

EFFECT OF SOLUTION EXTRUSION RATE ON MORPHOLOGY AND PERFORMANCE OF POLYVINYLIDENE FLUORIDE HOLLOW FIBER MEMBRANES USING POLYVINYL PYRROLIDONE AS AN ADDITIVE*

Chang-yu Tang^a, Wei Chen^{b, c}, Wen-qing Chen^{b, c**}, Qiang Fu^a, Zong-liang Du^c, Yang Ye^c,
Makoto Onishi^d and Naoki Abe^d

^a Department of Polymer Science and Materials, Sichuan University,
State Key Laboratory of Polymer Materials Engineering, Chengdu 610065, China

^b Department of Environment Science and Engineering, College of Architecture and Environment,
Sichuan University, Chengdu 610065, China.

^c SCU-HITACHI Environment Applied Technology Research Center, Sichuan University, Chengdu 610065, China

^d Hitachi Plant Technologies, Ltd, Tokyo 170-8466, Japan

Abstract Polyvinylidene fluoride (PVDF) hollow fiber membranes prepared from spinning solutions with different polyvinyl pyrrolidone (PVP) contents (1% and 5%) at different extrusion rates were obtained by wet/dry phase process keeping all other spinning parameters constant. In spinning these PVDF hollow fibers, dimethylacetamide (DMAc) and PVP were used as a solvent and an additive, respectively. Water was used as the inner coagulant. Dimethylformamide (DMF) and water (30/70) were used as the external coagulant. The performances of membranes were characterized in terms of water flux, solute rejection for the wet membranes. The structure and morphology of PVDF hollow fiber were examined by BET adsorption, dry/wet weight method and scanning electron microscopy (SEM). It is found that the increase in PVP content and extrusion rate of spinning solution can result in the increase of water flux and decrease of solute rejection. The improvements of interconnected porous structure and pore size are induced by shear-thinning behavior of spinning solution at high extrusion rates, which could result in the increase of water flux of hollow fiber membranes. The increase of extrusion rate also leads to the increase of membrane thickness due to the recovery effect of elastic property of polymer chains.

Keywords: Polyvinylidene fluoride; Polyvinyl pyrrolidone; Hollow fiber; Extrusion rate.

INTRODUCTION

In the past decades, the membrane technologies have been employed in a wide variety of applications, such as food purification, pharmaceutical extraction, gas separation and waste water treatment because of their excellent selectivity, low energy consumption, easily scaled production and little second pollution compared with conventional chemical and physical separation processes^[1]. Particularly, Hollow fiber membranes as an important branch of membrane separation field get more wide interests from academics and industries due to their unique benefits of high membrane packing densities, high mass flux, low fouling and flexibility in system design and operation^[2–4]. Most of polymeric hollow fibers are prepared by dry-wet spinning process using tube-in-orifice spinnerets^[5–8]. There is an air gap between the spinneret and the coagulation bath. Thus, the phase

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** Corresponding author: Wen-qing Chen (陈文清), E-mail: cwq69814@126.com

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inversion process starts immediately after extrusion from a spinneret at the inner surface of the hollow fiber by internal coagulant and then at the outer surface of the hollow fiber upon immersion in an external coagulation bath. However, the preparation of hollow fiber membranes is more complex than that of sheet membranes because it involves more controlling parameters during spinning, such as composition, temperature of external coagulant, composition of dope solution, temperature and flow rate of the bore fluid^[9, 10]. All these factors will affect the morphology and performance of the final membrane.

Polyvinylidene fluoride (PVDF), a semi-crystalline polymer, is popularly employed to fabricate asymmetric membranes using the Loeb-Sourirajan phase inversion method. Besides, the PVDF exhibits thermal stability, solvent and chemical resistance, particularly the oxidant resistance, which make it a new membrane material for waste water treatment^[11–13]. Since PVDF has a small critical surface tension, the solvent exchange rate of coagulations and spinning solution is restricted, which leads to thick skin layer and low porosity of the nascent membrane^[14]. Currently, much work was focused on the improvement of morphology and performance of membranes using varieties of hydrophilic additives/or porogen including polyvinylpyrrolidone (PVP)^[7], polyethylene glycol (PEG)^[15], lithium chloride (LiCl)^[14] and controlling composition and temperature of external coagulant, and composition of dope solution^[16]. However, to our knowledge, the effect of extrusion condition on the morphology and performance of hollow fiber membranes prepared from PVDF/PVP dope solution was rarely studied. When the polymer solution is flowed through a tube in orifice spinneret during hollow fiber spinning, shear stress is produced within the thin annular^[17, 18]. The highest shear stress is usually arisen from the wall of the spinneret, which could lead to the orientation of macromolecular chains on the outer surface of hollow fiber and formation of dense surface structure having high selectivity and low permeability due to tight molecular packing^[19, 20]. Generally, an increase in the dope extrusion rate results in an increase of shear rate; thus, the shear stress at the spinneret wall will also be increased. Meanwhile, the changed ratio of extrusion rate and internal coagulant flow rate will affect the solvent exchange between internal coagulant and spinning solution.

In this work, in order to better understand the effect of solution extrusion condition on the morphology and performance of membranes, the PVDF hollow fibers for ultrafiltration were prepared using PVP as an additive under different extrusion rates of spinning solution. The effects of extrusion rate on permeation properties, morphology and pore structure of the PVDF hollow fiber membranes were examined.

EXPERIMENTAL

Materials

Polyvinylidene fluoride (PVDF, Kynar K760 polymer pellets) was purchased from Elf Atochem, USA. The polymer was dried at 95°C under vacuum for at least 15 h before its use in the preparation of spinning solutions. Dimethylacetamide (DMAc) and acetone used as solvent were purchased from Kelong Chemical reagent plant (Chengdu, China). A mixture of dimethylformamide (DMF) and water (30/70) was used as the external coagulant. Polyvinylpyrrolidone (PVP-K30) with average molecular weight of 30000 used as an additive was purchased from Jinyu fine chemical Co., LTD (Tianjin, China). Bovine serum albumin (BSA) with molecular weight of 68000 was bought from Pengcheng BioTech Co., LTD (Guangzhou, China). All reagents were of analytical grade. Distilled water was used throughout.

Preparation of Hollow Fiber

PVDF pellets were slowly added into the mixed solvents of DMAc and acetone for over 30 min, followed by a mechanical stirring at a low speed of 200 r/min for 20 min in the first stage to make sure that each polymer pellet wetted thoroughly to avoid formation of polymer lump during dissolving PVDF. After that the stirrer speed was increased to 300 r/min and dope temperature was kept at 60°C until all polymer pellets dissolved in the solvent. As polymer viscosity was increased, the stirring was continued at a high speed of 500 r/min for 3 h. Then the desired amount of PVP was incorporated into the above mixed solution, followed by continuous stirring. The stirring was continued at the same speed for another 3 h to ensure complete dissolution of the polymer. Finally, the solution was kept at room temperature for at least 24 h to remove air bubbles.

In this study, hollow fiber was spun using a dry-wet spinning process as shown in Fig. 1. A tube-in-orifice spinneret with a spinneret of inside diameter of 0.68 mm and outside diameter of 1.2 mm was used to obtain hollow fiber membranes. The experimental parameters of hollow fibers were listed in Table 1. The air gap was kept at 19.5 cm for all the spinning runs. Water was used as a bore fluid (internal coagulant), and a mixture of dimethylformamide (DMF) and water (30/70) was used as the external coagulant for all spinning runs. The nascent hollow fiber membrane was passed through water bath to complete the solidification process and washed in water to remove residual solvent and PVP before all tests. The PVDF hollow fiber membranes prepared using different PVP contents (1% and 5%, respectively) were designed as P1 and P5, respectively. The different extrusion rates of 9.35, 11.77, and 16.94 mL/min were represented by V1, V2, V3, respectively.

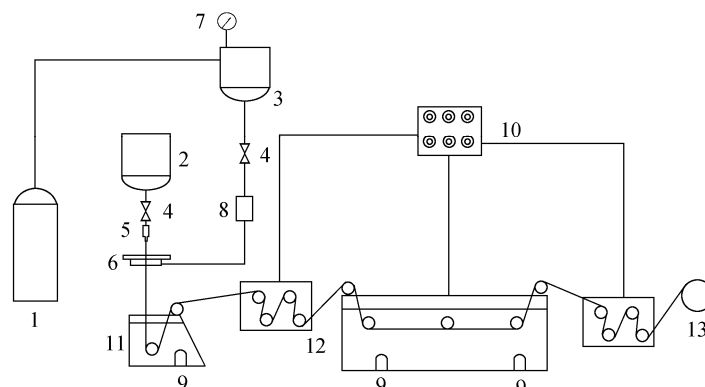


Fig. 1 Schematic diagram of hollow fiber spinning equipments: (1) nitrogen cylinder, (2) dope solution vessel, (3) bore liquid vessel, (4) dope solution valve, (5) rotor flowmeter, (6) spinneret, (7) pressure gauge, (8) regulating pressure valve, (9) heater, (10) electronic controller, (11) coagulation bath, (12) washing/treatment bath, (13) winding equipment

Table 1. Spinning parameters of PVDF hollow fiber membranes

Parameters	Operating conditions
Dope composition PVDF/PVP/DMAc/acetone	24%/1%–5%/61%–64%/10%
Dope extrusion rate	9.35, 11.77, 16.94 mL/min
Dope temperature	15°C
Bore fluid (internal coagulant)	Water
Bore fluid flow rate	14 mL/min
External coagulant	DMF/water (30/70)
External coagulant temperature	30°C
Air gap	19.5 cm

Permeation Test

The permeation performances for PVDF hollow fiber membranes were conducted in a cross-flow filtration set-up as shown in Fig. 2. Six fiber membranes were cut and potted at both ends with epoxy resin in a plastic module so that 20 cm was left as effective length for permeation. The feed solution (BSA) was pumped through the shell side of the module and the permeate solution was collected from the lumen of the fibers. The concentration of feed solution was 0.1 wt%, and all tests were carried out at room temperature and at a transmembrane pressure of 0.1 MPa. The solute concentration was obtained from the absorbance determined by UV-spectrophotometer (UV1100, Shanghai Puda Company).

Permeation flux of the membranes was calculated by the following equation:

$$J = \frac{V}{A \cdot t} \quad (1)$$

where J is the pure water flux ($\text{L}/(\text{m}^2 \cdot \text{h})$), V is the permeation volume of water (L), A is the effective membrane areas (m^2), t is the sampling time (h).

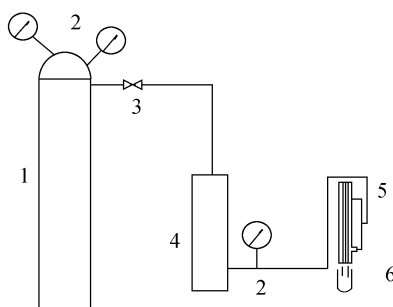


Fig. 2 Schematic diagram for UF experimental equipment: (1) nitrogen cylinder, (2) pressure gauge, (3) regulating pressure valve, (4) feed tank, (5) hollow fiber membrane module, (6) measuring cylinder for collecting permeate

The solute rejection (R) of the hollow fiber membrane was obtained from the following equation

$$R(\%) = (1 - c_1 / c_2) \times 100 \quad (2)$$

where c_1 and c_2 are the solute concentration of permeate and feed solution, respectively.

Scanning Electron Microscopy (SEM)

The cross-sections of the PVDF hollow fibers were observed by using a scanning electron microscope (SEM) (JSM-5900LV) under an acceleration voltage of 20 kV. Before being examined, the membrane samples were cryogenically fractured in liquid nitrogen and coated with gold.

Effective Porosity Measurements

The porosities of the PVDF hollow fiber membranes were measured by determining their swelling in isopropanol and using the following expression^[21]:

$$\text{Porosity} = \frac{W_2 - W_1}{S \cdot d \cdot d_i} \times 100\% \quad (3)$$

where W_1 and W_2 stand for the weights of the membranes in the dry and wet states, respectively; S and d represent the area and the average thickness of the membrane in the wet state, respectively; d_i is the density of isopropanol at room temperature.

Pore Size Measurements

The mean pore size of hollow fiber surface was determined by BET method using a Micromeritics Tristar-3000 instrument.

Rheological Measurements

The rheological properties of spinning solutions were investigated by an advanced rheological extension system (ARES) (Rheometrics, TA, USA) using 40 mm diameter parallel plate. The gap between the plates was 0.2 mm during measurement. The sample was allowed to equilibrate for at least 5 min at 25°C before steady shear measurements. Shear viscosity and normal stress difference for each spinning solution was obtained at a shear rate range of 10–1600 s⁻¹.

The shear rate profile of each spinning solution in the spinneret was estimated by the computational fluid dynamics (CFD) model reported by Cao *et al.*^[22]. This CFD model accounts for the flow of a fluid which obeys the power law within a concentric annulus. The shear rate at the outermost of the spinneret outlet was selected for consideration. On a basis of this method, the extrusion rates of spinning solution (9.35, 11.77, and 16.94 mL/min) used in this experiment were translated to the shear rates (781, 983.1, 1415 s⁻¹).

RESULTS AND DISCUSSION

To measure the relationship between shear rate and rheological properties, the extrusion rates (9.35, 11.77, and 16.94 mL/min, respectively) of spinning solutions were translated to the shear rate at spinneret wall (781, 983.1, and 1415 s^{-1} , respectively). Figure 3(a) shows the shear viscosities of PVDF spinning solutions with 1% and 5% PVP as a function of shear rate. One can see that the viscosity of PVDF solutions increases with increasing PVP content and these two solutions exhibit shear-thinning behavior like most non-Newtonian fluids. The shear rates applied in our spinning process fall in the range of 600–1600 s^{-1} , which can be observed in the inset of Fig. 3(a). With increasing shear rate from 781 s^{-1} to 1415 s^{-1} , the viscosity of PVDF solution with different PVP content decreases sharply by over 50%. This result indicates that the extrusion rates applied in our spinning condition significantly affect the viscosity of spinning solution, which could lead to the obvious difference in membrane morphologies. In general, polymer melt or solution is not an ideal viscous liquid, which exhibits dual visco-elastic behavior. Normal stress difference can directly reflect the elastic effect of polymer during shearing^[23]. The relationship between normal stress difference and shear rate for PVDF solutions with different PVP contents is shown in Fig. 3(b). Normal stress difference in all PVDF spinning solutions increases with increasing shear rate, which indicates the increase of elastic effect of PVDF solutions. In all range of shear rate, the normal stress difference in PVDF solution with 5% PVP is higher than that in PVDF solution with 1% PVP. It demonstrates that increase of PVP content can increase the elastic property of spinning solutions, which is maybe due to the interaction between PVDF and PVP.

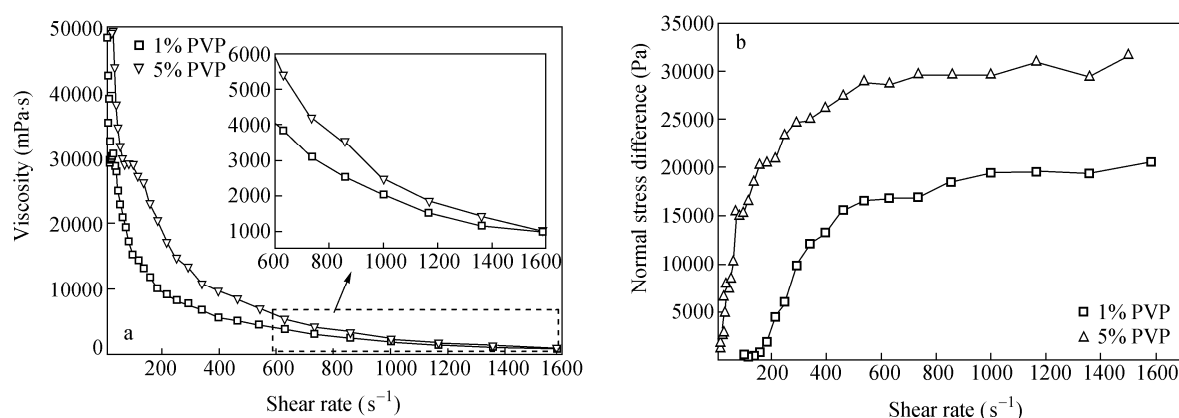


Fig. 3 (a) The shear viscosities and (b) the normal stress difference of PVDF spinning solutions with 1% and 5% PVP as a function of shear rate

The data about inner, external diameters and wall thickness of PVDF hollow fibers prepared at different PVP contents and extrusion rates were calculated from the SEM image of overall cross-section of hollow fiber (see Fig. 4) and listed in Table 2. For the PVDF hollow fibers with same PVP content, the inner, external diameters and wall thickness increase with increasing the extrusion rate of spinning solution. This is attributed to the recovery effect of elastic property of polymer chains^[23]. It is well known that macromolecular chains will be oriented along the flow direction of solution under the shear stress produced in the spinneret, when the polymer solution flows through a tube in orifice spinneret during hollow fiber spinning^[19]. After the spinning solution comes out from the spinneret, the relaxation of stretched polymer chains leads to the increase of the dimension of hollow fiber in the absence of the high shear stress. It can be seen that the recovery effect of elastic property of polymer chains becomes stronger with the increase of extrusion rate. Meanwhile, it is found that the increase of PVP content in spinning solution also results in the increase in dimension of hollow fiber at same extrusion rate of spinning solution, which could be related to the stronger visco-elastic behavior of spinning solution containing high PVP content (*i.e.* 5 wt%), which agrees with the rheological results shown in Fig. 3(b).

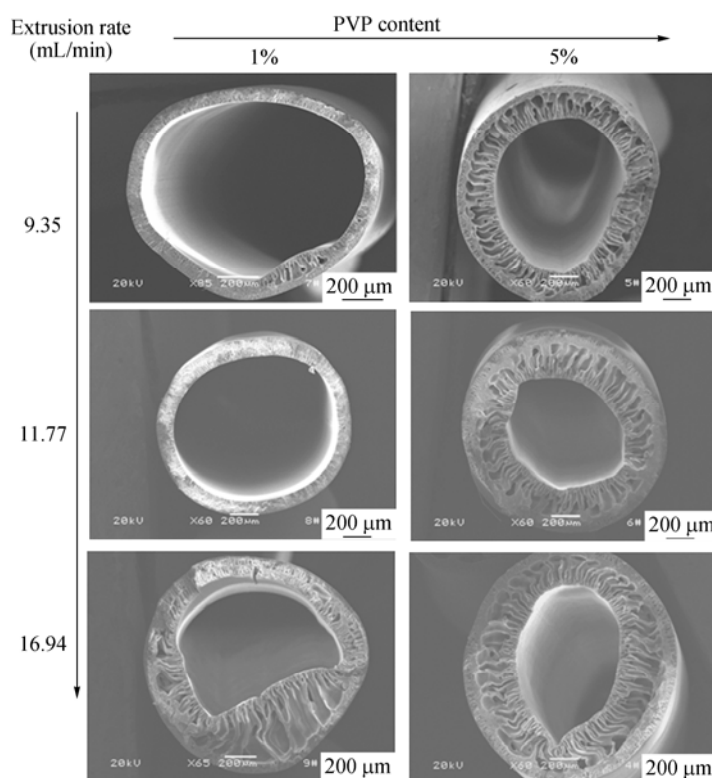


Fig. 4 The overall cross-section of hollow fiber membranes prepared from spinning solutions with 1% and 5% PVP at different extrusion rates (9.35, 11.77, 16.94 mL/min)

Table 2. Characteristic parameters of PVDF hollow fiber membranes

Sample	Extrusion rate (mL/min)	Outer diameter (mm)	Inner diameter (mm)	Thickness (mm)
P1V1	9.35	1.06	0.93	0.13
P1V2	11.77	1.22	1.06	0.16
P1V3	16.94	1.30	1.03	0.27
P5V1	9.35	1.25	1.00	0.25
P5V2	11.77	1.50	1.21	0.29
P5V3	16.94	1.58	1.26	0.32

The scanning electron microscopy was used to study the structure and morphology of PVDF hollow fiber membranes. The SEM images of cross-section of membranes at various magnifications are shown in Figs. 4–5. As can be seen from Fig. 5, the PVDF hollow fibers exhibit asymmetric structures containing three layers (outer, middle, and inner layers). For an extrusion rate of 9.35 mL/min, the sponge-like porous structure in middle layer disappeared and more interconnected finger-like macrovoid formed, when the PVP content of spinning solution increased from 1% to 5%. Because PVDF has a small critical surface tension of about 25×10^{-3} N/m, the penetration of the coagulant (water) into the nascent membrane is restricted, thus, the coagulation rate of nascent membrane is slow due to weak interaction between the coagulant (water) and the polymer^[14]. Here, the increased hydrophilicity of PVDF solution due to the hydrophilic nature of PVP led to an increase in the precipitation rate, thus, larger macrovoids and cavities were formed near both the inner and outer skins, and a thinner skin layer was obtained. In the case of spinning solution containing 1% PVP, it is found that the thickness of middle layer in the cross-section of hollow fiber reduces and finger-like cavities become larger as the extrusion rate of spinning solution increases. This is due to the decreased viscosity of polymer solution resulted from shear-thinning effect. In the dry/wet phase separation process, the low viscosity of PVDF solution

is favor of improving the phase separate rate and PVP is easily removed, which leads to the formation of more macrovoid and high interconnection of porous structure. Similar trend also appears in the PVDF hollow fiber prepared from spinning solution with 5% PVP.

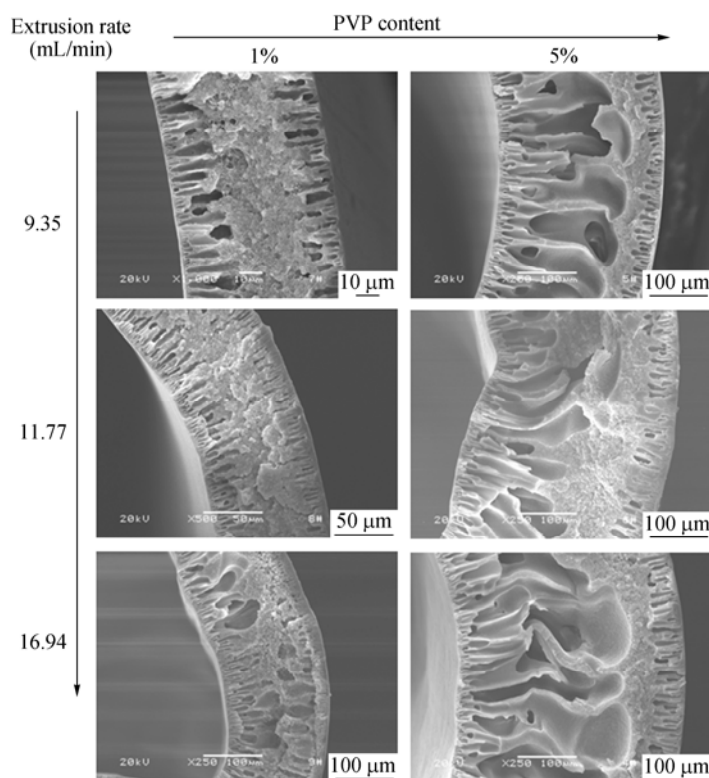


Fig. 5 The cross-section of hollow fiber membranes prepared from spinning solutions with 1% and 5% PVP at different extrusion rates (9.35, 11.77, 16.94 mL/min)

The mean pore sizes of both the internal and external surfaces of the PVDF hollow fibers and their porosity are summarized in Table 3. The mean pore size of surface and porosity of PVDF hollow fiber membranes increase with increasing the PVP content. The increase of extrusion rate also results in the increase of surface pore size and porosity in PVDF hollow fiber. In the case of spinning solution with 1% PVP, the porosity of hollow fiber obviously increases as extrusion rate increases, especially at an extrusion rate of 16.94 mL/min. This maybe due to the sharp reduce in viscosity of spinning solutions at an extrusion rate of 16.94 mL/min (as shown in Fig. 3a), which results in the formation of more porous structure as described in SEM results. However, PVDF hollow fibers prepared from spinning solution with 5% PVP have almost same porosity (77.3%–86.1%) in the extrusion rate range of 9.35–16.94 mL/min. In this case, the PVDF hollow fiber membrane exhibits highly interconnected finger-like structure without sponge-like middle layer at low extrusion rate (9.35 mL/min), as shown in Fig. 5. The further increase in extrusion rate does not significantly affect the porosity of membranes. It is demonstrated that the high porosity mainly arises from high PVP content rather than the decrease in viscosity of the spinning solution at high extrusion rates. It is noted that our results are different from some previous reports^[18, 24–26]. Some researchers found that the hollow fiber membranes spun with enhanced extrusion rate had a lower permeability and higher selectivity with denser surface (smaller pore size) due to closer pack of orientated polymer chains induced by high shear stress. But, the extrusion rate of spinning solution in our experiments is higher than that in these reports (< 5 mL/min), indicating that the low viscosity nature of dope arising from shear-thinning behavior dominates the final structure formation of hollow fiber membranes rather than the orientation of polymer chains in skin layer induced by high shear after a critical

extrusion rate.

Finally, the PVDF hollow fiber membranes prepared from spinning solution with 1% or 5% PVP at different extrusion rates were characterized by solute transport method using ultrafiltration of pure water and aqueous solutions containing 0.1 wt% BSA with molecular weight of 68000. The obtained water flux and solute rejection values are presented in Table 3. As can be seen, the increase of PVP content results in the membrane with high flux and low rejection. This result may be attributed to the increase of the surface pore size and porosity described in Table 3. It is found that the flux and porosity of PVDF hollow fiber increase with increasing the extrusion rate for the spinning solution with same PVP content. The extent of increased flux in hollow fiber prepared from spinning solution with 1% PVP is more than that of increased flux in hollow fiber prepared from spinning solution with 5% PVP, which is according to the changing trend of pore size and porosity as shown in Table 3. Generally, the water flux of membrane decreases as the membrane thickness increases according to the Hagen-Poiseuille equation^[1]. In this case, it seems that the water flux of membrane increases with the increase of membrane thickness, which does not follow the conventional theory. But it is noted that the calculated thickness of hollow fiber membrane increases accompanying an increase of pore size and porosity. It is demonstrated that the pore size and porosity is the determined factor for the water flux of membranes. Here, hollow fiber membranes having larger pore sizes exhibit lower solute rejection values according to previous most studies.

Table 3. Properties of PVDF hollow fibers membranes prepared from spinning solutions with 1% and 5% PVP at different extrusion rates

Sample	Pore size (nm)	Porosity (%)	Flux (L/(m ² ·h))	Rejection (%)
P1V1	12.02	59.3	34.39	86.3
P1V2	12.98	63.6	46.73	84.9
P1V3	13.50	79.2	60.02	82.9
P5V1	16.70	77.3	174.30	22.7
P5V2	22.56	81.5	239.90	10.2
P5V3	23.30	86.1	274.13	7.7

CONCLUSIONS

In summary, PVDF hollow fiber membranes were prepared from spinning solutions with different PVP contents at different extrusion rates by wet/dry phase process. The increase in PVP content and extrusion rate of spinning solution can result in the increase of water flux and decreased solute rejection. When the PVP content and extrusion rate of spinning solutions were controlled at 1% and 16.94 mL/min, respectively, high permeation flux and good solute rejection for BSA with a molecular weight of 68000 could be obtained. In this work, the improvement of interconnected porous structure and pore size induced by shear-thinning behavior of spinning solutions could result in the increase of water flux of hollow fiber membranes. The increase of extrusion rate also leads to the increase of membrane thickness due to the recovery effect of elastic property of polymer chains.

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