE was about 350 °C due to the relatively low decomposition temperature of PDMS. Overall, however, all four hollow fiber membranes exhibited good thermal stability at temperatures below 300 °C. In other words, for the experimental temperature at 120 °C, the thermal property of four types of PTFE hollow fiber membranes was enough.

3.1.5. Gas permeability

The carbonylation of formaldehyde is a gas–liquid reaction which consumes CO gas, so the gas permeability of various membranes was measured. As shown in Fig. 7, the gas permeability of porous PTFE hollow fiber membranes (*i.e.*, M1, M2 and M3) decreased with the decrease of stretching ratio. The lower the stretching ratio, the smaller the pore size, and the lower the gas permeability. As the stretching ratio decreased from 65% to 10%, the mean pore radius decreased from 73 to 8 nm, and the CO permeability at 1.0 MPa decreased from 0.54 to 0.14 mol·m^{-2}·s^{-1}. Different from the mass transfer mechanism of Knudsen diffusion in porous membranes, the gas permeation in dense membrane (M4) followed the mechanism of solution-diffusion. As a result, the CO permeability of M4 was much lower than that of M1, M2 and M3. It was only 1.97 × 10^{-4} mol·m^{-2}·s^{-1} at 1.0 MPa. However, the permeability above was enough compared to the theoretical consumption quantity of CO (1.0 × 10^{-5} mol·m^{-2}·s^{-1}, assuming that TOX was fully converted) under the following experimental conditions: 0.2 g of TOX and 1.0 g of HPW in 25.0 g of sulfolane with reaction time of 60 min.

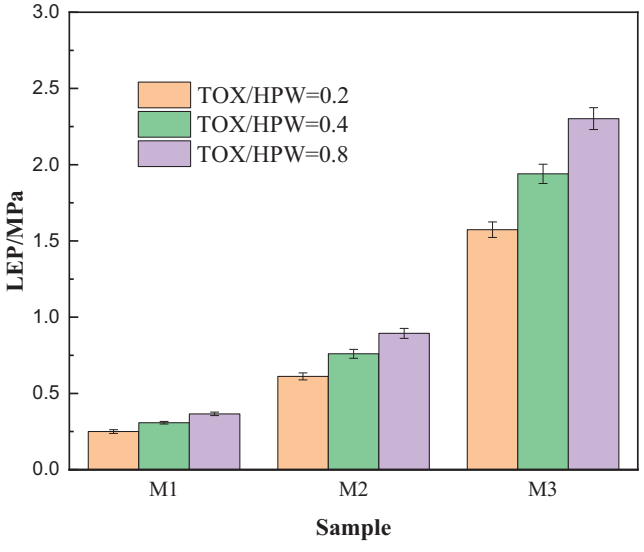

Fig. 5. Effect of reactant concentration on LEP of porous membranes.

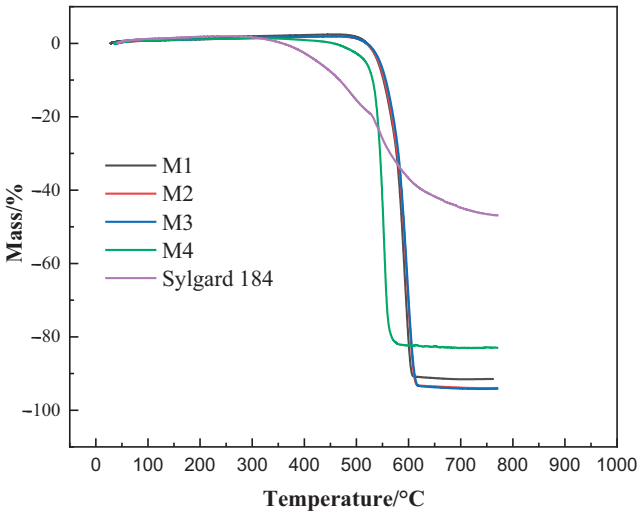

Fig. 6. TG analysis of four PTFE hollow fiber membranes.

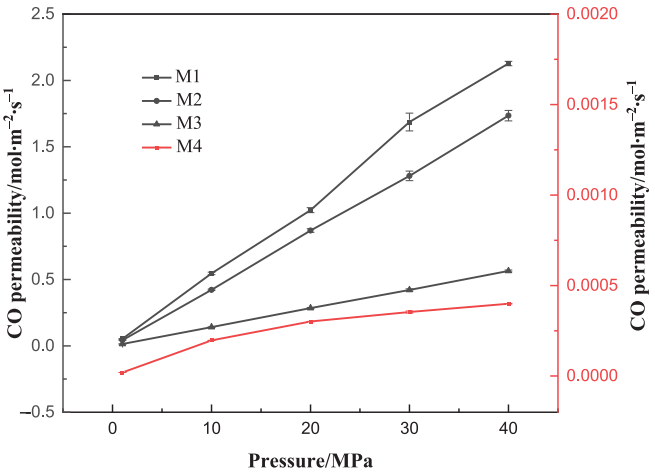

Fig. 7. CO permeability of various PTFE hollow fiber membranes.

3.2. Formaldehyde carbonylation

3.2.1. Effect of operation pressure

Because of the low solubility and diffusion coefficient of CO in a traditional solvent, the formaldehyde carbonylation reaction is usually carried out under relatively high pressures (8–25 MPa) [36]. By selecting solvent (sulfolane) and catalyst (HPW) as well as introducing membrane contactor, the reaction pressure of formaldehyde carbonylation could be reduced to less than 5 MPa [28,29]. In this study, the effect of operation pressure on the yield of glycolic acid was investigated using four types of PTFE hollow fiber membranes. The experimental conditions were listed as below: 0.2 g of TOX and 1.0 g of HPW in 25.0 g of sulfolane; reaction temperature of 120 °C; reaction time of 60 min. The results were summarized in Fig. 8.

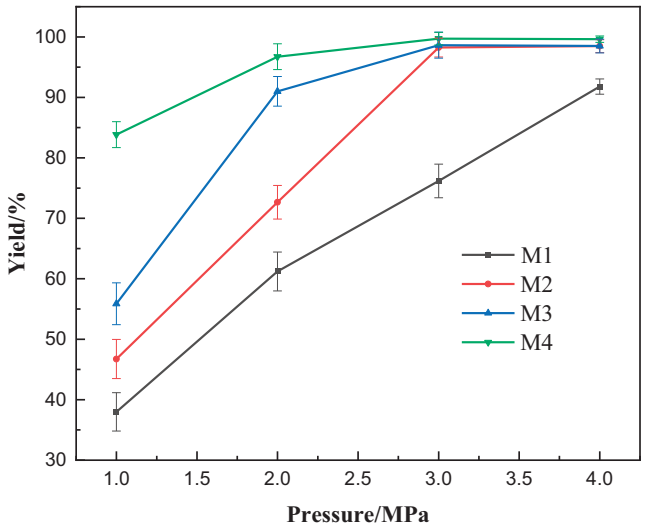

Fig. 8. Effect of operation pressure on the yield of glycolic acid in membrane contactors (reaction condition: 0.2 g of TOX and 1.0 g of HPW in 25.0 g of sulfolane at 120 °C for 60 min).

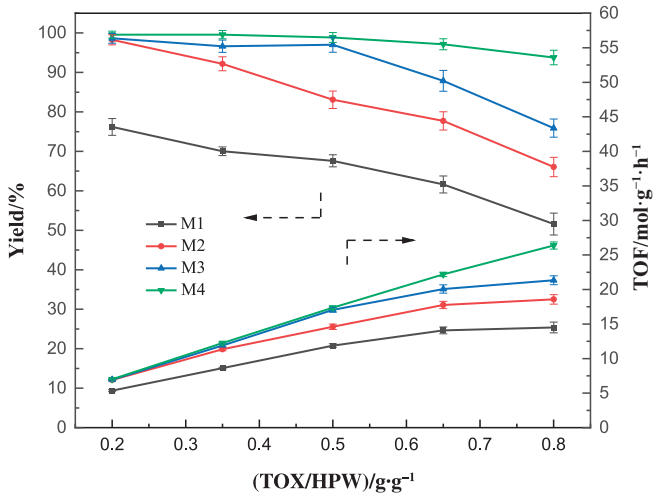

Fig. 9. Effect of TOX concentration on the yield of glycolic acid in membrane contactors (reaction condition: 1.0 g of HPW in 25.0 g of sulfolane, 3.0 MPa, 120 °C, 60 min).

First, the yield of glycolic acid increased with the increase of operation pressure for all types of PTFE hollow fibers. High operation pressure could enhance the solubility of CO in solvent, which was advantageous to the reaction because the carbonylation of formaldehyde is a first-order reaction for CO [28]. Second, the performance was improved with the decrease of membrane pore size. For example, as the operation pressure was 2.0 MPa, the yield of glycolic acid for M1, M2, M3 and M4 was 61.2%, 72.7%, 91.0% and 96.7%, respectively. Since the gas permeability exhibited opposite order according to Fig. 7, the difference in performance should be due to the different degree of membrane wetting. In experiments, the pressure difference between liquid phase and gas phase was basically the same, so the wetting behavior would be negatively correlated to the pore size. The larger the pore size, the more severe the wetting degree, and the higher the mass transfer resistance. The yield of glycolic acid in M1 membrane contactor was lowest. For the PDMS/PTFE composite hollow fiber, the dense PDMS layer on surface could effectively prevent membrane from wetting. Meanwhile, the CO permeability was sufficient for the reaction. Therefore, it exhibited best performance. Third, as the operation pressure reached 3.0 MPa, the yield of glycolic acid was all higher than 98% for M2, M3 and M4 due to the complete consumption of TOX in reaction solution. In the following section, we varied the concentration of TOX for further comparison. Moreover, the experimental results also indicated the good process intensification potential of membrane contactor technology.

3.2.2. Effect of TOX concentration

For the catalytic reactions, the feed ratio of a small amount of catalyst and a large amount of reactant is desired in industrial applications. The mass ratio of HPW in sulfolane was fixed at 1:25. The dosage of TOX was varied from 0.2 to 0.8 g to investigate the effect of TOX concentration on the yield of glycolic acid. The operation pressure was 3.0 MPa in experiments. According to the results shown in Fig. 9, the yield of glycolic acid exhibited a decreasing trend as the TOX concentration increased for all types of PTFE hollow fiber membranes, but meanwhile, TOF gradually increased. For example, as the mass ratio of TOX and HPW increased from 0.2:1 to 0.8:1, the yield of glycolic acid in M3 membrane contactor decreased from 98.2% to 66.1%, while the turnover frequency (TOF) increased from 6.93 to 21.34 $mol \cdot g^{-1} \cdot h^{-1}$. Among four types of PTFE membranes, M4 exhibited the best performance. The yield of glycolic acid maintained higher than 90% and the highest TOF was up to 26.37 $mol \cdot g^{-1} \cdot h^{-1}$. In addition, the performance difference among M2, M3 and M4 became obvious with the increase of TOX concentration, implying the different membrane wetting behavior, which was consistent with the analysis of Fig. 8. These results revealed that the reduction of pore size and the construction of dense layer on membrane surface was beneficial to the inhibition of membrane wetting in formaldehyde carbonylation process. The PDMS/PTFE composite hollow fiber membrane exhibited best potential in the practical application.

3.3. Analysis on membrane wetting

According to the experimental results above, for the porous PTFE hollow fibers including M1, M2 and M3, the yield of glycolic acid increased with decreasing pore size, which was due to the improvement of wetting resistance. As we know, the diffusion coefficient of CO in gas phase was much larger than that in liquid phase. When membrane pores were occupied partially by the reaction solution, the mass transfer of CO in membrane phase would be greatly affected. As a result, the yield of glycolic acid was reduced. As the pore size increased, the entry depth of sulfolane in membrane pores increased, leading to the decrease of yield of glycolic acid. Similar phenomenon was also reported in gas absorption using membrane contactor. For example, Wang *et al.* [37] reported that a marginal wetting of 5% could lead to a significant decrease of CO_2 absorption efficiency. Mavroudi *et al.* [38] also found that when 13% of membrane pores were occupied by liquid, the mass transfer resistance would account for higher than 98% of total membrane phase resistance.

The introduction of dense PDMS layer in composite hollow fiber could thoroughly prevent the solvent from entering membrane pores, thus eliminating the membrane wetting. Therefore, the composite membrane exhibited the best performance. It should be noted that, although the dense layer will inevitably reduce the gas permeability and increase the mass resistance of membrane phase in conventional gas absorption using membrane contactors [13,14], the negative influence in this study could be ignored because the amount of CO required for the reaction was very low. According to the theoretical calculation, the consumption quantity of CO in experiments was 1.0×10^{-5} $mol \cdot m^{-2} \cdot s^{-1}$ (0.2 g of TOX and 1.0 g of HPW in 25.0 g of sulfolane with reaction time of 60 min), which was much lower than the CO permeability at

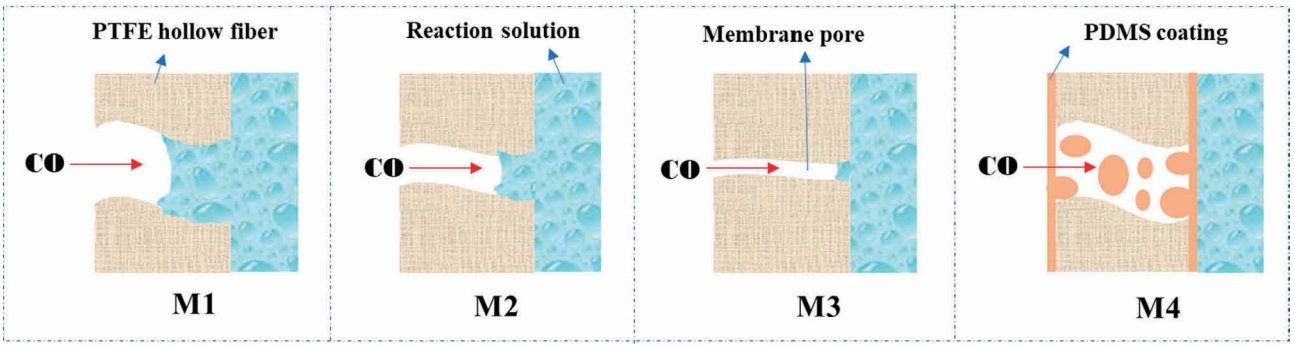

Fig. 10. Schematic diagram of antiwetting mechanism in PTFE membrane contactor for formaldehyde carbonylation.

1.0 MPa, *i.e.*, 1.97×10^{-4} mol·m^{-2}·s^{-1}. Therefore, after solving the problem of membrane wetting, the PDMS/PTFE composite hollow fiber membrane exhibited the best process performance. The schematic diagram of antiwetting mechanism in this study was shown in Fig. 10.

4. Conclusions

In summary, three porous PTFE hollow fiber membranes with different pore sizes and one PDMS/PTFE composite hollow fiber membrane with dense layer were prepared and employed to investigate the effect of microstructure on formaldehyde carbonylation performance in membrane contactors. For porous membranes, the yield of glycolic acid increased with the decrease of membrane pore size thanks to the improvement of membrane wetting. However, even for the PTFE hollow fiber with mean pore radius of only 8 nm, the wetting problem was not fully avoided due to low surface tension of solvent. The construction of PDMS/PTFE composite hollow fiber with dense layer was an effect approach prevents the solvent from entering membrane pores, thus exhibiting the best performance. At reaction temperature of 120 °C and operation pressure of 3.0 MPa, the yield of glycolic acid could be always higher than 90% when the mass ratio of TOX and HPW increased from 0.2:1 to 0.8:1, and the highest TOF was up to 26.37 mol·g^{-1}·h^{-1}. This study provided a reference for the understanding and optimization of membrane microstructure for formaldehyde carbonylation using membrane contactors.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

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.

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