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Preparation, characterization and performance of phenolphthalein polyethersulfone ultrafiltration hollow fiber membranes

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ABSTRACT

Phenolphthalein polyethersulfone (PES-C) is potentially an excellent candidate as a membrane. This assumption is based upon its mechanical and thermal properties. Here we report the manufacture of hollow-fiber membranes using the PES-C using a dry–wet spinning technique. The influence of different hollow-fiber contact forming conditions including solvent, composition of PES-C temperature, internal quench medium extrusion pressure and winding-up velocity on the structure and properties of prepared membranes were investigated. The content of PES-C in the spinning solution affects the properties of the membranes prepared, including porosity, average pore diameter and water flux. These decrease with increasing content of PES-C. Water flux of membrane increases with casting solution temperature. When the temperature reaches 40°C, water flux is maximum while retention reaches a minimum. Furthermore, water flux increases with increasing internal quench medium extrusion pressure, while inner and outer diameters increases and wall thickness decreases with increasing internal quench medium extrusion pressure. The inner and outer diameters of hollow membrane decreases with increasing winding-up velocity, the outer diameter decreases more than the inner diameter, which leads to a decrease of membrane wall thickness.

Keywords: Phenolphthalein polyethersulfone; Hollow-fiber membrane; Ultrafiltration; Internal quench medium extrusion pressure; Biaxial stretch

1. Introduction

Membranes play a critical role in our daily lives: "If you are tired of membranes, you are tired of life" [1]. In industrial separation processes membranes play a more and more important role. Thus the development of new applications using synthetic membranes requires polymers with outstanding properties. Polymer materials not only have to resist high pressures and high temperatures, but also have the appropriate chemical properties that lead to high flux and high selectivity membranes for application. Phenolphthalein polyethersulfone (PES-C) is a newly developed high-performance engineering thermoplastic that has been used as a potential membrane material due to its excellent mechanical and thermal properties [2]. Fig. 1 demonstrates its repeating unit.

Nowadays the hollow-fiber configuration is a favourite choice in membrane separation systems. The major advantages are seen when hollow-fiber membranes are compared to flat-sheet membranes [3]: (1) hollow fibers have a much larger ratio of membrane area to unit volume, and hence higher productivity per unit volume of membrane module. (2) They are self-supporting, which can be back-flushed for liquid separation. (3) They are flexible when used. The polymeric hollow fiber system has already been used in reverse osmosis, ultrafiltration,

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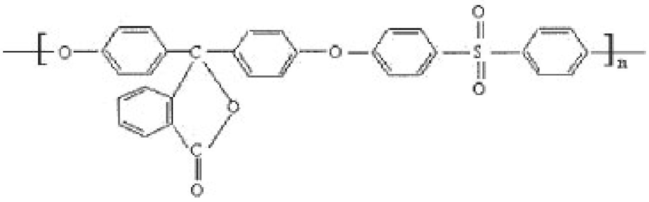

Fig. 1. Structural formula of PES-C.

microfiltration, hemodialysis, gas separation and gas absorption. The key technological factor is the development of appropriate hollow-fiber membranes. However, the preparation of this membranes is more complicated than flat-sheet membranes because it involves more controlling parameters variable when preparing the hollow fiber.

Although hollow-fiber membrane preparation techniques are well known, the precise membrane preparing procedure are not available for several polymer candidate. The aromatic polysulfone family of polymers is extensively used for UF membrane preparation due to their wide temperature, pH and chlorine tolerance. They are a class of polymers essentially comprises of ether, sulfone and substituted or unsubstituted methylene groups that are joined through aromatic groups in para-para orientation in varying proportions. Unlike polysulfone and polyethersulfone [4–22], PES-C are not widely reported. There are few works that outline PES-C in membrane materials [23–25]. This paper describe the preparation, characterization and performance of PES-C UF membranes. The results of our experiments will be useful in preparing PES-C hollow-fiber membranes.

2. Experimental

2.1. Materials and chemicals

PES-C (T_g = 255.8°C) was supplied by Xuzhou Engineering Plastics (Xuzhou, China.) PES-C has a reduced solution viscosity of 0.68 dl/g in chloroform at 25 GPC measurement; the polymer possesses a molecular mass of Mn = 12,000 and Mw = 32,000. Polyvinylpyrrolidone (PVP K90, Mn = 36,000) was supplied by BASF Shanghai (Shanghai, China). Dimethyl acetamide (DMAc, analysis grade), dimethylformamide (DMF, analysis grade), and 1-methyl-2-pyrrolidone (NMP, analysis grade) were used as solvents. All the solvents, bovine serum albumin (BSA, M_w = 67,000) and other remaining reagents were purchased from Shanghai Chemical Reagent (Shanghai, China).

2.2. Preparation of hollow-fiber membranes and modules

In this study the dry–wet spinning process was used to manufacture the hollow fibers. The spinning apparatus developed in laboratory is shown in Fig. 2. Before use the PES-C powder was dried at 120° for 24 h with vacuum. The casting dopes were made from PES-C with PVP dissolved in solvent. The solvents used in this work were DMAc, DMF and NMP. Distilled water was used as internal quench medium. The concentration for PVP(wt%) was a constant 5% in the experiments.

The casting dope was prepared and loaded into the dope tank. The dope was gas pumped (under air pressure) into a coaxial conic bottom tube spinneret (shown in Fig. 3), while the internal quench medium was forced through the inner tube. The internal quench medium was the inner coagulant and supported the hollow fiber before it was formed. The dope temperature and the internal quench medium extrusion pressure were both set by considering the viscosity of the polymeric mixture and other preparing conditions. The spinneret was maintained at 500 mm from the coagulation bath. The dope flow rate was maintained at 9.6 m/min while the temperature of coagulation bath and internal quench medium was maintained at 30°C in this study. The temperature of the first water bath was 45°C and the temperature of the second water bath was 65°C. The solvent, composition of PES-C, casting dope temperature, internal quench medium extrusion pressure and winding-up velocity were changed in this work in order to investigate their effects on the structure and properties of prepared hollow fiber membranes.

The hollow fibers formed were kept in a second water bath for 24 h. After this period, the fibers were washed at 25°C for two periods of 24 h each, for the first period with water, and for the second, water with an added 30% of glycerol aqueous solution. Finally, the fibers were dried in a vacuum dryer at room temperature.

To test quantitatively the hollow-fiber separation performance in terms of permeation flux and rejection, permeation modules were prepared. Each module consisted of 20 fibers with a length of 25 cm. The shell sides of the two ends of the bundles were glued into two stainless-steel tees using a normal-setting epoxy resin. These modules were left overnight for curing before testing. To eliminate the effect of the residual glycerol on module performance, each module was immersed in water for 1 day, and run in the test system for 90 min before any sample collection. All the tests were conducted at room temperature (25°C).

2.3. Characterization of membrane

2.3.1. Pure water flux and retention to BSA

Pure water flux (PWP) of the hollow-fiber membrane was measured under a pressure of 0.1 MPa at 25°C on permeation modules. Pure water flux was calculated by Eq. (1).

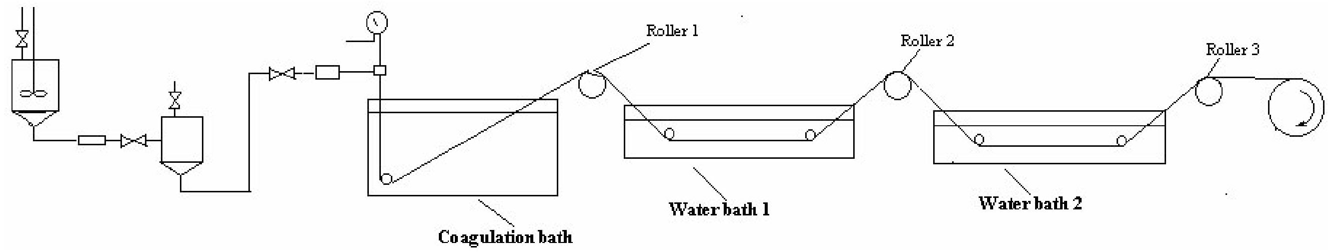

Fig. 2. Schematic diagram of hollow-fiber spinning apparatus.

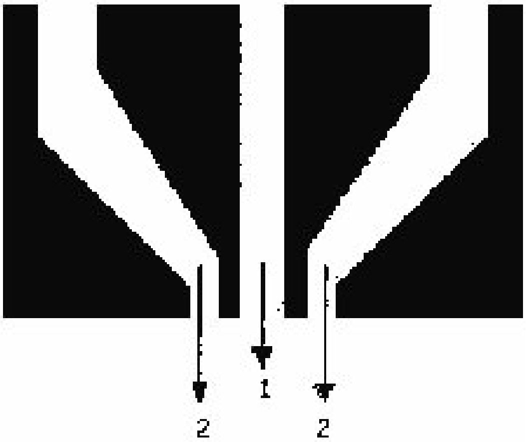

Fig. 3. Schematic diagram of spinneret used in spinning apparatus. 1 internal quench medium, 2 dope.

$$PWP = \frac{\text{Water permeated volume (L)}}{\text{Membrane area (m}^2\text{)} \times \text{time (h)}} \quad (1)$$

The retention of BSA is an important parameter when the membrane is used in the plasma separation and the ascites UF concentration process. The retention ratio of hollow-fiber membranes was tested with 0.5 mg/l BSA. The absorbance of original liquids and permeated liquids was obtained using a 7500 ultraviolet visible spectrometer ((Shanghai Tianmei Technology) at 280 nm. The retention ratio was calculated from Eq. (2):

$$\text{Retention ratio } (R) = \left(1 - \frac{2 \times c_2}{c_0 + c_1}\right) \times 100\% \quad (2)$$

where c_1 and c_2 refer to the concentration of the remaining solution and the permeated solution after ultrafiltration separately; c_0 is the original concentration before filtration.

2.3.2. Membrane cross-section morphology

The hollow fibers were broken in liquid nitrogen and coated with gold. Membranes were observed using a JEOL-500 scanning electron microscope.

3. Results and discussion

3.1. Influence of solvents

Table 1 shows the forming conditions for preparing the hollow fibers used in 3.1. The pure water flux and retention to BSA of hollow-fiber membranes cast from different solvents is shown in Table 2. When using DMAc as solvent, the membrane gave a higher pure water flux and a lower retention. However, membranes cast from DMF had a lower pure water flux and protein macromolecules were impermeable.

Cast solutions are polymer concentrated solutions, and there are many entanglements existing among macromolecules due to the interactions of molecular chains. Flow of the solution tends to align the sections of chains between coupling points, therefore elastic energy will be stored in the sections of chains between entanglements. The energy will be released when the flow stops after a time τ. The formation process of hollow-fiber membranes was so short that much stress was corrected between the entanglements in the nascent hollow fiber. The stress will be released as its temperature increases during the post-treatment process. The solubility parameter (δ_{sp}) and polarity parameter (δ_{pp}) of solvents used are listed as follows [26]: DMF: δ_{sp} =24.8 MPa$^{1/2}$, δ_{pp} = 13.7 MPa$^{1/2}$;

Table 1
Forming conditions in 3.1

PES-C content, % wt	18
Spinning solution temperature, °C	40
Internal quench medium extrusion pressure, Pa	2.5×10^4
Winding-up velocity, m/min	32

Table 2
Pure water flux and retention of membranes cast from different solvents

Solvent	J_w, L/m^2.h	R, %	δ_{sp}, MPa$^{1/2}$	δ_{pp}, MPa$^{1/2}$
DMF	148.0	90.3	24.8	13.7
NMP	164.0	84.0	22.9	12.3
DMAc	193.8	81.5	22.7	11.5

NMP: δ_{sp} = 22.9 MPa$^{1/2}$, δ_{pp} = 12.3 MPa$^{1/2}$; DMAc: δ_{sp} = 22.7 MPa$^{1/2}$, δ_{pp} = 11.5 MPa$^{1/2}$. PES-C is a polar polymer and more entanglements would be formed on one molecular chain when a solvent with higher solubility and polarity parameter was used. This is due to the stronger interaction that occurs between polymer molecules and solvent. The solubility parameter and polarity parameter of DMF are higher than the other solvents we used. Therefore, more stress is fixed between entanglements in the membrane cast with DMF and more shrinkage occurs during post-treatment process and the shrinkage give the hollow-fiber membrane a lower flux and a higher retention.

These findings indicate that hollow-fiber membranes cast from DMAc have the highest flux and the lowest retention. This result is similar to the observation of Yoew et al. [27] in PVDF membranes. Therefore, DMAc was chosen as the solvent for further investigation.

3.2. Influence of PES-C content in the spinning solution

Table 3 shows the forming conditions for preparing the hollow fibers used in 3.2. As shown in Fig. 4, pure water flux decreases quickly with increasing PES content in the solution. The tendency slows down when the solid content reaches 18%, which may be due to phase separation in the membrane formation process. PES-C macromolecules can exist in the casting solution in two states: one is a macromolecular network formed by a certain number of macromolecules through intermolecular interaction and macromolecular entanglement; the other is a micelle aggregate (micro-cell) formed through macromolecular approach and macromolecular entanglement and aggregation.

There are two kinds of pores on the skin layer surface of membranes formed by macromolecules corresponding to the two aggregating states: one is a network pore formed by chain segments network with smaller dimension and larger number. The other is micro-cell pore with larger dimension but smaller number. As concentration increases, the density of macromolecules increases, this leads to a density increase of macromolecular network. The macromolecular entanglement among neighboring micro-cells also increases and the average aperture of both kinds of pores decreases. This leads to a decrease of porosity and appears as a decrease of water flux. This increases the retention macroscopically. In addition, the wall of the network pore formed from casting solution at higher concentrations is thicker, which leads to an increase of resistance when water passes through. The rate of water penetration and pure water flux decrease.

Table 3
Forming conditions in 3.2

Solvents	DMAc
Spinning solution temperature, °C	40
Internal quench medium extrusion pressure, Pa	2.5×10^4
Winding-up velocity, m/min	32

3.3. Influence on the spinning solution temperature

Table 4 shows the forming conditions for preparing the hollow fibers used in 3.3. As shown in Fig. 5, the pure water flux reaches a maximum level at 40°C whereas the retention is at minimum point. Furthermore with increasing spinning solution temperature, the viscosity of the solution decreases and fluidity of the solution increases. This results in the increase of the interdiffusion velocity between the solvent and coagulating agent. The pore diameter decreases and the porosity increases with

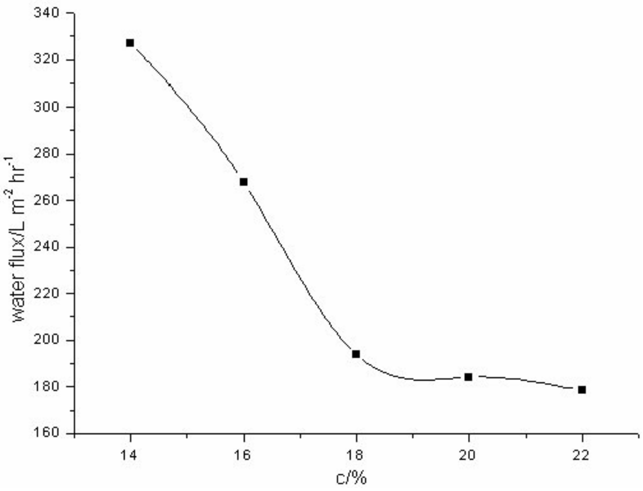

Fig. 4. Dependence of pure water flux on PES-C content in the solution.

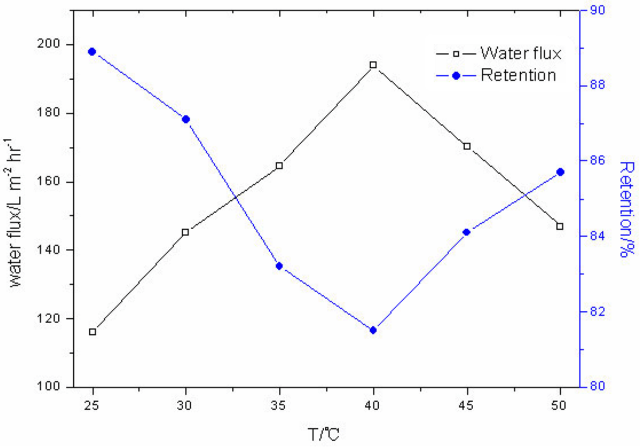

Fig. 5. Dependence of membrane performance on the temperature of spinning solution.

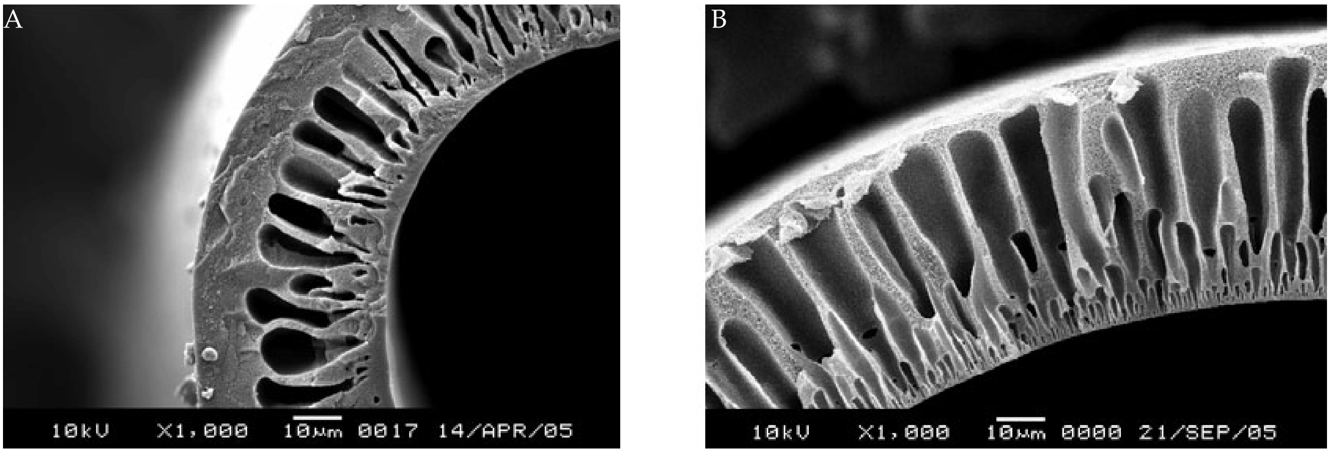

Fig. 6. SEM photos of cross section at different internal quench medium extrusion pressures. A. Low extrusion pressure. B. High extrusion pressure.

increasing spinning solution temperature thus leading to an increase of pure water flux and decrease in retention. When the temperature of spinning solution reaches 40°C, the effect of solvent evaporation increase is bigger than the increase of the interdiffusion velocity between the solvent and coagulating agent. Therefore, pure water flux decreases and retention increases accordingly.

Table 4
Forming conditions in 3.3

Solvents	DMAc
PES-C content, %wt	18
Internal quench medium extrusion pressure, Pa	2.5×10^4
Winding-up velocity, m/min	32

Table 5
Forming conditions in 3.4

Solvents	DMAc
PES-C content, %wt	18
Spinning solution temperature, °C	40
Winding-up velocity, m/min	32

Table 6
Internal quench medium extrusion pressure effect on the dimension of hollow fibers

Internal quench medium extrusion pressure, 10^4Pa	External diameter µm	Inner diameter µm	Wall thickness, µm
1.5	334	250	42
2.0	350	260	45
2.5	390	286	52
3.0	396	290	53
3.5	436	324	56

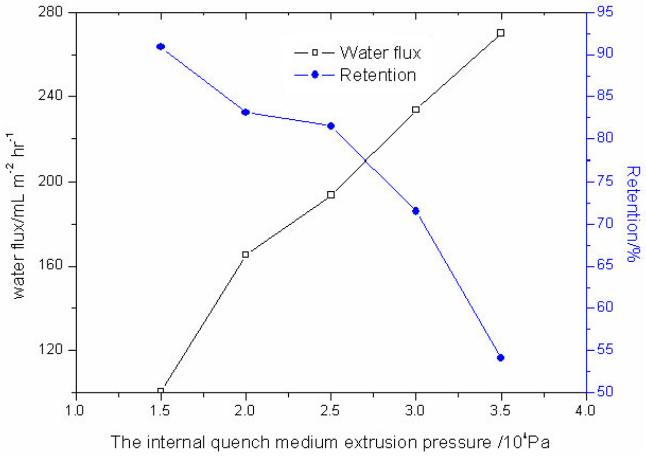

Fig. 7. Dependence of membrane performance on internal quench medium extrusion pressure.

3.4. *Influence of internal quench medium extrusion pressure*

Table 5 shows the forming conditions for preparing the hollow fibers used in 3.4. In this study a coaxial conic bottom tube spinneret was used to spin the hollow-fiber membrane and the inner tube was filled with the internal quench medium. The internal quench medium provides not only inner support for the as-spun hollow fiber but also acts as inner coagulation bath, which affects the structure on the inner surface and the performance of hollow fiber membrane. The dimensions of the hollow fiber, i.e. inner and outer diameter, wall thickness can be varied through the internal quench medium extrusion pressure as seen in Table 6 and Fig. 6. The inner and outer diameters of hollow fiber increase with increasing internal quench medium extrusion pressure. The inner diameter increases rapidly which leads to a decrease of membrane wall thickness; the thickness of sponge structure adjacent to outer wall decreases quickly, with its porosity and the

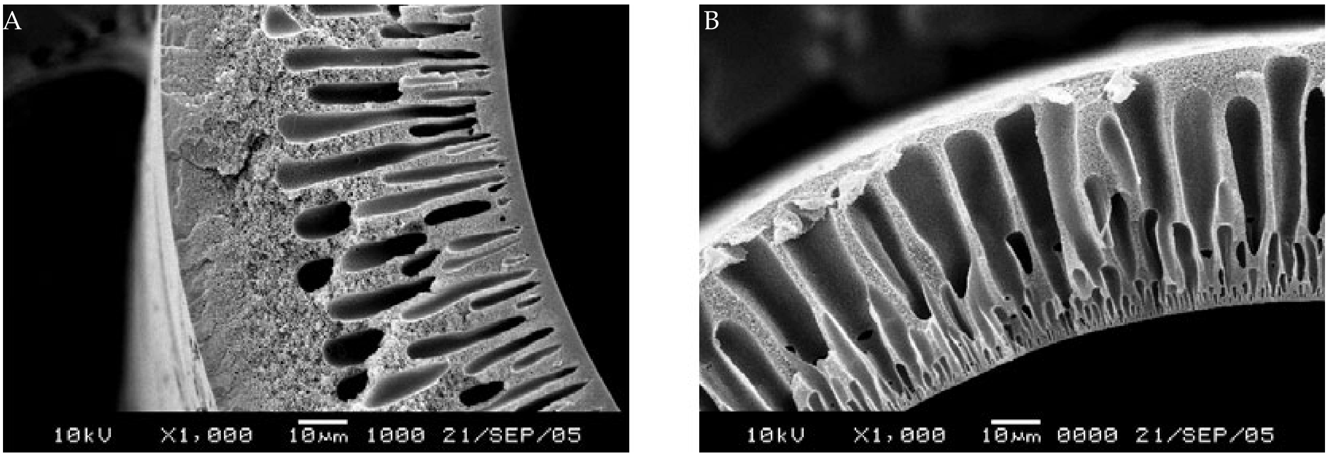

Fig. 8. SEM photos of membrane cross section at different winding-up velocities. A Without stretch. B. After stretch.

Table 7
Forming conditions in 3.5

Solvents	DMAc
PES-C content, %wt	18
Spinning solution temperature, °C	40
Internal quench medium extrusion pressure, Pa	2.5×10^4

diameter of finger pore increases. As shown in Fig. 7, pure water flux increases with increasing internal quench medium extrusion pressure. Wall thickness and mass transfer resistance decreases and the rate of water penetration increases with increasing internal quench medium extrusion pressure; consequently, the flow rate of internal quench medium increases with increasing internal quench medium extrusion pressure. This leads to an increase of concentration difference between solvent and coagulation bath at the border of the membrane. The rate of interdiffusion and membrane formation, the porosity and pore dimension increases, whereas pure water flux increases and retention decreases. Internal quench medium extrusion pressure can be varied according to the use of the membrane.

Biaxial stretch in hollow fiber was first reported in our laboratory [28]. Enough axial strength is required for clothing and industrial fiber, which can be obtained through axial stretch. Both axial and cross sectional stretches are necessary for hollow fiber membrane due to its special uses. If the hollow membrane is just stretched axially, firstly the pore on the membrane surface will deform, secondly the axial dimension will increase and thirdly the cross sectional dimension will decrease, which influences the filtering property of the membrane. Also the cross sectional strength of membrane will decrease. In this study the hollow-fiber membrane is first stretched cross sectionally according to the change of internal quench medium extrusion pressure; then plasticizing stretch and multi-stretch are carried out to obtain biaxial stretch of the hollow fiber membrane.

3.5. Dependence of membrane properties on winding-up velocity

Table 7 shows the forming conditions for preparing the hollow fibers used in 3.5. As winding-up velocity increases, both inner and outer diameters decrease. The outer diameter decreases which leads to a decrease in membrane thickness, resulting in its decrease of mass transfer resistance and the increase of water penetration rate and water flux. As seen in Fig. 8, the thickness of transfer layer adjacent to the outer wall of the hollow membrane without stretch is thicker.

4. Conclusions

PES-C is a developing membrane material. In this study PES-C hollow-fiber membranes were prepared by the dry–wet spinning technique. We have demonstrated that a PES-C hollow- fiber membrane cast from DMAc has the higher flux and the lowest retention. The PES-C content increase in the spinning solution has affected its membrane properties in terms of pure water flux decrease. The pure water flux of the membrane goes through a maximum, and the retention through a minimum, at a casting solution temperature of 40 °C. Pure water flux increases with increasing internal quench medium extrusion pressure. Inner and outer diameters increase and wall thickness decreases with increasing internal quench medium extrusion pressure. Finally, the inner and outer diameters of hollow-fiber membranes decrease with increasing winding-up velocity. This leads to outer diameter decreasing more, which results in a decrease of membrane wall thickness.

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