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Pervaporation Separation of Thiophene–Heptane Mixtures with Polydimethylsiloxane (PDMS) Membrane for Desulfurization

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Abstract Cross-linked polydimethylsiloxane (PDMS)–polyetherimide (PEI) composite membranes were prepared, in which asymmetric microporous PEI membrane prepared with phase inversion method was acted as the microporous supporting layer in the flat-plate composite membrane. Membrane characterization was conducted by Fourier transform infrared and scanning electronic microscopy analysis. The composite membranes were employed in pervaporation separation of *n*-heptane–thiophene mixtures. Effect of amount of PDMS, cross-linking temperature, amount of cross-linking agent, and cross-linking time on the separation efficiency of *n*-heptane–thiophene mixtures was investigated experimentally. Experiment results demonstrated that 80–100°°C of cross-linking temperature was more preferable for practical application, as the amount of cross-linking agent was up to 20 wt.%, and 25 wt.% of PDMS amount was more optimal as far as flux and sulfur enrichment factor were concerned. In addition, the swelling degree of and stableness of composite membrane during long-time operation were studied, which should be significant for practical application.

Keywords Polydimethylsiloxane · Pervaporation · Thiophene–heptane mixtures · Desulfurization

Introduction

Ultra-deep removal of sulfur from transportation fuels, particularly from gasoline and diesel, has become very important in petroleum-refining industry worldwide. The need for cleaner burning fuels has resulted in a continuing worldwide effort to reduce the sulfur levels in gasoline and diesel fuels [1–3]. The reduction of gasoline and diesel sulfur has been considered to be an important means for improving air quality [4–6]. Sulfur present in gasoline results in SO_x air pollution, which is directly responsible for acid rain [7]. Fluid catalytic cracking (FCC) gasoline, which accounts for 30–40% or more of the total gasoline pool, is by far the most significant sulfur contributor, especially in China.

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A number of solutions, such as hydrotreating, adsorption [8], and extraction [9], has been suggested to reduce sulfur in gasoline, but none of them proved to be ideal. Traditionally, hydrotreating process is the most effective technology used for removal of organosulfurs present in gasoline. However, this technology suffers from the high investment and operating costs. Further, alkene and cyclic alkane are susceptible to hydrogenation during hydrotreating, which leads to a significant loss in octane number since alkene and cyclic alkane mean higher octane number than paraffin. It should be important to find advanced technology to remove the organosulfurs present in gasoline.

Pervaporation (PV) technology, compared to traditional separation technology such as distillation, molecular sieve, and extraction, has many advantages: (1) high separation efficiency, (2) low energy consumption, (3) simple operation, and so on [10, 11]. Based on solubility parameter analysis, Kong et al. applied cross-linked polyethylene glycol membranes for sulfur removal from FCC gasoline [12–14]. In our previous work [15–17], polydimethylsiloxane (PDMS)–polyacrylonitrile composite membranes were studied and applied for pervaporative desulfurization for model gasoline. PDMS has been extensively investigated for the separation of various mixtures, and scientific researches have been made to modify PDMS membranes in different ways to enhance the pervaporation performance [18].

Real gasoline is a rather complex mixture composed of alkanes, olefins, cycloparaffins, and aromatics ranging from C_5 to C_{14}. Typical sulfur compounds in gasoline include mercaptans, thiophenes, and the ramifications thereof. In this work, *n*-heptane was selected to stand for gasoline, while thiophene was chosen as the representative organosulfurs. In this study, the PDMS–polyetherimide (PEI) composite membrane was prepared and employed to simulate desulfurization process of gasoline. The influences of amount of PDMS, cross-linking temperature, amount of cross-linking agent, and cross-linking time on the separation efficiency of *n*-heptane–thiophene mixtures were investigated experimentally in order to obtain a more practical membrane preparation condition for the scale-up of membrane separation technology, which was the most important point for practical application.

Experimental

Materials

PEI (Ultem®-1000), as shown in Fig. 1, was purchased from General Electric (USA). *N*-methyl pyrrolidone (NMP) used was obtained from Beijing Yili Fine Chemicals Co. Ltd., China. In order to simplify the experiment and to simulate the actual desulfurization process simultaneously, *n*-heptane (Beijing Chemical Company, China) and thiophene (Tianjin Chemical Company, China) were chosen as the representative components to form the

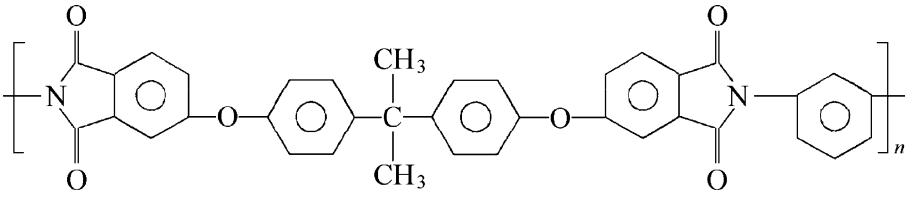


Fig. 1 The chemical structure of PEI

model gasoline. PDMS (viscosity 20 Pa s), ethyl orthosilicate, and dibutyltin dilaurate (Beijing Chemical Company, China) were purchased from Beijing Chemical Company for the preparation of PDMS membrane. All other chemicals used in the experiments were of reagent grade and were used without any further purification.

Membrane Preparation

PEI-Supporting Membrane Preparation

PEI was used as a membrane material after drying in vacuum at 150 °C for 6 h. Twenty weight percent of PEI was dissolved in NMP at 80 °C with stirring for 12 h and then the casting solution was filtrated to get rid of impurity. To remove air bubbles, the casting solution was kept at room temperature for 24 h under vacuum. After degassing, the casting solution was cast on a polyester nonwoven fabric with a scraper having 150-μm thickness. The nascent membrane was dried for 10 s at 25±1 °C. And then, it was immersed into deionized water at 25 °C. After the immersion, the precipitated membranes were washed for 12 h to remove residues of solvent mixtures from the membranes.

PDMS–PEI Composite Membrane Preparation

PDMS, cross-linking agent ethyl orthosilicate, and catalyst dibutyltin dilaurate were dissolved in *n*-heptane at room temperature. After being degassed under vacuum, the solution was cast onto the PEI membrane. The membrane was first vulcanized under room temperature to evaporate the solvent and then introduced into a vacuum oven to complete cross-linking. Controlling the PDMS concentration or the coating amount could produce membranes with variable top-layer thickness. The thickness of the top skin layer could be determined by means of scanning electronic microscopy (SEM) photographs.

Membrane Characterization

Scanning Electronic Microscopy Spectroscopy

In order to investigate the membrane structure, SEM characterization of the prepared membranes has been carried out. For this purpose, the membrane samples were fractured in liquid nitrogen and then coated with Au–Pd under vacuum conditions. The cross section and surface membrane morphology were taken by SEM (JSM-6301F scanning electron microscope).

Fourier Transform Infrared Spectra (FTIR-ATR)

Information about the presence of specific functional groups of the prepared membrane surfaces was obtained by a Nicolet IR 560 spectrometer with horizontal attenuated total reflectance (ATR) accessory equipped with a ZnSe crystal. For evaluation, a total of 32 scans were performed at a resolution of 4 cm^{-1} at a temperature of 25±1 °C. Meanwhile, Fourier transform infrared (FTIR) spectra were recorded within the range of 4,000–400 cm^{-1}.

Swelling Experiments

A piece of membrane sample was cut out and dried at the 60 °C in vacuum drying oven at least 48 h until constant weight, when its mass was noted as m_1. Then, the piece of

membrane was immersed into the feed and soaked. When the sample kept constant weight, it was carefully blotted between filter papers to remove surface liquid, and then the weight of the swollen membrane was quickly measured and its mass was noted as m_2. All experiments were repeated at least three times, and the results were averaged. The percent degree of swelling was calculated as

$$\eta = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

where η is the swelling degree; m_1 and m_2 are the mass of dry membranes and swollen membranes, respectively.

Pervaporation Experiments

The pervaporation apparatus used in this study is shown in Fig. 2. The membrane was installed in the pervaporation cell, and the effective membrane area in this cell was 22.4 cm^2. The feed solution was continuously circulated from a feed tank to the upstream side of the membrane in the cell at the desired temperature by a pump. Vacuum on the permeate side was maintained about 200 Pa and was monitored with a digital vacuometer. Two cold traps were set in parallel allowing the collection of permeate without rupture of the vacuum. About 1 h after starting the pervaporation process, the feed temperature, PV performance, and mass transfer equilibrium was stable. During the third hour, permeate was collected and samples from the feed tank were taken for analysis.

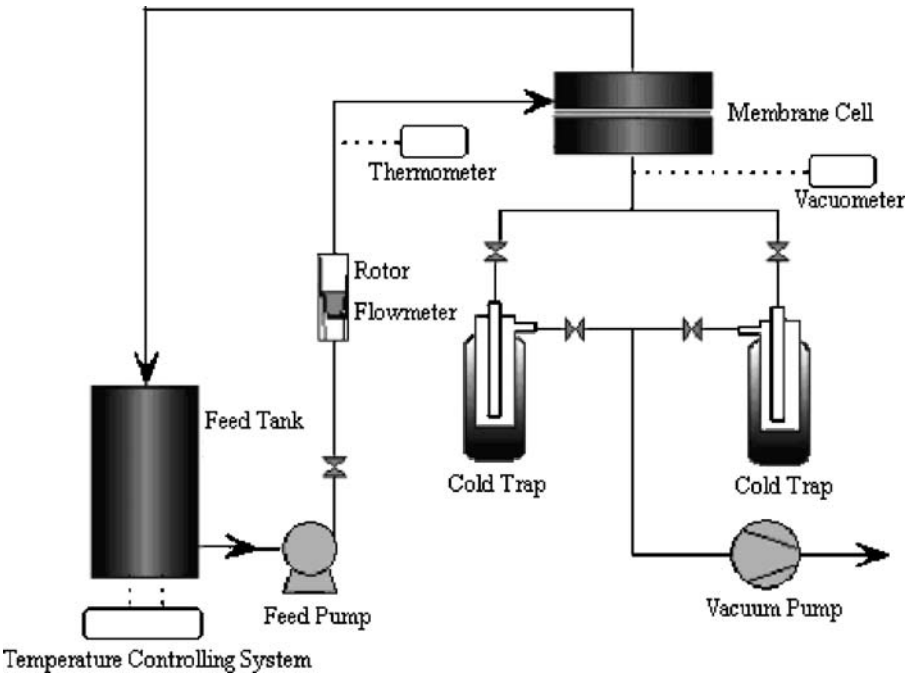


Fig. 2 Scheme of the pervaporation apparatus

The permeate total flux J was determined by measuring the weight of permeate collected in the cold trap and divided by time and the membrane's surface area as shown in Eq. 2:

$$J = \frac{\Delta m}{A \cdot \Delta t} \tag{2}$$

where Δm is the total amount permeated during the experimental time interval, Δt at steady state, and A is the effective membrane area. J used in the paper means total permeation flux if no special clarification. The total flux was determined gravimetrically with an experimental error of 1–2%.

The total sulfur content of feed and permeate was analyzed by Micro-Coulometric Analysis Instrument (Jiangsu, China). Each sulfur concentration determination was based on three or four different injections. The sulfur enrichment factor, β, is defined as

$$\beta = \frac{C_{\mathrm{p}}}{C_{\mathrm{f}}} \tag{3}$$

where C_{f} and C_{p} are the total sulfur content of feed and permeate samples, respectively.

In this study, the operation temperature was maintained at temperature of 80 °C using a thermostat and the thiophene concentration in feed mixtures was 100 ng/μL if no special clarification.

Results and Discussion

SEM Photographs of PDMS–PEI Composite Membrane

The cross section morphology of the PDMS–PEI membrane was shown in Fig. 3. As demonstrated in the SEM photographs, there is a clear boundary between the PDMS top layer and the PEI support layer. Meanwhile, the cross-sectional structure of the PDMS–PEI composite membrane consisted of an ultrathin skin layer and a porous finger-like structure. Moreover, the thickness of the PDMS top layer was determined to be about 4 μm from the SEM photograph by the scale tab. The surface morphology of the PDMS–PEI membrane was shown in Fig. 4. From this figure, the originally porous surface of the PEI substrate

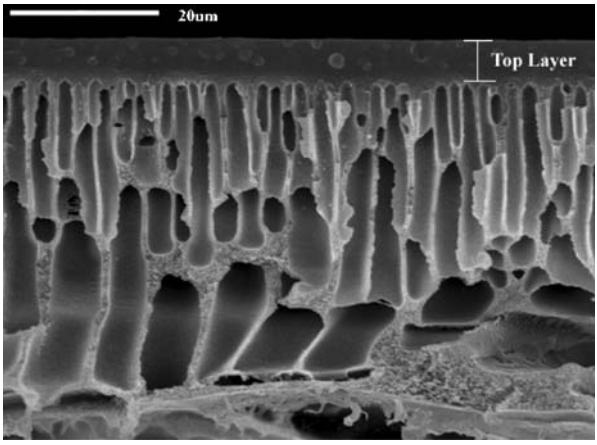


Fig. 3 The cross section morphology of the PDMS–PEI composite membrane

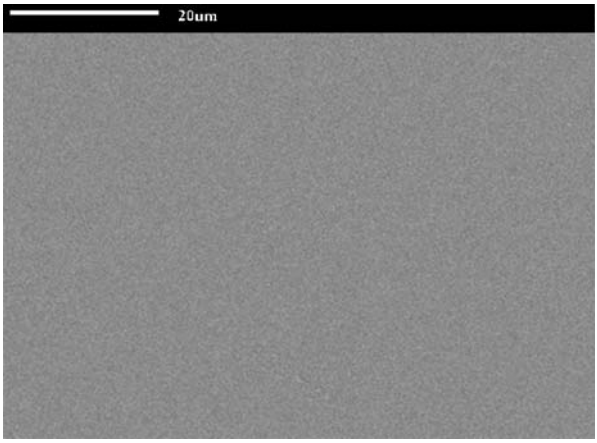
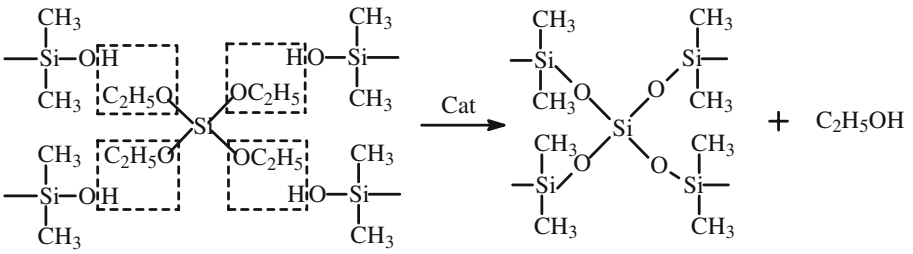


Fig. 4 The surface morphology of the PDMS–PEI composite membrane

was covered by a flat featureless PDMS layer, and the top PDMS layer, functioning as the basis of selectivity, had a nonporous and tight structure. The surface of the PDMS–PEI composite is dense and there is no pinhole or crack, which is important for the practical application.

FTIR Spectra of PDMS–PEI Composite Membrane

The attenuated total reflection Fourier transform infrared spectroscopy is a commonly used method to characterize the chemical structure of the surface [19]. The ATR technique enables the identification of specific molecules and groups located within 100 nm from the surface layer. In order to obtain detailed information about the structural changes of PDMS–PEI membranes resulting from cross-linking modification, FTIR spectra of the surface of PDMS–PEI membranes were recorded in Fig. 5 using the ATR technique. From Fig. 5a, a peak at 1,260 cm^{-1} was assigned to CH_3 (two CH_3 of Si–CH_3) symmetric deform. It also displayed three new absorbance signals at 850–730 cm^{-1} (CH3 out-of-plane bending and Si–C stretching), 2,890–3,000 and 1,000–1,150 cm^{-1} (Si–OH stretching), and 860–920 cm^{-1} (Si–OH angle bending vibration), respectively. Compared to the non-cross-linked membrane (from Fig. 5a), the spectra of the cross-linked membranes (from Fig. 5b) displayed absorbance signals of Si–OH evidently weakened. These changes were the evidences of the cross-linking reaction of PDMS [20]. The following formula (Eq. 4) showed the cross-linking reaction:



(4)

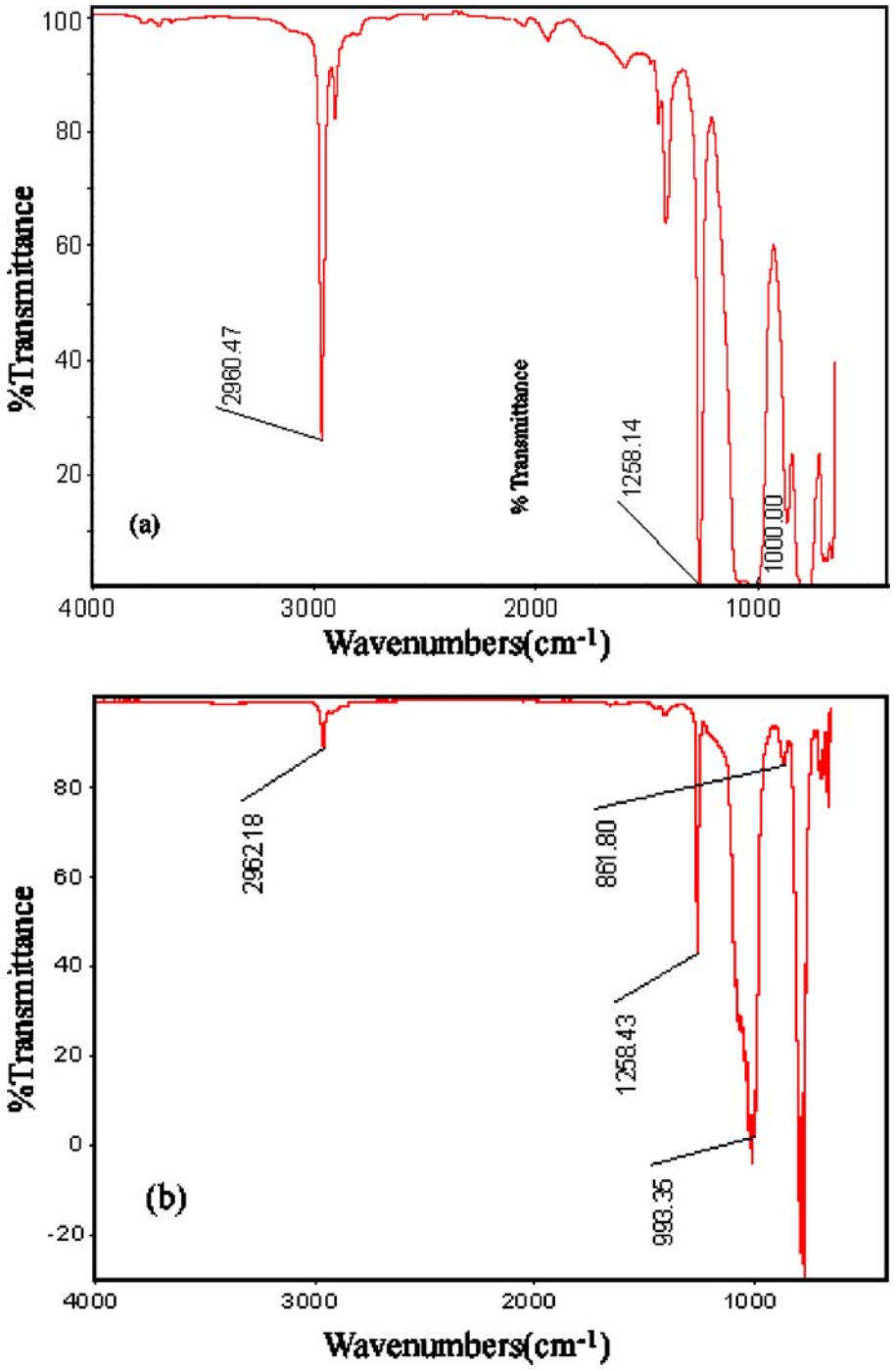


Fig. 5 FTIR spectra of PDMS–PEI composite membrane. **a** Before cross-linking modification, **b** after cross-linking modification

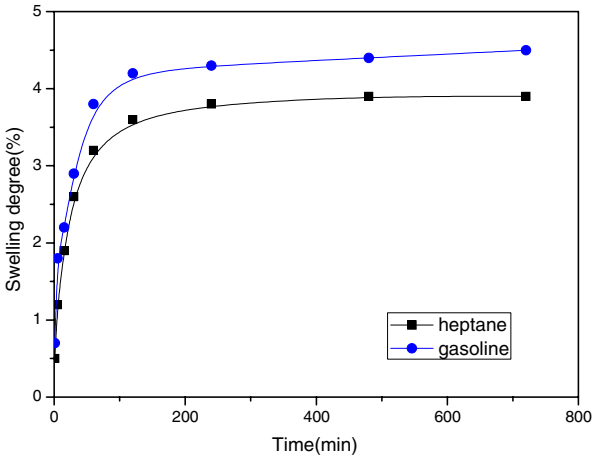


Fig. 6 Exhibits swelling behavior of the PDMS–PEI composite membrane (preparation condition: PDMS content (30 wt.%), cross-linking temperature (100 °C), cross-linking content (20 wt.%), cross-linking time (20 h))

Results of Swelling Experiments

The swelling results of different feed were given in Fig. 6, where it could be observed that the degree of swelling increased with increasing the time and then reached the equilibrium slowly within 240 min. From Fig. 6, the maximum of the swelling degree in heptane was no more than 4% and in gasoline no more than 5%, which should be suitable for practical application. It has also been shown that the swelling degree of membrane in gasoline was more a little than the swelling degree of membrane in heptane. These phenomena were contributed to gasoline contents many kinds of organic substances, and some of organic substances were easily dissolvable in PDMS membrane, so the membrane was easy to swell. That is to say, complicated hydrocarbons in gasoline stimulated the membrane swelling further. As described above, according to the comparison on PV performance of PDMS before and after modification as well as the swelling experiments, cross-linking was an effective modification way for PDMS membrane applied in gasoline desulfurization.

Effect of Amount of PDMS on Pervaporation Performance

Figure 7 revealed the effect of amount of PDMS on pervaporation performance. As shown in Fig. 7, with the increase of PDMS content, the flux decreased relatively sharply. However, enrichment factor increased at the beginning and then decreased tardily. This result implied that, when the PDMS content increased, more PDMS chains occurred in cross-linking reaction, and the top PDMS layer, functioning as the basis of permselectivity, became a nonporous and very tight structure. Accordingly, the free volume of PDMS membrane decreased, which led to the flux decrease. Meanwhile, top-layer thickness increased as the PDMS concentration increased. By all given reasons, the flux decreased as PDMS content increased. However, enrichment factor had a point of transition at 30 wt.% of PDMS content. It could be explained that the feed penetrated very difficultly when the free volume of PMDS membrane decreased at a definite degree. Also, this can be understood within the frame of solution–diffusion mechanism, which gives a quantitative description for the concentration dependence of the diffusivities as well as a better

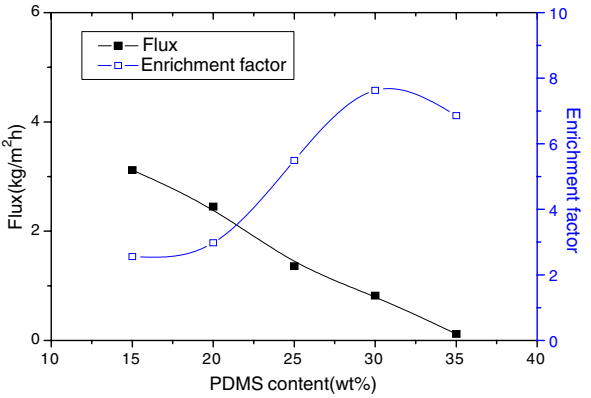


Fig. 7 Effect of PDMS content on pervaporation performance for separation of thiophene–heptane mixture (preparation condition: cross-linking temperature(100 °C),cross-linking content (20 wt.%), cross-linking time (20 h))

representation of polymer-phase equilibrium. Since sulfur enrichment factor was for key consideration, 25 wt.% of PDMS amount should be more practical and recommended.

Effect of Cross-linking Temperature on Pervaporation Performance

Impact of cross-linking temperature on pervaporation performance was depicted in Fig. 8. It can be found that the flux decreased and enrichment factor increased with the increasing of cross-linking temperature. From Fig. 8, at the range of 50–80 and 100–120 °C, the flux decreased severely. From 50 to 80 °C, the cross-linking reaction accelerated sharply with the increase of temperature, and then the cross-linking reaction reacted slowly since the reaction was up to equilibrium. From 100 to 120 °C, it should be supposed that excessive cross-linking reaction occurred which led to lessened free volume. The sulfur enrichment factor increased distinctly by cross-linking modification, which was the effective method for improving pervaporation performance. Although sulfur enrichment factor was for key consideration, 80–100 °C of cross-linking temperature was more preferable because the flux was too little for practical application when cross-linking temperature exceeded 100 °C.

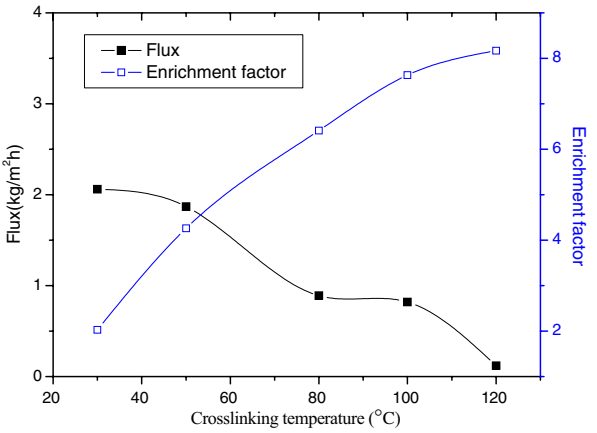


Fig. 8 Effect of cross-linking temperature on pervaporation performance for separation of thiophene–heptane mixture (preparation condition: PDMS content (30 wt.%), cross-linking content (20 wt.%), cross-linking time (20 h))

Effect of Amount of Cross-linking Agent on Pervaporation Performance

Figure 9 revealed the effect of amount of cross-linking agent on pervaporation performance. As shown in Fig. 9, flux decreased and sulfur enrichment factor increased at the certain range with the increase of amount of cross-linking agent. However, sulfur enrichment factor decreased when amount of cross-linking agent exceeded 20 wt.%. Cross-linking influenced the structure of PDMS membranes since the chemical connection occurred between macromolecules and reticular spatial structure formed, which has important influence on pervaporation performance. Interchain free volume lessened with the addition of cross-linking agent, which led to the permeation of feed decreased. Especially, at the range of 15–20 wt.% of cross-linking agent, the flux and enrichment factor changed sharply since cross-linking agent reached equilibrium saturation. Furthermore, exorbitant addition of cross-linking agent brought out lower enrichment factor in respect that the decrease speed of sulfur species was more than that of hydrocarbon species. As the amount of cross-linking agent was up to 20 wt.%, flux and enrichment factor could be more practical and efficient.

Effect of Cross-linking Time on Pervaporation Performance

Effect of cross-linking time on pervaporation performance was illustrated in Fig. 10. As the cross-linking time increased, flux decreased and enrichment factor increased according to Fig. 10. Meanwhile, flux and enrichment factor changed notably within 10 h of cross-linking reaction and there was almost no change after 20 h of cross-linking reaction. Consequently, 20 h of cross-linking time could fulfill the experiment.

Stable Investigation of PDMS–PEI Membranes

A desired PDMS–PEI composite membrane was prepared according to the above optimal preparation condition of membrane, and the effect of long-time operation on pervaporation performance of the membrane was shown in Fig. 11. It was indicated from Fig. 11 that separation performance of the membrane was stable during the 180 h long-time operation of pervaporation. The results show that the composite membrane prepared in this paper was steady, which was consistent with the swelling results shown in Fig. 6 where the maximum

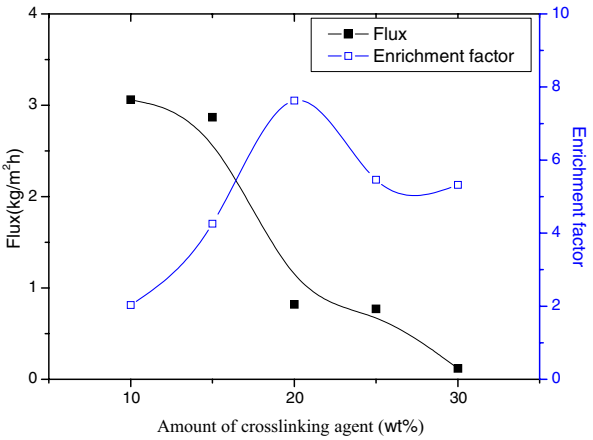


Fig. 9 Effect of amount of cross-linking agent on pervaporation performance for separation of thiophene–heptane mixture (preparation condition: PDMS content (30 wt.%), cross-linking temperature (100 °C), cross-linking time (20 h))

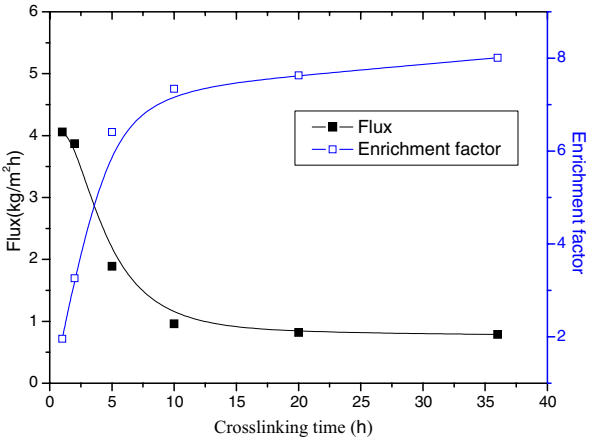


Fig. 10 Effect of cross-linking time on pervaporation performance for separation of thiophene–heptane mixture (preparation condition: PDMS content (30 wt.%), cross-linking temperature (100 °C), cross-linking content (20 wt.%))

of the swelling degree of the membrane in heptane was no more than 4% and in gasoline no more than 5%. Sulfur enrichment factor of the prepared membrane came to 7.6, with the corresponding flux of 0.8 kg/(hm^2). The PDMS–PEI composite membrane could be used for FCC gasoline desulfurization effectively.

Conclusion

Cross-linked PDMS–PEI composite membranes were prepared and employed in pervaporation separation of *n*-heptane–thiophene mixtures. The swelling and stable experiment results of the membranes demonstrated that the sulfur enrichment factor increased distinctly and the membrane performance was stable after cross-linking modification of the membrane. Furthermore, to prepare a desired PDMS–PEI composite membrane, the experimental conditions were confirmed by the present investigation: (1) 80–100 °C of cross-linking temperature was more preferable for practical application; (2) as the amount of cross-linking agent was up to 20 wt.%, the flux and enrichment factor could be more

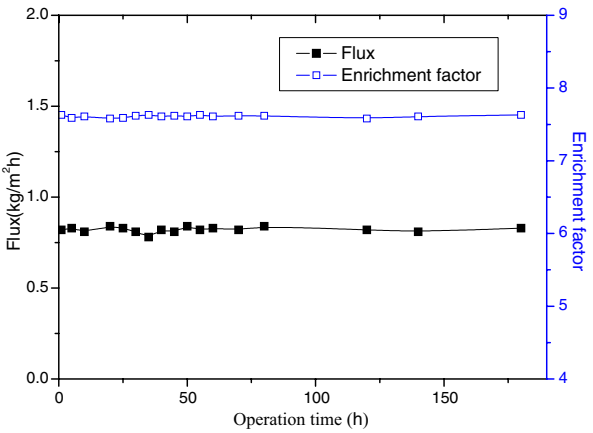


Fig. 11 Effect of long-time operation on pervaporation performance for separation of thiophene–heptane mixture (preparation condition: PDMS content (30 wt.%), cross-linking temperature (100 °C), cross-linking content (20 wt.%), cross-linking time (20 h))

practical and efficient; and (3) as far as flux and sulfur enrichment factor were concerned, 25 wt.% of PDMS amount was more practical and recommended.

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