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Pervaporation of phenol wastewater with PEBA–PU blend membrane

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ABSTRACT

The compatibility of polyether block amide (PEBA) and polyurethane (PU) was investigated with the calculation of their Flory–Huggins interaction parameter. The results showed that PEBA and PU are compatible at different content of PEBA. Then, PEBA–PU blend membranes were prepared. Scanning electron microscopic characterization showed that the blend membranes were dense and applicable for pervaporation. The swelling degree of the blend membrane increased with the phenol concentration, which suggested that the blend membrane has preferential permeation for phenol. Pervaporation experiments showed that the separation factor of blend membranes had been enhanced. When the blend membrane with 50 wt% PEBA content is used to separate 0.1 wt% phenol aqueous solutions at 308.15 K, the separation factor (phenol to water) is 9.7 and the permeation flux is 84.1 g m^{-2} h^{-1}.

Keywords: Pervaporation; Phenol; PEBA; PU; Blend

1. Introduction

Phenols constitute a variety of aromatic hydroxyl compounds which are very important raw materials in petrochemical, pharmaceutical, plastic and pesticide industries. On the other hand, phenols are also common pollutants usually found in industrial wastewater from petroleum refineries, coal chemical plants, as well as the production of phenolic resins, dyes and paper. In order to prevent environment pollution and make full use of phenols, the separation and recovery of phenols from effluents before discharge is of significant meaning [1,2].

General methods for phenol separation from effluents include solvent extraction, air stripping and several conventional oxidation processes [3,4]. However, these approaches are not applicable for low concentration wastewater treatment because of their relatively high cost. As an alternative technique for wastewater treatment, membrane separation has attracted wide concern in recent years [5]. Pervaporation is a promising membrane process that applies to homogeneous liquid mixture separation. It has many advantages such as less energy consumption, no need of regeneration process and no secondary contamination, which make it more competitive than traditional separation techniques [6].

Growing interest is shown in applying pervaporation for recovering phenol from wastewater, meanwhile, membranes based on various sorts of polymers have been investigated extensively [7–10]. Polymers with weak polarity, low surface energy and small solubility parameter are usually considered to be permselective membrane material for wastewater containing organic pollutants [11]. Membrane materials for phenol pervaporation such as polyurethane (PU), polyether block amide (PEBA) and polydimethylsiloxane (PDMS) were studied. Gupta et al. [8] investigated Hydroxyterminated polybutadiene (HTPB) based PU

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membranes cross-linked by excess –NCO groups. Results showed that the membranes had preferential selectivity for phenol while the flux is less than 35 g m^{-2} h^{-1}. Hoshi et al. [12] studied the pervaporation of a phenol–water mixture with a PU membrane. High phenol selectivity was obtained due to the high solubility of phenol in the 1,6-diisocyanatohexane–polytetramethyleneglycol (HMDI–PTMG) membrane.Sinha et al. [13] prepared porous PU membrane via addition of lithium chloride, which acted as the regulator of pore size and pore number per unit area, in contrast with dense HTPB–PU membrane, porous PU membrane had higher flux. However, with the increase of porosity, selectivity of this membrane reduced accordingly.

PU is a sort of attractive polymer material for its good mechanical properties and chemical resistance; it is also well established as elastomer block copolymer with alternating soft and hard segments. And PEBA is another hydrophobic and organophilic polymer which has a strong sorption capacity to aromatic compounds. Both of PU and PEBA are thought to be applicable materials for pervaporation. Blend is a promising modification method to get better membrane since not only it can be easily achieved, but also it may eliminate drawbacks of single-component polymer. Theoretical analysis of polymer compatibility is necessary for blend membrane preparation. Flory–Huggins interaction parameter is generally used to estimate the compatibility of blending polymers. Such theoretical calculation can be implemented through molecular simulation. Over the recent years molecular simulation has become a widely used tool to investigate molecular structure and behavior of polymeric membrane. Tamai et al. [14] calculated the excess chemical potentials of methane, water and ethanol in PDMS and polyethylene by Widom method. Solubilities of methane, water and ethanol in polymers were calculated from excess chemical potentials, showing that diffusion coefficients, solubilities and permeation rates were in reasonable agreement with experimental data. Ethanol has a smaller diffusion coefficient than water while ethanol has a larger permeation rate for its higher solubility in PDMS.

In this research, PEBA and PU, two suitable materials to form dense membrane, were selected as compositions to form blend membranes. To estimate their compatibility, Flory–Huggins interaction parameter of PEBA and PU at different contents was calculated. Then PEBA–PU blend membranes were prepared and their performance was tested in the pervaporation experiments of phenol wastewater. The blend membranes were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Mechanical properties, swelling properties and pervaporation performance of blend membrane were also discussed.

2. Compatibility analysis of PU and PEBA

2.1. Method and relative parameters

Compatibility of PU and PEBA was analyzed with the application of Material Studio software. Its database provides different types of force fields. Basically, all-atom model was built up for PU–PEBA blend. Compatibility of PU–PEBA was evaluated through calculating the solubility parameter and Flory–Huggins interaction parameter.

COMPASS force field was applied in this study, which was one of the effective force fields for condensed matter systems. Atom-based method and Ewald method were used for van der Waals force and Coulombic force, respectively. On the other side, Andersen method for temperature control and Berendsen method for pressure control were applied in the dynamic equilibrium stage. Initial velocity of every single molecule was sampled according to Maxwell distribution; it could be solved by using velocity Verlet algorithm. Cutoff distance for the calculation was set at 0.95 nm, the spline width and buffer width for the cutoff distance were 0.1 and 0.05 nm, respectively.

2.2. Construction of model and calculation of solubility parameter

Solubility parameter (δ) of polymer, which corresponded to the interaction of molecular chains, is defined as square root of cohesive energy density (CED):

$$\delta = \sqrt{\text{CED}} = \sqrt{\frac{E_{\text{coh}}}{V}} \tag{1}$$

where E_{coh} represents the cohesive energy and V is the molar volume.

Monomer structure models of PEBA and PU were constructed via using material visualizer module. Polymer that had a certain polymerization degree was obtained and subjected to geometry optimization afterwards within convergence precision of 0.1 kcal mol^{-1} $Å^{-1}$ (Fig. 1). In an effort to minimize the chain-end effect [15], amorphous structure that had a polymer chain was constructed in amorphous cell module.

Basically, five different kinds of configuration were created separately for every single polymer system. Structure with a lowermost energy was the object of simulation. Then the geometry optimization was conducted on established amorphous structure. When the optimization reached a certain convergence precision, the molecular dynamics were worked out in a stepwise manner: first, NTV ensemble (i.e., canonical ensemble, in which the temperature T, volume

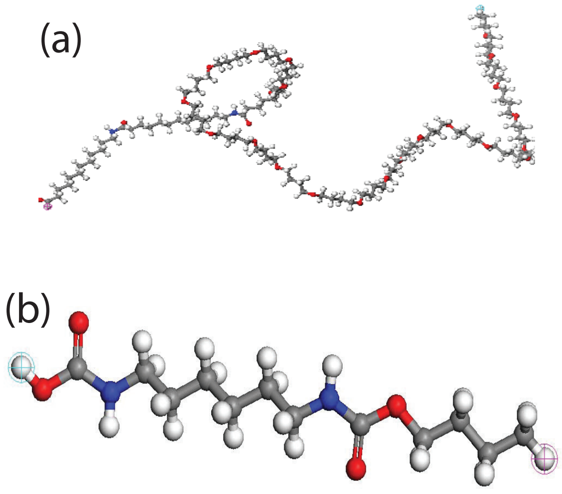

Fig. 1. Atomic models of (a) PEBA and (b) PU.

V and number of particles N_m are fixed) molecular dynamics calculation of 50 ps at 1,000 K; then, NTV ensemble molecular dynamics calculation of 50 ps at 298 K; finally, NTV ensemble molecular dynamics calculation of 100 ps at 298 K. CED and solubility parameter were estimated based the data got in the last step of molecular dynamics calculation.

A proper polymerization degree must be determined in the calculation process of polymer thermodynamic properties. The higher the polymerization degree is, the closer the system is to a real system. However, high polymerization degree would result in great computational burden. It is suggested that the polymerization degree is sufficient for calculation when the solubility parameter change little with it [16].

Figs. 2 and 3 present the solubility parameters of PU and PEBA at different polymerization degrees. According to these figures, when the repeating units of PEBA and PU reached 3 and 40, respectively, the solubility parameter showed little variation. Therefore, the polymerization degrees of PEBA and PU for further calculation were determined to be 3 and 40.

On the other hand, according to Hansen's theory, the solubility parameter was determined by dispersion solubility parameter, polar solubility parameter and hydrogen bonding solubility parameter. Their relation is as follows:

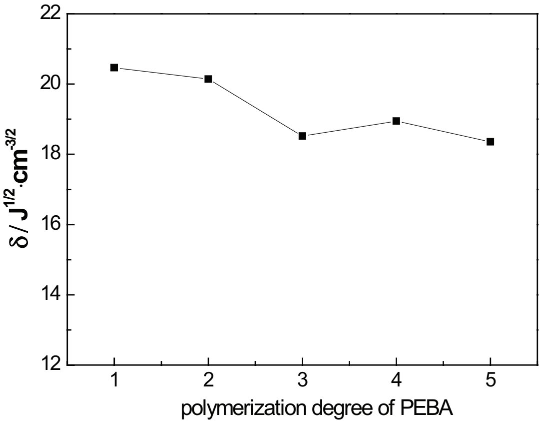

Fig. 2. Solubility parameters at different polymerization degree of PEBA.

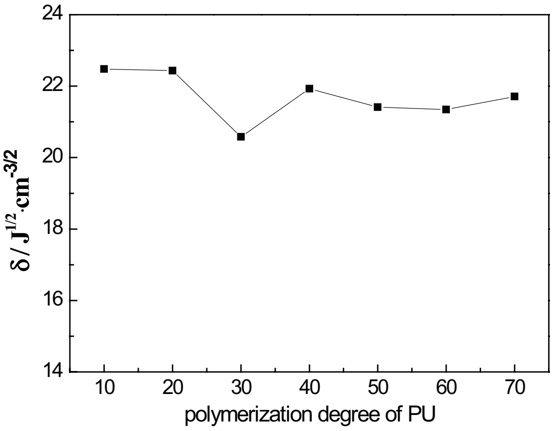

Fig. 3. Solubility parameters at different polymerization degree of PU.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{2}$$

where δ_d is the dispersion solubility parameter; δ_p is the polar solubility parameter and δ_h is the hydrogen bonding solubility parameter.

The terms in Eq. (2) can be estimated by group contribution method.

$$\delta_d = \sum F_{\mathrm{di}} / \sum V_i \tag{3}$$

$$\delta_p = \sqrt{\sum F_{\mathrm{pi}}^2} / \sum V_i \tag{4}$$

$$\delta_h = \sqrt{\sum E_{\mathrm{hi}} / \sum V_i} \tag{5}$$

where F_{di} is the group contribution for dispersion solubility parameter; F_{pi} is the group contribution for polar solubility parameter; E_{hi} is the group contribution for hydrogen bonding solubility parameter and V_i is the molar volume of group.

The values of F_{di}, F_{pi}, E_{hi} and V_i for PEBA and PU can be found in Brandrup et al. [17]. Then with the application of Eq. (2) to Eq. (5), the solubility parameter of PEBA and PU can be derived (Table 1).

Compared the solubility parameter values derived from molecular simulation with the values based on Hansen's method and literature value (Table 2), it was clearly seen that they were in rational agreement, therefore, the polymer models are suitable for further calculation.

2.3. Calculation of Flory–Huggins interaction parameter

χ represents the Flory–Huggins parameter, which is an important index to judge the compatibility of polymer materials. Generally, the less the value of χ is, the better compatibility of the polymer materials have. χ can be calculated according to the mixed energy by Eq. (6):

$$\chi = \left(\frac{\Delta \mathrm{E}_{\mathrm{mix}}}{RT\phi_{\mathrm{A}}\phi_{\mathrm{B}}} \right) V \tag{6}$$

V is the molar volume of repetitive unit. Usually V takes the lower molar volume of the two polymers in the blend material [18]. ϕ_{A} and ϕ_{B} are volume fractions of pure substances A and B, respectively. ΔE_{mix} expresses the magnitude of mixed energy, which can be calculated as follows:

Table 1
Solubility parameters of PEBA and PU (Hansen's method)

	PEBA	PU
δ_d ($\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$)	17.48	18.45
δ_p ($\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$)	1.24	3.66
δ_h ($\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$)	6.38	9.90
δ ($\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$)	18.7	21.3

$$\Delta E_{\text{mix}} = \phi_A\left(\frac{E_{\text{coh}}}{V}\right)_A + \phi_B\left(\frac{E_{\text{coh}}}{V}\right)_B - \left(\frac{E_{\text{coh}}}{V}\right)_{\text{mix}} \tag{7}$$

Subscripts A, B and mix denote the pure substance A, B and their blend.

For polymer blends, critical value of Flory–Huggins parameter serves as a criterion to determine the degree of compatibility. It can be calculated by the following formula [18,19]:

$$(\chi_{AB})_{\text{critical}} = \frac{1}{2}\left(\frac{1}{\sqrt{m_A}} + \frac{1}{\sqrt{m_B}}\right)^2 \tag{8}$$

Here, m is the polymerization degree, subscripts A and B represent PEBA and PU. On the basis of Flory–Huggins theory, if $\chi < (\chi_{AB})_{\text{critical}}$, it is considered that the polymer blends are theoretically compatible. Based on the previously determined polymerization degree, critical value of interaction parameter for PEBA and PU was calculated to be 0.27.

In this work, six models were built including pure PU, pure PEBA and PEBA–PU blends with PEBA mass fractions of 10.80%, 37.80%, 54.90% and 75.20%, respectively. With the application of amorphous cell module, mixed CED can be derived. Then the mixed energy was obtained from Eq. (7). Finally, Flory–Huggins interaction parameters of PEBA–PU blend at different mixed ratios were shown in Table 3. Blending density was estimated based on the density and volume fraction of monomers [20].

$$\rho_{\text{blend}} = \phi_A\rho_A + (1-\phi_A)\rho_B \tag{9}$$

Table 2
Comparison of calculated solubility parameters with literature value

Polymer	Solubility parameters ($J^{1/2}$ $cm^{-3/2}$)		
	Molecular simulation	Hansen's method	Literature value
PEBA	18.5	18.7	–
PU	21.9	21.3	20.5 [17]

The detailed information and calculation results of these six models were listed in Table 3. According to the simulation results, the mixed Flory–Huggins interaction parameters were less than $(\chi_{AB})_{\text{critical}}$ (0.27) at 298 K for all blend models. PEBA and PU have good compatibility. They could be used to form blend pervaporation membrane in any PEBA content. Furthermore, it was evident that χ increased at first then decreased with the increasing PEBA content. The value of χ reached its maximum when PEBA content was 54.90 wt%. This illustrated that when PEBA content was 54.90%, although PEBA and PU are still compatible, but the compatibility was not as good as other PEBA–PU blend.

3. Experimental

3.1. Materials

PEBA2533 was purchased from Arkema Co., Ltd. (France). PU1185A10 was received from BASF Co., Ltd. (Shanghai, China) 1-Methyl-2-pyrrolidone (NMP, CP), *N,N*-dimethylformamide (DMF, AR) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and deionized water was self-made.

3.2. Selection of proper solvent

PEBA and PU are polar polymers. Based on "like dissolves like" principle, and comparing the solubility parameter of different solvents [21] (Table 4), the solubility parameter of NMP was close to that of PU or PEBA. Therefore, NMP was selected to be the solvent for the following preparation of PEBA–PU blend membrane.

Table 4
Solubility parameters of the polymers and solvents

Polymer	δ_d ($J^{1/2}$ $cm^{-3/2}$)	δ_p ($J^{1/2}$ $cm^{-3/2}$)	δ_h ($J^{1/2}$ $cm^{-3/2}$)	δ ($J^{1/2}$ $cm^{-3/2}$)
PEBA	17.48	1.24	6.38	18.65
PU	18.45	3.66	9.90	21.25
DMF	17.40	13.70	11.30	24.80
NMP	18.00	12.30	7.20	22.90
Butanol	16.00	5.70	15.80	23.10
Ethyl acetate	15.80	5.30	7.20	18.10
Phenol	18.00	5.90	14.90	24.10
Water	15.50	16.00	42.30	47.80

Table 3
Simulation information of PABA, PU and PEBA–PU blends

Number	Molar fraction (PEBA %)	Ratio of chains (PEBA/PU)	Mass fraction (PEBA %)	Volume fraction (PEBA %)	Density (g/cm^3)	$\chi_{PEBA/PU}$
1	0.00	0/1	0.00	0.00	1.12	–
2	0.17	1/5	10.80	11.90	1.11	–6.32
3	0.50	1/1	37.80	40.30	1.08	–2.92
4	0.67	2/1	54.90	57.40	1.06	0.12
5	0.83	5/1	75.20	77.10	1.03	–11.26
6	1.00	1/0	100.00	100.00	1.01	–

3.3. Preparation of PEBA–PU blend membrane

In view of molecular simulation results, PEBA can be blended with PU in various ratios due to their good compatibility. In this regard, representative membranes with PEBA content of 20%, 50% and 80% were prepared for experiment. Adding a certain proportion of dried PEBA and PU into NMP solvent, the two polymers were dissolved in solvent and stirred at 70°C for about 4 h to ensure their homogeneous mixing. Solution with a weight content of 7% was obtained after ultrasonic degassing for 30 min. After having been cooled to 40°C for a short while, the solution was cast on glass plate with a steel knife to obtain a wet membrane. The wet membrane was dried at room temperature for 48 h, then it was further dried in a vacuum oven for certain time to ensure the solvent was volatilized completely.

3.4. Membrane characterization

FTIR (Nicolet USA) measurement was performed. Each sample was grounded well to make KBr pellets under pressure. In each scan, the amount of KBr and membrane sample was kept constant in order to find the difference of the intensity of characteristic peak.

The surface and cross-section of the membrane morphologies were observed by SEM instrument (Hitachi S-4800 Japan).

The mechanical properties of the membranes were evaluated at room temperature on an Instron 4300 Universal Testing System. Then the tensile stress–strain curves can be derived.

3.5. Swelling studies

Degree of swelling (DS) of membrane is measured by immersing the membrane sample in phenol solution for a certain period of time and weighing the membrane mass before and after immersion. DS is defined with respect to the dry weight (W_d) and swollen weight (W_s) as follows:

$$\text{DS}\left(\%\right)=\frac{(W_s-W_d)\times 100\%}{W_d} \tag{10}$$

3.6. Pervaporation experiments

Membrane performance was evaluated in terms of permeation flux (J) and separation factor (a), which are defined as:

$$J=\frac{W}{A_t} \tag{11}$$

$$\alpha=\frac{C_{i2}/C_{j2}}{C_{i1}/C_{j1}} \tag{12}$$

where W is the weight of permeate sample collected over a given time t and A is the effective membrane area. C is feed (C_1) and permeate (C_2) phenol concentration (weight fraction), the subscripts i and j denote phenol and water component, respectively.

Pervaporation of phenol–water mixture was carried out in a pervaporation cell (Peiyang Chemical Equipment Co., Ltd., Tianjin, China) [22]. Membrane was supported on a sintered stainless steel plate which located at the joint of membrane cells. Feed temperature was sustained by heater and temperature control unit in the setup. Downstream pressure was maintained at 100 Pa by the vacuum pump. The effective area of membrane for pervaporation is 3.6 × 10^{-3} m^2. The permeate vapor was condensed in a glass tube which was cooled by a liquid nitrogen cold trap.

The concentration of permeates and feed was determined by gas chromatography (GC7890F, Techcomp (Holdings) Limited) equipped with a FID detector and HP-FFAP capillary column, with benzyl alcohol as internal standard. The weight of permeate was weighed by electronic balance (with the measurement accuracy of 0.1 mg).

4. Results and discussion

4.1. Characterization of PEBA–PU blend membrane

4.1.1. FTIR analysis

FTIR spectra of PEBA, PU and PEBA–PU membranes are demonstrated in Fig. 4. For PEBA, there were characteristic peaks at 3,307 cm^{-1} (N–H stretching absorption), 2,837 cm^{-1} (C–H of –CH$_2$– stretching vibration), 1,735 cm^{-1} (C=O stretching vibration), 1,128 cm^{-1} (C–O of –CH$_2$–O–CH$_2$– stretching vibration) and 722 cm^{-1} (C–H deformation vibration). For PU membrane, the band at 3,330 cm^{-1} is attributed to the stretching absorption of N–H. The peak at 1,692 cm^{-1} is assigned to the stretching vibration of C=O. And the peak at 1,595 cm^{-1} corresponds to amide group.

As shown in Fig. 4, N–H stretching absorption peak was reduced due to the blend of PEBA and PU, which was mainly caused by the hydrogen bond interaction between amide group of PEBA and urethane group of PU. PEBA–PU blend membrane was robust owing to the formed hydrogen bond between different chains.

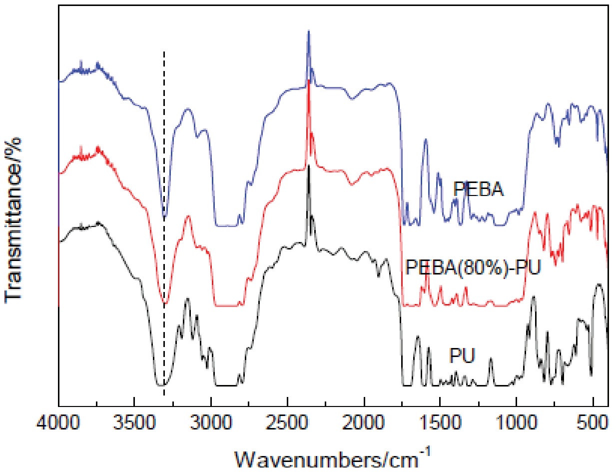

Fig. 4. FTIR spectra of PEBA, PU and PEBA-PU membranes.

4.1.2. SEM analysis

SEM images of surface and cross-section of membranes are presented in Fig. 5. All the PEBA–PU blend membranes show dense structure as pure PEBA or PU membrane, making them suitable for pervaporation application. PEBA (80 wt%)–PU and PEBA membranes had a similar cross-section structure, so did PEBA (20 wt%)–PU and PU membranes. The cross-section of PEBA (50 wt%)–PU membrane is a little rough. This might be caused by microphase separation of the blend polymers. It means that at this PEBA content, the blend of PEBA and PU is not so good, agreeing well with its Flory–Huggins interaction parameter is very close to the critical value.

4.1.3. Mechanical properties analysis

Fig. 6 shows uniaxial tensile stress–strain data for PEBA, PU and the PEBA–PU blend membranes. All the stress–strain curves have similar trend: the membrane experiences elastic deformation and plastic deformation successively before its fracture. And all the membranes have rather high tensile strength (higher than 14 MPa). Pure PEBA membrane exhibits the highest elongation at break. The tensile strength of blend membranes with 20 or 80 wt% PEBA content is close to that of PU membrane. The blend membrane with 50 wt% PEBA content shows decreased tensile strength and elongation at break. The reason for this may be that the blend membrane at this PEBA content has more free volume than other membranes, owing to the not so good compatibility based on theoretical calculation and SEM observation.

4.2. Swelling properties of the blend membranes

All the membranes can reach swelling equilibrium over a certain period of time. With the increase of PEBA content in PEBA–PU blend membrane, there was an enhanced DS (Fig. 7). Swelling degree of PU membrane was significantly fortified as a result of adding PEBA content. And PEBA membrane showed the highest swelling degree. Based on the swelling experiments, it can be speculated that PEBA has good phenol sorption selectivity. Fig. 8 illustrates the relationship between blend membranes and phenol solution concentration. The higher phenol concentration of aqueous solutions, the more swelling degree the membranes have. It seems that blend membranes preferred to adsorb phenol in its aqueous solutions. In this regard, they were suitable for the separation of phenol and water.

4.3. Pervaporation performance

The pervaporation experiments were operated at 30°C for phenol aqueous solutions with different concentration (0.1 and 0.7 wt%). Figs. 9 and 10 illustrate the effect of PEBA content on separation factor and permeation flux, respectively. The separation of phenol from its aqueous solutions by pervaporation follows solution–diffusion mechanism. Pure PEBA membrane showed better performance than pure PU membrane since PEBA has better phenol sorption selectivity. For the PEBA–PU blend membranes, the separation factor increased first with the content of PEBA. When PEBA content is 50 wt%, the separation factor reached highest value (7.79 for 0.7 wt% phenol solutions, 8.32 for 0.1 wt% phenol solutions at 30°C). Then separation factor decreased with the further increasing PEBA content. According to the preceding simulation results, compatibility of PEBA–PU blend was not so good when PEBA content was close to 50 wt%, which would make more fractional free volume for PEBA (50 wt%)–PU blend membrane. Therefore, the diffusion selectivity of phenol to water was strengthened. However, the permeation flux always increased with the increasing PEBA content considering integrated sorption and diffusion effects. And for the same membrane, the permeation flux at high phenol concentration (0.7 wt%) was larger than the flux at low phenol concentration (0.1 wt%). The reason might be at higher phenol concentration, the membrane had more swelling and higher driving force, thus water and phenol could permeate more easily.

Pervaporation performance at 20°C–40°C is listed in Fig. 11. Temperature is an important parameter that affect flux and separation factor. According to the experimental data, both permeation flux and separation factor increased with temperature. At 35°C, the separation factor is 9.7 and the permeation flux is 84.1 g m^{-2} h^{-1}.

The intrinsic stability of PEBA–PU blend membrane was assessed through sustained pervaporation at 35°C using a 0.1 wt% phenol feed. The pervaporation performance of PEBA (50 wt%)–PU blend membrane was rather stable for 120 h operation (Fig. 12). The permeation flux and separation factor changed little in long time experiments.

5. Conclusions

With the application of molecular simulation, the solubility parameters of PEBA and PU were calculated, which agreed well with the results obtained by Hansen's method. Then Flory–Huggins interaction parameters of PEBA–PU blends at different PEBA content were derived. All the interaction parameters of PEBA and PU are lower than critical value, which means that PEBA and PU are compatible. However, the compatibility of the blend with about 50 wt% PEBA content is not so good, which makes the membrane have higher free volume. Then a series of PEBA–PU blend membranes were prepared. SEM characterization showed that PEBA–PU blend membranes are dense and smooth. Separation of phenol from aqueous solutions through PEBA–PU blend membrane by pervaporation was feasible. The effects of PEBA content on swelling behavior and pervaporation performance of blend membranes were studied. The swelling degree increased with PEBA content and phenol concentration, which means phenol prefer to adsorb on the blend membrane. Compared with pristine PU or PEBA membrane, PEBA–PU blend membrane had a better separation factor. When PEBA content is 50 wt%, the blend membrane had better diffusion selectivity and showed the highest separation factor. And the permeation flux would increase with the increasing phenol concentration of the feed.

Acknowledgments

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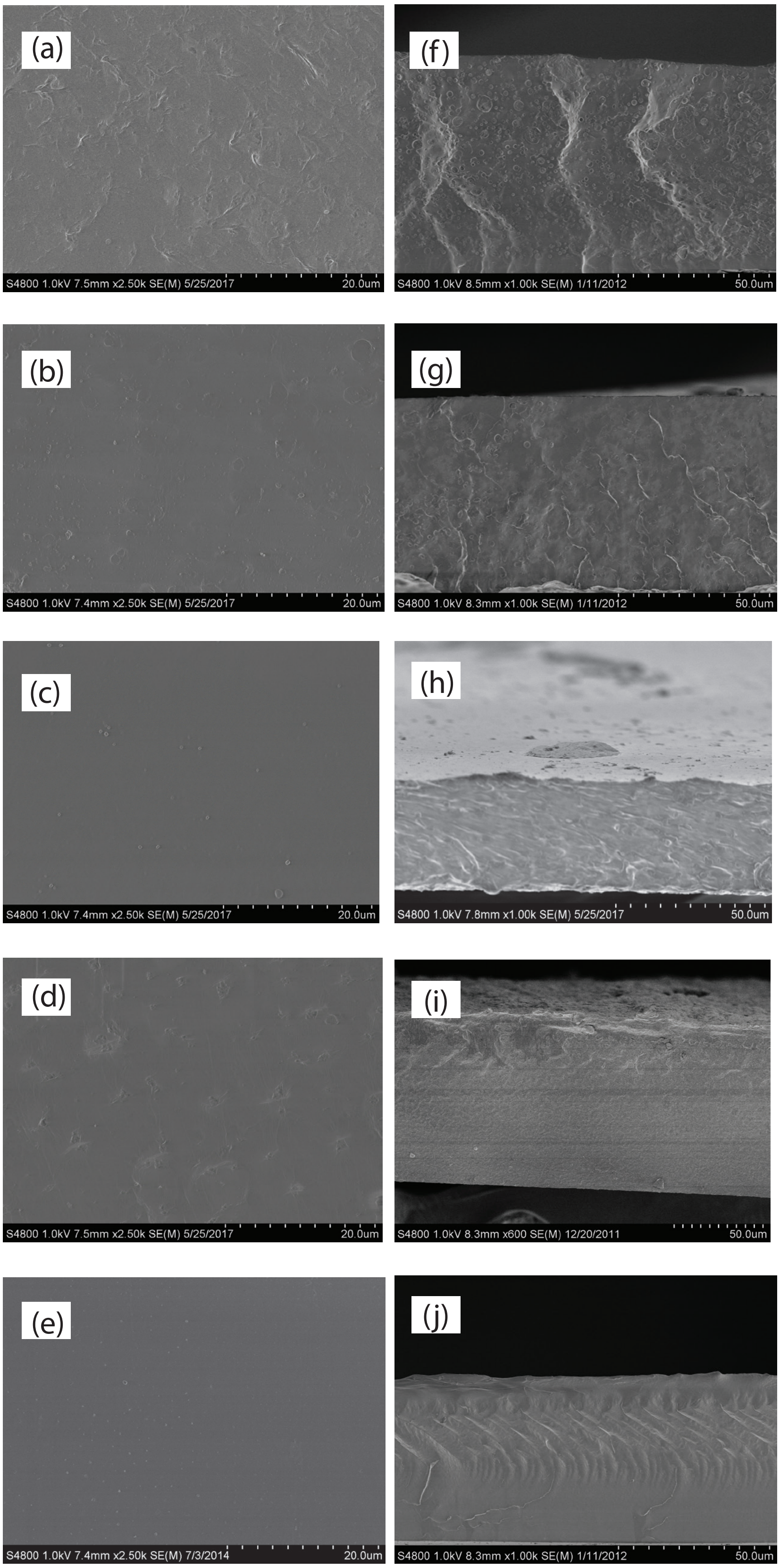

Fig. 5. SEM images of the surface and cross-section of PEBA, PU and PEBA–PU blend membrane. SEM images of the surface: (a) PU, (b) 20% PEBA, (c) 50% PEBA, (d) 80% PEBA and (e) PEBA. SEM images of the cross-section: (f) PU, (g) 20% PEBA, (h) 50% PEBA, (i) 80% PEBA and (j) PEBA.

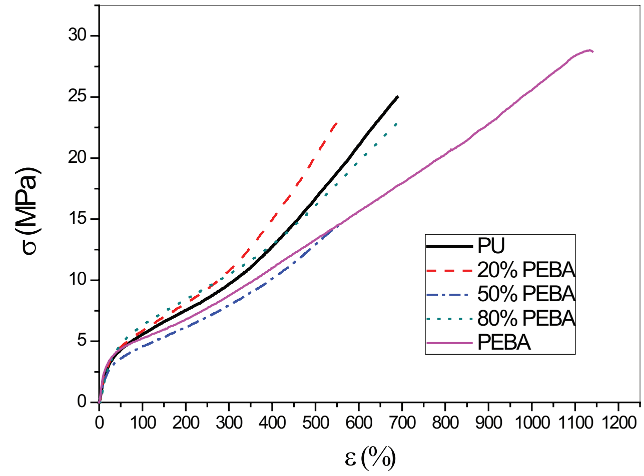

Fig. 6. Tensile stress–strain data for membranes.

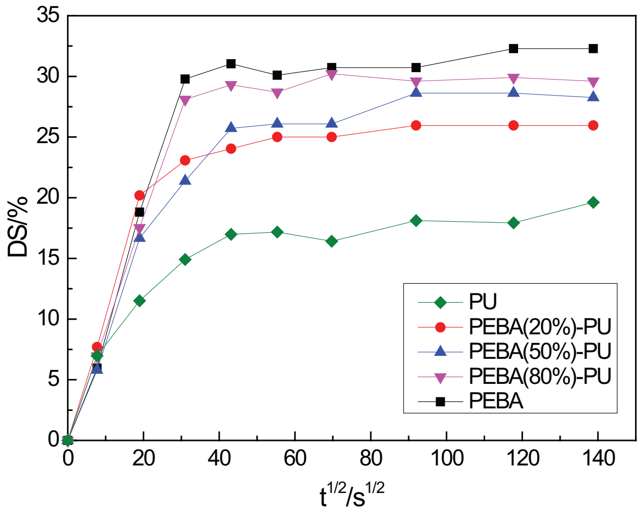

Fig. 7. Degree of swelling of different membrane variation with time.

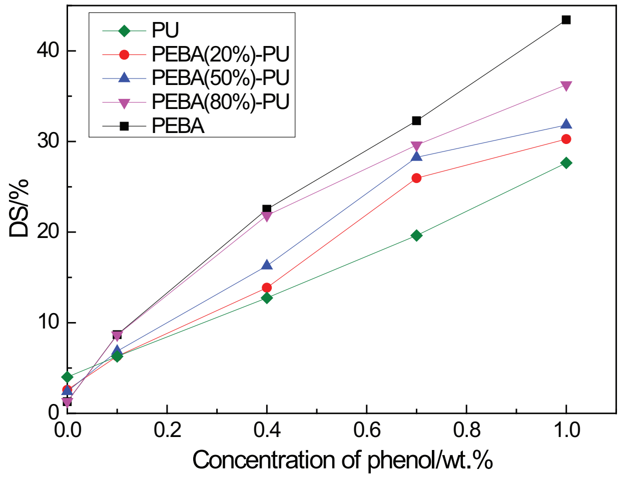

Fig. 8. Degree of swelling at different concentration of phenol aqueous solutions.

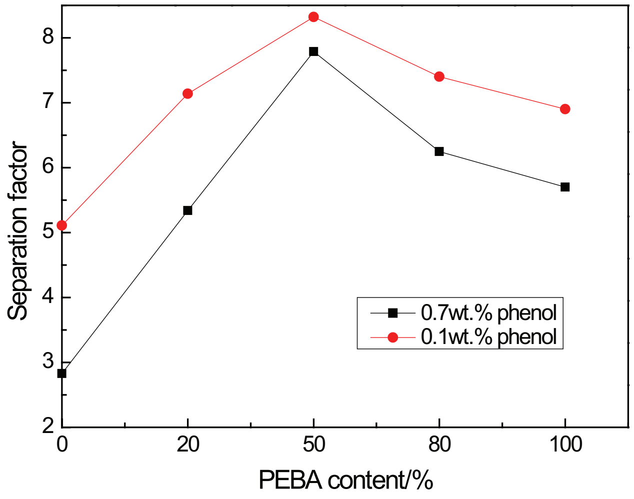

Fig. 9. Effect of PEBA content on separation factor of PEBA–PU blend membranes (30°C).

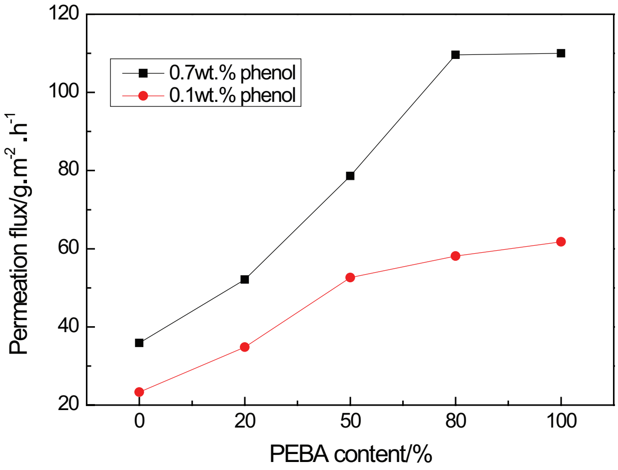

Fig. 10. Effect of PEBA content on permeation flux of PEBA–PU membranes (30°C).

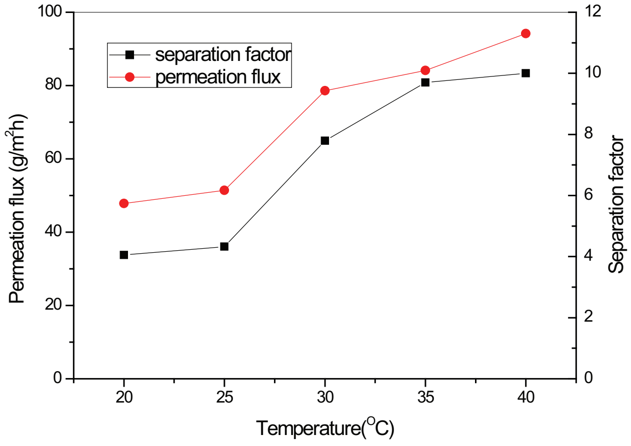

Fig. 11. Effect of temperature on the pervaporation of butanol (PEBA (50 wt%)–PU blend membrane and 0.1 wt% phenol solution).

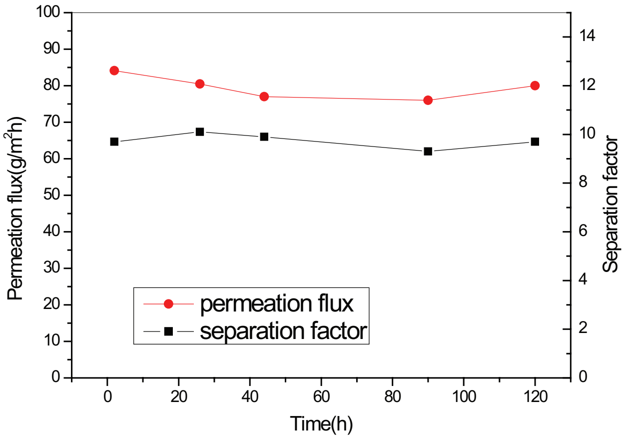

Fig. 12. Sustained pervaporation of PEBA–PU blend membrane (PEBA (50 wt%)–PU blend membrane, 35°C and 0.1 wt% phenol solution).

Symbols

A — The effective membrane area
C_1 — Phenol concentration of the feed (weight fraction)
C_2 — Phenol concentration of the permeate (weight fraction)
DS — Degree of swelling
E_{coh} — Cohesive energy
E_{hi} — The group contribution for hydrogen bonding solubility parameter
F_{di} — The group contribution for dispersion solubility parameter
F_{pi} — The group contribution for polar solubility parameter
M — Molecular weight of repetitive unit
m — Polymerization degree
t — Permeation time
V — The molar volume
V_i — The molar volume of group
W_d — Dry weight
W_s — Swollen weight
W — Weight of permeate sample
δ — Solubility parameter
δ_d^∞ — Dispersion solubility parameter
δ_p — Polar solubility parameter
δ_h — Hydrogen bonding
χ — Flory–Huggins parameter
ρ — Density
ϕ — Volume fractions of pure substances A or B
ΔE_{mix} — Mixed energy
$(\chi_{AB})_{critical}$ — Critical value of Flory–Huggins parameter
σ — Stress
ε — Strain

Subscripts

i — Phenol component
j — Water component
A — PEBA
B — PU

References

[1] I. Perez-Silva, C.A. Galan-Vidal, M.T. Ramirez-Silva, J.A. Rodriguez, G.A. Alvarez-Romero, M.E. Paez-Hernandez, Phenol removal process development from synthetic wastewater solutions using a polymer inclusion membrane, Ind. Eng. Chem. Res., 52 (2013) 4919–4923.

[2] X.G. Hao, M. Pritzker, X.S. Feng, Use of pervaporation for the separation of phenol from dilute aqueous solutions, J. Membr. Sci., 335 (2009) 96–102.

[3] M. Medir, A. Arriola, D. Mackay, F. Giralt, Phenol recovery from water effluents with mixed solvents, J. Chem. Eng. Data, 30 (1985) 157–159.

[4] V.K. Krishnakumar, M.M. Sharma, A novel method of recovering phenolic substances from aqueous alkaline waste streams, Ind. Eng. Chem. Process Des. Dev., 23 (1984) 410–413.

[5] M.T. Ravanchi, T. Kaghazchi, A. Kargani, Application of membrane separation processes in petrochemical industry: a review, Desalination, 235 (2009) 199–244.

[6] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, J. Hazard. Mater., 160 (2008) 265–288.

[7] P. Wu, R.W. Field, R. England, B.J. Brisdon, A fundamental study of organofunctionalised PDMS membranes for the pervaporative recovery of phenolic compounds from aqueous streams, J. Membr. Sci., 190 (2001) 147–157.

[8] T. Gupta, N.C. Pradhan, B. Adhikari, Separation of phenol from aqueous solution by pervaporation using HTPB-based polyurethaneurea membrane, J. Membr. Sci., 217 (2003) 43–53.

[9] M. Xiao, J.T. Zhou, Y.G. Zhang, X.J. Hu, S.F. Li, Pertraction performance of phenol through PDMS/PVDF composite membrane in the membrane aromatic recovery system (MARS), J. Membr. Sci., 428 (2013) 172–180.

[10] N.C. Pradhan, C.S. Sarkar, S. Niyogi, B. Adhikari, Separation of phenol-water mixture by membrane pervaporation using polyimide membranes, J. Appl. Polym. Sci., 83 (2001) 822–829.

[11] F. Lipnizki, S. Hausmanns, P.K. Ten, R.W. Field, G. Laufenberg, Organophilic pervaporation: prospects and performance, Chem. Eng. J., 73 (1999) 113–129.

[12] M. Hoshi, M. Ieshige, T. Saitoh, T. Nakagawa, Separation of aqueous phenol through polyurethane membranes by pervaporation. II. Influence of diisocyanate and diol compounds and crosslinker, J. Appl. Polym. Sci., 71 (1999) 439–448.

[13] B. Sinha, U.K. Ghosh, N.C. Pradhan, B. Adhikari, Separation of phenol from aqueous solution by membrane pervaporation using modified polyurethaneurea membranes, J. Appl. Polym. Sci., 101 (2006) 1857–1865.

[14] Y. Tamai, H. Tanaka, K. Nakanishi, Molecular simulation of permeation of small penetrants through membranes. 2. Solubilities, Macromolecules, 28 (1995) 2544–2554.

[15] E. Kucukpinar, P. Doruker, Molecular simulations of small gas diffusion and solubility in copolymers of styrene, Polymer, 44 (2003) 3607–3620.

[16] S.S. Jawalkar, T.M. Aminabhavi, Molecular modeling simulations and thermodynamic approaches to investigate compatibility/incompatibility of poly(l-lactide) and poly(vinyl alcohol) blends, Polymer, 47 (2006) 8061–8071.

[17] J. Brandrup, E.H. Immergut, E.A Grulke, Polymer Handbook, Wiley, New York, 1999.

[18] I.M.D. Arenaza, E. Meaurio, B. Coto, J.R. Sarasua, Molecular dynamics modelling for the analysis and prediction of miscibility in polylactide/polyvinilphenol blends, Polymer, 51 (2010) 4431–4438.

[19] L.Q. Liao, Y.Z. Fu, X.Y. Liang, L.Y. Mei, Y.Q. Liu, Diffusion of CO_2 molecules in polyethylene terephthalate/polylactide blends estimated by molecular dynamics simulations, Bull. Korean Chem. Soc., 34 (2013) 753–758.

[20] F.S. Moolman, M. Meunier, P.W. Labuschagne, P.A. Truter, Compatibility of polyvinyl alcohol and poly(methyl vinyl ether-co-maleic acid) blends estimated by molecular dynamics, Polymer, 46 (2005) 6192–6200.

[21] A. Bottino, G. Capannelli, S. Munari, A. Turturro, Solubility parameters of poly(vinylidene fluoride), J. Polym. Sci., Part B: Polym. Phys., 26 (1988) 785–794.

[22] Y.H. Wu, G.Q. Tian, H.F. Tan, X.T. Fu, Pervaporation of phenol wastewater with PVDF-PU blend membrane, Desal. Wat. Treat., 51 (2013) 5311–5318.