Preparation and characterization of poly(dimethylsiloxane)-polytetrafluoroethylene (PDMS-PTFE) composite membrane for pervaporation of chloroform from aqueous solution

De Sun*,**, Bing-Bing Li**, and Zhen-Liang Xu*,†

*State Key Laboratory of Chemical Engineering, Membrane Science and Engineering R&D Lab.,
Chemical Engineering Research Center, East China University of Science and Technology (ECUST),
130 Meilong Road, Shanghai 200237, China
**Department of Chemical Engineering, Changchun University of Technology, 2055 Yanan Street,
Changchun 130012, P. R. China

Abstract−Hydrophobic polydimethylsiloxane - polytetrafluoroethylene (PDMS-PTFE) flat-sheet membranes for pervaporation (PV) of chloroform from aqueous solution were successfully fabricated by solution casting method. The structures and the performance of the membranes was characterized by X-ray diffraction (XRD), scanning electron microscope combined with energy dispersive X-ray spectroscopy (SEM-EDXS), Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA) and the tests of contact angle and mechanical properties. The adding of PTFE particles (<4 μm) in the PDMS matrix enhanced the crystallinity, hydrophobicity, mechanical strength and thermal stability of the membranes. The examinations showed that the PTFE filled PDMS membranes exhibited striking advantages in flux and separation factor as compared with unfilled PDMS membranes. All the filled PDMS membranes with different PTFE content showed excellent PV properties for the separation of chloroform from water. When the content of the PTFE additive in PDMS composite membrane was 30 wt%, membrane performance was the best at feed temperature 50 °C and permeate-side vacuum 0.101 MPa. For the 30% PTFE-PDMS membrane, with the increase of the feed temperature from 30 to 60 °C, the total, water and chloroform fluxes as well as the separation factor increased, the apparent activation energy (ΔEa) of total, chloroform and water were 21.08, 66.65 and 11.49 KJ/mol, respectively, with an increase of chloroform concentration in the feed from 50 to 950 ppm, total, water and chloroform fluxes increased but the separation factor decreased.

Key words: Poly(dimethylsiloxane), Polytetrafluoroethylene, Membranes, Pervaporation

INTRODUCTION

The contamination of drinking and ground water by volatile organic compounds (VOCs), especially chlorinated organic compounds such as chloroform, dichloromethane and 1,1,2-trichloroethylene generated from household, agricultural and industrial purposes [1-3], is a major environmental and economic problem. It is well known that chlorinated organic compounds are potentially dangerous and increase the risk of cancer [4-7]; consequently, these chemicals have to be removed from contaminated water. For the separation of VOCs from low concentration contaminations, traditional technologies, such as distillation, adsorption and air stripping, might not be applicable for the reason of economy and second pollution, and pervaporation (PV) appears potentially attractive [8-11] for its low operating temperature, minimal energy expenditure, no emission to the environment and no second environment pollution [10-12].

Like other membrane materials, PV materials should also meet the requirements of high transport performance as well as thermal and structure stability over time [13]. PDMS is commonly used as VOCs-permselective membrane; its hydrophobic and rubbery prop-erties make it a very good PV membrane material with good PV properties of flux, selectivity and stability [14]. Its hydrophobicity can enhance organics' sorption and its rubbery property makes it favorable for the diffusion of dissolved organics. To make the PV process more economically attractive, many studies on PDMS modifications have been done to improve membrane organophilic properties [15-23]. The modification methods include filling [19,20], grafting [15,16,18], blending [17], coating [22,23] and so on. Ohshima et al. [15] prepared cross-linked poly(dimethylsiloxane) membranes usingpoly(dimethylsiloxane)dimethylmethacrylate macromonomer (PDMSDMMA) and divinyl compounds divinyl perfluoro-n-hexane (DVF) and used them in the separation of chloroform and water mixtures at a temperature of 40 °C for a 0.05 wt% chloroformfeed. It was found that these membranes exhibited a normalized permeation rate of 1.9×10^{-5} kg m/(m²·h) and a separation factor for chloroform/water of 4850, yielding a separation index of 9110. Uragami et al. [16] studied PV separation of chloroform/water mixtures using poly(methylmethacrylate)-poly(dimethylsiloxane) (PMMA-g-PDMS) graft copolymer membranes. It was shown that the chloroform-permselectivity and normalized permeation rate of the PMMA-g-PDMS membranes increased dramatically when dimethylsiloxane (DMS) content is more than 40 mol%. Lau et al. [18] prepared a silicone rubber membrane by crosslinking silylstyrene-oligomer containing

†To whom correspondence should be addressed.
E-mail: chemxuzl@ecust.edu.cn

-SiH groups with divinylpolydimethylsiloxane for the PV separation of chloroform-water. They obtained the highest separation factor of 2448 at the chloroform feed concentration of 60 ppm and the highest chloroform flux of 25.51 g/m²·h at the chloroform concentration of 700 ppm.

Among these modification methods, filling is very attractive because of its simplicity. Several kinds of filling materials which have the ability of organics absorption, such as polyphosphazene nanotube [24], carbon black [25] and nanosilica [19], have been added into PDMS. Investigations [15,26-28] showed that PV performance for the removal of organics from water had been enhanced by blending organophilic fluorinated polymers in base membranes making materials. Poly(tetrafluoroethylene) (PTFE) has been successfully used in the fabrication of PVDF-PTFE hollow fiber membrane for the desalination of sea water for its excellent thermal stability and super-hydrophobicity in nature [29].

In this study, novel composite membranes using PTFE filled PDMS as the active layer and PET non-woven fabrics as the support layer were developed. The membranes were used for the PV process of removing chloroform from aqueous solution in an expectation of achieving both high separation factor and high permeation flux. The effects of PTFE content and operating conditions including feed temperature and chloroform concentration on the separation performance of the filled composite membrane were examined.

EXPERIMENTAL

1. Materials

PET non-woven fabric as membrane support layer was obtained from Changzhou Haoxin Insulation Material Co. Ltd. (PR China). PDMS (Silicone Rubber 107, M_w5000), cross linking agent ethyl silicate and curing agent dibutyltin dilaurate were purchased from Shanghai resin Company (PR China). PTFE particles (Dyneon TF-9207) were used as the additive and their structural parameters are listed in Table 1 according to Minnesota Mining and Manufacturing Company (America). Reagent grade n-heptane and chloroform were obtained from Shanghai Ruen Jie Chemical Reagent Company (PR China).

2. Membrane Preparation

The PDMS membranes were prepared by solution casting method. For the preparation of unfilled PDMS membrane, a casting solution containing 17 wt% PDMS was prepared by dissolving PDMS, crosslinker (ethyl silicate) and curing agent (dibutyltin dilaurate) in the solvent (n-heptane) with a ratio of 10 : 1 : 0.5 (in weight). The solution was subjected to homogenization by magnetic stirrering of 3 hours; after the preparation of PDMS casting solution, it was poured onto the surface of non-woven fabric for 15 seconds. The PDMS coated flat sheet membrane was dried in the sterile room at room temperature for 24 hours, and then the cross linked unfilled

PDMS flat sheet composite membrane was prepared.

For the preparation of the PTFE filled PDMS membranes, PTFE particles were dried for 24 hours at 80 °C in a vacuum oven and then were evenly dispersed in the prepared PDMS solution by stirring for 3 hours. The rest of the preparation processes were the same as that of the unfilled membranes.

To investigate the effect of PTFE on physical characterization and PV performance of the PDMS membranes, the PTFE filled PDMS composite membranes with different PTFE contents were prepared. For simplicity, membrane samples were designated as 0% PTFE-PDMS, 10% PTFE-PDMS, 20% PTFE-PDMS, 30% PTFE-PDMS, 40% PTFE-PDMS and 60% PTFE-PDMS according to the PTFE content. In addition, to study the influence of the physicochemical properties of the filled membranes, unfilled/filled PDMS membranes without support were also prepared.

3. Membrane Characterization
3-1. SEM-EDXS

Membrane samples were fractured in liquid nitrogen and then coated with gold, top surface and cross-section structures and the distributions of chemical elements were observed by a scanning electron microscope (SEM) (JEOL Model JSM-5600 LV, Japan) equipped with an energy dispersive X-ray spectroscopy (EDXS) analysis system (EDAX-Falcon, America).

3-2. FT-IR

Fourier-transform infrared spectroscopy (FT-IR) spectra of the samples were recorded in the 500-4,000 cm⁻¹ range using a Nicolet-560 spectrometer (Nicolet, America).

3-3. XRD

X-ray diffraction spectra of the PTFE and the filled PDMS membranes were obtained at room temperature using a D-MAXIIA X-ray diffractometer (RIGAKU, Japan). The diffractograms were measured at a scanning speed of 10°/min in the 2θ range of 5-60° by means of a tube voltage of 40 kV and tube current of 30 mA.

3-4. Mechanical Property

The mechanical measurements were performed on QJ210A Stress Testing System (Shanghai Qingji Instrument Technology Co., Ltd., China) at room temperature. The flat sample of settled width of 15 cm was clamped at both ends and pulled in tension at a constant elongation speed of 50 mm/min with an initial length of 25 cm.

3-5. Contact Angle

The contact angle of water was measured by a JC2000D1 contact angle meter (CA-D type, Shanghai Zhongcheng Digital Technology Apparatus Co. Ltd., China) at RT and 60% relative humidity. Water droplets (sessile drops volume ca. 0.2 μL) were placed on the membrane for 10 seconds, and then the dimensions of the droplets were measured using the system software.

3-6. TGA

The thermal stability of the PTFE filled PDMS composite membranes was examined by PerkinElmer TG/DTA thermogravimetric analyzer from 30 to 800 °C at a heating rate of 10 °C min⁻¹ with a nitrogen flow of 25 mL min⁻¹.

4. Swelling Behavior

The membrane swelling experiments can help one to understand the interactions between the membranes and the liquid penetrants. Pieces of dried (un)filled PDMS membranes without support were weighed by a highly sensitive electronic balance (ALC-1100.2, Sartorius, Germany) with an accuracy of 0.0001 g and were immersed

Table 1. PTFE structure characteristics

Density/ (g/cm³)	Specific surface area/(m²/g)	Active component/ (%)	Particle size	
			Primary/ (nm)	Secondary/ (μm)
2.165	17	100	120	4

in a chloroform aqueous solution for 48 h at 50 °C. Taken out from the solution, the swollen membranes were gently wiped to get rid of the surface liquid and were weighed immediately. The data in this paper are average values of four to five measurements. The degree of swelling of the membrane, DS (wt%), was determined by

$$DS=(M-M_0)/M_0 \tag{1}$$

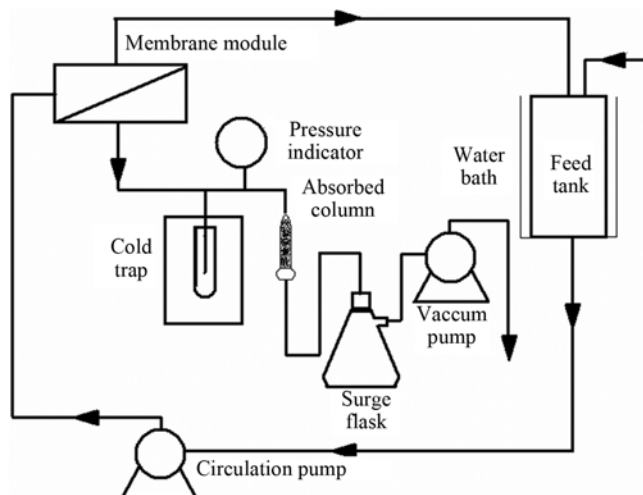where M is the mass of the swollen membranes and M_0 is the mass

of the dried membranes. In this study, the swelling behaviors of PTFE filled membranes with different PTFE content were studied in the condition of different feed concentrations.

5. PV Performance

Fig. 1 is the schematic diagram of homemade PV apparatus used in this case. PV experiments were conducted using a cross-flow laboratory scale flat membrane unit. The feed side is sealed by a Viton 'o' ring spacer with a relatively small effective membrane area of 27 cm². Before use, the Viton 'o' ring spacer was soaked in the feed solution for 24 hours. Dilute chloroform/water solution was used as the feed in a 3 L feed tank that is circulated by a pump. The feed solution was pumped into the membrane cell with a high flow rate of 50 L/h to minimize the effect of concentration polarization. The feed tank was kept in a water bath at a constant temperature controlled by a temperature controller. The permeate-side vacuum pressure was obtained through a vacuum pump. After the operation reached a steady state (about 1 hour after starting), the permeate vapor samples were collected in a liquid nitrogen trap which had been weighed previously. The cold trap with frozen sample was weighed, and then 100 mL pure water was poured into the cold trap. Thereafter, the sample was dissolved in the cold trap for 10 minutes under ultrasonic processing condition. The diluted sample was analyzed by gas chromatography with an electron capture detector (ECD) (Shimadzu, GC2014C) by headspace sampling (HS-16A, Shanghai Kemeiao Scientific Instrument Co. Ltd., China), and the permeate vapor sample was calculated through back-calculating method. The calculation of the permeation flux J (g·m⁻²·h⁻¹), separation factor

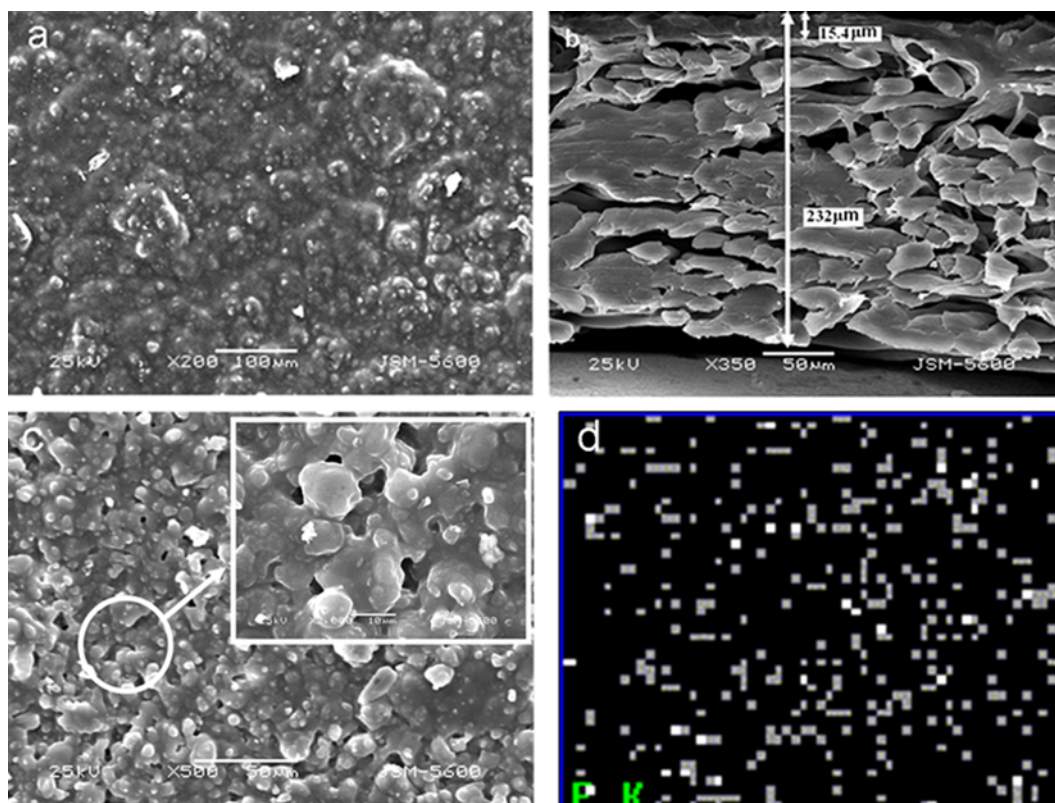Fig. 1. Schematic diagram of PV apparatus.

Fig. 2. SEM-EDXS photographs of the PTFE-PDMS composite membranes. (a) Top surface (200×) and (b) cross-section (350×) of the 30% PTFE-PDMS composite membrane; (c) top surface (500×) of the 40% PTFE-PDMS composite membrane; (d) fluorine element area profile of the 30% PTFE-PDMS composite membrane.

α and permeate separate index PSI is defined as

$$J=m/(\Delta t \times A) \qquad (2)$$

$$\alpha=(y_{chloroform}/y_{water})/(x_{chloroform}/x_{water}) \qquad (3)$$

$$PSI=(\alpha-1) \times J \qquad (4)$$

where m is the total amount of permeate collected during the experimental time interval Δt of 1 hour at steady state, A is the effective membrane area, x and y represent the mole fraction of a component in the permeate and in the feed.

RESULTS AND DISCUSSION

1. Membrane Characterization

1-1. SEM-EDXS Analysis

To investigate the morphology of PTFE filled PDMS membranes and the distribution of PTFE particles within them, SEM-EDXS characterizations of the composite membranes were perfomed. As shown in Fig. 2(a), the 30% PTFE-PDMS membrane is dense with no connected macroscopic voids and PTFE dispersed evenly (EDXS, shown in Fig. 2(d)) in PDMS matrix due to the good compatibility between organophilic PTFE particles and organophilic PDMS. The surface of the filled membrane has a rough appearance which increases effective contact area that could result in an enhanced flux [30,31]. However, the 40% PTFE-PDMS membrane exhibits a greater number of PTFE aggregates on the surface than the 30% PTFE-PDMS membrane does, and appreciable voids between PTFE and PDMS occurred as shown in Fig. 2(c). Fig. 2(b) shows that the PTFE filled PDMS top layer of about 15 μm in thickness tightly adhered to the surface of the non-woven fabric support layer.

1-2. FT-IR Analysis

Fig. 3 shows the FT-IR spectra of PTFE (a) and PTFE filled PDMS membranes with various PTFE contents (b). As seen in Fig. 3(a), the absorption peaks in the wave number region around 1,240 cm^{-1} and 1,150 cm^{-1} are originated from the C-F bond of the PTFE. The peaks of 640 cm^{-1} and 556 cm^{-1} represent the polarization region in PTFE [32]. We can see in Fig. 3(b), the absorption peaks at around 1,072 and 1,009 cm^{-1} in the filled membranes correspond to stretching vibrations of Si-O-Si. The peaks at 1,255 cm^{-1} and 1,415 cm^{-1}
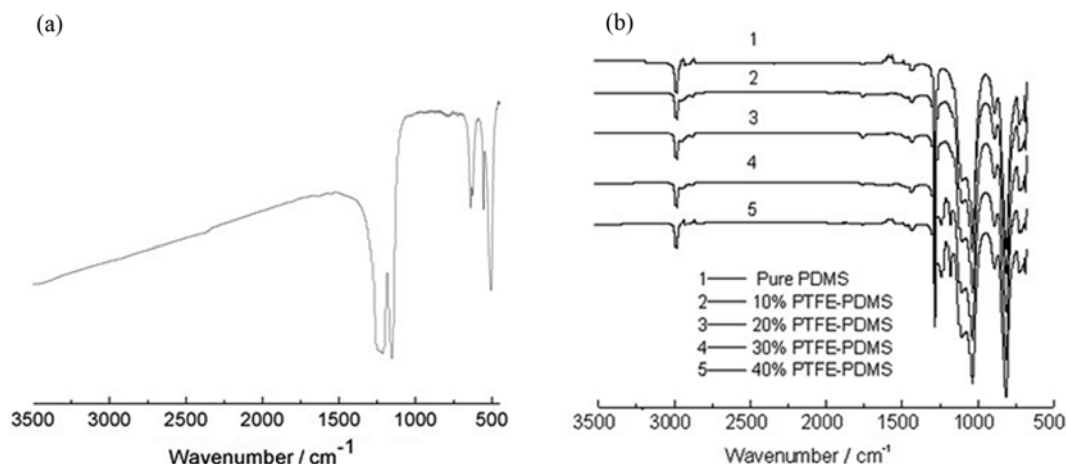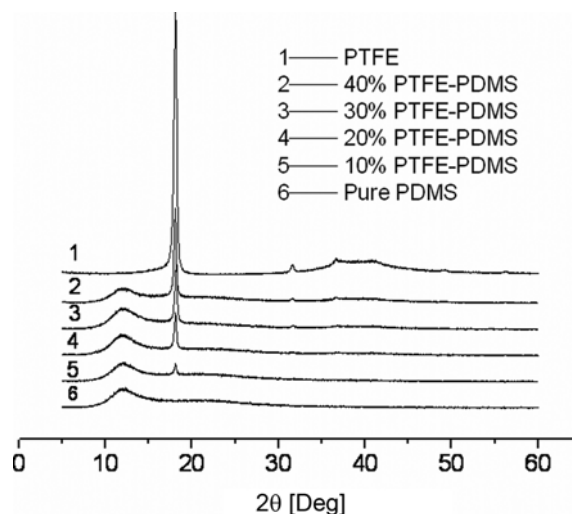

Fig. 4. XRD spectra of PTFE and filled PDMS membranes with various PTFE contents.

are assigned to deformation vibrations and dissymmetry deformation vibrations of the two methyls linked with Si. The characteristic peaks at around 786-872 cm^{-1} and 2,863-2,966 cm^{-1} represent the stretching vibrations of Si-C and C-H, respectively. Compared with the spectra of unfilled membrane, for the filled membranes, PTFE characteristic FT-IR absorption (1,240 cm^{-1}, 1,150 cm^{-1}) is obviously enhanced with the increase of PTFE content. Moreover, compared with the spectra of PTFE and PDMS, for PTFE filled PDMS membranes, no new absorption peak could be observed; this demonstrates that the PTFE is only physically blended in the polymer matrix [33].

1-3. XRD Analysis

The effect of PTFE particles on PDMS crystallinity was investigated. As illustrated in Fig. 4, the PTFE exhibit typical crystalline peaks at about 18.1°, 31.5° and 36.6° [34] and the unfilled PDMS membrane exhibit typical amorphous peaks in the 2θ range of 10.5°-15.6° [33]. PTFE filled PDMS membranes exhibit a more crystalline structure than the unfilled PDMS membranes. The increase of PTFE content led to a gradual increase in the peak intensities at about 18.1° which was in agreement with the XRD curve of PTFE. The
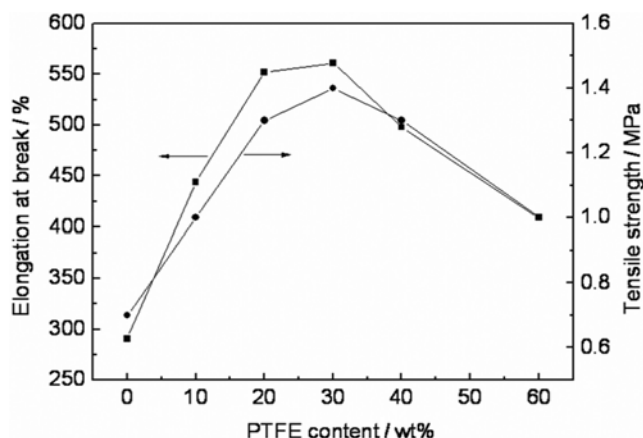

Fig. 3. FTIR spectra of PTFE (a) and filled PDMS membranes with various PTFE contents (b).

Fig. 5. Effect of PTFE contents on the mechanical strength of PDMF composite membranes.

Table 2. Water contact angles for PDMS filled membranes

PTFE content/wt%	0	5	20	30	40
The contact angle/°	109.5	110.0	113.0	116.5	119.0

Fig. 6. Effect of PTFE contents on the thermal stabilities of PDMS composite membranes.

XRD analysis results indicated that there was no change in the crystal diffraction angles for these membranes, and the incorporation of PTFE particles in PDMS membrane would not change the network of the cross-linked PDMS.

1-4. Tensile Property Analysis

Fig. 5 shows the tensile strength and elongation at break as a function of PTFE loading in PDMS membranes. As shown, the results of strength measurement illustrate that the mechanical strength of PDMS membranes was significantly enhanced by the incorporation of PTFE into PDMS. With the increase of PTFE content from 0 to 60 wt%, both the elongation at break and the tensile stress of the PTFE filled PDMS membranes were increased greatly at first and then decreased, and the maximum values of the two curves were reached when the PTFE content was 30 wt%.

Khan et al. [35] investigated the physical properties of ethylene-propylene-diene-rubber membranes which were filled with different kinds of PTFE micropowders that are similar in chemical compositions but distinctive in microstructural morphology. They found that PTFE particle's agglomerate morphology, dispersivity and interfacial compatibility with metric polymer are the key factors which influence physical properties of composite membranes. In this study, commercial PTFE particles with agglomerate morphology were used. Their primary particle size is 120 nm and secondary one is 4 μm as shown in Table 1. Also, SEM analysis (see section 3.1.1) showed that PTFE filled PDMS polymers have good properties of dispersion and interfacial compatibility. Besides, the increase of crystallinity could result in an increase of mechanical performance of composite membranes as we can see from the XRD analysis in section 3.1.3. As a result, when PTFE content is lower than 30 wt%, with the increase of PTFE content, both tensile stress and elongation of the filled membrane increased. But when the degree of filling is too high, PTFE particles can interconnect with each other and the continuity of PDMS in the membrane can be destroyed (shown in Fig. 2(c)). Consequently, when PTFE content is higher than 30 wt%, the network of the membrane is severely spoiled and mechanical strength appears to decline though the filled membranes have high crystallinity at the moment [36,37].

1-5. Contact Angle Analysis

Table 2 shows the experimental values of the contact angles on the air-side surface of the PTFE filled PDMS membranes with different PTFE content. The surface hydrophobicity of the 5% PTFE filled membrane is almost the same as the pure PDMS membrane's, which suggests that the surface of 5% PTFE filled membrane was covered by PDMS [38]. But when the PTFE content increases from 5% to 40%, the contact angles of the filled membrane surface increased from 110° to 119°, which suggests that the more PTFE content in filled PDMS membrane, the higher hydrophobicity of the filled membrane surface.
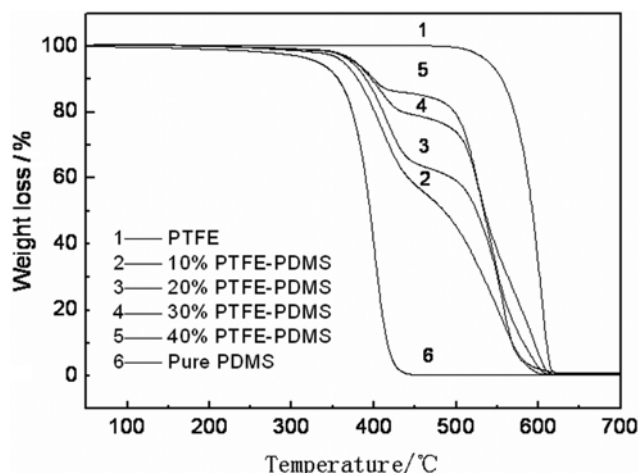
1-6. TG Analysis

The thermal stabilities and degradation behavior of the PTFE, PDMS and PTFE filled PDMS membranes were evaluated by TGA under nitrogen atmosphere. Fig. 6 shows that the adding of PTFE can enhance the thermal stability and retard the thermal degrading of PDMS membranes. With the increase of PTFE content, the thermal stability of the filled PDMS membranes improved significantly; similar results were also found in previous reports [31,38,39]. PTFE exhibited fine thermal stability with a rapid weight loss at 554.77-612.52 °C, pure. PDMS membrane exhibited a rapid weight loss at 349.25-426.01 °C, but there are two main degradation steps in the TG curves of PTFE filled PDMS membranes. The rst decomposition temperatures of PDMS occurred at 375.54-450.89 °C and the second one corresponding to PTFE occurred at 480.74-607.21 °C. We also can see, with the increase of PTFE content, the first decomposition temperature went up for filled membranes due to the contribution of the high thermal stability of PTFE.

1-7. Membrane Swelling Analysis

Swelling degree of PDMS composite membranes with different PTFE content in 100 ppm chloroform/water mixtures is presented in Fig. 7. Swelling degree decreases with the increase of PTFE content. Based on the analysis in sections 3.1.3, 3.1.4 and 3.1.6, the incorporation of PTFE particles in PDMS membrane can enhance crystalline, thermal stabilities and mechanical strength of the mem-
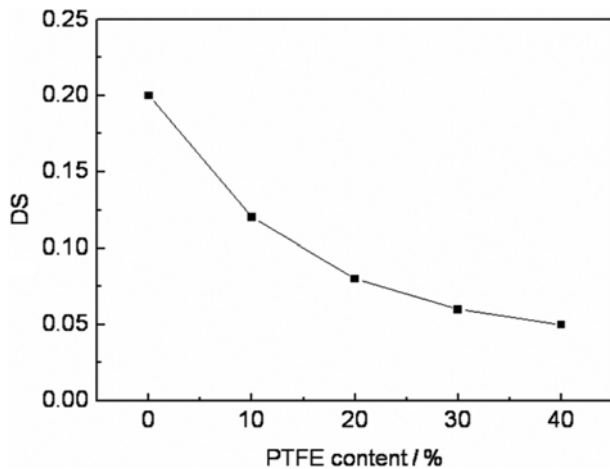
Fig. 7. Effect of PTFE contents on the degree of swelling of PDMS composite membranes.

brane, which proves that PTFE particles also act as reinforcing agent and physical crosslinker [44]. Thus, the movements of PDMS chain segment were obstructed by PTFE particles in filled membrane and serious swelling of filled membrane could be avoided when PTFE content is relative higher in membrane [20].

2. PV Performance

2-1. Effect of PTFE Content in Membrane on PV Performance

The effects of PTFE content on flux, separation factor and permeate separate index of PDMS composite membranes are shown in Fig. 8(a) and (b) at 100 ppm chloroform concentration, feed temperature 50 and permeate-side vacuum 0.101 MPa. As shown, the moderate PTFE filling in membrane exhibits striking advantages in the flux and the separation factor for PV separation of chloroform/water mixture compared with unfilled PDMS membrane. A similar effect was observed by Xia Zhan et al. [37], who found that, with the increase of chloroform concentration, the addition of the HF acid etched ZSM-5 can result in improvements in selectivity and flux for PV separation of ethanol aqueous solution.

As can be seen from Fig. 8(a), with the increase of PTFE content from 0 wt% to 40 wt%, the total and water flux increased gradually and the chloroform flux increased quickly to the maximum of 7.77 g/(m²·h) at 30 wt%, then decreased. The separation factor curve [Fig.

8(b)] shows a peak at 30 wt% PTFE content with the greatest value of 3215, a six-times improvement compared with unfilled PDMS membrane (535). When PTFE was added into PDMS membrane, as analyzed in section 3.1.5, it enhanced the hydrophobic of filled PDMS membrane, which increased the solubility of chloroform in the filled membranes. But when the PTFE content in the PDMS membrane reached 30 wt%, according to the analysis in section 3.1.4, the continuity of the PDMS membrane could be destroyed, which produces many voids of no selectivity. This causes the preferential permeation of the water molecules through the nonselective defect voids, as the kinetic diameter of water molecules (0.37 nm) was smaller than that of ethanol molecules (0.46 nm) [36,37,45]. That is why the chloroform flux and the separation factor first increased and then decreased as shown in Fig. 8. But for water flux, we obtained an interesting result which is contrary to several reported literatures [40-42]. According to the results of the analysis in section 3.1.5, with the adding of PTFE, the contact angle for water increased, which means an increase of hydrophobicity of PTFE filled PDMS membrane; accordingly, water flux should decrease monotonically with the increase of PTFE content. But obviously, this is contradictory to our experimental results, which suggests that pervaporation performance is associated with not only the surface characteristics but also the membrane bulk structure [33]. Lue et al. [43] reported that the particle agglomerates morphology might play important roles in impacting the final transport properties of permeants in mixed PDMS membranes. The PTFE particles used in this study showed the agglomerate morphology like the analysis in section 3.1.4, so there is a mass of interspaces among primary PTFE particles, which is favorable for the diffusion of small water molecules in PTFE filled membranes. As a result, the water flux always increased with the increase of PTFE content in PDMS membrane.

To evaluate the permeation performance of the PTFE filled membrane, we introduced the PSI parameter. As shown in Fig. 8(b), the PSI has a similar trend with separation factor, and the filled membrane containing 30 wt% PTFE has the best PV performance.

2-2. Effect of Feed Temperature on PV Performance

Fig. 9(a)-(c) shows the effects of feed temperature on PV performance for the 30% PTFE-PDMS membrane at the chloroform concentration 100 ppm, permeate-side vacuum 0.101 MPa. Generally, with the increase of operating temperature, the flux increases and separation factor decreases. That is because the higher the tem-
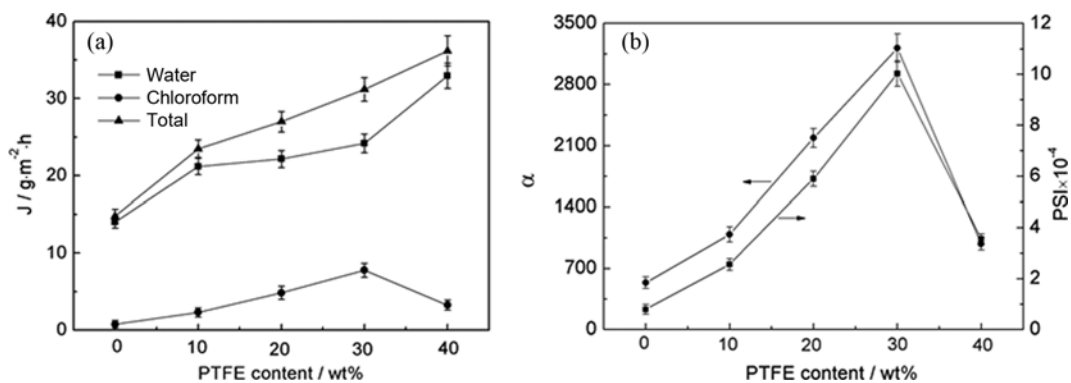

Fig. 8. Effects of PTFE content in membrane on PV performance. (a) Total, water and chloroform ux; (b) separation factor and permeate separate index.
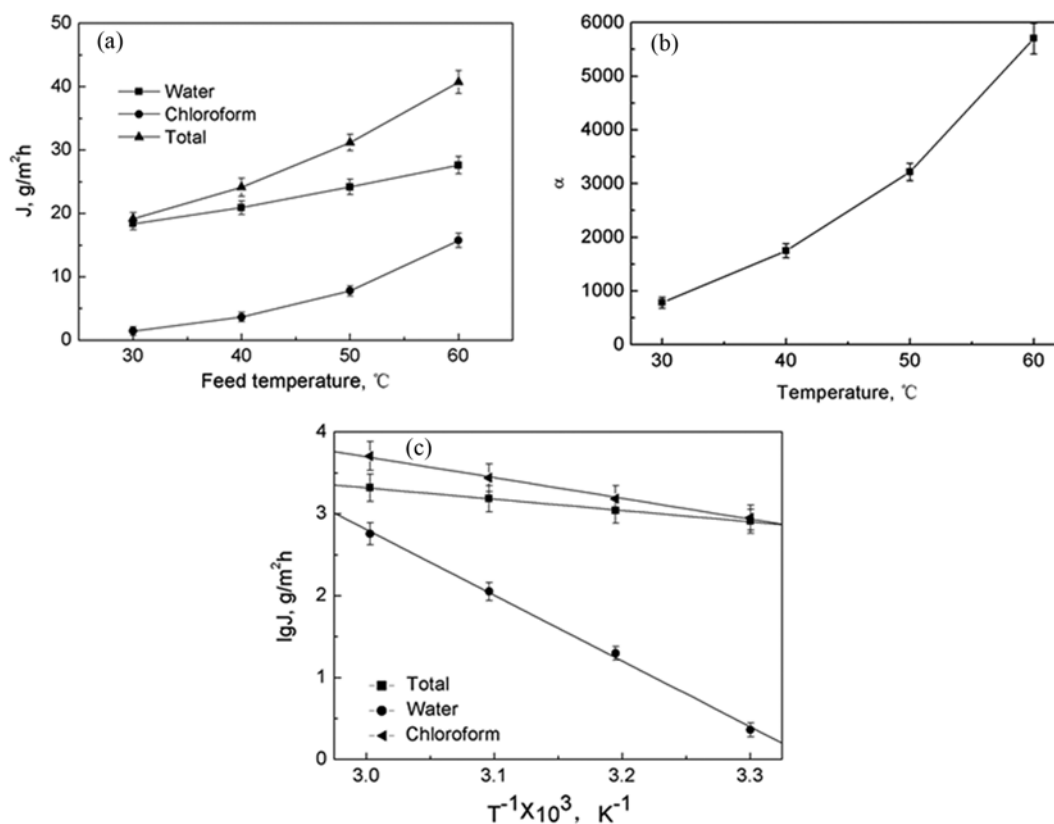
Fig. 9. Effects of operating temperature on PV performance. (a) Total, water and chloroform flux; (b) separation factor; (c) the relation between ln(J) and 1/T.

perature, the bigger the activity driving force across the membrane and the larger the free volume of membrane for diffusion [36,44]. But in this study, it appears that as the feed temperature increased, the total, water and chloroform flux increased, so did the separation factor as shown in Fig. 9(a) and (b). Studies [7,22,37] have demonstrated that the smaller the swelling degree is, the bigger the separation factors are; this is because the water permeation is restrained. The 30% PTFE-PDMS membrane used in this study has a small swelling degree, only 0.06 according to the analysis in section 3.1.7. Moreover, with the increase of feed temperature, the saturated vapor pressure of chloroform increased faster than that of water as shown in Table 3. Therefore, the activity driving force across the membrane of chloroform increased faster than that of water. So we can see that chloroform penetrates faster than water does in Fig. 9(a). Accordingly, we can observe that the separation factor increases with the increase of temperature in Fig. 9(b).

From the experiment results, according to the solution-diffusion mechanism, an Arrhenius type function can be used to express the effect of temperature on flux as follows: $J_i = J_0 \exp(-E_a/RT)$. Activation energy (E_a) represents the relative change of flux to the change of temperature. When the value of activation energy (E_a) is high, the flux will be more susceptible to the change of temperature. The plots of the total and partial permeation fluxes ($\ln(J_i)$) versus reciprocal temperature ($1/T$) are shown in Fig. 9(c). From Fig. 9(c), the variation of the permeation flux with the feed temperature follows the Arrhenius relationship. The activation energy values calculated from the slope are 21.08, 11.49 and 66.65 KJ/mol for total, water and chloroform, respectively, for the 30% PTFE-PDMS membrane. This indicates that the permeation of chloroform was more sensitive to the operation temperature than that of water for this membrane.

2-3. Effect of Feed Concentration on PV Performance

Fig. 10 shows the dependence of PV performance of the 30% PTFE-PDMS membranes on the feed composition from 50 to 950 ppm at a feed temperature of 50 °C and a vacuum pressure 0.101 MPa. With the increase of chloroform concentration, both chloroform and water flux increased. The increasing of chloroform flux is due to the increase in pressure-difference driving force of the chloroform vapor across the membrane according to the solution-diffusion theory, but for the water flux's increasing, it can be interpreted in terms of swelling effects. Separation factor decreased with the increase of chloroform concentration according to the data calculated by Eq. (3). This is because chloroform feed concentration increased faster than chloroform flux did.

The dried 30% PTFE-PDMS composite membrane samples were immersed in a feed solution ranging from 0 to 950 ppm. The results

Table 3. Saturated vapor pressure of water and chloroform, as obtained by using Antoine equation

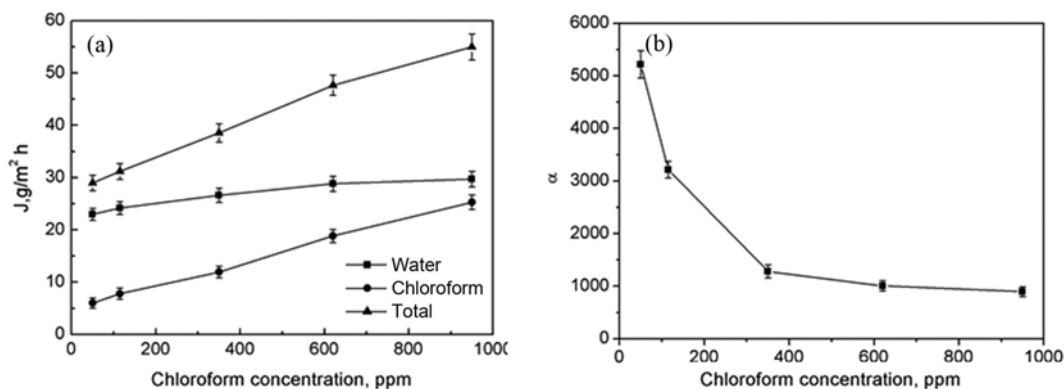|	Saturated vapor pressure/$\times 10^3$ KPa			
	30 °C	40 °C	50 °C	60 °C
Water	4.246	7.381	12.344	19.932
Chloroform	32.345	47.729	68.481	95.819

Fig. 10. The effect of the chloroform concentration in feed on PV performance. (a) The total, water, chloroform flux; (b) the separation factor.
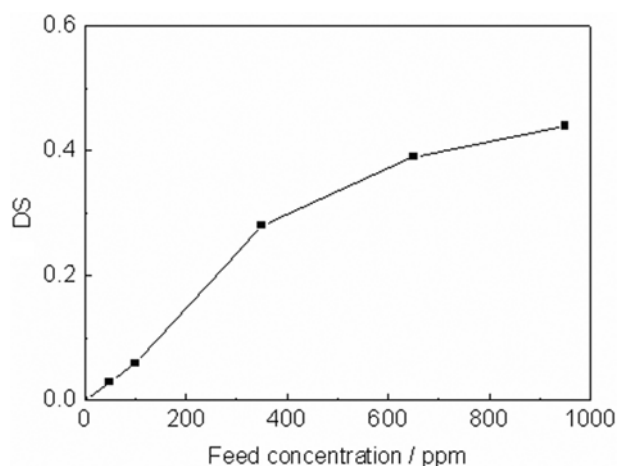

Fig. 11. Swelling degree of 30% PTFE-PDMS membrane in chloroform aqueous solution.

0 wt% to 40 wt%, the total and water flux increased from 14.78 to 36.18 $g/m^2 \cdot h$ and from 14.03 to 32.95 $g/m^2 \cdot h$, respectively; chloroform flux and separation factor increased quickly to the maximum then decreased. When PTFE content was 30 wt%, the separation factor reached the maximum value of 3215, which is six-times bigger than that of the unfilled PDMS membranes. That is because the PTFE particles can enhance the hydrophobicity of the filled PDMS membranes. As the operating temperature increased from 30 to 60 ℃, both the flux and the separation factor increased continuously for the tested 30% PTFE-PDMS composite membrane, under the condition of feed concentration of 100 ppm chloroform and permeate-side vacuum of 0.101 MPa. The variation of the permeation flux with the feed temperature followed the Arrhenius relationship and the activation energy values from the slope are 21.08, 11.49 and 66.65 KJ/mol for total, water and chloroform, respectively. When feed concentration was increased from 50 to 950 ppm, the permeation flux increased, but the separation factor decreased due to swelling effect in different feed concentrations.

of the swelling experiment are shown in Fig. 11. Due to the strong affinity of chloroform to the filled membranes, the swelling degree increased with the increase of chloroform concentration. As we know, a higher degree of swelling causes the increase of water flux, which reduces the solution selectivity [7,22,37], so we can see from Fig. 10(b), the chloroform separation factor decreased with the increase of chloroform concentration.

CONCLUSIONS

A novel composite membrane using PTFE filled PDMS as the top active layer and non-woven fabric PET as the support layer was developed for the PV of chloroform from water. SEM and EDXS graphs showed that PTFE dispersed evenly in the 30% PTFE filled PDMS composite membrane; the composite membrane was dense with no connected macroscopic voids. Both XRD and FT-IR observation verified that the PTFE was only physically blended with the PDMS polymer matrix and that the incorporation of PTFE into PDMS membrane enhanced the crystallinity, hydrophobicity, mechanical strength and thermal stability of filled PDMS membrane.

Incorporating PTFE into PDMS membranes could influence the PV properties significantly. With the increase of PTFE content from

REFERENCES

1. D. Luo, R. Corey, R. Propper, J. Collins, A. Komorniczak, M. Davis, N. Berger and S. Lum, *Environ. Sci. Policy.*, **14**, 585 (2011).
2. S. Preis, D. Klauson and A. Gregor, *J. Environ. Manage.*, **114**, 125 (2013).
3. S. C. Lee, H. Guo, S. M. J. Lam and S. L. A. Lau, *Environ. Res.*, **94**, 47 (2004).
4. G. Quijano, A. Couvert, A. Amrane, G. Darracq, C. Couriol, P. L. Cloirec, L. Paquin and D. Carrié, *Chem. Eng. Sci.*, **66**, 2707 (2011).
5. M. V. Templin, K. C. Jamison, D. C. Wolf, K. T. Morgan and B. E. Butterworth, *Cancer. Lett.*, **104**, 71 (1996).
6. C. Fang, M. Behr, F. Xie, S. Lu, M. Doret, H. X. Luo, W. Z. Yang, K. Aldous, X. X Ding and J. Gu, *Toxicol. Appl. Pharm.*, **227**, 48 (2008).

7. I. Rutkiewicz, W. Kujawski and J. Namiecœnik, *Desalination*, **264**, 160 (2010).

8. B. Bolto, M. Hoang and Z. L. Xie, *Water Res.*, **46**, 259 (2012).

9. G. L. Jadav, V. K. Aswal, H. Bhatt, J. C. Chaudhari and P. S. Singh, *J. Membr. Sci.*, **415-416**, 624 (2012).

10. S. Araki, S. Imasaka, S. Tanaka and Y. Miyake, *J. Membr. Sci.*, **380**, 41 (2011).

11. W. Wei, S. S. Xia, G. P. Liu, X. L. Dong, W. Q. Jin and N. P. Xu, *J. Membr. Sci.*, **375**, 334 (2011).

12. N. L. Le, Y. Wang and T. S. Chung, *J. Membr. Sci.*, **379**, 174 (2011).

13. P. Shao and R. Y. M. Huang, *J. Membr. Sci.*, **287**, 162 (2007).

14. M. Bennett, B. J. Brisdon, R. England and R. W. Field, *J. Membr. Sci.*, **137**, 63 (1997).

15. T. Ohshima, Y. Kogami, T. Miyata and T. Uragami, *J. Membr. Sci.*, **260**, 156 (2005).

16. T. Uragami, H. Yamada and T. Miyata, *J. Membr. Sci.*, **187**, 255 (2001).

17. S. J. Lue, T. H. Yang, K. S. Chang and K. L. Tung, *J. Membr. Sci.*, **415-416**, 635 (2012).

18. W. W. Y. Lau, J. Finlayson, J. M. Dickson, J. Jiang and M. A. Brook, *J. Membr. Sci.*, **134**, 209 (1997).

19. Y. Shirazi, A. Ghadimi and T. Mohammadi, *J. Appl. Polym. Sci.*, **124**, 2871 (2012).

20. X. L. Liu, Y. S. Li, Y. Liu, G. Q. Zhu, J. Liu and W. S. Yang, *J. Membr. Sci.*, **369**, 228 (2011).

21. B. Li, S. N. Yu, Z. Y. Jiang, W. P. Liu, R. J. Cao and H. Wu, *J. Hazard. Mater.*, **211**, 296 (2012).

22. G. P. Liu, W. Wei, W. Q. Jin and N. P. Xu, *Chinese J. Chem. Eng.*, **20**, 62 (2012).

23. H. J. Lee, E. J. Cho, Y. G. Kim, I. S. Choi and H. J. Bae, *Bioresour. Technol.*, **109**, 110 (2012).

24. Y. W. Huang, P. Zhang, J. W. Fu, Y. B. Zhou, X. B. Huang and X. Z. Tang, *J. Membr. Sci.*, **339**, 85 (2009).

25. D. Panek and K. Konieczny, *Sep. Purif. Technol.*, **57**, 507 (2007).

26. M. Khaye and T. Matsuura, *Desalination*, **148**, 31 (2002).

27. S. Simone, A. Figoli, S. Santoro, F. Galiano, S. M. Alfadul, O. A. Al-Harbi and E. Drioli, *Sep. Purif. Technol.*, **90**, 147 (2012).

28. Z. J. Yang, W. Y. Zhang, J. D. Li and J. X. Chen, *Sep. Purif. Technol.*, **93**, 15 (2012).

29. M. M. Teoh and T. S. Chung, *Sep. Purif. Technol.*, **66**, 229 (2009).

30. J. Li, G. J. Zhang, S. L. Ji, N. X. Wang and W. An, *J. Membr. Sci.*, **415-416**, 745 (2012).

31. W. C. Chao, S. H. Huang, Q. F. An, D. J. Liawc, Y. C. Huangc, K. R. Lee and J. Y. Lai, *Polymer*, **52**, 2414 (2011).

32. H. F. R. Ferreto, L. F. C. P. Lima, D. F. Parra, V. Zaia and A. B. Lugão, *Nucl. Instrum. Meth. B.*, **265**, 173 (2007).

33. B. Li, D. Xu, Z. Y. Jiang, X. F. Zhang, W. P. Liu and X. Dong, *J. Membr. Sci.*, **322**, 293 (2008).

34. R. K. Dhillo, S. Singh and R. Kumar, *Nuclear Nucl. Instrum. Meth. B.*, **268**, 2189 (2010).

35. M. Sohail Khan, R. Franke, D. Lehmann and G. Heinrich, *Tribol. Int.*, **42**, 890 (2009).

36. H. S. Hong, L. X. Chen, Q. W. Zhang and F. He, *Mater. Design.*, **34**, 732 (2012).

37. X. Zhan, J. Lu, T. T. Tan and J. D. Li, *Appl. Surf. Sci.*, **259**, 547 (2012).

38. H. L. Zhou, Y. Su, X. R. Chen, S. L. Yi and Y. H. Wan, *Sep. Purif. Technol.*, **75**, 286 (2010).

39. R. L. Guo, X. C. Ma, C. L. Hu and Z. Y. Jiang, *Polymer.*, **48**, 2939 (2007).

40. G. Liu, F. Xiangli, W. Wei, S. Liu and W. Jin, *Chem. Eng. J.*, **174**, 495 (2011).

41. F. B. Peng, Z. Y. Jiang, C. L. Hu, Y. Q. Wang, H. Q. Xu and J. Q. Liu, *Sep. Purif. Technol.*, **48**, 229 (2006).

42. S. L. Yi, Y. Su and Y. L. Wan, *J. Membr. Sci.*, **360**, 341 (2010).

43. S. J. Lue, C. F. Chien and K. P. O. Mahesh, *J. Membr. Sci.*, **384**, 17 (2011).

44. L. Liu, Z. Y. Jiang and F. S. Pan, *J. Appl. Polym. Sci.*, **101**, 90 (2006).

45. M. Eddaoudi, H. Li and O. M. Yaghi, *J. Am. Chem. Soc.*, **122**, 1391 (2000).