A new PDMS-b-PPO block copolymer membrane with novel *non-perforated* structure towards high flux for alcohol permselective pervaporation

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Abstract. The effective permselective pervaporation of alcohol is one of key technology for bio-alcohol industrial production. In this work, a new polydimethylsiloxane-block-polyphenylene oxide (PDMS-b-PPO) copolymer was first synthesized by a bridge reagent technique. Based on the copolymer structure confirmation, the asymmetric PDMS-b-PPO membrane was subsequently prepared by phase-inversion method in order to improve the anti-swelling capacity of PDMS. SEM observation indicated that the morphology of as-prepared membrane exhibited a ‘non-perforated’ structure, resulting from the phase-inversion and micro-phase separation of the PDMS-b-PPO copolymer in the membrane forming process. Furthermore, the structure changes of the membranes with different ratio of PDMS to PPO were investigated. This non-perforated structure in the membrane favored to reduce the diffusion resistance, together with the affinity of PDMS segment to alcohol during pervaporation process. Thus, the prepared PDMS-b-PPO membrane showed dramatically increased flux, in pervaporation separation of alcohol/water mixture. The flux of the PDMS-b-PPO membrane (PDMS content of 42.4%) can reach 3816.8 g/(m²·h), along with 8.53 of separation factor in pervaporation of 5 wt% alcohol/water mixture (60°C). This work may provide a new strategy to design and fabricate new copolymer membranes for improving alcohol permselective pervaporation.

Keywords: polymer membranes, alcohol permselective pervaporation, block copolymers, non-perforated structured membrane

1. Introduction

Bio-alcohol has been promoted as a benign environmental source to solve energy problem worldwide [1–4]. The coupling of pervaporation (PV) and fermentation for bio-alcohol production has received increasing attention because the produced bio-alcohol can be timely in-situ recovered from fermentation using pervaporation technology [5, 6], so that the inhibition of fermentation from high alcohol concentration can be effectively reduced. Thus, the alcohol permselective pervaporation membrane with higher separation efficiency is one of the most

important keys to accomplish the coupling of PV and fermentation.

Polydimethylsiloxane (PDMS) is one of the most representative membrane materials for pervaporation recovery of alcohols from their aqueous solutions, due to the advantages, such as high thermo-stability, hydrophobicity, low-surface tension, biocompatibility, and commercial availability. However, the wide utilization of PDMS is limited for its low glass transition temperature, difficult membrane-forming property, and poor cohesion, which lead to PDMS membrane cumbersome curing and lower anti-swelling

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[7–13]. A few of modifications on PDMS have been made to improve these deficiencies, such as crosslinking, filling, graft, and block copolymerization [14–19], of which graft or block copolymerization offered an appealing route to generate new types of materials that combine the superior properties of multiple polymers. For example, Dong *et al.* [15] prepared poly(1-phenyl-1-propyne) (PPP)/PDMS graft copolymer membranes, in order to improve the anti-swelling capacity of PDMS. This PPP/PDMS membrane showed excellent permselectivity towards alcohol, acetone, dioxane, acetonitrile, and pyridine by pervaporation separation, due to that the rigid PPP chains of PPP/PDMS endowed the membrane a good anti-swelling capacity. Jiang *et al.* [20] has investigated a new kind of fluoridated siloxane-imide block copolymer (PSI) membrane for organic-pervaporation. This fluoridated imide blocks in the PSI improved the mechanical strength of the PDMS membranes without reducing its separation factors. Moreover, the similar modification of PDMS were carried out to synthesize polydimethylsiloxane-block-polymethylmethacrylate copolymer [21], polydimethylsiloxane-graft-polymethylmethacrylate copolymer [22], and polydimethylsiloxane/polystyrene interpenetrating polymer network [23]. All these works demonstrated that the poor properties of PDMS can be effectively improved by graft or block copolymerization with other relatively rigid polymers.

Polyphenylene oxide (PPO) is a thermoplastic polymer, which shows excellent chemical and thermal stability, and has been widely applied in pervaporation separation. For example, the asymmetric PPO membrane, prepared by Schauer *et al.* [24], has been applied in pervaporation separation of alcohol/water, which can permeate alcohol, preferentially. Herein, we regarded the rigid PPO polymer as a good candidate to combine with PDMS through graft or block copolymerization. Our previous work has fabricated a novel PDMS/bromide-substituted PPO (BPPO) membrane by *in situ* crosslinking method [25]. The results showed that existence of PPO really improved the anti-swelling capacity of PDMS, and the resultant PDMS/BPPO membrane exhibited a high selectivity towards butanol. However, the flux of such PDMS/BPPO membrane was not satisfactory due to its densely crosslinked structure. Therefore, to further improve flux of the membrane, this work synthesized a series of polydimethylsiloxane-

block-polyphenylene oxide copolymers (PDMS-b-PPO) by reactive crosslinking method, using 2, 4-diisocyanatotoluene (TDI) as crosslinking reagent. Then, the asymmetric PDMS-b-PPO membranes were prepared by phase-inversion method. The morphologies and constituent of the membrane with tunable ratio of PDMS to PPO were investigated. The SEM results showed that the PDMS-b-PPO membrane presented a network porous structure both on the surfaces and in the cross-section, while the permeation and pervaporation tests showed that this porous membrane exhibited a ‘*non-perforated*’ structure (porous but the pores were not truly through holes). This novel ‘*non-perforated*’ structure led to a high flux in alcohol permselective pervaporation. This work may provide a new way to design and prepare asymmetric membrane with improved pervaporation performance, efficiently.

2. Experimentals

2.1. Materials

PDMS (KF-8008, average molecular weight of 11 400 g/mol, dual-terminated with aminopropyl group), was purchased from Japan’s Shin-Etsu Chemical Industry Company. PPO (average molecular weight of 16 000 g/mol) was purchased from Hao Di Chemical Trading Company (Kun Shan, China). 2,4-diisocyanatotoluene (TDI), dibutyltin dilaurate (DBTDL), and chlorobenzene were supplied by Tianjin Fuchen Chemical Reagents Company (Tianjin, China). Analytically grade chlorobenzene, chloroform, methanol, alcohol, 2-propanol, and butanol were purchased from Beijing Chemical Company (Beijing, China).

2.2. Synthesis of

polydimethylsiloxane-block-polyphenylene oxide copolymers (PDMS-b-PPO)

Calculated amount of PDMS, PPO and TDI were dissolved in chlorobenzene under stirring to obtain 10 wt% solutions, respectively. TDI solution was firstly transferred into a dried 500 mL flask. When the temperature of the flask was elevated at 80°C, the PPO solution was dropwise added into TDI solution under vigorous stirring and nitrogen atmosphere. Then, the PDMS solution together with 3 mL of DBTDL was added into the flask reactor. The temperature of the reaction system was elevated to 130°C and kept for 3 h. At last, the insoluble solids produced after cooled down to ambient temperature. The prod-

uct was filtrated and washed with methanol thoroughly, and the powder-like PDMS-b-PPO copolymers were collected and dried in a vacuum oven at 50°C for 48 h.

2.3. Preparation of PDMS-b-PPO membrane

The asymmetric PDMS-b-PPO membranes were prepared by phase inversion method. Typically, pre-calculated amount of PDMS-b-PPO and n-butyl alcohol was firstly dissolved in chloroform solvent to form a casting solution. The casting solution was spread on a level glass shutter by Gardner knife under ambient atmosphere. Then the glass shutter was immersed into a methanol coagulation bath. The as-obtained asymmetric PDMS-b-PPO membrane was peeled off and dried in a vacuum oven for 24 h.

2.4. Characterizations

The prepared PDMS-b-PPO copolymers were characterized by FTIR (Nicolet, 5DX instrument) and $^1\text{H-NMR}$ analysis (Avance 400M, Bruker, Germany). The content of PDMS was calculated by the area ratio of the characteristic elements (mass fraction was equal to the product of the unit molecular weight and unit mole ratio. In this work, the area ratio is the unit mole ratio). The morphologies of membranes were characterized by SEM (Hitachi S-4300, Japan).

2.5. Pervaporation experiments

The pervaporation apparatus in this work is presented in Figure 1. The membrane was installed in a glass pervaporation cell with an operational area of 28 cm². The feed was circulated through the pervaporation cell by a peristaltic pump. The downstream pressure was kept at approximately 0.1 kPa by a vac-

Figure 1. Scheme of experimental apparatus for pervaporation

uum pump. Permeate was collected through the condensation by liquid nitrogen. All the feeds are alcohol/water mixture with a ratio of 1:20 (5 wt % of the alcohol), and the operating temperature is 60°C. The feed and permeate compositions were analyzed by gas chromatography (GC7900, Tianmei Corporation, Shanghai, China), where the operating temperatures were 160°C in injector, 150°C in column and 160°C in detector. The separation factor was calculated from the quotient of the weight ratio of alcohol and water in the permeate, $Y_{\text{alcohol}}/Y_{\text{water}}$, and in the feed, $X_{\text{alcohol}}/X_{\text{water}}$ is given by Equation (1):

$$\alpha = \frac{\frac{Y_{\text{alcohol}}}{Y_{\text{water}}}}{\frac{X_{\text{alcohol}}}{X_{\text{water}}}} \quad (1)$$

The flux (J) was calculated through weight of permeate (W) at unit time (t) and unit area (A) by Equation (2):

$$J = \frac{W}{t \cdot A} [\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}] \quad (2)$$

2.6. Permeation experiment

Permeation experiments were used to prove the ‘non-perforated’ structure in the PDMS-b-PPO asymmetric membranes. The permeation test of PDMS-b-PPO membrane was conducted with an effective area of 26 cm². Deionized water and alcohol were used as the feeds. The experiments were carried out at a pressure of 0.6 MPa produced by a plunger pump. Permeations flux (F) were determined by measuring the volume of liquid collected over a measured time under steady-state conditions. F was calculated as shown by Equation (3):

$$F = \frac{V}{t \cdot A} [\text{mL} \cdot \text{m}^{-2} \cdot \text{h}^{-1}] \quad (3)$$

where ‘ V ’ is the permeate volume [mL], ‘ t ’ stands for the time [hours], and ‘ A ’ denote the effective membrane surface area [m²].

3. Results and discussion

3.1. Synthesis and structures of PDMS-b-PPO copolymer

As illustrated in Figure 2, PDMS-b-PPO was synthesized by the reaction of the isocyanate (–NCO) of TDI with aminopropyl (–CH₂CH₂CH₂NH₂) groups

Figure 2. The reaction scheme of the formation of PDMS-b-PPO copolymer

of PDMS and hydroxyl (–OH) groups of PPO to form urethane and substituted urea group, respectively. The synthesis process was controlled by two stages. In the first stage, the reaction system was controlled at temperature of 80°C for one of isocyanate (–NCO) of TDI to react with hydroxyl (–OH) group of PPO to form urethane, as well as in order to inhibit the self-polymerization of TDI. After the introduction of PDMS and dibutyltin dilaurate (DBTDL) solution, the other isocyanate (–NCO) of TDI would be attacked by the aminopropyl group of PDMS in presence of dibutyltin dilaurate (DBTDL) other than –OH group of PPO because of the steric hindrance. Thus, the initial PDMS-b-PPO copolymer segments were formed. For the second stage, the temperature was further elevated and kept for 3 hrs. in order to complete the reaction.

To evidence of the formation of the PDMS-b-PPO copolymer, the FTIR spectra of PDMS, PPO, TDI, and PDMS-b-PPO were illustrated as in Figure 3. The PDMS spectrum in Figure 3 indicated typically the Si–O–Si stretching peak, CH₃ bending peak, CH₃ rocking peak, and C–H stretching peak appeared at 1100–1000, 1260, 797.35, and 2989 cm^{–1}, respectively. The spectra of PPO showed the benzene ring peak, C–O stretching peak, and CH₃ rocking peak appeared at 1468, 1306, and 857 cm^{–1}, respectively. And the peak at 2261 cm^{–1} clearly indicated –N=C=O of TDI. In contrast, the characteristic peaks of PDMS and PPO are presented in the spectrum of PDMS-b-PPO copolymer. Meanwhile, the characteristic peak of TDI disappeared and a new peak appeared at 1711.9 cm^{–1}, which was ascribed to the produced urethane group. These results indicated that the PDMS-b-PPO was really formed.

Figure 3. FTIR spectra of PDMS, PPO, TDI and PDMS-b-PPO copolymers

The typical ¹H-NMR spectrum of the PDMS-b-PPO copolymers was shown in Figure 4. The peak at 7.256 ppm of Figure 4 was ascribed to the characteristic peak of deuterated chloroform solvent.

Figure 4. ¹H-NMR spectra of PDMS-b-PPO copolymer

And the two peaks at 6.469 and 2.087 ppm were ascribed to the proton of aromatic and methyl group of PPO, respectively, and the peak at 0.072 ppm was attributed to the proton of siloxane. The area ratio of the three signals at 6.469, 2.087 and 0.072 ppm was used to calculate the PDMS content.

3.2. The morphologies of as-prepared PDMS-b-PPO membrane

Generally, PDMS cannot be directly formed into an asymmetric membrane by phase-inversion method because of its poor mechanical property. However, our PDMS-b-PPO copolymer can form a wholly continuous non-substrate membrane by phase-inversion method, due to existence of more rigid PPO segments. As shown in Figure 5, the surface and cross-section morphologies of the membranes indicated that the surface morphology of PPO asymmetric membrane (Figure 5a) was very dense and com-

pact, and its cross-section (Figure 5b) exhibited a typical pear-shaped finger-like structure. In contrast, the surface of our PDMS-b-PPO membrane (prepared by the ratio of PDMS:PPO:TDI was 1.5:1:2) was porous-like (Figure 5c) with pore size of about 100 nm. But the enlarged image in the inset of Figure 5c indicated that the surface displayed much non-perforated pores. And the image of the cross-section (Figure 5d) showed a sponge-like network structure with pore size about 0.5–1.0 μm . The formed novel morphology of the PDMS-b-PPO membrane was mainly resulted from the specific hard and soft segments of the copolymers and the membrane-forming processes; that is, the microphase separation of the block copolymers and the phase-inversion process. As illustrated in Figure 6, when the casting solution consisting of PDMS-b-PPO dissolved in *n*-butyl alcohol and chloroform was spread onto a glass shutter and then immersed into methanol

Figure 5. The SEM of the surface and the cross-section of PDMS-b-PPO membrane. a) surface of PPO asymmetric membrane; b) cross-section of PPO asymmetric membrane; c) surface of PDMS-b-PPO membrane; d) cross-section of PDMS-b-PPO membrane (PDMS:PPO:TDI = 1.5:1:2).

Figure 6. Phase-inversion process of PDMS-b-PPO membrane

coagulation bath, the phase inversion occurred. The solvent displacement between liquid component and gel proceed due to the existence of poor and rich phase region in the PDMS-b-PPO membrane, resulting in the porous structure. Furthermore, during membrane forming process, the solvent of n-butyl alcohol could be partially displaced by methanol when immersed into methanol coagulation bath, due to the compatibility between PDMS and n-butyl alcohol. Thus, the cross section of the PDMS-b-PPO membrane appeared as sponge-like other than finger-like structure. Moreover, when the phase inversion finished, the PDMS domains in outer skin layer of PDMS-b-PPO were swollen by methanol and n-butyl alcohol. And these wrapped solvents evaporated during drying, resulting in the shrinkage of PDMS segment and occurrence of subsidence areas, much similar to the porous-like but non-perforated structure. Simultaneously, the micro-phase separation of the as-prepared PDMS-b-PPO, resulting from the soft PDMS segment and the rigid PPO chain, caused that PDMS micro-region was uniformly dispersed in the PPO matrix to form such porous-like structure. The component of this micro-region can be further demonstrated by EDS shown in Figure 7. The blue points of Si element and the red points of C element in Figure 7 obviously indicated that the PDMS component in the blue Si domains was uniformly dispersed in the PPO matrix.

Figure 7. EDS scanning image of the PDMS-b-PPO membrane (blue points standardized Si element and the red points standardized C element)

To further demonstrate the porous-like but *non-perforated* structure of the surface and the cross-section of PDMS-b-PPO membrane, the permeation of aqueous solution was performed. Both of PPO and the PDMS-b-PPO asymmetric membrane were prepared by the phase-inversion method under the same conditions. The results in Figure 8 indicated that the pores in Figure 5b and 5d were not truly through holes, and really exhibited a non-perforated structure. When the feed liquid was water, the permeations of PPO and PDMS-b-PPO membrane were 3.0 and 15.0 mL/(m²·h) under 0.6 MPa, respectively.

Figure 8. Permeation results of PPO membrane and PDMS-b-PPO membrane

The low permeation of pure water under relatively higher pressure demonstrated that the PPO membrane and PDMS-b-PPO membrane were dense and the water was difficult to permeate through. However, when the feed liquid was changed into alcohol, the permeation of the PPO membrane and PDMS-b-PPO membrane were increased to 10.0 and 60 mL/(m²·h) under the same pressure, respectively. This was due to the better affinity between PDMS and alcohol. And the PDMS-b-PPO membrane showed a relatively higher permeation for alcohol. Thus, we can deduce that the porous structure of the PDMS-b-PPO membrane in Figure 5 was really non-perforated.

3.3. The effect of raw material ratio on the structure of PDMS-b-PPO membranes

To investigate the effect of the soft and rigid segment in PDMS-b-PPO copolymers on the structure of the membrane, series of PDMS-b-PPO copolymers with different constituents were prepared by different ratio of PDMS to PPO. The PDMS content in the PDMS-b-PPO copolymer was measured using ¹H-NMR area ratio as shown in Table 1. The results of Table 1 indicated that the PDMS content was some close to the theoretical ones. The relatively low

PDMS contents in sample 3, 4, 5 of Table 1 may be probably due to that the excessive amount of TDI brought about the crosslinking structure, of which the long molecular chains increased the measurement error. Moreover, the content of PDMS in the copolymer increased with increasing the ratio of PDMS to PPO, indicating that the composition of soft PDMS segments and rigid PPO segments in PDMS-b-PPO copolymers could be effectively tuned by the ratio of PDMS to PPO.

The morphologies of PDMS-b-PPO membrane with different ratio of PDMS to PPO on were investigated by SEM. As shown in Figure 9, all the PDMS-b-PPO membranes exhibited ‘non-perforated’ porous-like structure. When the ratio of PDMS:PPO:TDI changed from 0.5:1:2 to 1.5:1:2, the PDMS content in PDMS-b-PPO increasing from 24.14 to 42.40 wt%, and the corresponding images shown in Figure 9A, 9B, and 9C, indicated that the irregular and small pores existed in the surface and cross-section of membrane with the ratio of PDMS:PPO:TDI as 0.5:1:2, due to the low amount of soft PDMS segment in the copolymer. When the soft PDMS segment of the copolymer chains increased, the pores in the surface and the cross-section of membrane became relatively lager (Figure 9B and Figure 9C), resulting from that the increased PDMS brought about higher degree of microphase separation. Moreover, when the ratio of PDMS:PPO:TDI changed from 1:1:2 to 1:1:4 as shown in Figure 9B, 9D, and 9E, the surface and cross-section of the PDMS-b-PPO membrane became denser and even compact (Figure 9D-s). This was attributed to that the excessive amount of TDI may produce some crosslinking structure in the membrane and resulted in the restricted micro-phase separation process during formation of membrane. Therefore, the results in Figure 9 indicated that the morphology of such ‘non-perforated’ PDMS-b-PPO membrane can be tuned by changing the ratio of soft PDMS and rigid PPO.

Table 1. The variation of PDMS content in the copolymers with different ratio of PDMS to PPO

Sample	PDMS:PPO:TDI (mole ratio)	PDMS [wt%]	
		Theoretically added	Measured
1	0.5:1:2	26.27	24.14
2	1:1:2	41.61	37.02
3	1.5:1:2	51.66	42.40
4	1:1:3	41.61	32.38
5	1:1:4	41.61	30.75

3.4. Pervaporation separation of the alcohol/water binary mixtures

Figure 10 showed the effect of TDI amount on the pervaporation performances in the separation of alcohol/water, 2-propanol/water, and t-butanol/water mixtures. It can be noted that the separation factor and flux PDMS-b-PPO membrane decreasing with the increased of TDI amount. This was in accordance with the gradually denser and more compact

Figure 9. The SEM images of the membranes with different ratios of PDMS: PPO: TDI. ‘s’ represent the surface and ‘c’ represent cross-section. (A) PDMS:PPO:TDI=0.5:1:2 polymer membrane, (B) PDMS:PPO:TDI=1:1:2 polymer membrane, (C) PDMS:PPO:TDI = 1.5:1:2 polymer membrane, (D) PDMS:PPO:TDI=1:1:3 polymer membrane, (E) PDMS:PPO:TDI=1:1:4 polymer membrane.

Figure 10. The effect of TDI amount on the pervaporation performances in the separation of alcohol/water, 2-propanol/water, and t-butanol/water mixtures

structure of Figure 9B, 9D, and 9E. Moreover, based on the results of Table 1, more usage of TDI resulted in some crosslinked PDMS-b-PPO. The micro-phase separation process of PDMS-b-PPO was then restricted, and the shrinkage of PDMS segment caused the surface and the cross-section became less porous and relatively compact. Thus, the separation factor and flux of PDMS-b-PPO membrane decreased. When the ratio of PDMS: PPO: TDI was 1:1:2 (PDMS content is 37.02%), the prepared membrane exhibited an optimum pervaporation performance. The separation factor (α) and flux (J) were 8.06 and 3150.7 g/(m²·h) for alcohol/water mixture, 11.35 and 3390.8 g/(m²·h) for 2-propanol/water and 12.7 and 3345.1 g/(m²·h) for t-butanol/water mixture, respectively, with 5 wt% of the feed concentration and at 60°C of operation temperature. Figure 11 showed the effect of PDMS content in PDMS-b-PPO on pervaporation performances in

Figure 11. The effect of PDMS content in PDMS-b-PPO on pervaporation performances

the separation of alcohol/water, 2-propanol/water and t-butanol/water mixtures. It was noted that the separation factor and flux PDMS-b-PPO membrane increased with increasing of PDMS content, which was also in accordance with the variation of morphologies of Figure 9A to 9C. This was probably due to that the more amount of PDMS led to a relatively larger PDMS domains on the surface and a looser and porous cross-section in the membrane (Figure 9C), which resulted in increased efficient contact areas and reduced mass transfer resistance of the membrane. Therefore, the flux of PDMS-b-PPO membrane was enhanced. This optimum pervaporation performance can be further illustrated from the porous ‘non-perforated’ structure of the membrane shown in Figure 9C. When the ratio of PDMS:PPO: TDI was 1.5:1:2 (PDMS content is 42.4%), the feed concentration was 5 wt%, and the operation temperature was 60°C, the optimum pervaporation separation behavior was achieved. The separation factor

Table 2. The pervaporation performance of membranes in reference (In the system of ethanol/water)

Membrane	Ethanol concentration [wt%]	Temperature [°C]	Flux [kg/(m ² ·h)]	Separation factor	Reference
Crosslinked PDMS containing vinyl groups	16.5	40	0.085	8	[26]
Crosslinked PDMS containing acetoxysilyl groups	8	30	0.0251	10.8	[11]
PDMS-PS IPN supported on PESF	10	60	0.16	5.5	[27]
PDMS film treated with octadecyldiethoxymethylsilane	4.0	25	0.016	16.3	[28]
PDMS supported on PTFE	1.5	60	1.53	14	[29]
PDMS supported on CA	5	40	1.3	8.5	[12]
PTMSP	6	30	0.44	15.1	[30]
PTMSP modified with PFA-g-PDMS	10	25	0.6	20	[31]
Plasma modified with octadecyldiethoxymethylsilane	4	25	0.015	18	[28]
PDMS-PI copolymer	10	60	0.56	10.6	[32]
PEO-CS blend polymer	8	20	0.9	4.4	[33]
Silicalite filled PDMS	5.5	22.5	0.05	16.5	[34]
PDMS-b-PPO asymmetric membrane	5	60	3.816	8.53	This work

and flux reached 8.53 and 3816.8 g/(m²·h) for alcohol/water mixture, 13.54 and 3650.0 g/(m²·h) for 2-propanol /water and 18.18 and 3571.0 g/(m²·h) for t-butanol/water mixture, respectively.

Table 2 shows the pervaporation performance of other polymeric membranes. As can be shown, our PDMS-b-PPO asymmetric membrane exhibit better flux than that of the reported polymeric membranes while the separation factors maintained on a relatively high level [26–34].

4. Conclusions

PDMS-b-PPO membranes were successfully prepared for pervaporation separation of alcohol/water mixtures. The membranes showed a ‘*non-perforated*’ structure and high flux in alcohol permselective pervaporation. With the increasing of PDMS content and the decreasing of TDI amounts, the sponge-like structure of PDMS-b-PPO membranes became looser and the PDMS shrinkage domains on surface increased, resulting in the improved separation performance. When the ratio of PDMS:PPO:TDI was 1.5:1:2, the separation factor and flux reached 8.53 and 3816.8 g/(m²·h) for alcohol/water mixture, 13.54 and 3650.0 g/(m²·h) for 2-propanol/water and 18.18 and 3571.0 g/(m²·h) for t-butanol/water mixture, respectively. This higher flux for alcohol was attributed to the specific ‘*non-perforated*’ structure, which enhanced efficient contact areas and reduced the mass transfer resistance of the membrane. This work provides a new way to design and develop the novel alcohol permselective pervaporation membranes.

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