



Effect of PVP Additive on PVDF/TPU Blend Hollow Fibre Membranes by Phase Inversion

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ABSTRACT

Asymmetric blend hollow fibre membranes were made from a new casting dope containing poly(vinylidene fluoride) (PVDF)/thermoplastic polyurethane (TPU)/*N,N*-dimethylacetamide (DMAc)/polyvinylpyrrolidone (PVP). The separation property, microstructure, crystalline phase of membranes, and membrane strength were characterized by bovine serum albumin (BSA) retention experiments, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR), differential scanning calorimetry (DSC) and tensile testing, respectively. PVP at low concentration (≤ 3 wt%) was a significant demixing enhancer which thermodynamically controlled the phase inversion process, improved flux, reduced α -form crystal structure, and decreased crystallinity of PVDF in membranes. At high concentration of PVP (> 3 wt %) due to viscosity buildup, kinetic hindrance overwhelmed the thermodynamic factor which suppressed the formation of macrovoids, reduction of flux, and increase in crystallinity of PVDF in membranes.

Key Words:

poly(vinylidene fluoride);
thermoplastic polyurethane;
polyvinyl pyrrolidone;
blend;
crystallization;
morphology.

INTRODUCTION

Polymeric membranes can be prepared by phase inversion process. The demixing of a polymer solution can be induced by compositional changes of constituents due to mass transfer in a system. One important goal in membrane technology is to control membrane structure and performance.

Due to its excellent chemical

resistance and good physical and thermal stability, PVDF hollow fiber membrane has been used widely in industrial waste treatment including oily emulsion, organic/water separations, gas absorption and stripping, membrane distillation, and ultrafiltration. PVDF membranes prepared were not of practical interest

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because of their low permeate fluxes [1]. In addition, they are nowadays too expensive to be considered for environmental depolluting applications.

Blending is frequently used for improving the properties of polymeric membranes [2-4]. Addition of a second polymer often leads to a significant change in the membrane morphology. Thermoplastic polyurethane, with properties covering from a high performance elastomer to tough thermoplastic and also low price, has been extensively used due to its superior physical properties (e.g., high tensile strength, abrasion and tear resistance, and low temperature flexibility) and high versatility in chemical structures [5]. TPU membranes have been used for clinical applications due to their superior cytocompatibility.

Addition of organic hydrophilic polymer in a casting dope to prepare porous membranes by phase inversion method has been an effective practice to improve the permeability and selectivity of ultrafiltration membranes. As far as we know, the additives such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) are widely used for structural control of membranes [1,6]. Low rejection and large pore size are caused by the fact that large molecular weight PVP tends to form thicker skin layer containing bigger pores [1,7]. Xu et al. have studied the effect of PVP with different molecular weights on morphology of polyetherimide hollow fibre membranes. They found when the higher molecular weight of PVP was added, the bigger pore was made [8]. On the other hand, Wienk et al. have showed that PVP is an agent for suppressing macropore formation in the phase inversion membranes [9]. There are much less studies on PVP which not only do not show the non-solvent characteristics (demixing enhancer) but do not reveal the property of suppressing macropore formation (demixing hindrance) either.

In the present research, the tensile strength and the elongation-at-break of PVDF/TPU blend membranes were higher than that of pure PVDF membrane. PVP was used as an additive in PVDF/TPU/DMAc solution system for the development of improved performance of hollow fibre membranes. The effect of PVP on the final structure and performance of the hollow fibre membrane were analyzed and it was found that PVP is thermodynamic enhancer and kinetic hin-

dering agent during phase inversion in the membrane preparation. Crystal forms of PVDF have been changed for dopes by the addition of PVP as revealed by FTIR-ATR which is due to the increase of viscosity, causing stress variation of nascent fibre. Variation of the heat of fusion (ΔH_f) and melting temperature of PVDF by DSC analysis of these membranes revealed that crystallinity of PVDF in membranes changed which is coherent relative to crystal structure variation obtained by FTIR-ATR. Furthermore, by addition of PVP in the dopes, it is found that morphology of the membranes' macrovoids varies with different PVP contents in the dope, which is examined using scanning electron microscopy technique. These morphological features are consistent with the measured water flux and retention data.

EXPERIMENTAL

Material

The polyvinylidene fluoride used was a commercial product (FR904). Thermoplastic polyurethane obtained from Townsend Corporation (RE-FLEX585-XU) was an amorphous polymer. *N,N*-Dimethylacetamide (DMAc, >99%, reagent) was employed as a solvent and distilled water was used as a non-solvent for the polymers precipitation. Polyvinylpyrrolidone (PVP) (K30) (MW= 25,000-40,000) was added to the casting dopes to modify the membranes structure. BSA (MW= 67, 000) was used to characterize the separation performance of hollow fibre membranes.

Preparation of PVDF/TPU Blend Membrane

The membranes were made by the phase inversion method. Casting dopes (80°C) were prepared by dissolving PVDF and TPU in the solvent and adding PVP to casting dopes under stirring. Dopes consisted of 16 wt% PVDF/TPU and 84 wt% PVP/DMAc mixtures. Their compositions and viscosities with different amount of PVP are shown in Table 1. Casting solutions were deposited at 50°C in a place out of sun light for one day for removing their air bubbles. The degassed dope was transferred to a stainless steel reservoir and pressurized to 0.1 MPa using nitrogen gas. In general, water as internal coagulant adjusted

Table 1. Cloud points and viscosity data of dopes with different PVP contents.

Composition (wt%)			Water content at cloud Point (wt%)	Viscosity (cps)
PVP	DMAc	PVDF/TPU		
0	84	12.8/3.2	16.67	3520
1	83	12.8/3.2	15.25	4653
3	81	12.8/3.2	13.04	5507
5	79	12.8/3.2	10.71	7020
7	77	12.8/3.2	9.09	7947
10	74	12.8/3.2	7.41	8687

at 3 mL/min, the air gap was kept at 14 cm for the spinning runs. The spinneret with an orifice diameter/inner diameter of 0.8/0.2 mm was used. The nascent fibre was guided through water baths at 25°C at a take-up velocity, carefully adjusted to match the free falling velocity to complete the solidification process. The detailed experimental procedures can be found elsewhere [10]. The formed membranes were washed in water bath for at least 24 h to remove the traces of PVP and DMAc.

Characterization of Membrane

The membranes prepared were characterized by the methods which are listed below:

- The viscosity of the prepared casting dope was measured using digital rheometer (Model NDJ-9S, Shanghai Precision Instruments Co., Ltd.) at the constant temperature of 25°C. The cloud points of the casting dopes were obtained by measuring the amount of precipitant, distilled water, added to the dopes until the solutions revealed the cloudy feature.

- Morphologies of the membranes were observed in cross-section views by SEM (JSM-5600LV, Jeol Ltd.).

- The thermal behaviours of membrane were observed using a differential scanning calorimeter (Perkin Elmer DSC-7, PerkinElmer, Inc.). The temperature was raised from 25 to 250°C at a rate of 5°C/min in a nitrogen atmosphere. The melting temperature and the heat of fusion (ΔH_f) were determined from the obtained thermograms.

- FTIR-ATR Spectra were obtained by a Nexus 670 (Nicolet Instruments Corp.) spectrometer with 4 cm⁻¹ resolution. This technique was employed to examine the residual PVP content in the formed membranes

and observe the transition of crystal type of PVDF.

- Membrane porosity was measured via the method of dry/wet weight.

- Water permeation of the membranes was measured in a dead-end ultrafiltration cup. The permeation performances of BSA through various membranes at transmembrane pressure of 0.1 MPa were measured to see the solute retention capabilities of membranes.

- The tensile strengths and elongation-at-breaks of the membranes were determined by tensile tester [xlw(1), Jinan Languang M&E Technology Co., Ltd]. The measurements were carried out at room temperature and pull rate of 5 mm/min.

RESULTS AND DISCUSSION

Mechanical Properties

The tensile strengths and elongation-at-breaks of the membranes are shown in Table 2. Both values were exceeded, obviously. Although the dopes including TPU content above 50% were also prepared, it is too viscous to spin. Thus, only those samples with TPU content below 40% were measured. Mechanical properties of both blend membranes were higher than those of pure PVDF membranes. Especially, in the case of 40% TPU content the elongation-at-break value was conspicuously promoted 5 times more than those of membranes without TPU. The behaviours indicated that adding TPU to a PVDF dope can improve the membrane's mechanical properties.

Thermodynamic and Dynamic Effect on Membrane-forming System by PVP

An additive PVP can induce a dual effect on a casting

Table 2. Mechanical properties of PVDF/TPU blend membranes.

Composition (wt%)				Tensile strength (MPa)	Elongation-at-break (%)
PVDF	TPU	PVP	DMAc		
16.0	0.0	0	84	5.15	28
12.8	3.2	0	84	6.51	34
11.2	4.8	0	84	7.23	60
9.6	6.4	0	84	7.92	171

dope. One of these effects is a thermodynamic variation due to the non-solvent effect and the other one is a rheological variation due to high molecular weight of PVP.

The cloud point data are shown in Table 1. The original binary dope of 16 wt% polymer (PVDF/TPU) in solvent (DMAc) was phase separated as water added into the dope reached to 16.67 wt%. By the addition of PVP, in the thermodynamic equilibrium, casting dope needed much less amount of water at the demixing point of phase inversion. The water content to demix PVDF/TPU dope decreased with the increasing PVP concentration. At 3 wt% PVP, the water concentration causing demixing was reduced to 13.04 wt% and at 5 wt% PVP it was reduced to 10.71 wt%. The cloud point data suggested that the PVP introduced to the casting dope could reduce the miscibility of dope with water and PVP can work in favour of the enhancement of the demixing of casting dope, thermodynamically.

The rheological (dynamic) behaviour was estimated by measuring the viscosity of dopes. The addition of PVP to casting dope increased its viscosity as shown in Table 1. At 3 wt% additive, the viscosity was increased up to about 56 % and by the addition of 10 wt% it was increased up to about 150 %. This effect was based on the type of additive and PVP's high molecular weight. The diffusion can be inhibited by PVP in the dope due to the increase of the kinetic hindrance or a delayed exchange between solvent (DMAc) and non-solvent (water) during the phase inversion process. Namely, it is concluded that PVP addition could function as the thermodynamical enhancer and kinetic hindrance in PVDF/TPU casting dope demixing. Thermodynamic and kinetic properties are correlative in the phase inversion system for the preparation of the PVDF/TPU hollow fibre membranes.

Crystal Structure and Vibrational Spectra

Both infrared and Raman spectra distinguish the different crystalline forms of PVDF and the presence of polymer chain defects, as shown by many studies [11,12]. Studies of the crystallization process and its dependence on solvent nature, temperature, and time indicate that the α -form is thermodynamically favoured, while β -form is kinetically favoured [12]. However, an actual PVDF sample, depending on the preparation condition, may present one or more of the different crystalline structures [12,13].

In Figure 1 the FTIR-ATR spectra of membranes prepared by immersing dopes containing no-additive, 3 wt%, and 10 wt% PVP, are respectively shown. When the dope was free of PVP, the membrane precipitated into α - and β - forms. Well known peaks of the α -form of PVDF located at 795 and 976 cm^{-1} could be recognized very distinctly. The peak at 1275 cm^{-1} of the β -form is seen clearly as well. By partial addition of PVP the α -form of PVDF in the membrane has been disappeared. At 3 wt% PVP content the α -form was disappeared where its peaks were located at 795 and 976 cm^{-1} .

When PVP content was added up to 10 wt% the related peaks were remained unchanged. It is revealed that crystallinity of PVDF in the membranes is reduced by the increase of PVP content. The reason is that during the spinning procedure, PVP addition increases the solution viscosity (Table 1) and the spinning speed slows down which causes stress variation of nascent fibres.

Since, this stress is the main factor brings about the crystalline transition structures [14]. It is also concluded that by the increase of PVP concentration, the effect of thermodynamic variation is much less dominant on membrane formation than the kinetic variation.

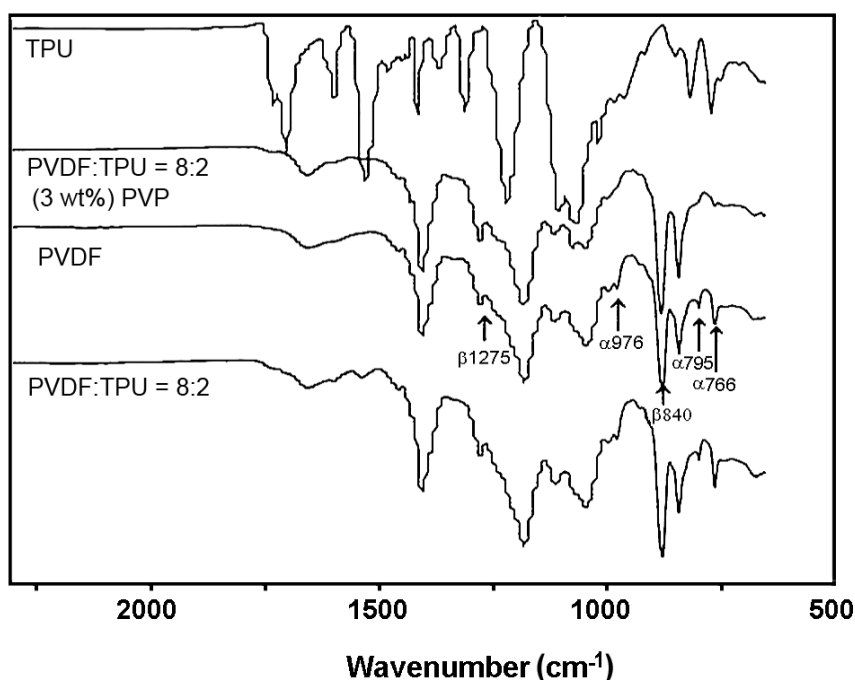


Figure 1. FTIR-ATR Spectra of membranes with the various amounts of PVP.

Thermal Behaviour of the PVDF/TPU/PVP Membranes

Melting temperature and the heat of fusion (ΔH_f) of PVDF in various membranes were determined by means of DSC thermal analysis. In Figure 2 were presented the thermograms of membranes at different PVP contents for which the scanning rate was 5°C/min in all experiments.

It can be seen that these membranes exhibit a melting behaviour with a progressive decrease of the

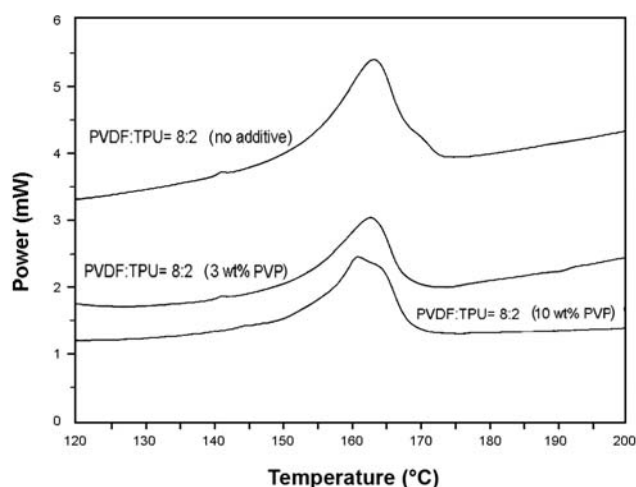


Figure 2. DSC Thermograms of membranes with various PVP concentrations.

average melting temperatures with the increase of PVP contents. The reason for this observation may be due to the difference in crystal structure during the processes of membranes formation. The similar results were obtained by Prest et al. when they studied the melting behaviour of melt-crystallized PVDF samples [15]. Membranes with different crystal forms (e.g., α - and β - forms) of PVDF crystallites also exhibit different melting temperatures. Laroche et al. have obtained that α - and β -forms of PVDF exhibit two melting peaks which are close to each other and it appears that the β -form has a lower melting point than α -form [16].

In Figure 2 it is also observed that when PVP concentration is added up to 10 wt%, two melting peaks are obtained which are close to each other and the average melting temperature is lowered. DSC Analysis reveals that α -form which displays higher melting temperature has a trend of reduction and lowers the melting temperature (Table 3) when PVP content increases. The result is also supported by crystal structure variation obtained by the FTIR-ATR spectra.

The crystallinity of each membrane prepared by different PVP contents was calculated based on the heat of fusion of ideal PVDF crystal ($\Delta H=105$ J/g) [17]. The crystallinity showed obvious changes as it is

Table 3. The heat of fusion and crystallinity of PVDF/TPU/PVP membranes.

Composition (wt%)				DSC			
PVDF/TPU	PVP	DMAc	PVDF/TPU	T _m (°C)	ΔH _f (membrane) (J/g)	ΔH _f (PVDF) (J/g)	Crystallinity (%)
12.8/3.2	0	84	12.8/3.2	163.29	26.06	32.58	31.02
12.8/3.2	3	81	12.8/3.2	162.84	18.35	22.94	21.85
12.8/3.2	10	74	12.8/3.2	161.04	22.74	28.43	27.07

revealed by peak area. ΔH_f of membranes is obtained directly from the DSC thermograms. ΔH_f of PVDF is obtained by dividing the ΔH_f of membrane by the weight fraction of PVDF in the membrane [18]. The results are shown in Table 2.

With addition of PVP up to 3 wt% in the casting dope, the crystallinity dropped to 30 %. While progressive increment of PVP content in the dope resulted in the increasing of the crystallinity of PVDF in membrane which impelled the crystallization process. The DSC measurement revealed that crystallization is more favourable at the high concentration of PVP. It is beneficial to suppress the polymer crystallinity in the membrane formation process [19]. Growth of polymer crystallinity has a detrimental effect on the final membrane transport properties. Since it decreases the free volume of amorphous region available for species transport and increases the membrane tortuosity [20].

Morphologies of PVDF/TPU Membranes

Figure 3 shows SEM micrographs of the cross-section of membranes prepared by increasing the PVP content. All membranes demonstrate the so-called asymmetric morphology characterized by a thin skin and a porous bulk. They comprise fully developed macropores extending to the central or even toward the bottom region of the membrane irrespective of the amount of added PVP in the casting dope. By increase of PVP content the asymmetric morphology exhibits evidently.

By adding 3 wt% PVP the macropores enlarge obviously (Figure 3b). The membrane prepared by 5 wt% PVP was led to a structure with macrovoids somewhat deeper (Figure 3b). While by 10 wt% PVP, the macrovoids in the membrane cross-section are suppressed and their structure stretch down like fingers from the underneath of membrane skin to the bot-

tom of its sub-layer (Figure 3d).

Thermodynamic and kinetic factors correlating each other during phase inversion are two dominating factors controlling the morphologies of membranes. At the low level of PVP in the casting dope, the thermodynamic driving force played a major role on solution demixing, inducing the demixing enhancement, corresponding to the acceleration of phase separation due to the PVP's non-solvent effect. Thus the PVP acts as a phase separation enhancer, resulting in macropore enlargement (Figure 3b).

At high levels of PVP, water, and DMAc concentrations, mutual diffusion was inhibited by PVP in solution due to the increase of the dope viscosity which affects the exchange between water and DMAc during the phase inversion. In this way, phase separation time increased and demixing was delayed. The DSC analysis also reveals that crystallization was more favourable at higher concentrations of PVP. Crystallization favoured to take place during the precipitation process. It takes a considerably long time for non-solvent to reach the bottom region to induce liquid-liquid demixing [21].

Under the delayed demixing condition, membranes can be expected to have low porosity and permeability, with suppressing formation of macrovoid [22]. PVP in the PVDF/TPU dope works as an agent for suppressing macrovoid formation (kinetic factor) at high concentration. While at a low concentration PVP enhances the macrovoid formation (thermodynamic effect). PVP cannot come to coherency with the demixing enhancement, because it fails to induce thermodynamic enhancement which is overwhelmed by kinetic hindrance [23].

Additionally, variation of macrovoid can be explained by the competitive thermodynamic and kinetic effects of PVP on the phase inversion process [24]. During the formation of hollow fibre mem-

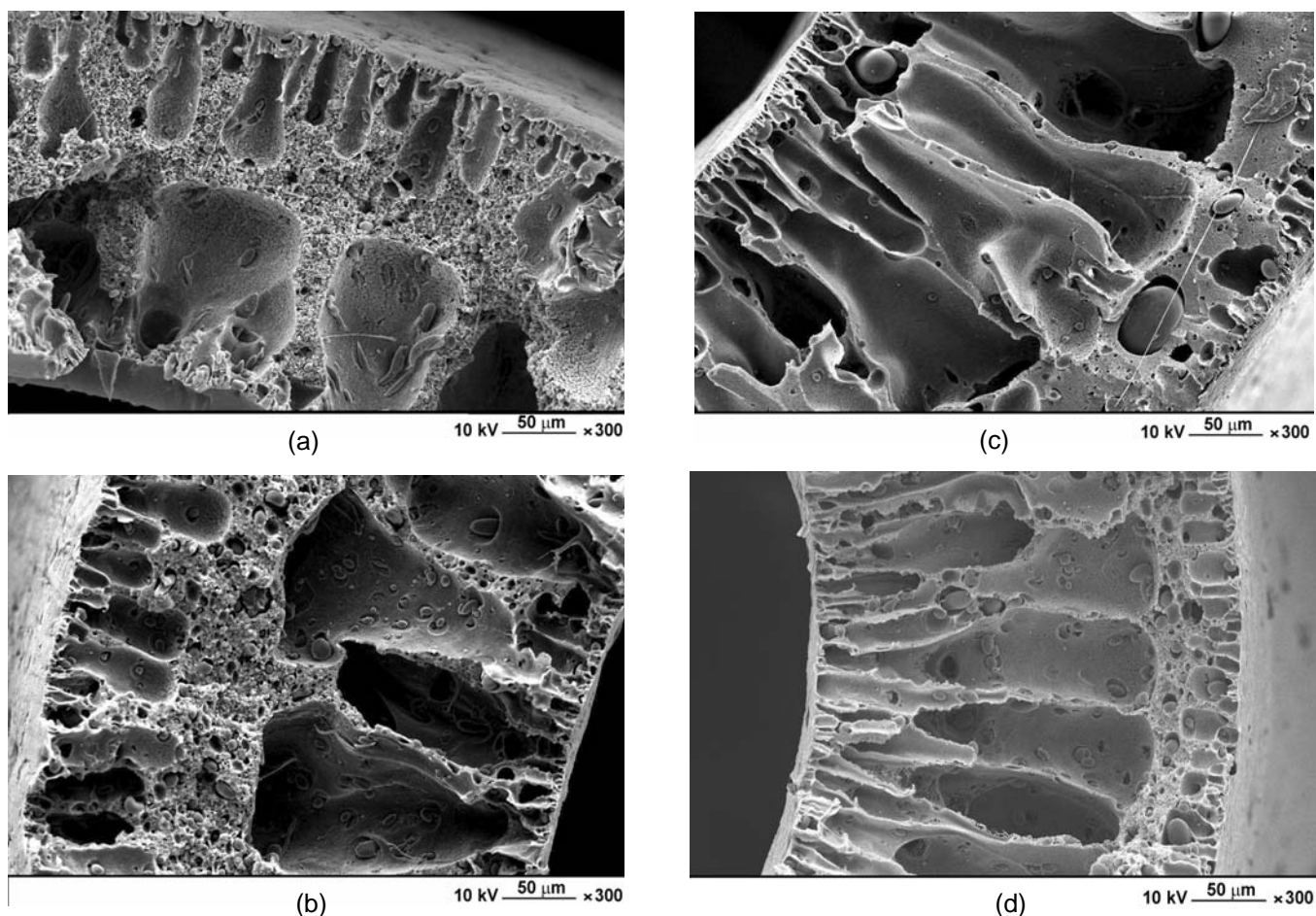


Figure 3. SEM Micrographs of membranes with different concentrations of PVP: (a) without additive, (b) 3 wt%, (c) 5 wt%, and (d) 10 wt% of PVP.

branes, due to an existing air gap, the mass transfer happened much earlier between the internal coagulant (water) and solvent (DMAc) than between the external coagulant (water) and solvent (DMAc). Smolders et al. have suggested that macrovoid growth is controlled by solvent diffusional flows and the macrovoids are formed at distances further away from the membrane top layer [25].

Thus, macrovoids generally grew near internal surface, varied significantly the morphology of the membrane top layer. In the case of adding 10 wt% PVP, owing to the increased viscosity of dope, the take-up speed slowed down and the time of solvent diffusion exposing in air is prolonged before fibres reach the coagulation bath. Macrovoids were expanded by solvent diffusion flows [25], hence the length of macrovoids became longer while the macropores were smaller in diameter, which resulted in more prominent asymmetric morphology.

Flux and Retention of Membranes

Membrane flux and retention were affected by the addition of PVP content. Marchese et al. have suggested that when PVP is entrapped by membrane materials, it should increase hydrophilicity and results in important changes in the performance of ultrafiltration membrane such as solute retention and fouling [26]. The results of permeation experiments were shown in Table 4. Below 3 wt% of PVP content the water flux is increased, after this point, however, the more PVP was in the casting dope, the less was the flux. Although at 3 wt% PVP content the water flux was maximum but retention had much lost. Even at 10 wt% of PVP, the water flux is close to the flux of membrane without PVP.

It is still argued that the entrapped PVP offers hydrophilicity to hydrophobic membranes and reduces the water flux due to the swelling of the pore-filled PVP [27]. The water flux of membranes increases

Table 4. Properties of membranes added different PVP content^a.

PVDF:TPU	PVP (wt%)	Water flux (L·m ⁻² ·h ⁻¹)	Retention (%)	Porosity (%)	Take-up speed (m·min ⁻¹)
100:0	0	9.25	83.34	56.0	13.00
80:20	0	28.25	82.54	69.52	11.30
80:20	1	55.41	80.0	79.05	10.00
80:20	2	321.55	79.0	82.00	8.00
80:20	3	440.43	77.24	83.60	7.50
80:20	5	346.73	86.88	81.40	6.50
80:20	10	32.47	80.22	69.22	5.90

(a) Polymer concentration is 16 wt%.

when higher amount of PVP is bleached out [28].

Growth of polymer crystallinity has a detrimental effect on the final membrane transport properties [20]. When PVP is added into PVDF/TPU membranes, by increase of PVP content, the crystallinity declined at first and then with the sharp increase of viscosity (10 wt%) led to the prolonged demixing time of casting dope and the crystallinity of PVDF is increased. Simultaneously, the permeate fluxes are enhanced first and then lessened (Table 4). PVP content operates as a permeate flux enhancer at a low level (< 3 wt%), but there is a sign that a high level of PVP (10 wt%) is less effective to improve the permeation flux in casting dope.

Retention to BSA of membranes prepared from the dopes with PVP is shown in Table 4. The presence of PVP had two different effects. A downhill of retention was found with PVP concentration below 3 wt%. When the amount of PVP was higher than 3 wt%, protein macromolecules hardly passed through the membrane and the retention was increased up to a maximum value. While PVP concentration exceeded 5 wt%, although the retention was slightly lowered, compared with additive-free PVDF/TPU membranes, the changes of retention were unobvious.

The membranes with PVP content above 5 wt% were found to have good ultrafiltration properties. This observation can be attributed to the variety of porosity shown in Table 4. From retention data it may be concluded that PVP at 3 wt% increases porosity but at 10 wt% it rather decreases porosity. The differences on porosity induced by the casting dopes and the presence of PVP resulted in various protein retentions properties.

CONCLUSION

Thermodynamic and kinetic variations are the keys factors to understand the phase inversion process which occurs by the addition of PVP into PVDF/TPU casting dopes. Thermodynamically, PVP worked as a demixing enhancer that accelerated the phase inversion, reduced α -form crystal structure which resulted in reduction of the crystallinity of PVDF in membranes, and contributed to the enlargement of macrovoid structure in the membranes which has improved the membrane flux. However, by further increment of PVP, kinetic impact was dominant. The demixing of the casting dope delayed and the crystallinity of PVDF increased which resulted in stretching down of finger like macrovoids from the underneath of membrane skin to the bottom of the sublayer. At high concentration, PVP suppressed macrovoid formation in the PVDF/TPU dope. The flux was decreased rather than increased and the membranes had higher retention due to decrease of porosity. It reveals that kinetic effect takes over thermodynamic enhancement.

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