Pervaporation Performance of Polydimethylsiloxane Membranes for Separation of Benzene/Cyclohexane Mixtures

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ABSTRACT: Crosslinked polydimethylsiloxane/polyetherimide (PDMS/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. The different function composition of the PDMS/PEI composite membranes were characterized by reflection Fourier transform infrared (FTIR) spectroscopy. The surface and section of PDMS/PEI composite membranes were investigated by scanning electron microscope (SEM). The composite membranes prepared in this work were employed in pervaporation separation of benzene/cyclohexane mixtures. Effects of feed temperature, feed composition, concentration of crosslinking agent on the separation efficiency of benzene/cyclohexane mixtures were investigated experimentally. In addition, the swelling rate and stableness of composite membrane during long time operation were studied, which should be significant for practical application. The results demonstrated that the pervaporation method could be very effective for separation of the benzene/cyclohexane mixtures. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2425–2433, 2009

Key words: benzene/cyclohexane; polydimethylsiloxane; polyetherimide; composite membrane; pervaporation

INTRODUCTION

Organic mixtures have conventionally been separated by extractive distillation, extraction, and adsorption process while these separation technologies need high capital investment and high energy consumption.[1] Pervaporation is a very promising membrane technology for separation of organic/organic mixtures, among which separation of aromatic hydrocarbons from aliphatic hydrocarbons is a very important target.[2] Especially, benzene/cyclohexane mixture is a tough system because both have very close boiling points (only 0.6°C difference) and approximately equal molecular volumes.[3] Consequently, a conventional distillation process is not practical for separation of benzene and cyclohexane on account of complexity, high energy consumption, and operating costs. Furthermore, high purity cyclo-

hexane is most often required by petrochemical industries, especially in the production of precursors of nylon (adipic acid, caprolactam) and also in paints and varnishes.[4] For all these reasons, the industry has always been eager to look for a viable alternative to the conventional benzene/cyclohexane separation processes.

Permeability through polymeric membranes is mainly dependent on solubility and diffusion differences between the components of the mixture. Because of the insignificant difference between diffusion of benzene and cyclohexane, a polymer with a high affinity toward one component of the feed is generally preferred as the membrane material, as it is expected to offer a good selectivity.[5] Therefore, in the separation of the benzene/cyclohexane mixtures by pervaporation, many polymer membranes have been studied through various ways including new material synthesis, membrane modification, using carriers to facilitate transport, and molecular dynamics simulation.[6–13] Besides choosing suitable membrane material for separating a given system effectively, the preparation technology of membranes is another very important issue, even in making dense membrane, such as the casting solvent, additive, crosslinking, temperature and moisture, and so on,[14,15] among which the casting solvent is
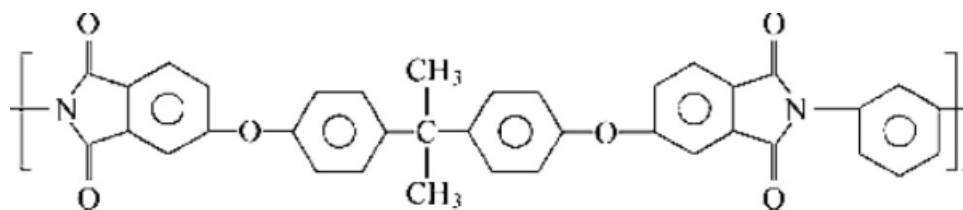
Figure 1 The chemical structure of PEI.

the key factor. High efficiency and low production costs favor composite membranes made up of a polymer layer and a porous carrier. In the field of environmental protection, polydimethylsiloxane (PDMS) membranes are used most often.[16] They display highly satisfactory properties to separate a wide range of solvents, especially those of hydrophobic nature.[17] Bai et al.[18] have studied separation of acetic acid/water mixtures by silicone rubber-coated polyetherimide membranes. It was found that the composite membrane could become either water selective or acetic acid selective, depending on the pore size of the support membrane and the condition of the silicone rubber coating. However, solubility parameter was not used to explain this result.

PDMS has not been extensively investigated for the separation of the benzene/cyclohexane mixtures in the previous research studies nevertheless, and few works on crosslinking modification of PDMS membranes to enhance the pervaporation performance were reported. In this study, microporous polyetherimide (PEI) ultrafiltration membranes were used as support layer of the composite membranes, while PDMS and PEI both have —O— bond so their interface can cement closely. Subsequently, PDMS/PEI composite membranes were prepared and employed to separate the benzene/cyclohexane mixtures. The influences of concentration of PDMS, crosslinking temperature, concentration of crosslinking agent, and crosslinking time, on the separation efficiency of benzene/cyclohexane mixtures were investigated experimentally to obtain 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 Figure 1, was purchased from General Electric (Shanghai, China). N-methyl pyrrolidone (NMP) was obtained from Beijing Yili Fine Chemicals, Beijing, China. n-Heptane was obtained from China Medicine (Group) Shanghai Chemical Reagent Corp. PDMS (viscosity 20 Pa s), ethyl orthosilicate, dibutyltin dilaurate were purchased from Tianjin Chemical Company of China

for the preparation of PDMS membrane. All the chemicals used in the experiments were of analytical grade and were used without any further purification.

Membrane preparation

PEI supporting membranes preparation

PEI was used as a membrane material after being dried in vacuum at 150°C for 6 h. 20 wt % of PEI was dissolved in NMP at 80°C by 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 of 150 μm thickness. The nascent membrane was dried for 10 s at 25 ± 1°C. And then, it was immersed into DI 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 membranes preparation

PDMS, crosslinking agent ethyl orthosilicate and catalyst dibutyltin dilaurate were dissolved in n-heptane at room temperature. After degassed under vacuum, the solution was cast onto the PEI membrane with a scraper of 20 μm thickness. The membrane was first vulcanized under room temperature to evaporate the solvent, and then an automatic electric oven was introduced to complete crosslinking. 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) spectroscopy.[19]

Membrane characterization

SEM spectroscopy

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
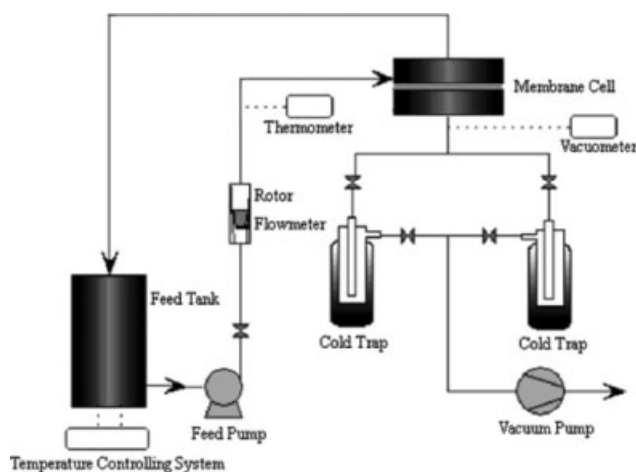
Figure 2 Scheme of the pervaporation apparatus.

with Au/Pd under vacuum conditions. The cross section and surface membrane morphology were taken by SEM (JSM-6301F SEM, JEOL, Japan).

Fourier transform infrared spectra-attenuated total reflection (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 ATR accessory equipped with a ZnSe crystal. For evaluation, a total of 32 scans were performed at a resolution of 4 cm^{-1} at temperature of 25 ± 1°C. Meanwhile, FTIR spectra were recorded within the range of 4000 cm^{-1} to 400 cm^{-1}.The software from Nicolet was used to record the spectra and for the selection of the corresponding backgrounds.

Swelling experiments

A piece of membrane sample was cut out and dried at the 60°C in vacuum drying oven for 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 swelling rate η was defined as

$$\eta = \frac{m_2 - m_1}{m_1} \times 100\% \tag{1}$$

Pervaporation experiments

Pervaporation experiment apparatus used in this study was shown in Figure 2.[20] The membrane was positioned in the stainless steel permeation cell, and the effective surface area of the membrane in contact with the feed mixture 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, and the feed temperature was monitored by a digital vacuometer. Pervaporation experiments were carried out by maintaining atmospheric pressure on one side (feed) and about 200 Pa using a vacuum pump on the other side (permeate). After a steady state was obtained (about 1 h after start-up), the permeation was collected in the cold traps and condensed by liquid nitrogen. The compositions of the feed solution and permeate were analyzed by gas chromatography (SHIMADZU, GC-14C). The results for pervaporation were reproducible, and the errors inherent in the pervaporation measurements were less than 2%. Separation performances of the membranes can be evaluated on the basis of total flux and separation factor.

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 mass of permeate during the operation time Δt at steady state, and A is the effective membrane area. Then, the selectivity of a membrane in a binary system is obtained as,

$$\alpha = \frac{y_a/y_b}{x_a/x_b} \tag{3}$$

where α is separation factor; x and y represent the weight fractions of corresponding solute in feed and permeate, respectively; subscripts a and b refer to the more permeable component (benzene) and the less permeable one (cyclohexane), respectively.

THEORY

The membrane material and its intrinsic properties are very pivotal for the separation applications. Especially for pervaporation process, solubility parameter is effective to characterize the interaction intensity between solvent and membrane, so it is an important way for membrane materials selection. Solubility parameter (δ) was proposed first by Hildebrand,[21] which was defined as the square root of cohesive energy for unit volume molecule. The solubility parameter which depended on chemical and physical structure of material is important to characterize the interaction intensity among simple liquids and closer solubility parameter results in

<div align="center">

TABLE I
Properties of Benzene and Cyclohexane

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	bf (°C)	Density at 25°C (g/mol)	Molar volume (cm³/mol)	Collision diameter (nm)	Solubility parameter $(J/cm^3)^{1/2}$			
					δ_d	δ_P	δ_h	δ
Benzene	80.1	0.87	89.4	0.526	18.4	0	2.0	18.6
Cyclohexane	80.7	0.78	108.7	0.606	16.8	0	0.2	16.8

higher attraction for permeation components in membrane phase. The closer solubility parameter between two substances, the better it will be for their mutual solubility. The δ value of certain substance can be represented by its three components: dispersion power (δ_d), polarity power (δ_P) and hydrogen bond power (δ_h). The relation is expressed as

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (4)$$

To a ternary system, including component A, component B and membrane, the component which is expected to preferred permeation should exert strong dissolution performance and have closer solubility parameter with polymer molecule. That is to say, whether or not the membrane can fulfill its separation goal depends on the relative permeation capability of the membrane to components. Higher attraction results in the increased solubility for permeation components in the membrane. However, ultra-strong affinity will lead to membrane swelling. In summary, it is a feasible way to evaluate the selectivity of the membrane by estimating the interaction between polymer and solvent molecule.

RESULTS AND DISCUSSION

Membrane materials selection for the separation of the benzene/cyclohexane mixtures

To select suitable membrane material for benzene/cyclohexane system, the molar volumes, collision diameters, solubility parameters, and some representative physical properties of benzene and cyclohexane are listed in the Table I by query.[22,23] The solubility parameters, shown in Table I, indicate that the hydrogen bonding component (δ_h) of benzene solubility is stronger than that of cyclohexane. It is expected that this high hydrogen bonding component of benzene interacts with free polar groups in the membrane, as explained by Yamasaki et al.[24] who compared the retention time of benzene, n-hexane, and cyclohexane through a column filled with PVA polymer. The solubility parameter of PDMS material is 21.01 $J^{1/2}/cm^{3/2}$,[25] which is closer to benzene than that of cyclohexane, so PDMS material act as top layer of the composite membrane. Generally, top layer controls the flux and selectivity of the composite membrane. The porous support membrane is

to provide the mechanical strength for the selective layer in high operational pressures, so it does not influence the permeation data in this work controls the flux and selectivity of the composite membrane. Therefore, PDMS/PEI membrane can fulfill the separation goal.

On the other hand, Huang et al. have reported that the molecular size of permeate has strongly influenced the permeation and separation of benzene/cyclohexane mixtures in pervaporation process.[26] Comparing benzene molecule with the cyclohexane molecule, the former has smaller molecular size than the latter as listed in Table I. Consequently, it is expected that the permeability of the smaller molecular size diffuse predominantly in the membrane.

SEM photographs of PDMS/PEI composite membrane

SEM permits imaging cross section and surface membrane morphology. The cross section morphology of the PDMS/PEI membrane was shown in Figure 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 ultra-thin skin layer and a porous finger-like structure. Moreover, the
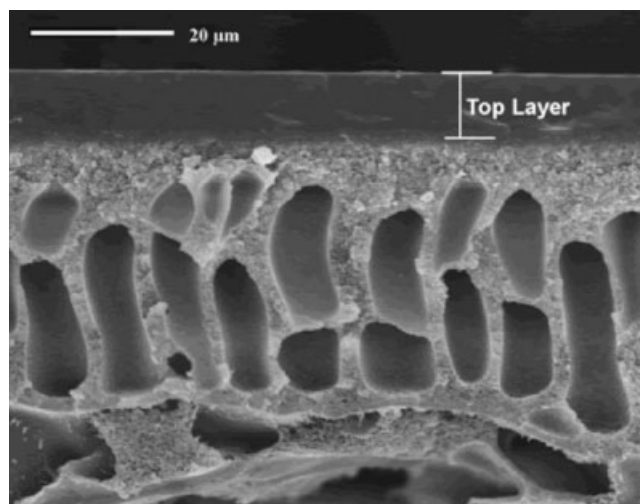

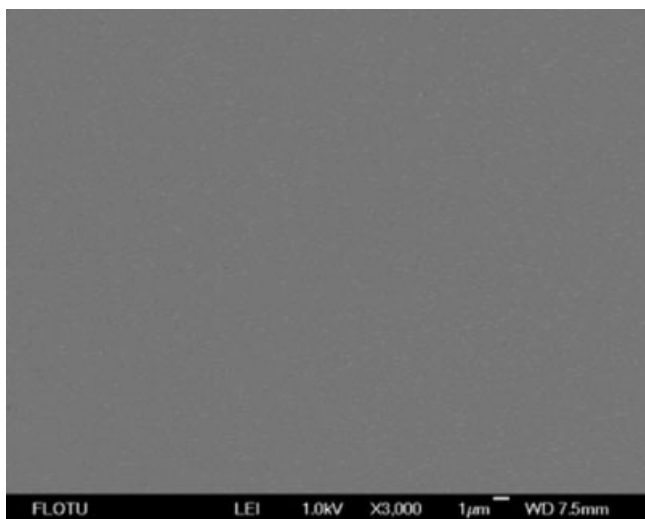**Figure 3** The cross section morphology of the PDMS/PEI composite membrane.

Figure 4 The surface morphology of the PDMS/PEI composite membrane.

thickness of the PDMS top layer was determined to be about 11 μm from the SEM photograph by the scale tab. The surface morphology of the PDMS/PEI membrane was shown in Figure 4. From this figure, the originally porous surface of the PEI substrate 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 any pinhole or crack, which is important for the practical application.

FTIR spectra of PDMS/PEI composite membrane

The attenuated total reflection FTIR spectroscopy is a commonly used method to characterize the chemical structure of the surface.[27] The ATR technique enables the identification of specific molecules and groups located within 100 nm from the surface layer. To obtain detailed information about the structural changes of PDMS/PEI membranes resulting from crosslinking modification, FTIR spectra of the surface of PDMS/PEI membranes were recorded in Figure 5 using the ATR technique. From Figure 5(a), a peak at 1260 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 cm^{-1} to 730 cm^{-1} (CH_3 out-of-plane bending and Si—C stretching), 2890–3000 cm^{-1} and 1000–1150 cm^{-1} (Si—OH stretching) and 860–920 cm^{-1} (Si—OH angle bending vibration), respectively. Comparing with the noncrosslinked membrane [from Fig. 5(a)], the spectra of the crosslinked membranes [from Fig. 5(b)] displayed that absorbance signals of Si—OH evidently weakened. These changes were the evidences of crosslinking reaction of hydroxyl-terminated PDMS

with tetraethylorthosilicate under dibutyltin dilaurate catalysis.[28] The crosslinking reaction is shown as the following formula:
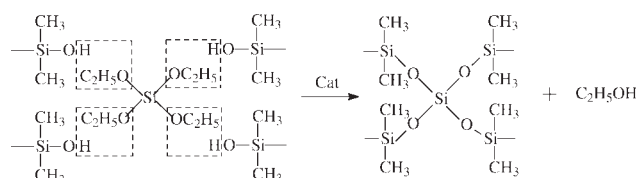
Results of swelling experiment

The swelling results of PDMS/PEI composite membranes in the different feed concentrations were given in Figure 6, where it could be observed that the rate of swelling increased with the increasing immerging time and then reached the equilibrium slowly within 5 h. It has also been shown that the swelling rate of membrane increased as benzene concentration increased. These phenomena indicated
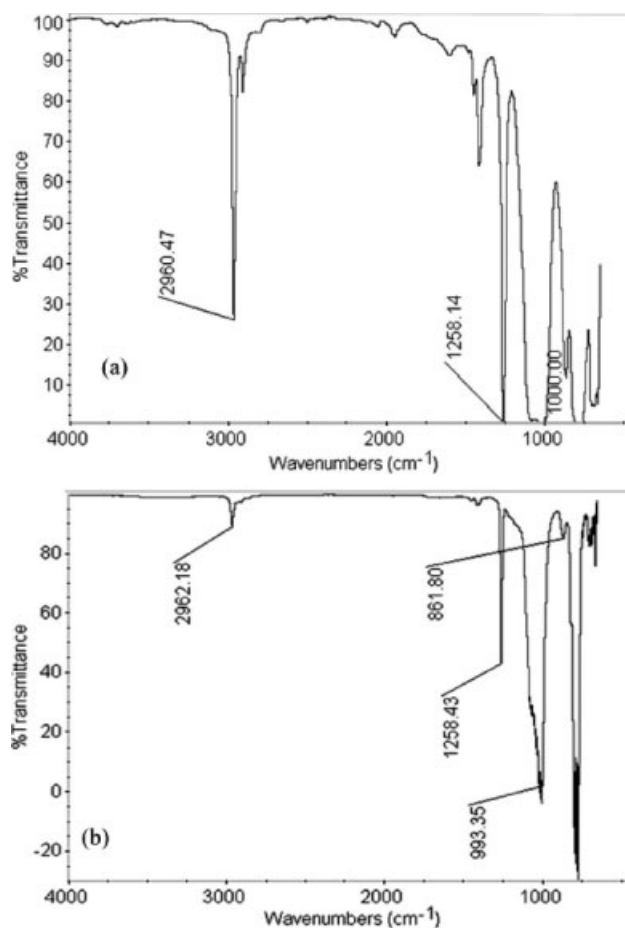

Figure 5 FTIR spectra of PDMS/PEI composite membrane. (a) Before corsslinking modification, (b) Afer crosslinking modification.
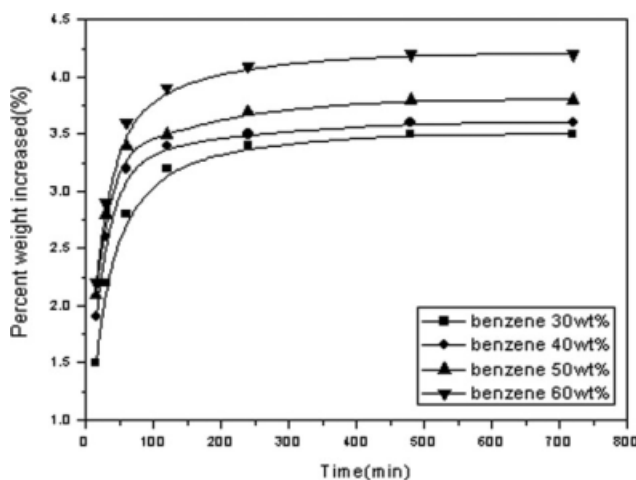
Figure 6 Swelling behavior of the PDMS/PEI composite membrane, [preparation condition: PDMS content (30 wt %), crosslinking temperature (100°C), crosslinking content (20 wt %), crosslinking time (20 h)].

Figure 7 Effect of feed temperature on total flux [preparation condition: PDMS content (30 wt %), crosslinking temperature (100°C), crosslinking content (20 wt %), crosslinking time (20 h)].

that benzene was more easily dissolvable in PDMS membrane, which was due to the stronger interaction between benzene and membrane according to the solubility parameter. All these experimental results showed consistence with the fact that benzene mainly stimulated the membrane swelling further and crosslinking was an effective modification way for PDMS membrane to reduce the swelling. Sun and Ruckenstein[29] also showed that the swelling of different membranes was mainly due to the sorption of benzene rather than cyclohexane. Moreover, it can be observed that the maximum swelling rate in the solution was not more than 5%, which should be suitable for practical application. Thus, all swelling behaviors aforementioned were attributed to better affinity of PDMS/PEI membrane for benzene rather than cyclohexane.

Effect of feed temperature on pervaporation performance

Figures 7 and 8 illustrate the effect of feed temperature on total flux and separation factor, respectively. It can be observed clearly that both permeation flux and separation factor changed significantly with the rise of feed temperature from 50 to 80°C. It can be also seen that the flux increased and separation factor decreased with feed temperature increasing, which was consistent with common rule.[30] As expected, all the experimental evidences confirmed an increase in permeability and a decrease in selectivity of membranes with increasing temperature.[31] One reason is that the increased mobility of the permeating molecules in the bulk feed solution with the feed temperature increasing from 50 to 80°C, results in higher partial vapor pressure and provides greater driving force for the permeating components.
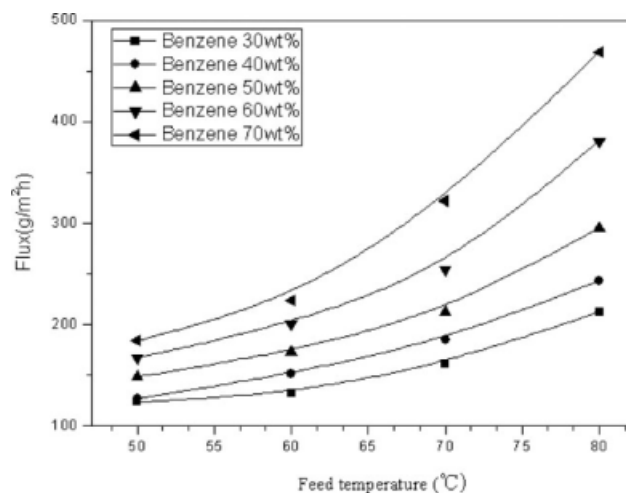
Also, the increased mobility of the permeating molecules within the membrane will facilitate the transfer of the components. The other reason is that the thermal motion of polymer chains became more violent at higher temperature and caused larger available free volume of polymer matrix for diffusion, leading to more availed components permeating trough the membrane. In a word, the increase in total flux with temperature was due to the increase of the mobility of individual permeating molecules caused both by the temperature and by the enhanced mobility of the polymer segments. On the other hand, the increase in the degree of swelling of the membrane with temperature results in more cyclohexane transport, which led to the decrease of selectivity toward
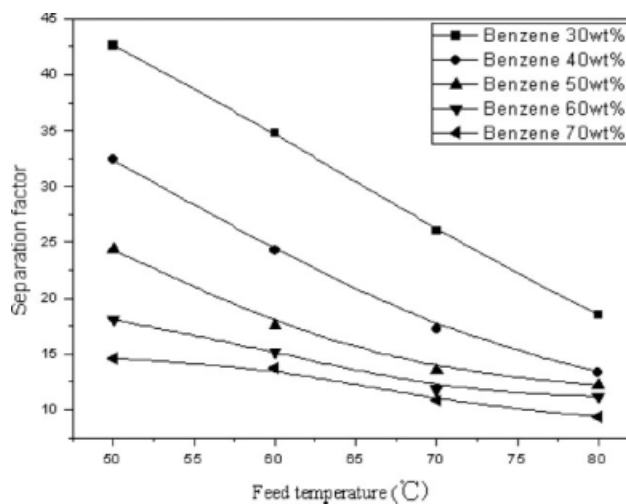

Figure 8 Effect of feed temperature on separation factor [preparation condition: PDMS content (30 wt %), crosslinking temperature (100°C), crosslinking content (20 wt %), crosslinking time (20 h)].
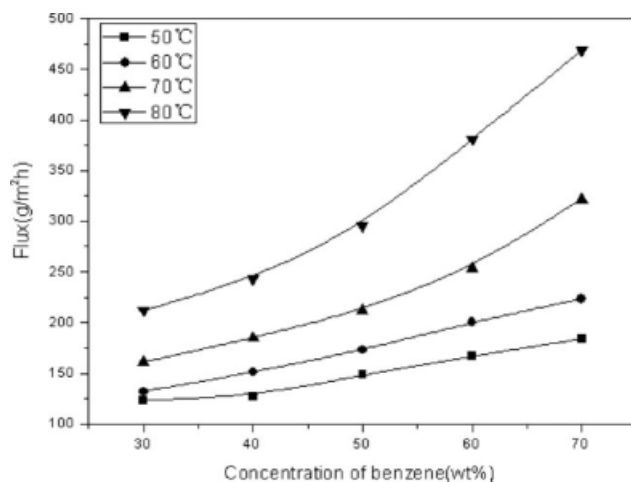
Figure 9 Effect of concentration of benzene on total flux [preparation condition: PDMS content (30 wt %), crosslinking temperature (100°C), crosslinking content (20 wt %), crosslinking time (20 h)].

benzene. By all given reasons, both mass transfer coefficients of components in the feed and sorption of components into the membrane increase with feed temperature,[32] so total flux increased with temperature. Moreover, the continuous increase of feed temperature weakened the difference of solubility and diffusion velocity of benzene and cyclohexane, and caused the decrease of separation factor.[33]

Effect of feed composition on pervaporation performance

The effects of benzene content in feed on the total flux and separation factor are depicted in Figure 9 and Figure 10, respectively. The corresponding benzene contents in the feed under consideration were in the vicinity from 30 to 70 wt %. From Figure 9, it can be found that the flux increased and separation factor decreased with increasing benzene content in feed. When the benzene content in feed increased, an extensive swelling of the membrane occurred due to the strong affinity of benzene to the membrane, which was attributed to the fact that benzene permeates more easily than cyclohexane at the same temperature. It is well-known that a remarkable swelling of polymer membranes leads to an opened membrane structure and consequently an enhancement of permeation in the polymer membranes. Therefore, total flux increased due to the enhanced activity of polymer chains and bonds.

From Figure 10, separation factor decreased with the increase of concentration of benzene. It is to say that the benzene permselectivity of the membranes was lowered with increasing benzene content. In general, the permselectivity of liquid mixtures through polymer membranes by pervaporation

depends on both the differences in the solubility of permeants in polymer membranes (the sorption separation process) and in the diffusivity of permeants in polymer membranes (the diffusion separation process), namely the solution-diffusion theory.[34] Accordingly, the permselectivity for the benzene/cyclohexane mixtures through the membrane depends on both solubility and diffusibility. In the first step, the benzene molecules which have a higher affinity for the membranes than the cyclohexane molecules are preferentially sorbed into the membrane in the sorption process. Then, in the second step the diffusivity of these molecules in the diffusion separation process is significantly dependent on the molecular size and shape. In this case, increasing benzene content led to a higher permeation rate and lower separation factor.

Effect of concentration of crosslinking agent on pervaporation performance

PDMS material behaved stronger affinity to benzene and this interaction increased the solubility of benzene in membrane to fulfill separation purpose. However, the affinity was so strong that the membrane was prone to present excessive swelling. In our experiments, swelling of uncrosslinked membrane was too severe so that the crosslinking modification was quite necessary. Considering the practical application, what is more important for crosslinking modification was that the swelling resistance of membrane and the steadiness of separation performance improved distinctly after crosslinking modification.

Figures 11 and 12 reveal the effect of concentration of crosslinking agent on pervaporation performance. As shown in Figure 11, flux decreased with the
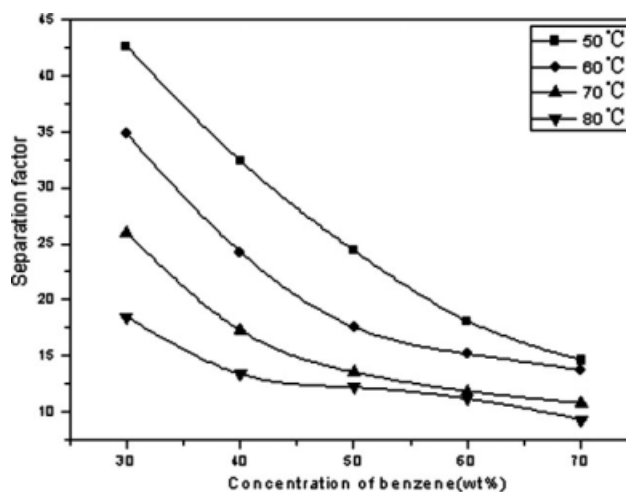

Figure 10 Effect of concentration of benzene on separation factor [preparation condition: PDMS content (30 wt %), crosslinking temperature (100°C), crosslinking content (20 wt %), crosslinking time (20 h)].
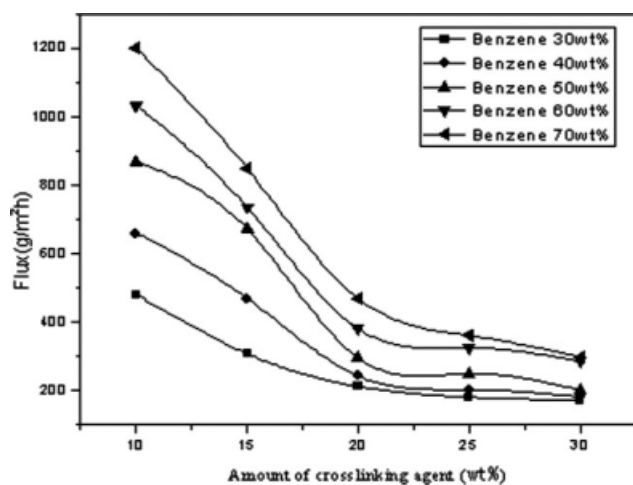
Figure 11 Effect of concentration of crosslinking agent on total flux [preparation condition: PDMS content (30 wt %), crosslinking temperature (100°C), crosslinking time (20 h)].

increase of concentration of crosslinking agent with increase from 10 to 30 wt %, and flux decreased sharply with crosslinking agent changing between 10 and 20 wt %. As shown in Figure 12, separation factor increased at the certain range with the increase of concentration of crosslinking agent. However, separation factor decreased when concentration of crosslinking agent exceeded 20 wt %. From FTIR spectrum results as shown in Figure 5, crosslinking 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 crosslinking agent, which led to the decrease of permeation of feed.
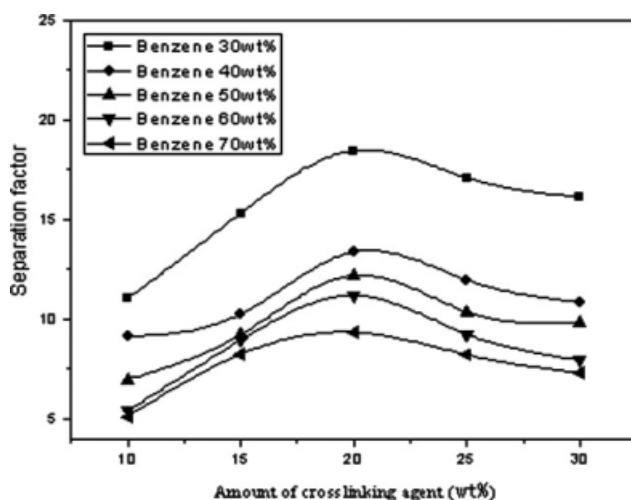

Figure 12 Effect of concentration of crosslinking agent on separation factor [preparation condition: PDMS content (30 wt %), crosslinking temperature (100°C), crosslinking time (20 h)].

Especially, exorbitant addition of crosslinking agent brought about lower flux and membrane intensity decrease for solubility restrict to crosslinking agent and these results were unfavorable for practical application. For this reason, at the range of 15–20 wt % of crosslinking agent, the flux and enrichment factor changed sharply since crosslinking agent reached equilibrium saturation. Furthermore, as the concentration of crosslinking agent was up to 20 wt %, total flux decreased to ultra low level. Under the 20 wt % of the crosslinking agent concentration conditions, flux and separation factor both exerted higher level. In conclusion, 20 wt % of crosslinking agent concentration was more practical and efficient since ultra low level flux was unwanted for the scale up of membrane technology.

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 as Figure 13. It was indicated from Figure 13 that separation performance of the membrane was stable during the 180-h-long time operation of pervaporation. The results revealed that this kind of membrane had the property of resisting pollution and the composite membrane prepared in this article was steady. After some time of run, swelling balance of the membrane reached to stable flux and separation factor, which was consistent with the swelling results shown in Figure 6 where the maximum of the swelling rate of the membrane in the feed was no more than 5%. To sum up, average separation factor of the prepared membrane came to 13.2, with the corresponding flux of 218 g/(m²h) during the long time operation of 180 h. From all
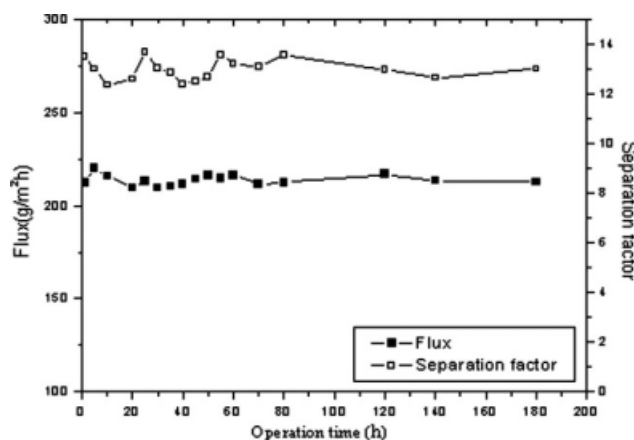

Figure 13 Effect of long time operation on pervaporation performance [preparation condition: PDMS content (30 wt %), crosslinking temperature (100°C), crosslinking content (20 wt %), crosslinking time (20 h)].

above results, the PDMS/PEI composite membrane could be used for separation of benzene/cyclohexane mixtures effectively.

CONCLUSIONS

Crosslinked PDMS/PEI composite membranes were prepared, characterized by FTIR, SEM, and employed in pervaporation separation of benzene/cyclohexane mixtures. The swelling experiment results of the membranes demonstrated: the degree of swelling increased with the increasing immerging time and benzene concentration; the maximum of the swelling rate in the solution was no more than 5%. Moreover, it was found that the increase in feed temperature yielded higher total fluxes and lower selectivity to benzene, and experiments also showed that PDMS membrane was more selective to benzene than to cyclohexane for the difference in solubility parameter. Experimental results indicated that, with the increase of the content of benzene in feed, the total flux increased correspondingly while the separation factor of benzene decreased simultaneously.

Crosslinking modification was important for the swelling resistance of membrane so that pervaporation performance depended on the condition of crosslinking. After crosslinking modification, not only the separation factor increased distinctly, but also the membrane performance was stable, which was the most significant point for practical application. Experimental results demonstrated that 20 wt % of crosslinking agent was optimal as far as flux and separation factor were concerned. Finally, a desired PDMS/PEI composite membrane was obtained with average separation factor of 13.2 and flux of 218 g/(m^{2}h) during the long time operation of 180 h. From all the earlier results, separation of benzene/cyclohexane mixtures can be conducted effectively by pervaporation using crosslinked PDMS/PEI composite membranes.

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