The Physical Properties of Hemofiltration Module Made from Polyether Sulfone Hollow Fiber Membrane

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ABSTRACT: Different membrane forming conditions including solid content, spinning solution temperature, the pressure of internal quench medium, concentration of coagulation bath, and winding-up velocity, etc. have different influence on the structure and physical properties of PES hollow fiber membranes prepared. Membrane properties i.e., void content and water flux decrease with increasing content of PES in the spinning solution. Water flux reaches a maximum while retention reaches a minimum when spinning solution temperature reaches 35°C. Water flux, inner and outer diameters increase and wall thickness decreases with increasing pressure of internal quench medium. Water flux reaches a minimum when the concentration of coagulation bath reaches 20%. The inner diameter of hollow fiber membrane increases and outer diameter does not change with increasing 1st godget velocity. The inner and outer diameters and membrane wall thickness decrease with increasing winding-up velocity. The clearance of creatinine and urea reaches 92 and 86% respectively. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3708–3714, 2007

Key words: polyether sulfone; hollow fiber membrane; hemodialysis

INTRODUCTION

Artificial kidneys prepared from cuprene and acetate hollow fibers have been widely used in medical treatment since 1960s. But these kinds of artificial kidney cannot clear the poisonous ingredients with middle average molecular weight in the blood, which leads to another kind of incurable illness. The researchers have been developing hemofiltration module prepared from new kinds of materials i.e., polysulfone to replace those made from cellulose and its derivatives since 1960s.[1–6]

According to some research, membrane made from polyether sulfone (PES) owns the following advantages in contrast to the membrane made from polysulfone, e.g., the pore dimension is easier to control with narrow distribution, stronger mechanical properties, longer durance under load, better chemical stability and blood compatibility, and smoother surface in case of gore. The sensitivity under working conditions is lowered apparently. Higher glass temperature enables it to be pasteurized under high steam pressure. The blood components of the experimental with low and middle average molecular weight can be cleared out. Therefore, PES is an excellent membrane material.

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The morphology, structure, and properties of the hollow fiber membranes prepared may vary with the composition of the spinning fluid and spinning conditions. However, the manuscripts concerning the fundamental research of hemofiltration module made from PES are few. There are just a few patents concerning about the preparation of hemofiltration module from PES blend system,[7–10] which give a wide scope and vague description. Here we will give a detailed report about the research of the membrane preparation condition on membrane properties.

EXPERIMENTAL

Materials and reagents

The PES Ultrason E6020P was supplied by BASF Co., Germany. Chemical-grade dimethyl sulfoxide was used as solvent, supplied by Nan-xin Chemical Regents, China. Medical-grade creatinine and urea were supplied by Shanghai Medicine, China. The average molecular weight of special-grade albumin bovine (supplied by Shanghai Biological Product Institute, China) was 67,000 Da. This serum protein was studied to determine the metabolite rejection properties of the prepared PES membranes in ultrafilteration. The polymer blending with PES was prepared in team's laboratory. Polyvinyl pyrrolidone (PVP) was supplied by BASF, Germany.

Preparation of blend solution

PES, blend polymer(1–20% wt of PES), PVP, and solvent were mixed under mechanically stirring until 15–25% (wt) transparent solution was obtained, which was then filtered through stainless mesh and deaerated under vacuum.

Preparation of hemofiltration module

Hollow fiber membrane was prepared on wet spinning machine prepared in our lab, washed by distilled water until solvent free and dried under vacuum at 50°C. The inner diameter and thickness of the hollow fiber membrane is controlled at 200–250 μm, 40–70 μm respectively. Hollow fiber membranes were cut into 30 cm and assembled into hemofiltration module with surface area 1.2 m^2. Polycarbonate was used as shell material. Polyurethane was used as potting material. Three hemofiltration modules were prepared with the same hollow fiber membrane.

Characterization of membrane structure and properties

SEM

A JSM-5600LV scanning electron microscope was used to study the cross and surface morphology of the membranes. The membranes were dried at room temperature and fractured in liquid nitrogen and sprayed with gold for test.

Inner and outer diameter

The inner and outer diameters and the thickness of the membrane were measured through a stereo microscope. The magnification range is 80.

Void content

Membrane void content (ε) was measured according to the following equation:

$$\varepsilon = (W_w - W_d)/\mathrm{n}\pi\left(R_0^2 - R_1^2\right)L\rho\mathrm{H2O}$$

where W_w and W_d are the weight of a bundle of wet and dry membrane respectively. R_0, R_1, and L are the inner, outer diameter, and length of the hollow fibers pieces respectively. ρ_{H2O} is the density of water at measured temperature, and n is the number of hollow fiber membrane pieces in the bundle (range of is around 50–100).

Ultrafiltration experiments and measurement of ultra-filtration flux

The solution for ultrafiltration (SU) was prepared as followed: 300 mg urea dissolved in a small amount of distilled water and 20 mg creatinine dissolved in a small amount of 0.1N hydrochloride acid. Both solutions were mixed together into a 200 mL flask, diluted to the scale by distilled water for use. Here SU is used as simulation blood and distilled water is used as dialyte. Hemofiltration module was prepared from hollow fibers and the properties of hemofiltration module were measured at 25°C in a recycle mode on dialysis machine prepared by our lab, equipped with glass bottle with marked scale. 6000 mL SU was put into the glass bottle. The flow rate of SU is 200 mL/min, the flow rate of distilled water is 500 mL/min. Transmembrane pressure (TMP) is − 13.3 kPa. Distilled water was put into the glass bottle continuously to keep SU solution in the bottle constant, the amount of water ΔV was recorded. The whole process lasted 4 h. Ultra-filtration flux U_f was got according to the following equation:

$$U_f = \frac{\Delta V}{\Delta t \times A}$$

where ΔV means the volume loss of SU during time interval Δt (here it is 4 h) under TMP, a means membrane area.

The whole process was repeated on three hemofiltration modules, the average was used and the error is no more than 10%.

Measurement of retention to bovine albumin

Retention experiment was performed in the same dialysis machine as described in Ultrafiltration experiments and measurement of ultra-filtration flux, where the flow rate of 500 ppm bovine albumin solution was 200 mL/min, TMP was 26.6 kPa. The whole retention process lasted 1 h and 5 mL permeated solution was collected, which was measured at 280 nm wavelength on a UV-7500 spectrophotometer (Shanghai Tian-mei Science Instrument Limited, China). From the absorption values of bovine albumin solution before and after ultrafiltration, we can get the corresponding bovine albumin concentrations and calculate the average retention as follows:

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

where c_1 and c_2 refer to the concentration of permeated and retained solution after ultrafiltration respectively, c_0 referred to the primary concentration before filtration. The whole process was repeated on three hemofiltration modules, the average was used and the error is no more than 10%.

Measurement of clearance of urea and creatinine

Clearance experiment was performed in the same dialysis machine as described in ultrafiltration

experiments and measurement of ultra-filtration flux. SU (6000 mL) was put into the glass bottle. The flow rate is 200 mL/min, TMP is 20 KPa. Distilled water was put into the glass bottle continuously to keep solution in the bottle constant, the amount of water was recorded. The whole process lasted 4 h. Elimination of urea and creatinine was measured at 430 and 510 nm respectively, on UV-7500 spectrophotometer. From the absorption values of the solution before and after dialysis, we can get the corresponding concentrations and calculate the removal of urea and creatinine. The equation used was described as following:

$$(\mathrm{CRR}) = (c_0 - c_2)/c_0 \times 100\%$$

where c_0 and c_2 has the same meaning as described before. The whole process was repeated on three hemofiltration modules, the average was used and the error is no more than 10%.

In the following discussion, all other experimental parameters are fixed for the change of a specific experimental condition. And the fabrication conditions are in the discussed range, which varied with practical conditions.

RESULTS AND DISCUSSION

The dependence of water flux, retention and void content on PES content in the spinning solution

As seen in Figure 1, void content decrease with increasing PES content. In Figure 2, retention increases and water flux decreases quickly with increasing PES content in the solution and the tendency slows down when PES content reaches 20% (wt), which may be concerned with the phase separation during the process of membrane formation. PES macromolecules exist in the casting solution in

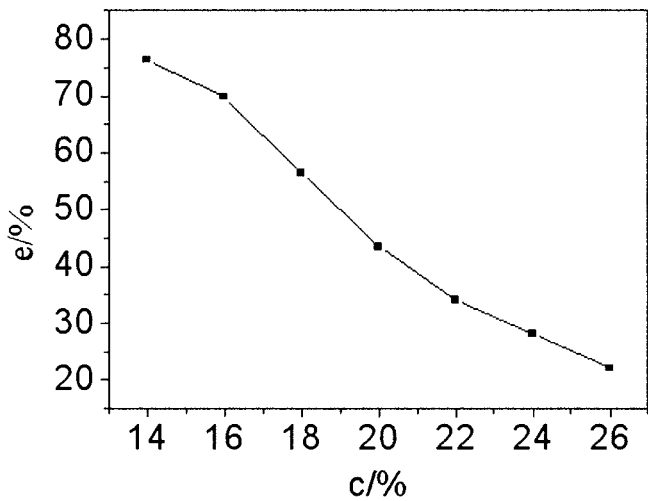

Figure 1 Dependence of void content on PES content.

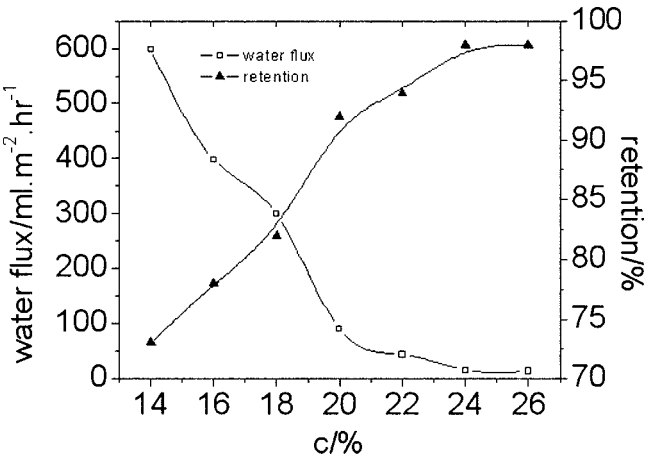

Figure 2 Dependence of water flux and retention on PES content in the solution.

two states, i.e., macromolecular network formed by a certain number of macromolecules through intermolecular interaction and macromolecular entanglement, and the other is micelle aggregate (micro-cell) formed through macromolecular approach and macromolecular entanglement and aggregation. So there exist two kinds of pores on the skin layer surface of membrane formed by macromolecules corresponding to the two aggregating states: one is network pore formed by chain segment network with smaller dimension and larger number; the other is micro-cell pore with larger dimension and smaller number. As concentration increases, not only does the density of macromolecules increase which leads to a density increase of macromolecular network, but also the macromolecular entanglement among neighboring micro-cells increases, the average aperture of both kinds of pores decreases, which leads to a decrease of void content and appears as a decrease of water flux and an increase of retention macroscopically. In addition, the wall of network pore formed from casting solution of higher concentration is thicker, which leads to an increase of resistance when water passes through, the rate of water penetration descends. Therefore, water flux decreases and retention increases, which is in accordance with the Barzin's[11] report about PES flat membrane structure change with spinning concentration. Sixteen percent PES solution was used to spin hollow fiber membrane in the following discussion.

Dependence of water flux and retention on the temperature of spinning solution

Figure 3 shows that water flux reaches a maximum while retention reaches a minimum when spinning solution temperature reaches 35°C. The interdiffusion velocity between solvent and coagulating agent increases with increasing spinning solution

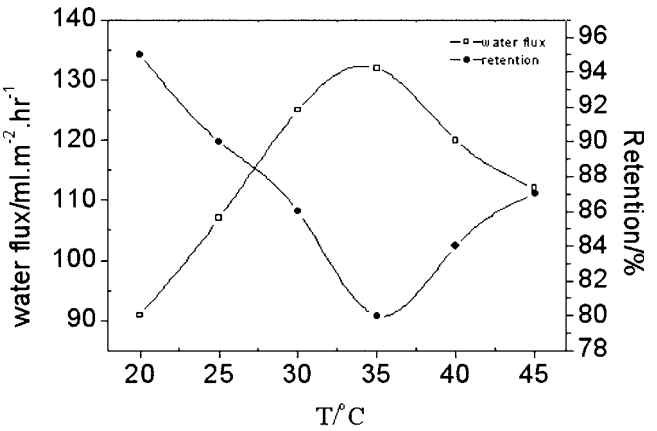

Figure 3 Dependence of water flux and retention on the temperature of spinning solution.

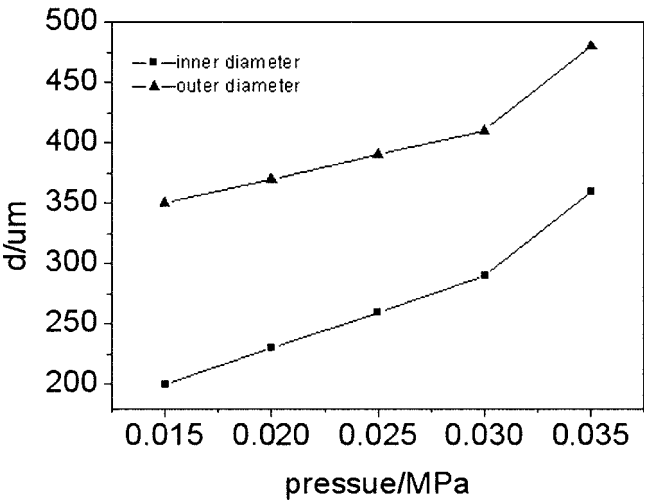

Figure 4 Dependence of hollow fiber dimension on the pressure of internal quench medium.

temperature before 35°C, which leads to an increase of pore diameter and water flux and a decrease of retention. When the temperature of spinning solution exceeds 35°C, the evaporation of solvent acts as a controlling factor, which leads to an increase of solution concentration. So water flux decreases and retention increases according to the above discussion. We use 35°C spinning solution.

Dependence of membrane properties on the pressure of internal quench medium

Canular spinnerette is adopted to spin hollow fiber membrane and the inner tube was filled with internal quench medium. The internal quench medium not only provides inner support for the as-spun hollow fiber but acts as inner coagulation bath, which leads to the formation of dense layer on the inner surface and assures the retention of blood corpuscle and albumin during dialysis. The dimension of hollow fiber, i.e., inner and outer diameter, wall thickness can be varied through the change of pressure of internal quench medium, as seen in Figure 4. The inner and outer diameters of hollow fiber increase with increasing pressure of internal quench medium, and the inner diameter increases more quickly that leads to a decrease of membrane wall thickness, the thickness of sponge structure adjacent to outer wall decreases quickly, void content, and the diameter of finger pore increases as seen in Figure 5. As seen in Figure 6, water flux increases with increasing pressure of internal quench medium.

Wall thickness and mass transfer resistance decreases, and the flow rate of internal quench medium increases with increasing pressure of internal quench medium, which leads to an increase of concentration difference between solvent and coagulation bath at the border of membrane, and the rate of

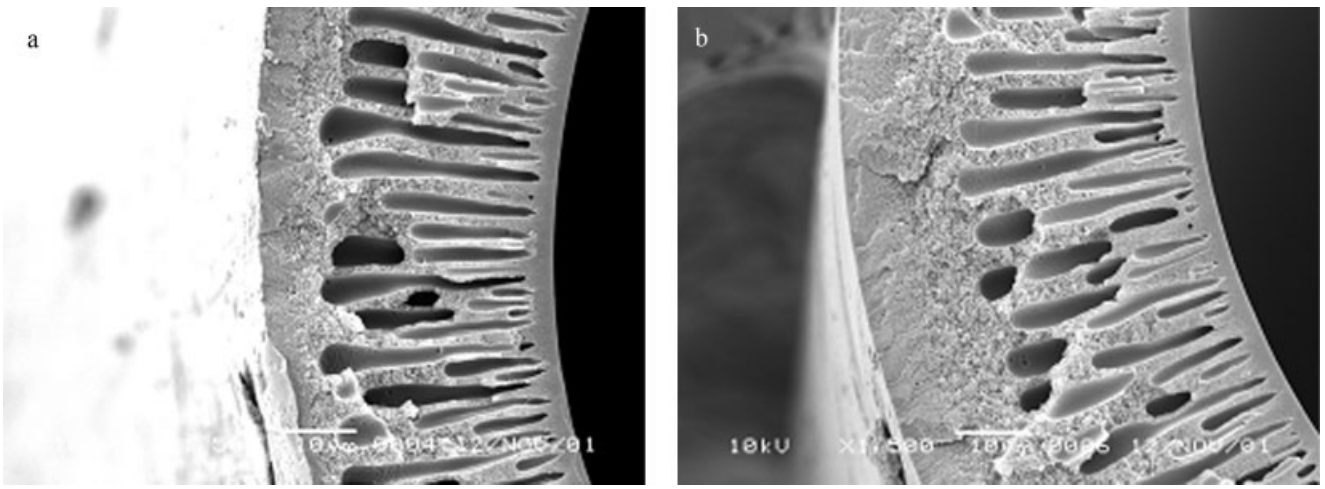

Figure 5 SEM photos of cross section at different pressure of internal quench medium (a) 0.030 Mpa internal quench medium and (b) 0.020 Mpa internal quench medium.

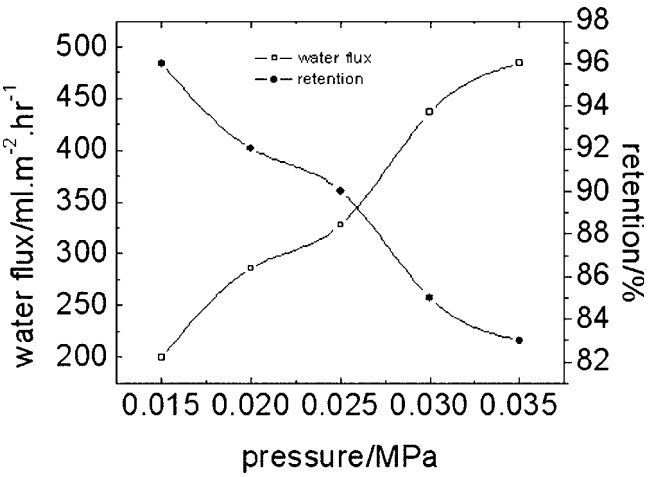

Figure 6 Dependence of water flux and retention on the pressure of internal quench medium.

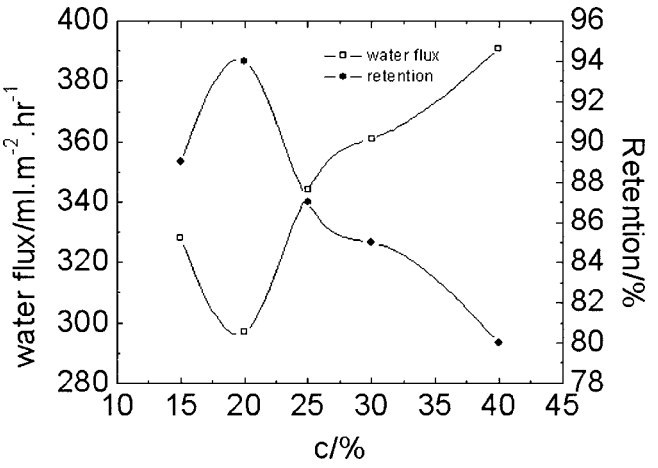

Figure 7 Dependence of water flux and retention on the concentration of coagulation bath.

interdiffusion increases, which leads to an increase of void content, pore dimension and water flux and a decrease of retention. The pressure of internal quench medium can be varied according to membrane use and here 0.025 Mpa is used.

The conception of Biaxial Stretch in hollow fiber is put forward here. The enough axial mechanical strength is necessary for ordinary fiber, which can be obtained through axial stretch. However, hollow fiber is seldom stretched axially because both axial and radial stretch is necessary for hollow fiber membrane because of its special uses under tension. If hollow fiber is only axially stretched, radial strength decreases. At the same time the pore on the membrane surface will deform, i.e., axial dimension will increase and cross-sectional dimension will decrease. The pores may close at the most, which have bad influence on the filtering property of membrane greatly. Here radial stretch is practiced through the change of the pressure of internal quench medium and axial stretch is carried out by plasticizing stretch and multi-stretch. Thus, Biaxial Stretch of hollow fiber membrane is realized. There exist large number of stable pores and the mechanical properties of hollow fiber increase.

Dependence of membrane properties on coagulation bath concentration

The structure of hollow fiber membrane is also controlled by the constitution of inner and outer coagulation bath. Figure 7 shows that water flux reaches a minimum at 20% (wt) coagulation bath concentration. As seen in Figure 8, the pore of membrane prepared from 25% coagulation bath is rather rough and pore size is larger than that prepared form 20% coagulation bath while inner and outer diameters of hollow membrane keep constant, which is in

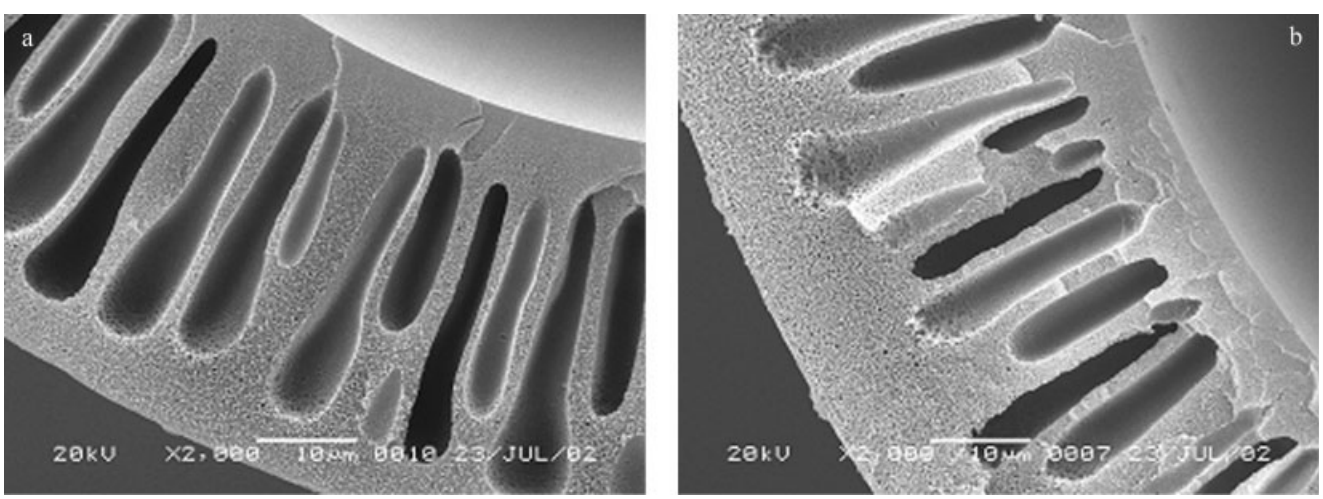

Figure 8 SEM photos of cross section with different coagulation bath concentration (a) 16% coagulation bath concentration and (b) 21% coagulation bath concentration.

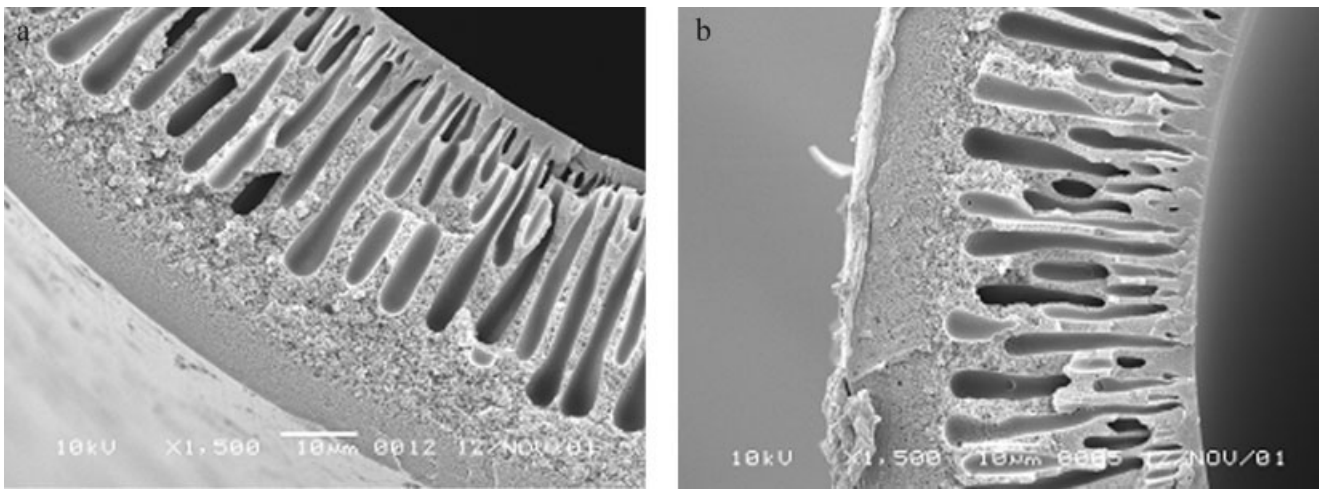

Figure 9 SEM photos of cross section at different 1st godget velocity (a) low 1st godget velocity (22 m/min) and (b) high 1st godget velocity (27 m/min).

accordance with the results in Figure 7. Here we use 17% DMSO solution as coagulation bath.

It is because that solvent concentration difference between spinning solution and coagulation bath decreases with increasing coagulation bath concentration, the interdiffusion rate and phase separation rate decreases, which leads to a dense membrane structure. Therefore, water flux decreases and retention increases. When the coagulation bath reaches a critical value 20%, water flux reaches a minimum. Later on, the solidification rate of membrane decreases with increasing coagulation bath and there is still a lot of solvent remained in the membrane and the membrane is in swelling state. So the macromolecules in the membrane still have enough space to move and get an equilibrium, which leads to a decrease of retention and an increase of water flux.

Dependence of membrane properties on 1st godget velocity

The total drawing ratio and its distribution in different spinning process influence the membrane properties and structure. If the total stretching ratio is kept constant, drawing ratio in plasticizing bath decreases and draw ratio in coagulation bath increases with 1st godget velocity, the inner diameter increases and the outer diameter does not change, membrane thickness decreases and membrane is becoming dense as seen in Figure 9, which leads to an increase of mass transfer resistance and decrease of water penetration rate and water flux (Fig. 10).

Dependence of membrane properties on winding-up velocity

As winding-up velocity increases, both inner and outer diameters decrease and the outer diameter decreases more, which leads to a decrease of membrane thickness and mass transfer resistance, an increase of water penetration rate and water flux. As seen in Figure 11, the thickness of transfer layer adjacent to the outer wall of the hollow membrane without stretch is thicker than that after stretch, the pore is rough and the pore size is larger than that of the hollow fiber membrane after stretch. We chose 18 m/min as favorite winding velocity.

Clearance of urea and creatinine

Clearance of urea and creatinine is an important data for the measurement of membrane material used for hemofiltration module. As seen in Table I, the hemofiltration module prepared from PES hollow fiber membrane has a high clearance rate of urea and creatinine, i.e., 92 and 84% for clearance of urea and creatinine respectively, which is higher

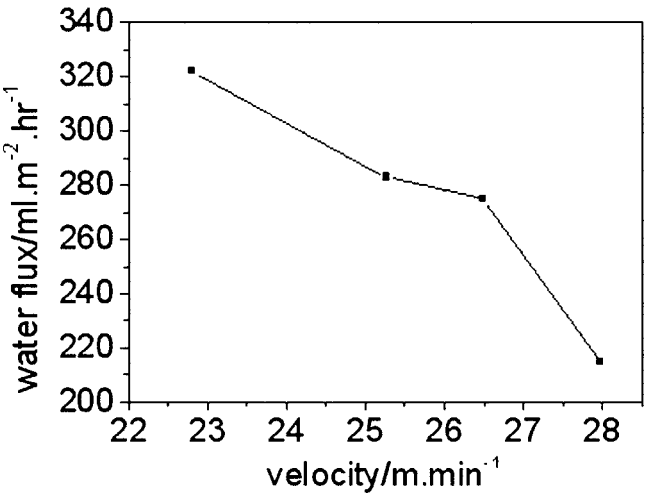

Figure 10 Dependence of water flux and retention on 1st godget velocity.

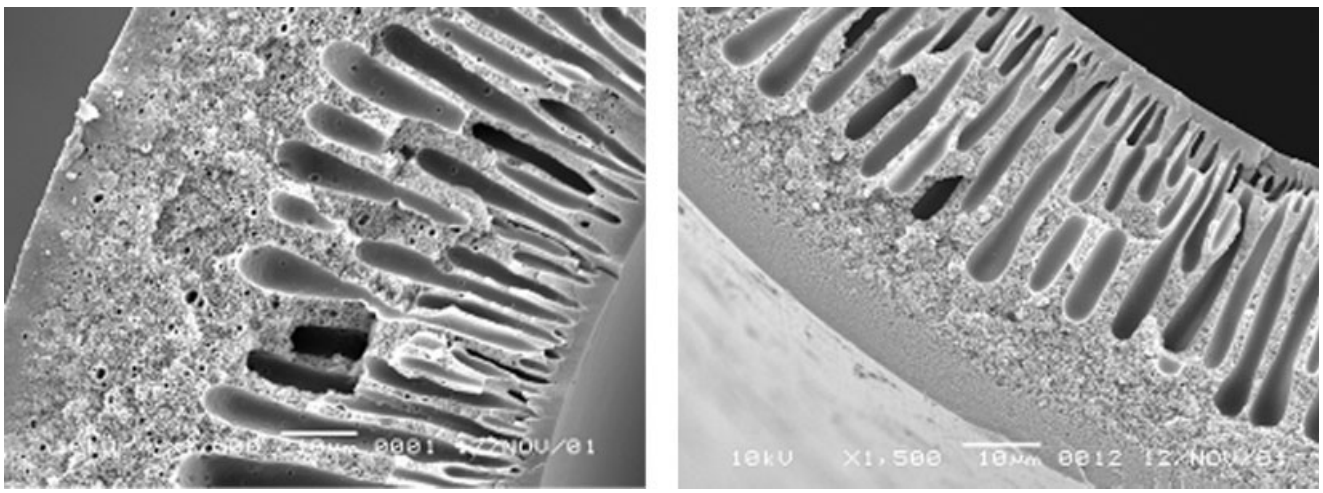

Figure 11 SEM photos of cross section at different winding-up velocity No stretch stretch ratio : 12%.

than the results from Barzin et al.[12] Barzin et al. prepared membrane at lower PES concentration (12%) and rather loose membrane structure was got, which favored the clearance of uremic toxins at the price of lower mechanical properties. The data we got for the clearance of urea and creatinine fits the national clinical standard in China and implies that PES hollow fiber membrane can be used in the preparation of hemofiltration module in China.

The SU just contains the poisonous components of the real blood, which is still somewhat different from the real blood. Therefore it is of great interest to studying the performance of the hemodialysis modules with human serum (as Barzin et al. did), since it would be closer to the clinical practice conditions in which fouling may occur and compromise clearance. We propose to use human serum to compare with our present results in the near future.

CONCLUSIONS

1. PES content in the spinning solution has apparent influence on membrane properties prepared, i.e., void content and water flux decrease, retention increases with increasing PES content.
2. Water flux reaches a maximum while retention reaches a minimum when solution temperature reaches 35°C.
3. Water flux, inner and outer diameters increase and wall thickness decreases, retention increases with increasing pressure of internal quench medium.
4. Water flux reaches a minimum when concentration of coagulation bath is 20%.
5. The inner diameter increases, outer diameter does not change with increasing 1st godget velocity.
6. The inner and outer diameters of hollow membranes decrease with increasing winding-up velocity, and the outer diameter decreases more which leads to a decrease of membrane wall thickness.
7. PES hollow fiber membrane has a high clearance rate of urea and creatinine, i.e., 92 and 84% for clearance of urea and creatinine respectively.

TABLE I
The Comparison of Clearance of Creatinine and Urea

	Experiment	J. Barzin et al.[12]
PES concentration (%)	21	12
Additive in the spinning solution	Blend polymer, 5% (wt % of PES)	PVP, 2.8% (wt % of PES)
Coagulation bath (°C)	40	60
Membrane area (m^2)	1.2	0.0005
Whole processing time (h)	4	5
Clearance of urea (%)	92	84
clearance of creatinine (%)	86	53

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