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Pervaporation of phenol wastewater with PVDF–PU blend membrane

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ABSTRACT

The compatibility of poly (vinylidene fluoride) (PVDF) and polyurethane (PU) was studied based on the theoretical analysis of solubility parameter and mixing enthalpy. The results showed that PVDF and PU are partially compatible. Then, the blend membranes of PVDF–PU with 5, 10, and 80 wt.% PVDF content were prepared with the application of solution blending in solvent N, N-dimethylacetamide (DMA). The membranes were characterized by Fourier transformed infrared spectroscopy (FT-IR) to assess the intermolecular interactions. And the morphology of the membranes was studied by scanning electron microscope (SEM). 80wt.% PVDF–PU membrane was porous. However, 5% and 10% PVDF–PU membrane were suitable for pervaporation. The study showed that the degree of swelling (DS) of PVDF–PU membrane increased with the phenol concentration, which suggested that these membranes have stronger sorption capacity to phenol. Then, the pervapration performance of the membranes was examined. The results showed that the pevaporation performances of the blend membranes have been improved comparing with the plain PU membrane.

Keywords: PVDF; PU; Blend; Pervaporation; Phenol

1. Introduction

Phenol and phenolic derivatives are widely used in chemical industry. In 2010, about nine million ton phenol was produced worldwide, with a significantly increasing trend. Phenol is a kind of common organic pollutants. It is highly toxic and cannot been easily degraded biologically at high concentration. Phenol can be rapidly absorbed through the skin. Phenol can affect the liver, kidneys, lungs, and vascular system. Comas, convulsions, and death may result from overexposing to the environment with high phenol concentration. A large volume of aqueous effluents containing phenol is produced in various fields, such as coal processing, petrochemical, pharmaceutical, pulp and paper industries etc., which will pollute our environment severely [1]. Phenol-containing wastewater may not be conducted into open water without treatment because of its toxicity. In China, the phenol limits for wastewater emissions are 0.3 mg/l (0.3 ppm), while the limit for phenols in potable and waters is 0.002 mg/l [2].

In order to make full use of the industrial value of phenol and protect human health and environment, the separation or recovery of phenol from wastewater has

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attracted lots of concerns. Conventional methods used for phenol recovery are extraction, adsorption, and distillation. Among them, distillation procedures are quite energy demanding. Extraction and adsorption are usually uneconomical to use when the phenol concentration is low [3]. Recently, pervaporation has attracted attention as an alternative technique for the removal of low volatile organics from wastewater, showing many advantages: minimal energy consumption, no secondary contamination, high efficiency and easy operation. By now, pervaporation with siloxane (especially polydimethylsiloxane (PDMS)) membranes, urethane polymers, and poly (ether block amide) (PEBA) membranes have been investigated extensively. Bakhshi et al. [4] dealt with the separation of binary water–phenol mixtures and ternary water–phenol–ethanol mixtures by pervaporation with PDMS membranes. Because phenol has a higher solubility parameter in silicone membranes, the membrane was highly efficient for the PV separation of phenol from dilute aqueous solutions. Gupta et al. [5] synthesized hydroxyterminated polybutadiene (HTPB)-based polyurethane (PU) and polyurethaneurea membranes and investigated their pervaporation performance. When pervaporation was carried out at 60°C, polyurethaneurea membrane synthesized with 50 mol% diamine showed about 97% phenol selectivity in permeate but relatively low flux ($<10\,\mathrm{g\,m^{-2}\,h^{-1}}$). In 2009, pervaporation using poly (ether block amide) (PEBA 2533) membrane was studied as a means of recovering phenol from wastewater streams. This membrane showed high permselectivity to phenol due to its high solubility selectivity [6]. In order to increase the permeation flux, incorporating porosity into the polymer membrane by treatment with lithium chloride and then leaching it out in hot water was investigated. The porous membrane showed better pervaporation separation efficiency than the corresponding dense membrane [7,8].

In this article, blend membrane, an effective way of developing new material that will exhibit combinations of properties superior to either of the pure components alone [9], was prepared and used in the pervaporation of the model phenol wastewater. As porous membrane may have potential use in pervaporation, poly (vinylidene fluoride) (PVDF), an excellent material to form porous membrane, was selected as a composition of blend membrane. And PU, a unique polymer comprising of flexible soft segment and rigid hard segment, was used as the other composition. The compatibility of PVDF and PU was analyzed theoretically through solubility parameter method and mixing enthalpy method. Then, the PVDF–PU membrane was synthesized and characterized. The swelling properties and pervaporation performance of PVDF–PU blend membrane were also investigated.

2. Theoretical analysis

2.1. The structure of PU and PVDF

PU is a class of thermoplastic elastomer, which consisted of rigid hard and flexible soft segments, having microphase separated structure. This unique structure makes it has good mechanical property, thermal stability, and chemical stability. In this article PU1185A10, a kind of polyether-based polyurethane was used. It has affinity for organics. The structure of PU1185A10 is listed as follows (Fig. 1).

PVDF is the homopolymer of vinylidene fluoride. It is a kind of crystalline polymer with excellent mechanical properties, tenacity and film forming ability. It has been widely used to get microfiltration or ultrafiltration membrane. Its structure was listed in Fig. 2.

2.2. Calculation of solubility parameter

The solubility parameter of a polymer equals to the sum of molar attraction constant of each group in repeat unit divide the molar volume. In polar polymer system, dipole or hydrogen bond would influence the intermolecular force. So Hansen [10] proposed that the solubility parameter was composed of three parts: dispersion solubility parameter, and polar solubility parameter, hydrogen-bonding solubility parameter. Their relation is as follows,

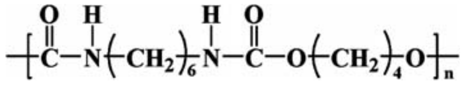
$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

δ_d is the dispersion solubility parameter, δ_p is the polar solubility parameter and δ_h is the hydrogen-bonding solubility parameter.

Each term in Eq. (1) can be estimated by group contribution methods. They can be calculated by Eqs. (2)–(4):

$$\delta_d = \sum F_{di} / \sum V_i \tag{2}$$

$$\delta_p = \sqrt{\sum F_{pi}^2} / \sum V_i \tag{3}$$



$$-\!\!\left[\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}\left(CH_2\right)_6\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O\left(CH_2\right)_4O\right]_n$$

Fig. 1. The structure of polyurethane.

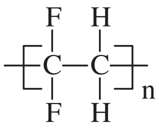

$$-\!\left[CF_2-CH_2\right]_n\!-$$

Fig. 2. The structure of PVDF.

$$\delta_h = \sqrt{\sum E_{hi}/\sum V_i} \tag{4}$$

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, V_i is the molar volume of group.

The values of F_{di}, F_{pi}, E_{hi} and V_i for PU can be found in [11]. Then, with the application of Eqs. (1)–(4), the solubility parameter of polymer PU can be derived. While the solubility parameter of PVDF was $23.2\,\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$ according to Ref. [12]. Both the solubility parameters of PU and PVDF were listed in Table 1.

Based on the blending theory, if $|\Delta\delta|$ of the two polymers is less than $0.5\,\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$, they are completely compatible. Otherwise, the polymer mixture may be partly compatible, needing evaluation through other methods. According to the calculation results of Table 1, the value of $|\Delta\delta|$ of PVDF and PU is $1.95\,\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$, which is greater than $0.5\,\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$. So we need to do further investigation on the compatibility of PU and PVDF.

2.3. The mixing enthalpy of PU and PVDF

Schneier [13] suggested that the mixing enthalpy of two blended components could be calculated as follows:

$$\Delta H_m = \left\{ X_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \left[\frac{X_2}{(1 - X_2) M_2 \rho_2 + (1 - X_1) M_1 \rho_1} \right]^2 \right\}^{1/2} \tag{5}$$

where X_i, ρ_i, M_i and δ_i ($i = 1, 2$) are mass fraction, density, molecular weight of repeat unit and solubility parameter respectively. The critical value of ΔH_m for thermodynamic compatibility is $0.0418\,\mathrm{J\,mol}^{-1}$. When different polymers were mixed, if ΔH_m value was less than the critical value, the system would be compatible completely. If ΔH_m value was greater than the critical value, the system would be incompatible completely. While the intersection of $\Delta H_m \sim X$ curve and the horizontal line means that the system was partly compatible.

After estimation of PU–PVDF blend with different weight fraction, $\Delta H_m \sim X$ curve can be got (Fig. 3). In Fig. 3, $\Delta H_m \sim X$ curve and the critical line intersected. So PVDF and PU are partly compatible. When the weight fraction of PVDF was less than 10% or greater than 40%, PVDF is compatible with PU, which means that PVDF and PU can be used to get PVDF–PU blend membrane at this PVDF content range.

3. Experimental

3.1. Materials

PU1185A10 was supplied by BASF The Chemical Company. PVDF (PR904) was purchased from Shanghai 3F New Materials Co., LTD. Phenol and dimethylacetamide (DMA) of analytical purity was supplied by Sinopharm Chemical Reagent Co., Ltd. Deionized water was selfmade.

3.2. Solvent selection

PVDF and PU are both polar polymer. So the appropriate solvent selection follows the polarity similarity principle. Solubility parameter method could be also applied to solvent selection. The most widely used polar solvents in the preparation of membrane are N, N-DMA, N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP). Besides, *n*-butanol was always used as solvent for PEBA membrane preparation. The solubility parameters of polymer and different solvents were listed in Table 2 [11].

PU and PVDF were tested their solubility in the above-mentioned solvents. The resulting dissolution situations were listed in Table 3. According to the solubility parameter and the actual solving performance of different solvents, DMA was selected as the solvent for PVDF–PU blend membrane.

3.3. Preparation of PU–PVDF blend membrane

In this article, PU–PVDF blend membrane was prepared through solution-blended process. Dried PU

Table 1
Solubility parameters of PEBA and PU

Polymer	δ_d ($\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$)	δ_p ($\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$)	δ_h ($\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$)	δ ($\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$)
PU	18.45	3.66	9.90	21.25
PVDF	17.2	12.5	9.2	23.2

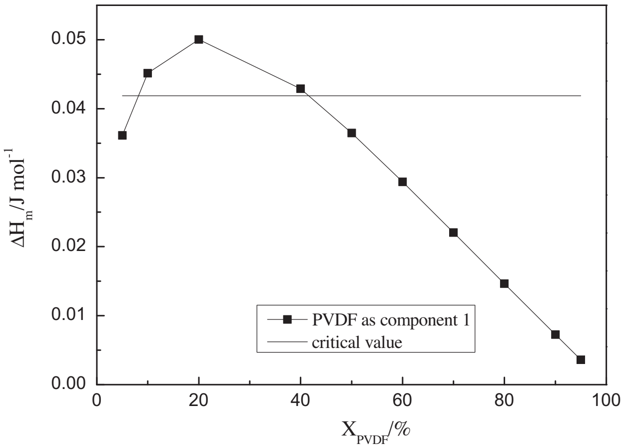


Fig. 3. Mixing enthalpy vs. weight percentage of component 1 in PVDF–PU blends.

and PVDF at a ratio were added into DMA solvent and stirred at 70℃. After the polymer dissolved completely by stirring, the prepared 10 wt.% casting solution was deaerated and then toppled on a horizontal glass plate and casted with a scraper. The solvent was evaporated in the atmosphere for 48 h. And then the membrane was further dried at 70℃ in a vacuum oven.

According to the above analysis and calculation, PVDF and PU are partly compatible when the PVDF weight fraction is less than 10% or greater than 40%. Hence, in this article PVDF–PU blend membrane with the PVDF weight fraction of 5, 10, and 80% were prepared. Pure PU membrane was considered as the plain membrane. The membrane with high PVDF content (80%) was apparently porous membrane, with the pore diameter of 5–10 μm which was not suitable for pervaporation application.

3.4. Membrane characterization

FT-IR spectral measurements were performed using NEXUS FT-IR spectrometer (Thermo Nicolet, USA). Each sample was grounded well to make KBr pellets under pressure. In each scan, the amount of membrane sample and KBr were kept constant in order to find the changes in the intensities of characteristics peaks.

Hitachi S4800 scanning electron microscopy were used to observe the surface and cross-section morphologies of the membranes.

3.5. Swelling studies

The dried PVDF–PU membrane was weighed and immersed in phenol aqueous solution at 35℃. Then, the membrane sample was periodically taken out and wiped carefully with Kimwipes (Kimberly-Clark) to remove the liquid on surface. After weighed, the sample was put back into aqueous solution again until the sample weight was unchanged. The degree of swelling (DS) was determined by

Table 2
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 ($J^{1/2}cm^{-3/2}$)
PU	18.45	3.66	9.90	21.25
PVDF	17.2	12.5	9.2	23.2
DMA	16.8	11.5	10.2	22.7
DMF	17.4	13.7	11.3	24.8
NMP	18	12.3	7.2	22.9
n-Butanol	16	5.7	15.8	23.1
Ethyl acetate	15.8	5.3	7.2	18.1
Phenol	18.0	5.9	14.9	24.1
Water	15.5	16.0	42.3	47.8

Table 3
Dissolution of the polymers in different solvents

$T = 70$℃	Ethyl acetate	NMP	*n*-Butanol	DMA	DMF
PU	Insoluble	Soluble	Non-soluble	Soluble	–
PVDF	–	–	–	Soluble	Soluble

$$\mathrm{DS}\ (\%) = \frac{W_s - W_d}{W_d} \times 100 \tag{6}$$

where W_s and W_d are the mass of swollen and dry membranes, respectively.

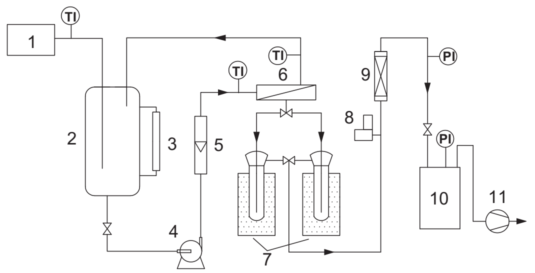
3.6. Pervaporation experiments

The pervaporation apparatus was shown in Fig. 4. The feed liquid storing in the reservoir was sent to the membrane cell by a pump. Some of the feed went through the membrane and evaporated in vacuum environment on the downstream side. The permeate vapor was condensed and collected in the cold trap with liquid nitrogen. The retentate was recirculated to the liquid tank. During the experiments, the upstream side of the membrane cell was maintained at atmospheric pressure and the downstream side pressure was kept 320 Pa. The feed temperature is controlled through a temperature-controller, and the feed rate was monitored by a rotameter. The temperatures at the entrance and exit of the membrane module were measured with two thermocouples. The effective membrane area is $3.6 \times 10^{-3}\,\mathrm{m}^2$.

The concentrations of permeates and feed were determined by gas chromatography (GC7890F, TECHCOMP (HOLDINGS) LIMITED) equipped with a FID detector and using HP-FFAP capillary column, with benzyl alcohol as internal standard. The weight of permeate was weighed by electronic balance (with the accuracy of 0.1 mg).

The pervaporation performance of a membrane is usually evaluated in terms of separation factor α and permeation flux J, which are determined as follows:

$$\alpha = \frac{(C_i/C_j)_{\mathrm{Permeate}}}{(C_i/C_j)_{\mathrm{Feed}}} \tag{7}$$



1. thermal controller; 2. liquid reservoir;3.level gauge; 4.liquid pump; 5.rotameter; 6.membrane cell; 7.cold trap; 8.pressure sensor; 9.dryer; 10. buffer tank; 11. vacuum pump

Fig. 4. Schematic diagram of the pervaporation experimental equipment.

$$J = \frac{W}{At} \tag{8}$$

where C_i and C_j are the mass fractions of *n*-butanol and water components, respectively; W is the mass of the permeate, g; A is the effective membrane area, m^2; t is the permeation time, h.

4. Results and discussion

4.1. FT-IR analysis

Fig. 5 shows the FT-IR spectrum of PU sample, 5% and 10% PVDF–PU sample. After the blending, the stretching vibration band of N–H at $3{,}330\,\mathrm{cm}^{-1}$ in PU spectra framework got narrower and weaker. The reason was that there is NH–CO group in PU, which contained proton donor NH- and proton accepter –CO simultaneously. At the same time, the fluorine atom in PVDF has strong electronegativity, which can form hydrogen bond with PU.

4.2. Scanning electron microscope analysis

The scanning electron microscope (SEM) images of the surfaces of PU and 5%, 10% and 80% PVDF–PU sample were shown in Fig. 6.

From Fig 6, the 80% PVDF–PU membrane was apparently porous, and the pore size was about 5–10 μm. Phenol and water both can permeate the membrane easily. PU plain membrane was a dense homogeneous membrane with a very smooth surface. The microphase separation phenomena appeared in 5% and 10% PVDF–PU membrane, which might be beneficial to enhance the permeation flux.

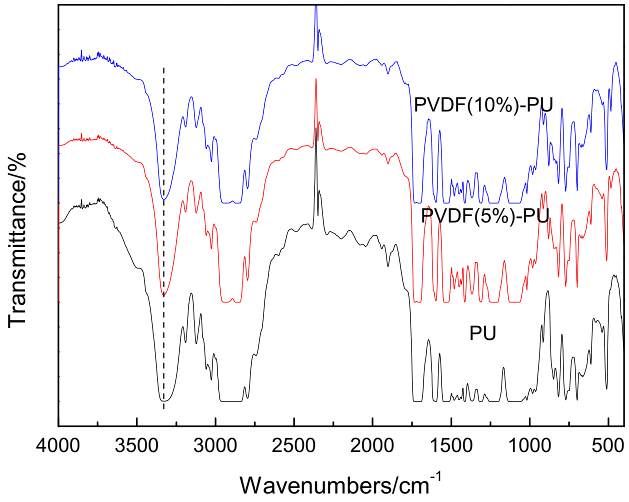
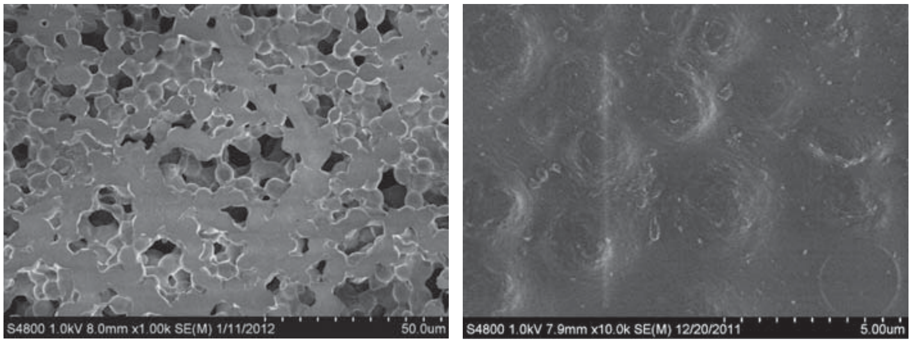
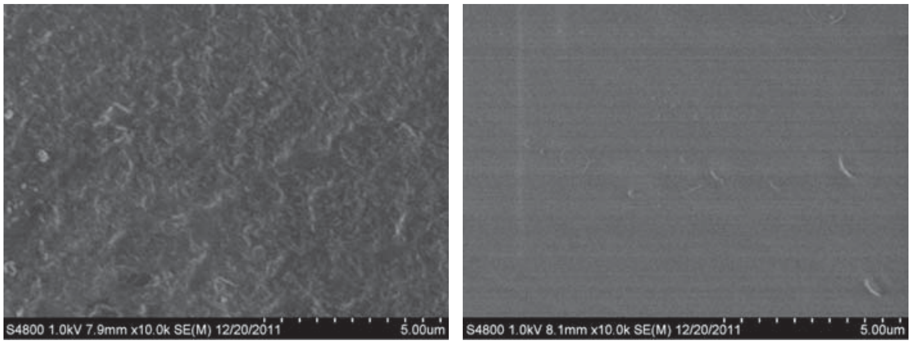


Fig. 5. FTIR spectra of PU and PVDF–PU membranes.



(a) 80%PVDF-PU (b) 5%PVDF-PU



(c) 10%PVDF-PU (d) PU

Fig. 6. The SEM images of surfaces of PU and PVDF–PU blend membranes.

The cross-section SEM image (Fig. 7(a)) of 80% PVDF–PU further confirmed its porous structure, while PU, 5%, 10% PVDF–PU were all dense membrane, which could be used in pervaporation experiment. And compared with 10% PVDF–PU blend membrane, 5% PVDF–PU membrane showed more uniform structure, which meant the blending effect of this membrane was better (Fig. 7).

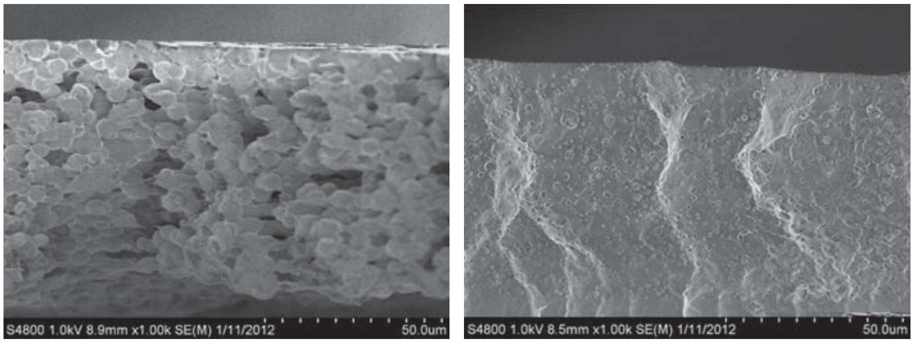
4.3. Swelling properties

Fig. 8 shows that the swelling properties of PU and PVDF–PU blend membrane in phenol aqueous solution at different phenol concentration. The swelling degree of all the membranes increased with phenol concentration evidently, reflecting that they had certain organophilic property. The swelling behavior of these three membranes made them exhibit phenol permselective property in pervporation process.

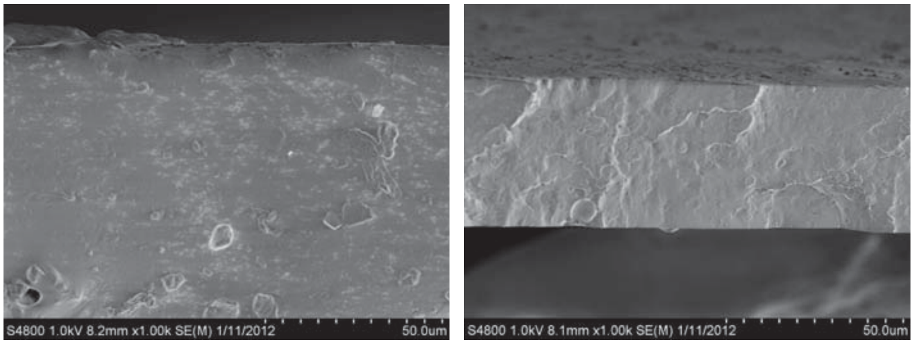
4.4. Pervaporation performance

PU, 5% and 10% PVDF–PU membrane were used to pervaporate phenol solution at 35℃. The effects of the membrane composition on the separation factor and permeation flux were shown in Fig. 9. The separation factor of PVDF–PU blend membrane was greater than that of PU plain membrane. With the increasing of PVDF weight fraction, the separation factor first increased and then decreased. When the feed concentration was 0.7 wt.% and the flow rate was $50\,\mathrm{l\,h^{-1}}$, 5% PVDF–PU membrane had the highest separation factor 8.5. Because there is hydrogen formed between PVDF and PU, suppressing water diffusion in the membrane. The separation factor of 10% PVDF–PU membrane dropped obviously. The reason might be that the compatibility of 10% PVDF–PU was not so good as that of 5% PVDF–PU membrane. Meanwhile, on the whole the permation flux of PVDF–PU blend membrane was higher than that of PU plain membrane. Because with blending, the membrane had a tendency to form porous structure, the free volume of the blend membrane increased, promoting the transport process in the membrane and increasing the permeation flux.

In order to investigate how temperature influence the separation factor and permeation flux, PU, 5% and 10% PVDF–PU membrane were tested their pervaporation performance at different temperatures. From Fig. 10, the separation factor of PU and 5% PVDF–PU membrane increased with temperature. While 10% PVDF–PU membrane showed an opposite



(a) 80%PVDF-PU (b) 5%PVDF-PU



(c) 10%PVDF-PU (d) PU

Fig. 7. The SEM images of the cross section of PU and PVDF–PU membranes.

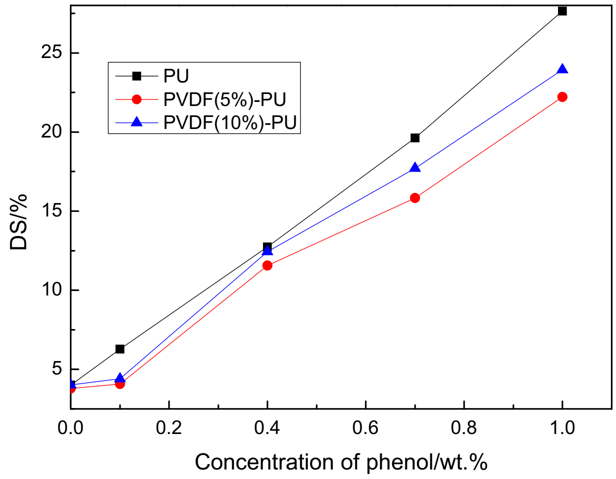


Fig. 8. Swelling degree of the different PVDF–PU membranes vs. concentration of phenol solution.

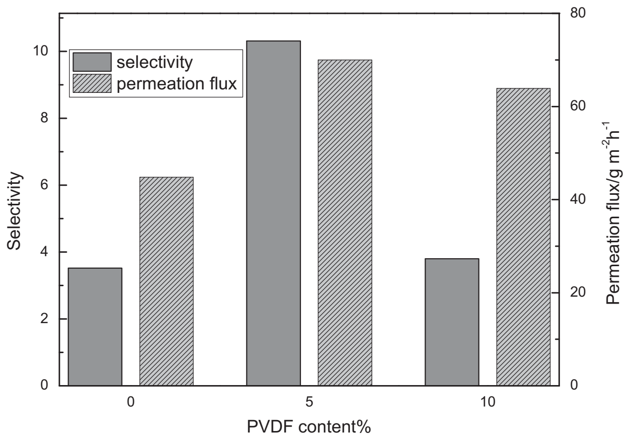


Fig. 9. Effect of PVDF content on permeation flux and selectivity of PVDF–PU blend membranes.

trend on separation factor. The reason was that the compatibility of PVDF and PU was not so good that the membrane structure was more likely be porous. When temperature increased, the motion of water and phenol molecule both were accelerated, which make them get through the membrane more easily. Therefore, the separation factor decreased with temperature.

Fig. 11 shows the influences of temperature on permeation flux. 5% PVDF–PU membrane with good compatibility displayed higher permeation flux. Moreover, the permeation flux of the three membranes increased with temperature.

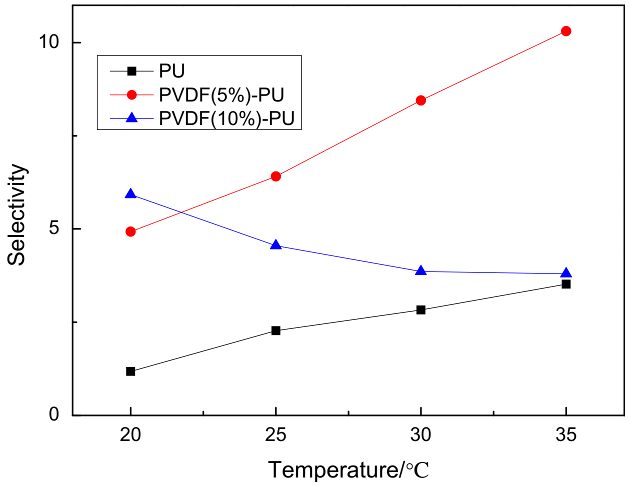


Fig. 10. Effect of temperature on the selectivity of phenol solution for PVDF–PU membrane.

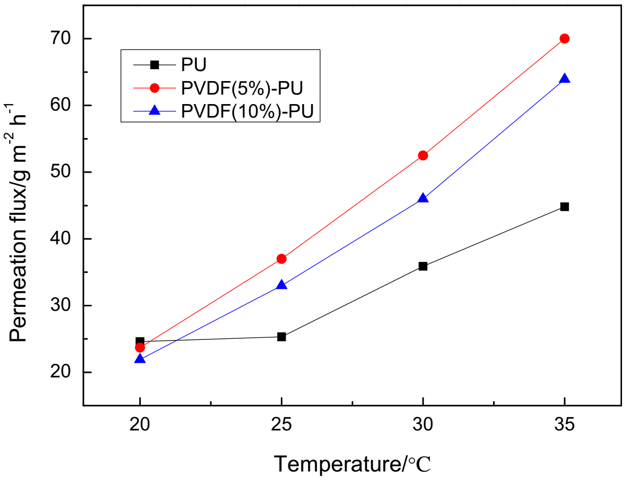


Fig. 11. Effect of temperature on the flux of phenol solution for PVDF–PU membranes.

5. Conclusions

The compatibility of PVDF–PU blend was investigated based on the calculation and analysis of their solubility parameters and mixing enthalpy. The results showed that PVDF, a hydrophobic membrane material, can be blended with PU partly. It was compatible with PU when the weight fraction of PVDF was less than 10% or greater than 40%. Then, PVDF–PU blend membranes were prepared and characterized. The structure and morphology of the membranes were characterized by FT-IR and SEM. The blend membrane with high content of PVDF was porous. However, 5% and 10% PVDF–PU membrane were suitable for the application of pervaporation. The effects of the ratio of blend membrane on swelling behavior and pervaporation performance were investigated. The swelling degree of PU and PVDF–PU membranes increased with phenol concentration, which meant that they all had certain organophilic property. Compared with PU plain membrane, pevaporation performance of blend membranes has been enhanced. And the flux and separation factor of 5% PVDF–PU blend membrane both increased with feed temperature evidently.

Acknowledgments

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