

Effects of Operation Conditions, Solvent and Gelation Bath on Morphology and Performance of PPESK Asymmetric Ultrafiltration Membrane

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ABSTRACT: The effect of gelation temperature, evaporation time, solvent and gelation bath on the structure and performance of poly(phthalazinone ether sulfone ketone) (PPESK) asymmetric ultrafiltration membrane via phase inversion are investigated; the relationship between gelation thickness of dope solutions (X) and time for several polymer solutions with different solvents and gelation bath by online optical microscope-CCD camera experimental system (OM-CC system) are obtained. The results show that gelation temperature has much stronger influence on aperture opening ratio of membrane surface (AOR) and average diameter of membrane surface (AD) than evaporation time, whereas evaporation time has greater effect on the structure factor of membrane cross-

section (S). Bovine serum albumin rejection (R) is mainly determined by surface structure; however, pure water flux (J) is controlled not only by the structure of surface and cross-section, but also the connectivity of the pores. PPESK membranes with fine performance can be fabricated under appropriate gelation temperature and evaporation time. In addition, the membrane structure and performance vary widely when various solvents and gelation bath are employed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3662–3669, 2008

Key words: poly(phthalazinone ether sulfone ketone); phase inversion; membrane formation; gelation kinetics; membrane structure and performance

INTRODUCTION

Poly(phthalazinone ether sulfone ketone) (PPESK), synthesized by Jian et al.,^{1,2} is a novel polymer power with rigid heterocyclic configuration. It has high-transition temperature ($T_g = 279^\circ\text{C}$), high-molecular weight ($M_w = 218,900$), and superior mechanical strength. As a result, the ultrafiltration and nanofiltration membranes prepared by this kind of material^{3–5} have great performance of heat-resistance, chemical stability, and high flux, and can be a kind of promising material for ultrafiltration membrane.

Preparation of asymmetric ultrafiltration membrane by wet-phase inversion is a complicated multicomponent transportation process accompanied by phase transformation; therefore, different operation conditions, concentrations and types of solvents, gelation

bath, and additives all affect the membrane structure and performance. The effects of additives on PPESK membrane structure and performance have been reported a lot in previous research; in addition, Qin et al.^{6,7} investigated the gelation kinetics of PPESK ultrafiltration membrane formation and got a different conclusion from Strathmann et al.⁸ However, few researchers attempt to study the effect of the operation conditions, variations of solvents and gelation bath on membrane structure and performance. To study the detailed mechanism of PPESK membrane formation and find the relationship between preparation, structure and performance, more data concerning the effect of other factors are needed. In this article, by means of gelation kinetic experiments performed by Qin, and membrane structure image analysis software developed by ourselves, the effect of gelation temperature, evaporation time, solvents and gelation bath on membrane morphology and performance is studied.

EXPERIMENTAL

Materials

PPESK powder (see Scheme 1) was purchased from Dalian Polymer new Material, Liaoning Province, People's Republic of China. *N*-Methyl pyrrolidone (NMP), *N,N*-dimethyl acetamide (DMAc), pyridine,

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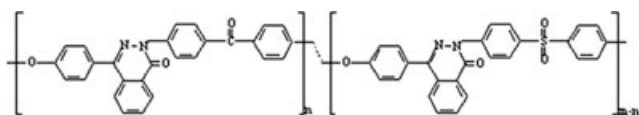
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Scheme 1 Structure of poly(phthalazinone ether sulfone ketone) (PPESK).

morpholine, polyethylene glycol 600 (PEG600), methanol, ethanol, *n*-propanol, and *n*-butanol, analytically pure, were purchased from Beijing Yili Fine Chemicals, Beijing, People's Republic of China. Ultrapure water was obtained from Microelectronic Institute of Tsinghua University.

Membrane preparation

PPESK polymer is dissolved and stirred for at least 1 day, and after the impurities present in the solutions are filtrated and bubbles are removed in vacuum drying chamber, the dope solutions are cast onto nonwoven fabrics by means of membrane-preparation machine developed by Tsinghua University. PPESK ultrafiltration membranes are prepared by wet-phase inversion, with ambient temperature 25°C and ambient humidity less 20%, and the knife gap of the casting knife is set as 150 μm. Details of preparation parameters of three kinds of dope solutions are listed in Table I.

Characterization of membrane morphology and performance

The surface and cross-section images of membranes are observed by scanning electron microscope (SEM, Flotu JSM-7401F). For cross-section analysis the mem-

TABLE I
Preparation Parameters of Three Kinds of PPESK Dope Solutions

1	Polymer	PPESK (16 wt %)
	Solvent	NMP
	Additive	PEG600 (3 wt %)
	Gelation bath	H ₂ O
	Gelation temperature	10°C, 20°C, 30°C, 40°C, 50°C, 60°C
	Evaporation time	6 s, 30 s, 60 s, 90 s, 120 s, 150 s
2	Polymer	PPESK (16 wt %)
	Solvent	NMP, DMAc, pyridine, morpholine
	Additive	No additive
	Gelation bath	H ₂ O
	Gelation temperature	24°C
	Evaporation time	15 s
3	Polymer	PPESK (16 wt %)
	Solvent	NMP
	Additive	No additive
	Gelation bath	Methanol, ethanol, <i>n</i> -propanol, and <i>n</i> -butanol
	Gelation temperature	24°C
	Evaporation time	15 s

brane samples are freeze-fractured in liquid nitrogen. All samples are sputter-coated with gold before observed.

The aperture opening ratio (*AOR*) and average diameter (*AD*) of membrane surface are counted by image analysis software developed by ourselves, and the structure factor of membrane cross-section (*S*) are calculated according to the definition given below (see Fig. 1):

$$S \text{ (structure factor)} = \frac{L_s \text{ (thickness of sponge layer)}}{L \text{ (thickness of membrane)}}$$

Membrane performance is characterized by pure water flux (*J*) and bovine serum albumin rejection (*R*) (the molecular weight of bovine serum albumin is 67,000 Da) by means of equipments made by Tsinghua University.

Measurement of *J*: membrane is preloaded under 0.2 MPa for 1 h, afterward the water flow rate is determined under 0.1 MPa and 25°C, and *J* is calculated by the formula given below:

$$J = \frac{V}{A \cdot t}$$

Measurement of *R*: *R* is determined under 0.1 MPa using 300 mg/L bovine serum albumin solution, and then the concentrations of feeds and permeates are measured separately at intervals, and *R* is calculated by the formula given below:

$$R = \frac{C_f - C_p}{C_f}$$

Gelation kinetics experimental

The gelation process can be visually investigated in online optical microscope-CCD camera experimental system (OM-CC system) including an Olympus IX71 optical microscope, a CCD camera, a personal com-

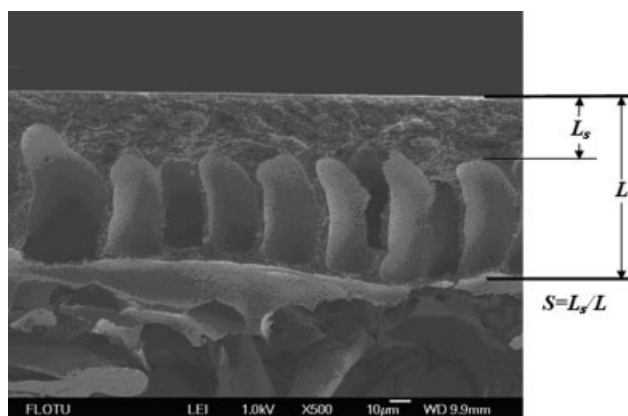


Figure 1 Sketch map of structure factor of membrane cross-section, $0 < S < 1$, it will be finger pores completely when $S = 0$, and sponge pores completely when $S = 1$.

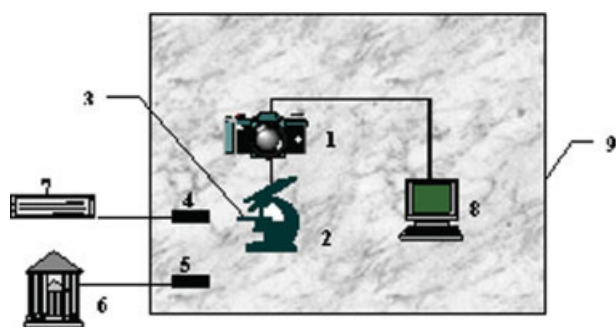


Figure 2 Gelation kinetics experimental settings. (1) CCD camera, (2) optical microscope, (3) special microscope accessory, (4) temperature sensor, (5) humidity sensor, (6) dehumidifier dehumidity unit, (7) air-conditioner, (8) personal computer and software, (9) clean room. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

puter, and a specially designed microscope slide¹⁰ (see Fig. 2). When ambient temperature is 25°C and ambient humidity is less than 20%, 10- μ L polymer solution is placed in a compartment made by two specially designed microscope accessories, and then 1-mL distilled water is injected into the compartment by a syringe. From the recording gelation thickness of dope solution (X), we can distinguish the gelation rates of different dope solutions.

RESULTS AND DISCUSSION

The effect of gelation temperature and evaporation time on membrane morphology and performance

Thirty-six sheets of membranes are obtained at every pair of gelation temperature and evaporation time. The

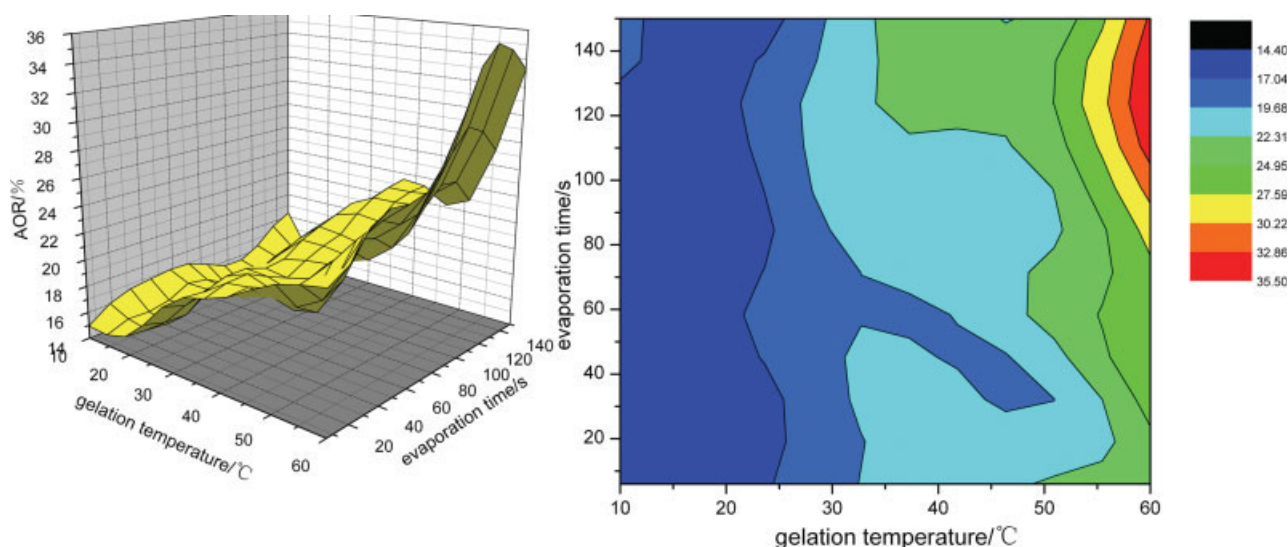


Figure 3 Surface diagram and contour map of AOR as a function of operation conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tridimensional surface diagram and contour map of AOR, S , J , and R as a function of gelation temperature and evaporation time are illustrated in Figures 3–6.

From Figures 3–6, some correlation of operation conditions, membrane morphology, and performance are obtained.

AOR of membrane surface increase along with the increase of gelation temperature, but it has a little change along with the increase of evaporation time, which indicates that gelation temperature has much stronger effect than evaporation time on AOR.

Structure factor of membrane cross-section (S) is affected by both evaporation time and gelation temperature, but the effect of evaporation time seems more significant. The sponge layer becomes thicker along with the increase of evaporation time.

Pure water flux (J) varies inversely with bovine serum albumin rejection (R). Fine ultrafiltration membranes will be obtained at appropriate gelation temperature and evaporation time.

Generally, R is decided by AOR, which means the rejection will be low when AOR is high; while J is affected not only by AOR and S , but also the connectivity of pores. The study for the characterization of pores connection will be carried through in the following research.

The effect of different solvents on membrane morphology and performance

The gelation kinetics experiments of PPEsk/H₂O dope solutions with four different kinds of solvents are carried out, and the profile of gelation thickness of dope solutions (X) against time is illustrated in Figure 7.

Figure 7 shows that the order of X is DMAc > NMP > pyridine > morpholine. To some extent, the

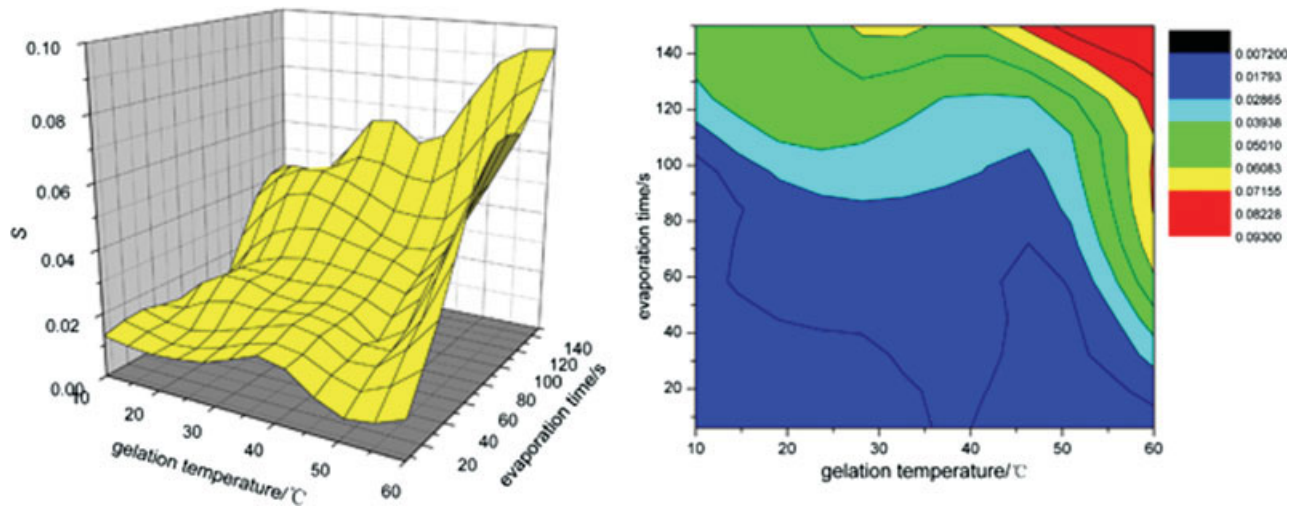


Figure 4 Surface diagram and contour map of S as a function of operation conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

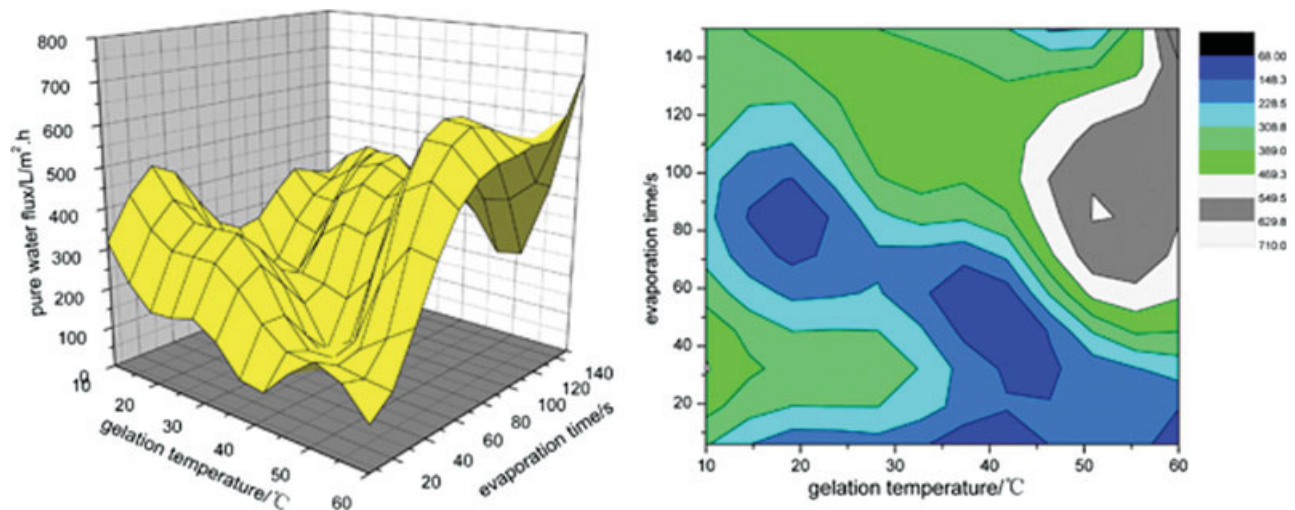


Figure 5 Surface diagram and contour map of J as a function of operation conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

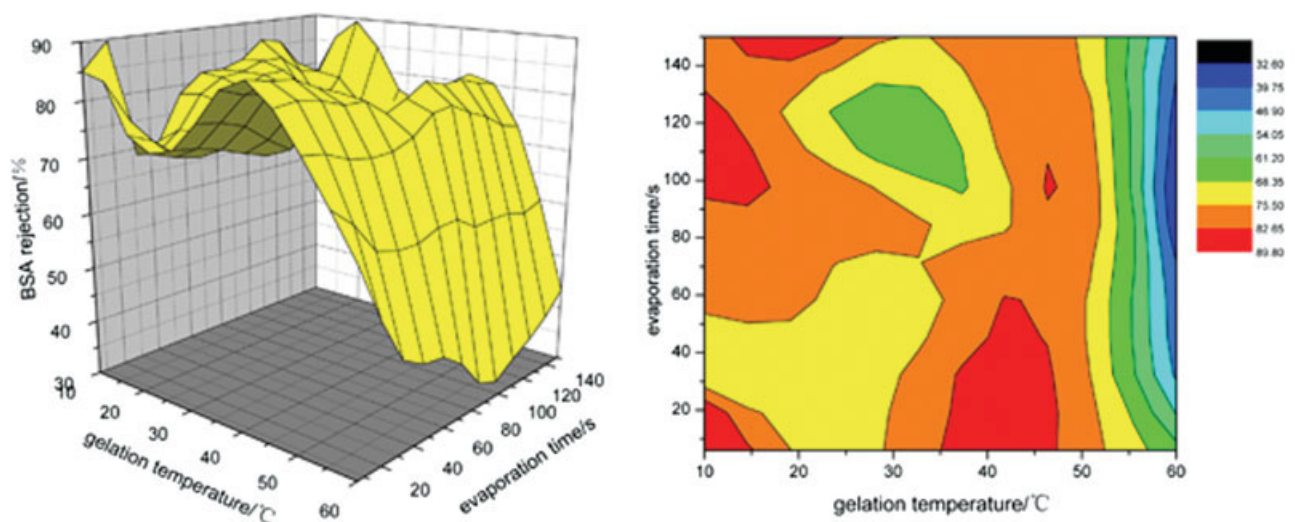


Figure 6 Surface diagram and contour map of R as a function of operation conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

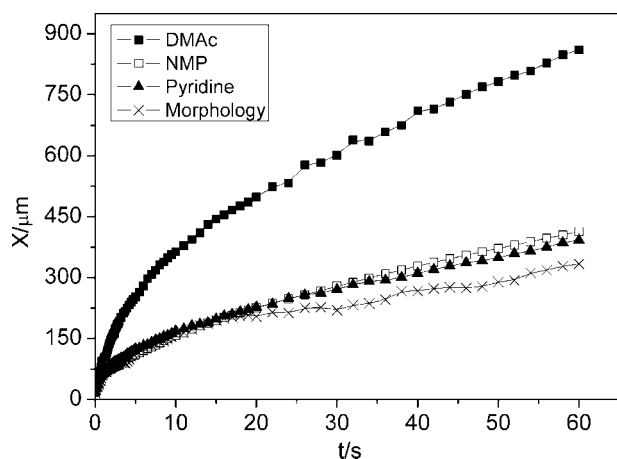


Figure 7 Gelation kinetic curves of polymer solutions by H₂O with different solvents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

gelation rate is determined not only by the viscosity of either dope solutions or gelation bath, but also the interaction between solvents and gelation bath. The gelation rates will become faster when the dope solutions and gelation bath have a low viscosity, and there exists strong interaction between them.

To compare the viscosity of the four different dope solutions and the interaction between solvents and gelation bath, the viscosity of dope solutions and distribution coefficient of solvent between polymer and gelation bath, measured by HPLC, and solubility parameters of the four solvents⁹ subtracted from H₂O are listed in Table II. Because the same gelation bath, which is H₂O, is employed, only the viscosity of dope solutions is considered. We can see that both the viscosity of dope solutions and distribution coefficients increase along with the order of DMAc > NMP > pyridine > morpholine, showing that the gelation rate increase gradually. The solubility parameters subtracted from H₂O also increase except DMAc, which indicates the interactions between solvents and H₂O become weaker, which results in the decrease of *X*. As an exceptional case, the solubility parameter subtracted from H₂O of DMAc is not the smallest, but it has the maximal *X*. This result may be due to the fact that DMAc is not a good solvent for PPESK, and there has already existed many tiny phase-separations before mem-

brane preparation⁹ which make the gelation rate become faster.

Surface and cross-section images of PPESK membranes with four kinds of solvents are illustrated in Figure 8.

The comparisons of surface and cross-section structure parameters with membrane performance are listed in Table III.

As to the surface structure of the membranes, AOR and AD seems larger when taking DMAc and morpholine as solvents, while smaller when taking NMP and pyridine as solvents. Because the gelation bath is the same, the surface structure is mainly determined by thermodynamic property of dope solutions. At the moment the dope solutions are immersed into H₂O, the solvents in the surface of dope solutions are exchanged by H₂O so rapidly that polymer chains have no time to shrink and rearrange, therefore the polymers are solidified immediately. In a general way, relaxing polymer chains in good solvents will result in homogenous cross net surface structure, however, contractive polymer coils in poor solvents will result in loose surface structure. What is more, large numbers of phase-splittings occurred in DMAc solvent will bring large aperture in membrane surface. Furthermore, the cloud points in DMAc and morpholine are very small, according the binodal curve is very close to the polymer-solvent axis, and hence phase-inversion is easy to happen.

In regard to the cross section structure, dense surface will result in finger pores, but loose surface brings sponge pores. Because dense surface suppress the exchange of solvent and gelation bath, therefore, solvents existed in polymer solutions are difficult to pass through the interface of polymer solution and gelation bath, and then make polymer to have more time to shrink and make the pores grow gradually; whereas loose surface make gelation bath enter into polymer solutions conveniently, and the rate of nucleation is faster than that of growth, consequently, sponge pores are formed.

The effect of different gelation bath on membrane morphology and performance

The gelation kinetics experiments of PPESK/NMP dope solutions with four different kinds of gelation bath are implemented, and the gelation thickness of

TABLE II
Thermodynamic and Kinetic Properties of PPESK Polymer Solutions with Different Solvents

Solvent	DMAc	NMP	Pyridine	Morpholine
Viscosity (cP)	924	1,337	3,667	4,094
Distribution coefficient (PPESK/H ₂ O)	0.3526	0.4014	0.4421	4.2299
Solubility parameters subtracted from H ₂ O (MPa ^{1/2})	25.1	24.9	26.0	26.3

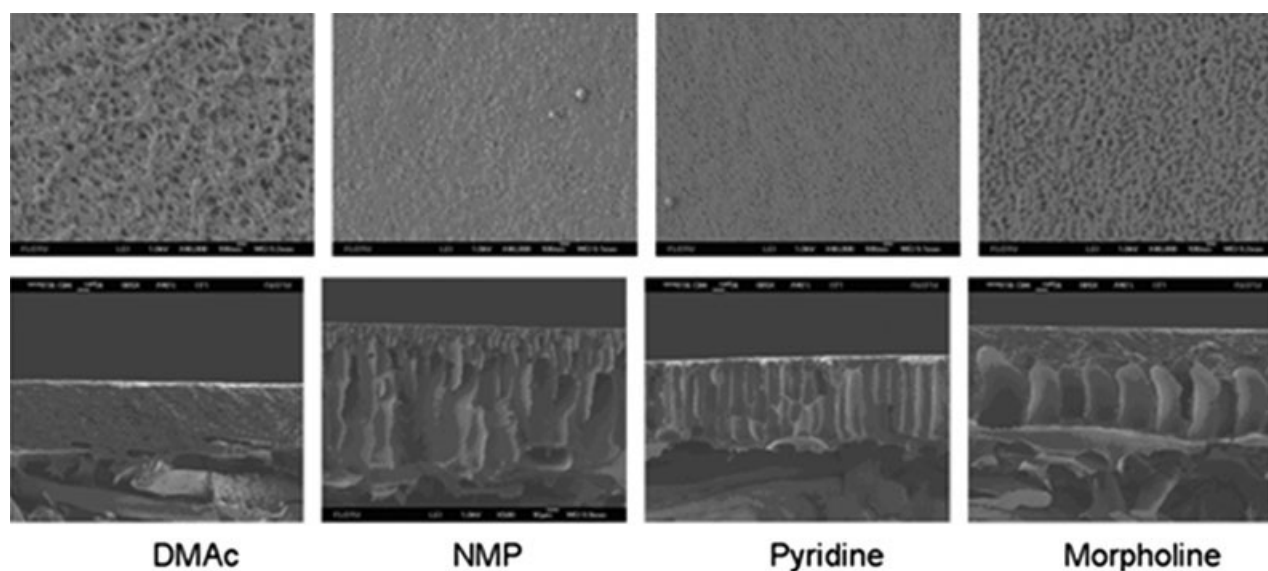


Figure 8 Surface and cross-section images of PPEsk membranes with different solvents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dope solutions (X) as a function of time is illustrated in Figure 9. It shows that the trend of X decreases along with the increase of normal carboatomic number. For the same dope solutions, gelation rate is determined by the viscosity of gelation bath and the interaction between solvents and gelation bath. From the thermodynamic properties of gelation bath (see Table IV), the viscosities of methanol, ethanol, *n*-propanol, and *n*-butanol increase along with the increase of normal carboatomic number, but the interaction between solvents and gelation bath become stronger according to the solubility parameters subtracted from NMP. So it seems that the viscosity of gelation bath have stronger influence on gelation rate than interaction between solvents and gelation bath.

Four kinds of ultrafiltration membranes are fabricated when taking methanol, ethanol, *n*-propanol, and *n*-butanol as gelation bath. The SEM images of surface and cross-section are illustrated in Figure 10, and the characterization of membrane structure and performance are listed in Table V.

TABLE III
Structure Parameters and Performance of PPEsk Membranes with Different Solvents

Solvents	DMAc	NMP	Pyridine	Morpholine
AOR (%)	22.73	15.33	15.00	21.17
AD (nm)	23.88	16.14	15.56	27.70
S	1	0.01	0.09	0.28
Cloud point*	0.280	1.724	0.759	0.341
J (L/m ² h)	295	330	427	439
R (%)	20.56	71.34	91.67	28.75

* Unit: g/20 g 0.8 wt % PPEsk solutions.

From Figure 10 and Table V, we can see AOR decrease along with the increase of normal carboatomic number. Since the same solvent is employed, the thermodynamic properties of four kinds of dope solutions are the same; therefore, the difference of surface structure is determined by the property of gelation bath and gelation kinetics. The cloud points of dope solutions with alcohols are larger than H₂O, which implies that more alcohols can be accommodated than water in the same dope solutions; as a result, the relaxation time delays and it will take more time to reach phase separation, which is also the reason why X descends. During this period before phase separation, polymers incline to shrink and form larger surface pores.

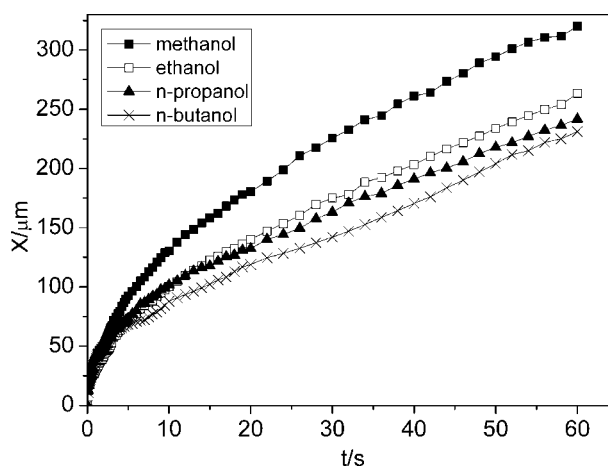


Figure 9 Gelation kinetic curves of PPEsk/NMP polymer solutions by different gelation bath. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Thermodynamic Properties of Different Gelation Bath

Gelation bath	Methanol	Ethanol	<i>n</i> -Propanol	<i>n</i> -Butanol
Solubility parameters subtracted from NMP (MPa ^{1/2})	6.2	3.5	1.5	0.3
Viscosity (cP)	0.59	1.17	2.26	3.38

In addition, S decrease in the upside of the membrane, while increase in the downside, which means sponge structure of membrane sublayer become thinner and that of the membrane bottom become thicker. The alcohols are encumbered to enter into polymer solutions with the increase of the viscosity of alcohols; as a result, finger pores cannot reach the bottom of the membrane. The decrease of AOR and the increase of sponge layer thickness of cross-section make J descend.

CONCLUSIONS

The effect of operation conditions, solvents and gelation bath on the morphology and performance of PPESK asymmetric ultrafiltration membrane via phase-inversion is investigated in this article. On the one hand, preparation conditions have a great effect on the final membrane structure: the structure of membrane surface is mainly affected by gelation temperature, while the structure of cross-section is influenced by both gelation temperature and evaporation time, with the effect of the latter more significant. To be specific, the AOR of membrane surface increases when the temperature of gelation increases,

and, at the same time, the sponge sublayer become thicker gradually, which means the structure factor of membrane cross-section (S) increases with increasing evaporation time. On the other hand, we can also find the relationship between structure and performance: bovine serum albumin rejection (R) is controlled by AOR ; while pure water flux (J) is affected by the connectivity of the pores, as well as AOR .

Both solvents and gelation bath have a great influence on membrane structure and performance. For the same gelation bath, surface structure is determined by thermodynamic properties of polymer solutions (such as whether the solvent is good or poor, and whether the viscosity of dope solutions is high or low); however, for the same solvents, surface structure is mainly determined by the viscosity of gelation bath. The structure of cross-section has an effect on the structure of surface. In the same way, R is determined by AOR , but J is decided not only by surface and cross-section morphology but also pores connectivity.

In addition, it seems that the gelation thickness of dope solutions (X) is mainly controlled by the viscosity of polymer solutions and gelation bath, instead of the interaction between solvents and gelation bath. Moreover, X does not have certain effect on the membrane performance.

Unfortunately, our results cannot characterize the connectivity of pores which is an important factor that affects the pure water flux, and we will make a further study aiming at this point. Despite this limitation, our results have provided some more data of membrane formation mechanisms which could contribute to the research of PPESK asymmetric ultrafiltration membranes.

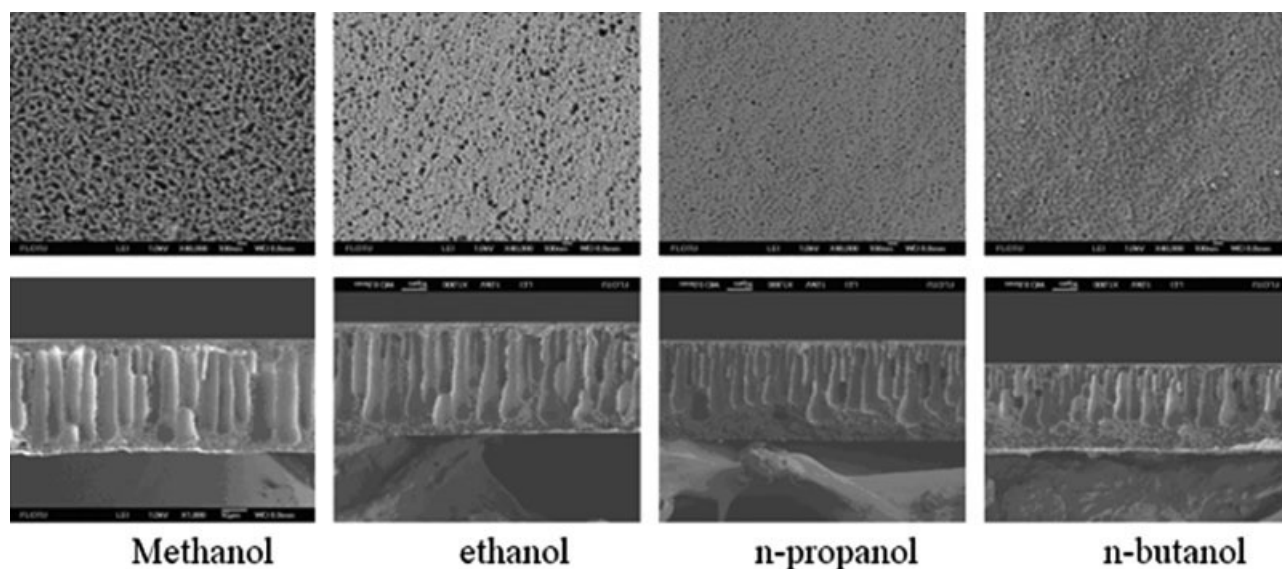


Figure 10 Surface and cross-section structure of PPESK/NMP polymer solutions with different gelation bath. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Structure Parameters and Performance of PPESK
Membranes with Different Gelation Bath

Gelation bath	Methanol	Ethanol	<i>n</i> -Propanol	<i>n</i> -Butanol
AOR (%)	29.87	20.91	19.26	19.10
AD (nm)	39.86	27.30	20.81	25.14
S (upside of membrane)	0.08	0.06	0.06	0.03
S (downside of membrane)	0.05	0.10	0.16	0.29
Cloud point*	5.4	5.9	6.4	6.6
<i>J</i> (L/m ² h)	97	86	75	64

* Unit: g/25 g 1 wt % PPESK solutions.

NOMENCLATURE

AOR	Aperture opening ratio of membrane surface (%)
AD	Average diameter of membrane surface (nm)
S	Structure factor of membrane cross-section
<i>J</i>	Pure water flux (L/m ² h)

R	Bovine serum albumin rejection (%)
X	Gelation thickness of dope solutions (μm)

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