Preparation and Performances of Poly(phthalazinone ether sulfone ketone) Hollow Fiber Membranes with Excellent Thermotolerance

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ABSTRACT: The cloud points of PPESK/NMP/H_2O ternary system at different temperatures were measured by titrimetric method. The binodal lines in the ternary phase diagram of the poly(phthalazinone ether sulfone ketone (PPESK) dope system was determined, on the basis of the cloud point experimental data being linearly fitted with the semiempirical linear cloud point correlation. Furthermore, phase separation behavior during the phase inversion of PPESK membrane-forming system was discussed in terms of the phase diagram. Then, dry–wet spinning technique was employed in manufacturing PPESK hollow fiber membranes by immersion precipitation method. The cross-section morphologies of hollow fibers were observed by scanning electronic microscopy. Also, the effects of dope solution composition and spinning parameters, including the coagulant composition and the spinning temperature on the separation performances of fibers, were evaluated by permeability measurements. The thermotolerance of the PPESK hollow fiber membranes prepared in the work was examined for the permeation operation at different temperatures and pressure differences. The experimental results showed that pure water flux increases several fold along with the temperature increases from 20 to 80°C at different operation pressures, while the solute rejection only decreases slightly. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 878–884, 2006

Key words: poly(phthalazinone ether sulfone ketone); hollow fiber membranes; phase diagrams; dry–wet spinning

INTRODUCTION

The polymers used as ultrafiltration (UF) and nanofiltration (NF) membrane materials mainly included cellulose acetate, polysulfone, poly(ether sulfone) (PES), polyolefin (containing PP, PE), PVC, PAN, PVDF, PTFE, and polyetherimide.[1,2] The majority of these materials can be used to prepare porous membranes (flat or hollow fiber) by phase inversion method, except for some unsolvable polymers such as PP and PTFE. But the application of these available materials is limited, because such-and-such shortcomings always adhere to them. Therefore, it is necessary and significant to develop new membrane materials that are applicable in some special separation fields or rigorous operation situation.

Owing to the thermal instability of polymers, most polymeric membranes have been limited to application at low operation temperatures (usually below 50°C).[3] However, in some areas, such as gas separation, reverse osmosis, UF, and NF, high-temperature separation is advantageous and needful.[4–6] The treatment of some high-temperature wastewater, such as the effluents from dye industry, the black liquor from pulp mills, requires the separation membrane to possess good thermal stability.[5,7] Furthermore, the high-temperature cleaning of the thermotolerable membrane and the lower operation pressure of the hot fluid separation would reduce the treatment time and cost.

A serial polymer of poly(phthalazinone)s containing phthalazinone moiety were synthesized by X.G. Jian and coworkers[8,9] and Meng et al.[10] Poly-(phthalazinone ether sulfone ketone) (PPESK), a member of poly(phthalazinone)s, is a sort of amorphous polymer, and it demonstrated excellent comprehensive properties as membrane materials in gas separation, UF, and NF. Some studies showed that PPESK could be applied for dyes and salts separation at high operation temperature, because of its outstanding thermal stability.[11–15] The excellent solubility makes PPESK to be easily fabricated to a flat porous membrane for UF and NF by immersion phase inversion method. Most reports[8–15] about PPESK concentrated on its chemical modification for the purpose of preparing flat separation membrane with better properties. As reported by several authors,[12,13] UF and composite NF membranes were prepared by combining PPESK with sulfonated PPESK (SPPESK). As the sulfonic group is introduced, SPPESK exhibits better

thermal stability and hydrophilicity than does PPESK. SPPESK composite NF membrane could be applied in the separation of inorganic salts such as Na_2SO_4 and $MgCl_2$. Y. Su et al.[14] made use of quaternized PPESK as membrane material for salt separation. Also, the SPPESK and other sulfonated poly(phthalazinones) were applied for proton exchange membrane materials.[15,16]

In the present work, the thermodynamics of PPESK/NMP/H$_2$O ternary system was studied by means of a phase separation diagram. Further, PPESK hollow fiber membrane was produced and characterized. The effects of the dope solution compositions and membrane-fabricating parameters on the hollow fiber morphologies and separation performances were investigated. Finally, the thermal tolerance of PPESK hollow fibers is studied by the permeability experiments at different operating temperatures. The excellent thermal stability endows PPESK hollow fiber membrane with a potential application at high temperature and at high flux NF and UF.

EXPERIMENTAL

Materials and reagents

PPESK (S : K = 1 : 1, $[\eta]$ = 0.65 dL/g) was purchased from Dalian New Polymer (P.R. China). Commercially available N-methyl-2-pyrrodone (NMP) (Shanghai Wulian chemical plant, P.R. China, reagent grade) served as the solvent. Poly(ethylene glycol) (PEG) with a MW of 10,000 was provided by Sigma. The polymeric additive, PVP(K30), was from Sinapharm Group. Both ethanol and n-hexane used in the experiments were analytical reagents.

Cloud point and phase separation diagram

Titrimetric method was employed on the determination of cloud point of PPESK/NMP/H$_2$O ternary system.[17,18] In the method, with NMP acting as a solvent, a series of solutions containing a certain amount of PPESK (0.5–15 wt %) was prepared and put into a tailor-made glass bottle. The solution temperature was stabilized at 20, 40, and 60°C, respectively, using a thermostatic water bath. The nonsolvent, namely deionized water, was added to the solution with a microsyringe and stirred vigorously. The addition of water was stopped when the solution became visually turbid. Then the solution temperature was elevated to make the solution transparent again. When the solution temperature descends to the original level, the turbidity of PPESK solution was measured with a nephelometer (LST200, Hangzhou Milden photo instrument, P.R. China). Water was added again, and the above course was repeated until the turbidity took place. The relative contents of PPESK, NMP, and H$_2$O

TABLE I
Spinning Parameters for PPESK Hollow Fibers

Dope flow rate (mL/min)	3.0
Dope and spinneret temperature	Kept consistent with coagulant
External coagulant	Ultrafiltrated water
Internal coagulant composition	Water or water/NMP mixture
Internal coagulant flow rate (mL/min)	1.5
Spinneret parameters (mm)	o.d.: 1.0; i.d.: 0.5
Air gap (cm)	10

of the ultimate solution were considered as the cloud point.

The experimental data of the cloud point of PPESK/NMP/H$_2$O ternary system were fitted linearly on the basis of the linearized cloud point (LCP) correlation suggested by Boom et al.[19] The LCP correlation is given as follows:

$$\ln\frac{\phi_1}{\phi_3} = b \ln\frac{\phi_2}{\phi_3} + a \tag{1}$$

where φ is the weight fraction of the component. The subscripts 1, 2, and 3 refer to the nonsolvent, solvent, and polymer, respectively. The cloud point curves in ternary system are approximate to the binodal lines in the phase diagram. Therefore, the binodal lines in a wider concentration range would be calculated according to the expression[1] if the system agreed with the LCP correlation. The cloud point curves, namely binodal lines, are helpful in analyzing the phase separation course when only the liquid–liquid phase separation occurs.

Hollow fiber membrane preparation

The dry–wet spinning method and protocol have been detailed in the previous reports.[20] A clear and transparent dope solution was prepared by mixing a certain amount of PPESK with NMP and additive, and thereafter stirring the mixture fully while heating. The dope was filtrated with nonwoven fabrics and put into the material kettle of the spinning equipment. The PPESK hollow fiber was spun in the parameters listed in Table I.

All nascent fibers were gathered up with no extension. The as-spun hollow fibers were stored in ultrafiltrated water for at least 1 day, to remove the residual solvent. Some fibers were immersed in a 50 wt % glycerin aqueous solution for 24 h and dried at air for permeability test usage. When used for porosity and scanning electron microscope (SEM) study, the PPESK hollow fibers were treated with ethanol and n-hexane

for 24 h, respectively, and then vacuum dried at 50°C for 24 h.

Fiber diameters and porosity

The outer and inner diameters of PPESK hollow fiber membranes were measured using an optical microscope (XSP-16A, Jiangnan instrument plant, P. R. China). The porosity was determined by weighing methods described in the following sections.[21] At first, a small amount of PPESK resin was hot-pressed in a rounded mold to form a flake. The density of polymer PPESK, ρ_P, was calculated by measuring the weight and volume of the flake. Then, some PPESK fibers which had been precisely evaluated (length, about 100 cm) were vacuum dried at 80°C, until the weight of these fibers was constant. The porosity, P, was calculated as follows:

$$P = \frac{V_m - W_m/\rho_P}{V_m} \qquad (2)$$

where W_m refers to the weight of the dried fibers; V_m is the volume of the fiber samples, which was calculated by the equation: $V_m = \pi(R_0^2 - R_i^2)L$, where R_o and R_i are separately the outer and inner radius of the hollow fiber; L is the total length of fibers.

Membrane morphologies

A field-emitting SEM (Sirion-100, FEI Co., Netherlands) was used to study the morphologies of PPESK hollow fiber membranes. The fiber samples were fractured in liquid nitrogen and sputtered with gold after they were immersed and washed with ethanol and n-hexane, to observe the fiber cross sections.

Pure water permeation flux and solute rejection

For each fiber sample, three permeation modules were prepared to test the pure water flux and solute rejection, and the average of the test data was reported.[20,22,23] Ten hollow fibers with a length of 20 cm were encased in a glass tube. Then the two tube ends were sealed with epoxy resin. All permeability tests were carried out under cross-flow and feed solution in the shell side. Deionized water and 100 ppm of PEG10,000 aqueous solution were respectively used for the flux and solute rejection study. In this article, the operation pressure is a constant value of 0.1 MPa, unless it is specially indicated. The permeation flux, F, was calculated according to the equation: $F = V/(A \times t)$, where V is the total volume of filtrate at the operation time t and A is the membrane area which can be calculated in terms of the fiber outer diameter and length. Solute rejection, R, was obtained as fol-
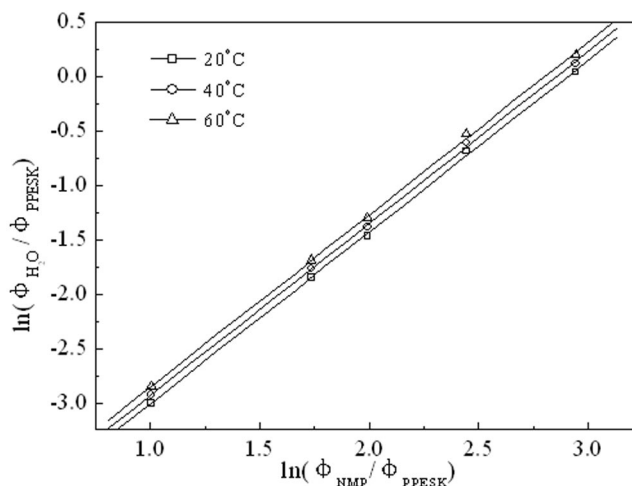

Figure 1 LCP relations of PPESK/NMP/H$_2$O system at different temperatures.

lows: $R = (1 - C_p/C_f) \times 100\%$, where C_p and C_f are the PEG concentration in the filtrate and feed, separately. The PEG concentration in the feed and filtrate was measured with a spectrophotometer (Shimadzu, UV-1601), following the usual protocol.

RESULTS AND DISCUSSION

LCP correlation and ternary phase diagram of PPESK/NMP/H$_2$O system

The thermodynamics and kinetics of membrane-forming systems have a great effect on the membrane morphologies and performances in preparing phase inversion membranes by means of immersion precipitation.[24–28] The thermodynamics mainly throws an effect on the porosity of the membrane, while the diffusion kinetics of solvent and nonsolvent mainly works on the size and distribution of the membrane holes.[26–28] Ternary phase diagram is a very useful tool for studying the thermodynamic behavior of liquid–liquid phase separation system. Through the phase diagram, some information about the phase inversion path and the critical compositions of the membrane-forming system is able to be expressed and transferred. On the basis of the phase separation study, the appropriate membrane-forming parameters may be chosen for fabricating the membranes with the desired morphology and performance.

In the phase diagram of ternary system, the cloud point curve denotes the critical composition of the dope system from the thermodynamic stable to unstable. Some cloud point data of PPESK/NMP/H$_2$O system at 20, 40, and 60°C, respectively, were obtained by nonsolvent titrimetric method. Figure 1 presents the LCP correlation of the ternary system. In terms of the expression,[1] the results of linear fitting on the experimental data are listed in Table II. The values of corre-

TABLE II
Linear Fitting Results of LCP Relation of PPESK/NMP/
H_2O System

Temperature (°C)	Intercept a	Slope b	Correlation index R
20	-4.578 ± 0.097	1.575 ± 0.042	0.99931
40	-4.503 ± 0.093	1.578 ± 0.040	0.99936
60	-4.430 ± 0.095	1.581 ± 0.040	0.99933

lation indexes being very close to 1 showed that the system is in good agreement with LCP relation. In the meantime, Boom et al.[19] also suggested that the slope b is a function of the molar volumes of the component v (in m^3/mol): $b = (v_1 - v_3)/(v_2 - v_3)$, based on the Flory–Huggins solution theory. So the value of b would be larger than 1. The data of slope b in Table I agree with this conclusion.

More cloud point data, in a more wide concentration range, were calculated by the LCP equation, according to the value of a and b. The binodal lines in the ternary phase diagram (Fig. 2) were drawn by combining the experimental cloud point data with the calculated data. From Figure 2, it was found that the cloud point curve (namely binodal line) is more close to the polymer–nonsolvent axis when the system temperature increases. This showed that the membrane-forming system became thermodynamically more stable when the system temperature was elevated. That is to say, when the coagulant temperature is higher, more exchanges of nonsolvent and solvent are required for gelation in the course of membrane forming. Therefore, the dope and coagulant temperature have an important influence on the gelation velocity, namely the kinetic behavior of the membrane-forming system. The ultimate morphology and performance of the membrane attribute to the combining effect of the system's thermodynamic state and kinetic behavior.

Effect of spinning solution composition on membrane morphologies and performances

PPESK hollow fiber membranes were manufactured with respect to the spinning parameters listed in Table I. A series of spinning solutions with different compositions, showed in Table III, was used to investigate the effect of dope composition on the morphologies and properties. Ultrafiltrated water was employed as the internal and external coagulant, and the coagulant temperature was kept at 20°C. The pure water permeation flux and the PEG10,000 rejection were also measured at 20°C, and the results are listed in Table III. Moreover, the corresponding SEM images of the hollow fiber cross section morphologies were showed in Figure 3.

From Table III and Figure 3, it was found that the spinning solution composition has a great effect on the structure and performance of PPESK hollow fibers. When the concentration of the polymer, PPESK, was elevated, the membrane morphology was inclined more tightly and the porosity was less; also the pure water flux decreased and PEG rejection increased. All these might be mainly caused by the dope becoming more viscous and the bidirectional diffusion of solvent–nonsolvent being slower at the time of gelation. Accordingly, the membrane with a thicker skin layer and bigger pore was formed.

The addition of the water-soluble additive, PVP, in the dope contributed to the PPESK membranes a greater porosity and larger pure water flux. It is well known that PVP easily leaches out from the membrane in the course of the complete exchange of solvent and nonsolvent, and more cavities are left. When a small amount of nonsolvent was added to the spinning solution, the dope composition was more close to the binodal line, and the membrane-forming system became more unstable. Consequently, the velocity of the phase separation was more rapid and the porous surface layer came into being.

Effect of the internal coagulant composition and spinning temperature on membranes

A dope solution of the weight fraction PPESK : PVP : NMP : H_2O = 15 : 5 : 79 : 1 was used to spin the hollow fibers, for investigating the effect of the coagulant composition and spinning temperature on membrane performances. The dope and spinneret temperature were always kept uniform with both the coagulants. In the course of spinning, the composition of the internal coagulant varied by adjusting the weight fraction of NMP in the bore fluid. Water alone was used as
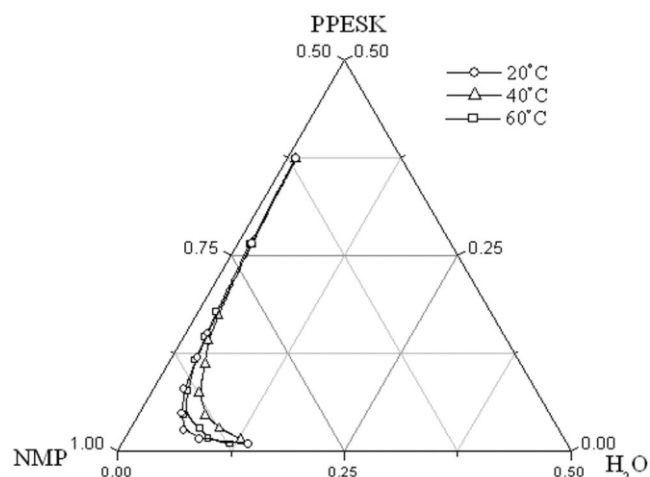

Figure 2 Ternary phase diagrams of PPESK/NMP/H_2O system at different temperatures.

TABLE III
Performance Parameters of Fibers That Were Produced with Different Dope Solution Composition

No.	Spinning solution composition/w.t PPESK : PVP : NMP : H$_2$O	Pure water flux (L m^{-2} h^{-1})	PEG10,000 rejection (%)	Porosity (%)
1	12 : 8 : 80 : 0	22.7	80	55.0
2	12 : 8 : 78.5 : 1.5	25.9	68	62.8
3	15 : 5 : 80 : 0	14.6	84	53.1
4	18 : 2 : 80 : 0	8.1	91	48.3

the external coagulant. The pure water permeation and solute rejection were determined at 20°C and 0.1 MPa.

Figure 4 shows the flux and solute rejection of PPESK hollow fiber membrane which were fabricated on the different internal coagulant composition at 20°C. It was found that, with the ascending of NMP content in the bore fluid, the flux has a great decline, while PEG10,000 rejection exhibits a slight increase. Because of the addition of the solvent, NMP, into the internal coagulant, the coagulant power of the bore fluid was weakened, and the delayed demixing phase inversion would more probably occur in the exchange of solvent and nonsolvent.[4] Accordingly, tighter mem-

brane with higher solute rejection and lower water flux was formed.

The ternary phase diagram mentioned earlier indicates that the spinning temperature has an influence on the formation and performance of PPESK hollow fiber membrane. To investigate the effect of spinning temperature, pure water was chosen as both internal and external coagulant. During spinning, the temperature of the internal and external coagulant was elevated by the heater. As shown in Figure 5, the water flux increases greatly, while the solute rejection descends with the higher spinning temperature. The increase of spinning temperature made the dope solution less viscous and the diffusion of solvent–nonsol-
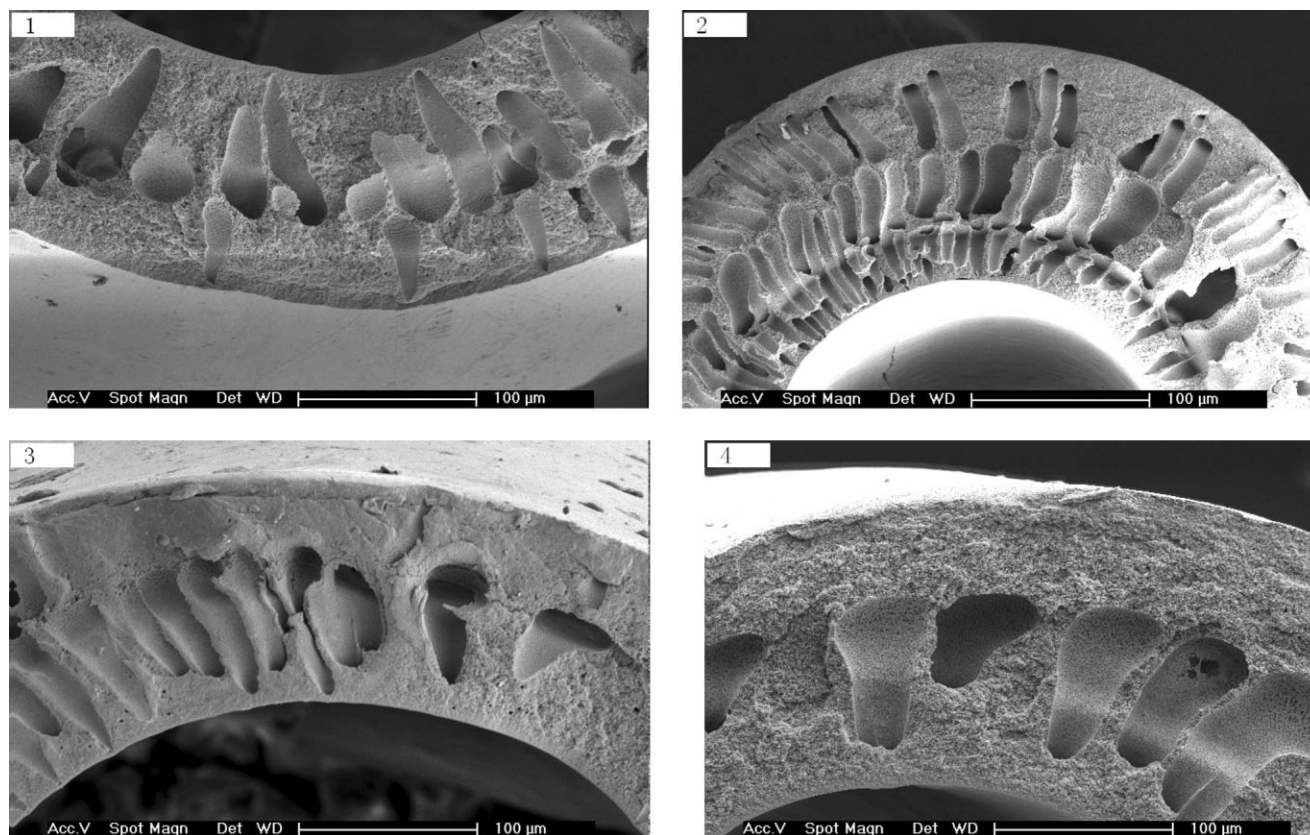

Figure 3 Effect of spinning solution composition on the cross-section morphologies (the numbers are corresponding to Table III).
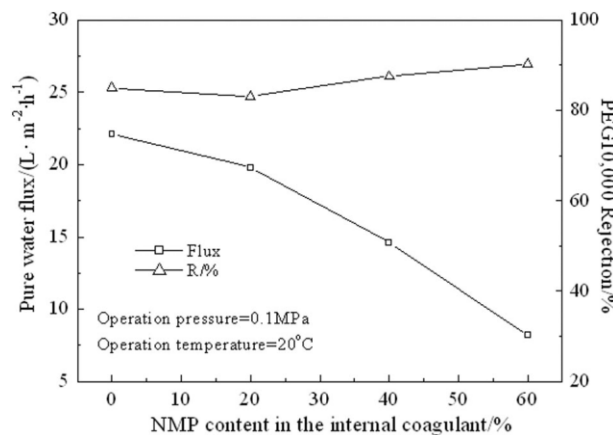
Figure 4 Effect of NMP concentration in the internal coagulant on separation performances of PPESK hollow fiber membranes.

Figure 6 Effects of operating temperature on pure water permeation flux of PPESK membrane at different operation pressures.

vent more rapid. The instantaneous liquid–liquid demixing process might occur, and the formation of more macrovoids brought greater water flux to the hollow fibers.

Thermal stability of PPESK hollow fibers

To investigate the thermal tolerance of PPESK hollow fiber membrane, a membrane which was posttreated with ethanol and *n*-hexane was used to evaluate the pure water flux and PEG10,000 rejection at operation temperatures 20, 40, 60, and 80°C and operation pressures 0.1, 0.15, 0.2, 0.25, and 0.3 MPa, respectively. The results are showed in Figures 6 and 7. It was discovered that the flux increases from 18.4 L m^{-2} h^{-1} at 20°C to 53.2 L m^{-2} h^{-1} at 80°C when the pressure difference is 0.1 MPa, an approximate 2.9-fold increase, while the solute rejection only changes slightly. Also, similar conclusion could be taken at the other operation pressure. This demonstrates that the PPESK
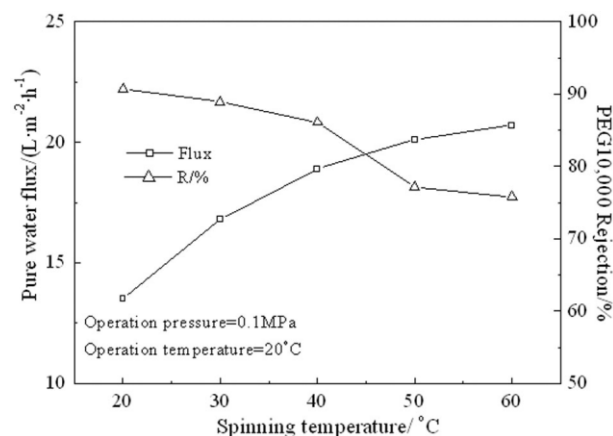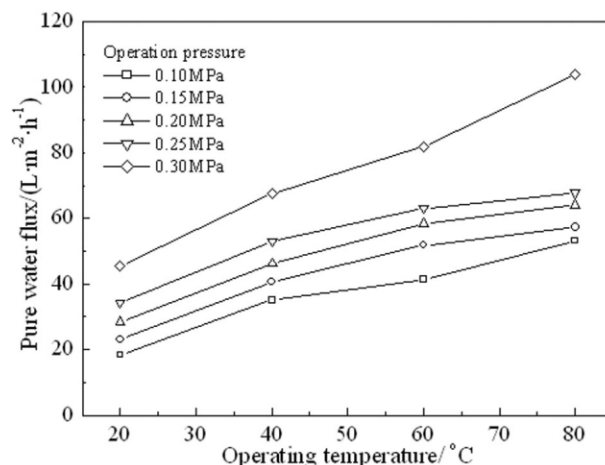
hollow fiber membranes hold excellent thermotolerance.

In the meantime, an obvious increase occured to the permeation flux, with only a diminutive decrease of solute rejection when the operation pressure was raised, as also shown in Figures 6 and 7. It suggested that the PPESK hollow fiber membrane could be applied in the condition of high temperature and high pressure for high permeation flux.

CONCLUSIONS

The experimental data confirmed that the cloud points of PPESK/NMP/H$_2$O ternary system agree very well with the LCP correlation. The binodal lines in the ternary diagram showed that the temperature has a great influence on the thermodynamically stability of
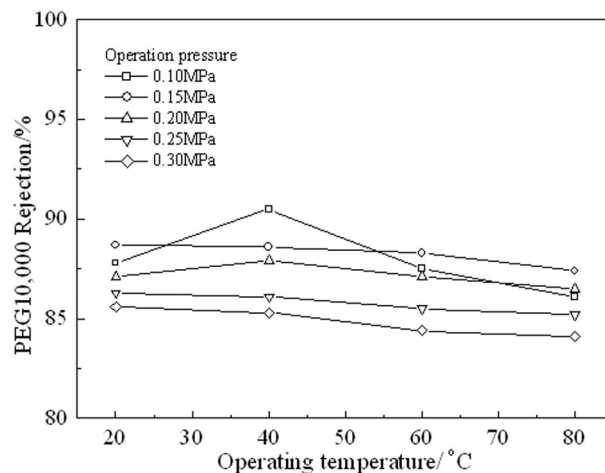

Figure 5 Effect of the spinning temperature on separation performances of PPESK hollow fiber membranes.

Figure 7 Effects of operating temperature on PEG10,000 rejection of PPESK membrane at different operation pressures.

membrane-forming system. PPESK hollow fiber membranes were manufactured by dry–wet spinning technique. The separation performances and the cross-section morphologies of PPESK membranes that were fabricated in different dope composition were evaluated by permeability measurements and SEM observation. Based on the study of phase separation behaviors, the effect of spinning parameters containing the internal coagulant composition and the spinning temperature on the pure water permeation flux and solute rejection of hollow fibers were investigated and discussed. Furthermore, it was demonstrated that the PPESK hollow fiber membrane exhibits excellent thermal stability in the operation temperature range of $20-80°C$.

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