

# Preparation of Polysulfone Hollow Fiber Affinity Membrane Modified with Mercapto and Its Recovery Properties. I. Synthesis and Preparation of Hollow Fiber Matrix Membrane

Bing Wang,<sup>1,2</sup> Bowen Cheng,<sup>1,2</sup> Yongfang Cui<sup>1</sup>

<sup>1</sup>School of Materials Science and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China

<sup>2</sup>Key Laboratory of Hollow Fiber Membrane Material and Membrane Process (Tianjin Polytechnic University), Ministry of Education, Tianjin 300160, People's Republic of China

Received 2 March 2005; accepted 5 July 2005

DOI 10.1002/app.23455

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Several kinds of chloromethyl polysulfones (CMPSF) with different chlorinity and reactive groups were synthesized by Friedel-Crafts reaction, which could be utilized as reactivity matrix membrane materials. The CMPSF hollow matrix membranes were prepared with phase inversion by utilization of the CMPSF/additive/DMAC casting solution and CMPSF as membrane materials. The rheological behavior of CMPSF/additives/DMAC spinning casting solution was studied. The experimental results showed that the spinning casting solution was a pseudoplastic fluid, the apparent viscosity of the spinning casting solution decreased with the increase of shearing rate, and the viscous flow activity energy of the spinning casting solution was inclined to unchange at high shearing rate. The effects of composition of spinning casting solution and process parameters of dry-wet spinning on the structure of CMPSF hollow fiber matrix membrane were investigated. The pore size, porosity, and water flux of membrane decreased with the increase of additive content, bore liquid, and dry spin-

ning distance. With the increase of extrusion volume outflow, the external diameter, wall thickness, and porosity of the hollow fiber matrix membrane increased, but the pore size and water flux of the membrane decreased. It was also found that the effects of internal coagulant composition and external coagulant composition on the structure of CMPSF hollow fiber matrix membrane were different. The experimental results showed that thermal drawing could increase the mechanical properties of CMPSF hollow fiber matrix membrane and decrease the pore size, porosity, and water flux of the CMPSF hollow fiber matrix membrane, and the thermal treatment could increase the homogeneity and stability of the structure of the CMPSF hollow fiber matrix membrane. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 758–771, 2006

**Key words:** adsorption; membranes; matrix; fibers; separation technique

## INTRODUCTION

An affinity membrane with chelating groups can be used to treat industrial waste water and recover metal ions because it integrates the advantages of both modern separation membrane techniques and affinity chromatography techniques.<sup>1–6</sup> PSF is an important membrane material known for its good physical and chemical stability, mechanical behavior, preferable performance to form membrane, and its cheapness. In

our previous article,<sup>7</sup> the high quality heterogeneous polysulfone affinity plate filter membranes with chelating groups were prepared by phase separation by using blends of the chelating resin and polysulfone. Then, PSF was used as the starting materials to synthesize chloromethyl polysulfone (CMPSF) with Friedel-Crafts reaction and CMPSF was converted into plate membrane using phase inversion technology.<sup>8</sup> The CMPSF plate matrix membrane reacted with sulfocarbamide and was then hydrolyzed under alkaline conditions to afford the mercapto-modified polysulfone as homogeneous chelating affinity plate membrane and its adsorption properties for Hg<sup>2+</sup>. At present, the studies on hollow fiber chelating affinity membrane for removing metal ions have not been reported. As everyone knows, the loadability of the unit volume of hollow fiber membrane surface is much larger than that of plate membrane, and the intensity of hollow fiber membrane is hard enough to support itself, while plate membrane is not. Thus, in

Correspondence to: B. Wang (Bingwang666@yahoo.com.cn).

Contract grant sponsor: Natural Science Foundation, Tianjin; contract grant number: 05YFJMJC04200.

Contract grant sponsor: Emphasis Item of Science and Technical Research, Ministry of Education, China; contract grant number: 205011.

this study, it has both the theoretical and practical significance to study on CMPSF hollow fiber membrane, which could be utilized as reactive matrix membrane materials of chelating hollow fiber affinity membrane modified with mercapto, based on the chelating plate membrane.

## EXPERIMENTAL

### Materials and reagents

Dichloromethane and 1,2-dichloroethane (Tianjin Chemical Reagent Plant), chloromethyl ether (Nankai University Chemical Plant), zinc chloride (Chemical Reagent Plant), and polyethylene glycol (Tianjin Chemical Reagent Plant) were all analytical reagents and were used without any further purification. The other solvents were analytical grade and used without any further purification.

### Main apparatuses

Capillary Rheometer of Vapor Pressure Type was made by Chengdu Science and Technology University, China. XL30 ESEM (environmental scanning electron microscope) was made by PHILIPS. HD-201 Electronic Strand Strength Meter was made by Hongda laboratory apparatus, China. Dry-wet spinning equipment was made by Tianjin Polytechnic University, China.

### Synthesis of chloromethyl polysulfone

A given amount of dried PSF was dissolved in dichloromethane (or 1,2-dichloroethane) and the solution of anhydrous zinc chloride/chloro-methyl ether was added dropwise. The reaction temperature was slowly increased to 40°C and the reaction was carried out at 40°C for 6 h. The solution was slowly dropped into methanol after the reaction system was cooled to room temperature. CMPSF was precipitated from the system as lump and was washed by hot distilled water repeatedly until no bubbles appeared. The rough chloromethyl polysulfone (CMPSF) was dried in vacuum oven between 60 and 70°C. Then the rough CMPSF was sheared into small pieces and dissolved in DMAC. The solution was poured into the distilled water of 70–80°C with stirring to get the white stripe or floc precipitate. The refined CMPSF was filtered and washed with distilled water for three times and dried in the vacuum oven at 60–70°C till constant weight was reached.

### Preparation of the CMPSF spinning casting solution

The CMPSF, PEG (or NH<sub>4</sub>Cl), and DMAC were put into the dissolution kettle, stirred for 5 h at 50°C to be

dissolved, and then was filtered, made to stand still, and deaerated.

### Measurement of the CMPSF spinning casting solution flow curve

The CMPSF casting solution at a given temperature was put into the capillary rheometer of vapor pressure type, and then the weight  $W$  of the CMPSF casting solution was determined when it went through the capillary (whose length and radius were  $L$  and  $R$ , respectively) in  $t$  seconds. The shearing stress  $\sigma_t$  is calculated from eq. (1).

$$\sigma_t = \frac{\Delta P/R}{2L} = \frac{P + 98(Hd_0)}{2L}R \quad (1)$$

Where  $P$  is the gauge pressure,  $\Delta P$  is the differential pressure of the double ends of the capillary,  $R$  and  $L$  is the radius and length of the capillary, respectively,  $H$  is the height of the liquid in the material duct,  $d_0$  is the solution density at experimental temperature, and  $98(Hd_0)$  is the solution deadweight pressure in the material duct. The shearing velocity  $\dot{\gamma}$  is calculated from eq. (2).

$$\dot{\gamma} = \frac{\sigma_t}{\eta} = \frac{4w}{\pi R^3 t d_0} \quad \dot{\gamma}_{\text{check}} = \frac{3n+1}{4n} \dot{\gamma} \quad (2)$$

where  $t$  is the time that the solution went through the capillary, and  $W$  is the weight of the solution that passes through the capillary in time  $t$ .

The non-Newton exponent  $n$  is calculated from eq. (3).

$$\sigma_t = K\dot{\gamma}^n \quad (3)$$

$$\log \sigma_t = \log K + n \log \dot{\gamma}$$

Plotting the  $\log \sigma_t$  versus  $\log \dot{\gamma}$ , the curve slope  $n = d \log \sigma_t / d \log \dot{\gamma}$  is just a non-Newton exponent.

The apparent viscosity  $\eta_a$  is calculated from eq. (4).

$$\eta_a = \frac{\sigma_t}{\dot{\gamma}_{\text{check}}} \quad (4)$$

The structural viscosity exponent  $\Delta \eta$  is calculated from eq. (5).

$$\Delta \eta = \left( \frac{d \log \eta_a}{d \dot{\gamma}_{\text{check}}^{1/2}} \right) \times 10^2 \quad (5)$$

Plotting the  $\log \eta_a$  versus  $\dot{\gamma}_{\text{check}}^{1/2}$  flow curve, and the  $\Delta \eta$  can be evaluated by the slope of the curve.

The flow activation energy  $\Delta E_\eta$  is calculated from eq. (6):

$$\eta = A \exp \left[ \frac{\Delta E_{\eta}}{RT} \right] \quad (6)$$

where  $A$  is a constant,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $\Delta E_{\eta}$  is the flow activation energy of the macromolecular solution under a given shearing rate. Plotting  $\log \eta$  versus  $1/T \times 10^3$ , the value of  $\Delta E_{\eta}$  could be calculated by the slope of the curve.

#### Preparation of the CMPSF hollow fiber matrix membrane

The dry-wet spinning method was adopted to prepare the hollow fiber matrix membrane in the spinning equipment. The CMPSF, the solvent (DMAC), and additives were blended to a scale, were stirred at given temperature until they were totally dissolved, were made to stand still, and then used. Then, the spinning casting solution was put into the storage tank and deaerated under negative pressure. The high pressure nitrogen as the pressure source to push out the CMPSF casting solution that had been measured from the spinning head; at the same time, the core liquid went from the central cavity of the spinning head into the hollow fiber cavity as its supporter and inner coagulum medium under the pressure of head tank. Lastly, the CMPSF spinning dope went away from the spinning head, passing the air clearance between the spinning head and coagulating bath tank, into the coagulating bath tank; when it had been coagulated into mold completely, by hot drawing and heat setting treatment, the hollow fiber matrix membrane would be prepared. The CMPSF hollow fiber matrix membrane should be preserved in hygrometric state.

#### Measurement of mechanical property of the CMPSF hollow fiber matrix membrane

Mechanical property measurement was preformed with HD-201 Electronic Strand Strength Meter, and the given length of the sample is 500 mm.

#### Measurement of flux of the hollow fiber matrix membrane

The hollow fiber matrix membrane was installed on the self-made hollow fiber matrix membrane module, and when the pure water permeated from outside to inside of the membrane under a given pressure of the circulating pump, the pure water volume through given membrane area was noted in the given time. The flux (permeate rate) could be calculated by the following eq. (7).

$$Q = \frac{V}{At} \quad (7)$$

where  $Q$  is the flux ( $L/m^2h$ ),  $V$  is the volume of the permeate liquid ( $L$ ),  $A$  is the effective membrane area of the hollow fiber matrix membrane, and  $t$  is the ultrafiltration time (s).

#### Measurement of porosity of the hollow fiber matrix membrane

The experiment was carried out by the gravimetric method and the glycerol was used as the soak solution of the hollow fiber matrix membrane.<sup>9</sup> A piece of given area ( $S$ ) hollow fiber hygrometric state membrane was sheared and weighted  $W_d$  (wet weight) after glycerol being wiped off from the membrane surface, and then the membrane was moved into vacuum drying oven to a constant weight  $W_d$  (dry weight of the membrane) and the porosity is calculated by the following eq. (8)

$$P_r = \frac{W_w - W_d}{sd\rho} \times 100\% \quad (8)$$

where  $d$  is the average thickness of the membrane and  $\rho$  is the glycerol density.

#### Measurement of pore size of the hollow fiber matrix membrane

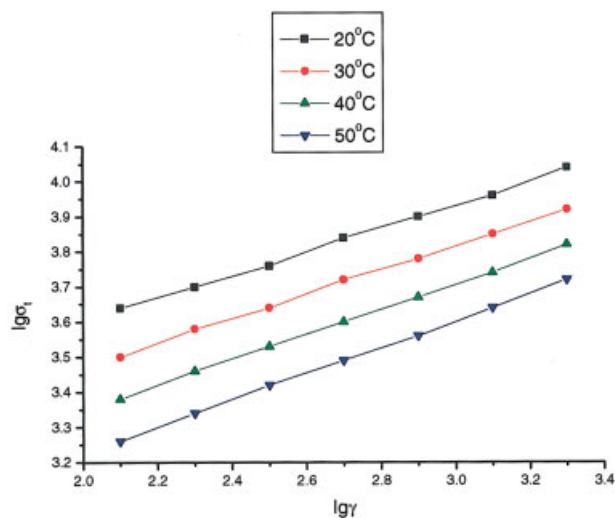
The pore size of the hollow fiber matrix membrane was determined by the filtering velocity method.<sup>9</sup> The membrane pore diameter  $r_f$  was calculated from eq. (9):

$$r_f = \sqrt{\frac{8 \times (2.90 - 1.75P_r)\mu LQ}{P_r \Delta P A}} \quad (9)$$

where  $P_r$  is the porosity (%);  $L$  is the membrane thickness;  $\mu$  is the viscosity of the permeate liquid (Pa s);  $Q$  is the flux ( $m^3/s$ );  $\Delta P$  is the pressure (Pa); and  $A$  is the permeated area ( $m^2$ ).

#### ESEM of the CMPSF hollow fiber matrix membrane

The CMPSF hollow fiber matrix membrane was immersed in 50% aqueous glycerol for 24 h. Then the membrane was taken out and the glycerol on its surfaces was wiped away. The membrane was dehydrated stepwise by the mass fraction of 50, 70, 90, and 100% ethanol, sequentially. The ESEM characterization was performed on a coating film by ion-sputtering after the membrane was frozen in liquid nitrogen and fasten on the sample table and the thickness was about 20 nm. The pore size and size distribution of the membrane were obtained from the observation of the morphological structure of the cross section of the



**Figure 1** The relationship between  $\log\sigma_t$  and  $\log\gamma$  of CMPSF spinning solution at different temperatures (solid content 16%). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

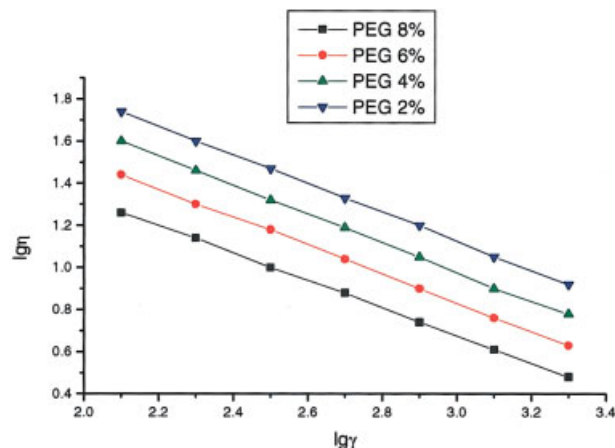
matrix membrane, with a XL30 ESEM (environmental scanning electron microscope).

## RESULTS AND DISCUSSION

### The rheological behavior of the CMPSF spinning casting solution

It counted much for chemical fiber forming that the rheological behavior and the extrusion course of the spinning liquid; while the rheological behavior may be used to discriminate good from bad for the spinning liquid. The study on the rheological behavior of the CMPSF spinning casting solution has an important guiding significance for spinning of CMPSF hollow fiber matrix membrane.

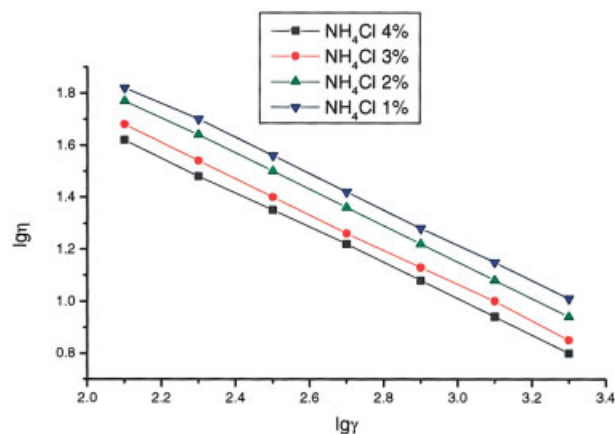
The spinning of CMPSF hollow fiber matrix membrane was carried out at flow state and it was influenced by the rheological behavior of the polymer (including the additive PEG) concentrated solution. In the polymer concentrated solution, the macromolecules twist and agglomerate to form the supramolecular structure. The size of the molecular group, the degree of twisting and their interactions decide the rheological behavior of the polymer concentrated solution (spinning casting solution). Figure 1 is the  $\log\sigma_t$ - $\log\gamma$  rheogram of the same CMPSF spinning casting solution at different temperatures. Figure 1 shows that  $\log\sigma_t$  and  $\log\gamma$  of the CMPSF spinning casting solution exhibits a linear relationship, and  $\log\sigma_t$  increases with the increase of  $\log\gamma$ , and accords with the power law and  $n < 1$ . It proves that the CMPSF spinning casting solution is a pseudoplastic fluid. Figure 1 also shows that the shearing stress of the CMPSF spinning casting solution decreases with



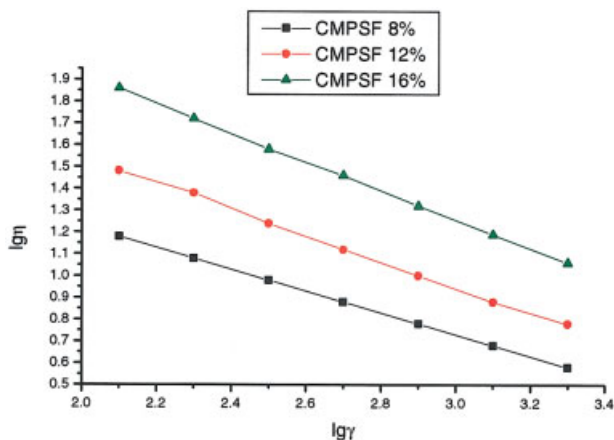
**Figure 2** Flow curves of CMPSF spinning casting solution with different additive PEG content (PEG molecular weight, 10,000; CMPSF concentration, 16%; and temperature, 30°C). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the increase of temperature. The reason is that increase of temperature increased the activity of the macromolecular chain and repelled the decrease of the shearing stress of the spinning casting solution.

Figure 2 is  $\log\eta$ - $\log\gamma$  rheological diagram of the CMPSF spinning casting solution constitute systems with different additive PEG (molecular weight is 10,000) content at the same temperature, and Figure 3 is  $\log\eta$ - $\log\gamma$  rheological diagram of CMPSF spinning casting solution constitute systems with different additive  $\text{NH}_4\text{Cl}$  content at the same temperature. It can be concluded from Figures 2 and 3 that the relationship of  $\log\eta$  and  $\log\gamma$  of the CMPSF spinning casting solution system is that of a typical pseudoplastic flow, and  $\log\eta$  decreases with the increase of  $\log\gamma$  that is the



**Figure 3** Flow curves of CMPSF spinning casting solution with different additive  $\text{NH}_4\text{Cl}$  content (CMPSF concentration, 16%; and temperature, 30°C). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

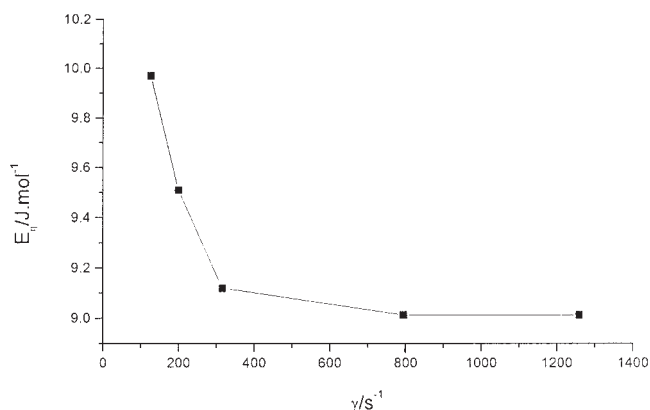


**Figure 4** Flow curves of CMPSF spinning casting solution with different CMPSF concentration (additive content, 0%; and temperature, 30°C). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

so-called “shearing force rarefying” phenomenon. In general, the shearing force rarefying of polymer solution is considered when the polymers are rheological and there is a velocity gradient between each liquid layer. If the slender macromolecules go through a few liquid layers with different flow velocity at the same time, the various part of the macromolecule will go forward at different speed, but, apparently, this would not be for long. Therefore, while flowing, each long chain molecule strives to put itself into the liquid layer of the same velocity of flow, and the parallel distribution of different velocity layer results in the tropism of the flow direction. At the same time, the additives PEG and  $\text{NH}_4\text{Cl}$  accelerate this process, and so the viscosity of the CMPSF spinning casting solution system decreases. At the same temperature and shearing rate, the effects of various contents of PEG and  $\text{NH}_4\text{Cl}$  to  $\eta$  are complex relatively, but they all make the viscosity of the spinning casting solution systems below that of pure spinning casting solution systems (free of additives) and enhance spinnability of the spinning casting solution. The flow of the macromolecule polymer in polymer concentrate solution carried out by the cooperative motion of the molecule segments and the cooperative transition of the molecule segment is dependent on two factors: one is the ability of the transition segment, and the other is whether there is space to accept it around the transition segment. The addition of PEG could decrease the viscosity of the polymer concentrate solution as a plasticizer. The relative slippage of  $\text{NH}_4\text{Cl}$  grains results in the increase of free volume among the molecular chains may also decrease the viscosity of the system. Furthermore, for the macromolecular concentrate solution, the increase of the shearing force may result in desolvating effect and reduce the macromolecular effective size.

For polymer concentrated solution, the concentration of solution affects not only the viscosity but also the shape of the flow curve. Figure 4 shows the change of  $\log \eta$ – $\log \gamma$  of the CMPSF spinning casting solution system with CMPSF concentration at 30°C. From Figure 4 it can be seen that with the increase of the CMPSF concentration, the viscosity of polymer solution increases, and the liquid generally transits from Newtonian fluid to non-Newtonian fluid. The larger the CMPSF concentration, the smaller the critical shearing rate  $\log \gamma$  when the shearing force rarefying appears. The CMPSF spinning casting solution system as a macromolecular concentrated liquid system has a twisting phenomenon, and the solution could be considered as a transient crosslinking network structure. With increase of concentration of the CMPSF system, number of the molecules that contact others in the unit volume increase, and density of the tangling points increases. When concentration of the liquid increases from 2 to 10%, the liquid totally shows behavior of the pseudoplastic liquid in shearing rarefying phenomenon.

Based on the relationship of the apparent viscosity and temperature at a constant decreasing speed, the  $E_\eta$  of the CMPSF spinning casting solution system could be obtained. Figure 5 is the plot of the flow activation energy  $E_\eta$  of the CMPSF spinning casting solution. The flow activation energy reflects the dependence of the apparent viscosity of the casting solution system on temperature. In general, the more rigid the molecular chain, or the greater the force among the molecules, the higher the flow activation energy, and the viscosity of this kind of polymer is a little more sensitive on temperature. From Figure 5 it can be learned that with the increase of the shearing rate, the flow activation energy of the CMPSF spinning casting solution system decreases and the change of the flow activation energy is minor at high shearing rate. We can make out that the dependence of the flowing



**Figure 5** The relationship between  $E_\eta$  and  $\gamma$  of CMPSF spinning casting solution (additive content, 0%; and CMPSF concentration, 16%).

**TABLE I**  
The Effect of Temperature and Shear Rate on the Structural Viscosity Index  $\Delta\eta$  of the CMPSF Spinning Casting Solution<sup>a</sup>

$\dot{\gamma}$ (s <sup>-1</sup> )	$\Delta\eta$		
	30°C	40°C	50°C
125	3.30	3.18	3.41
501	2.47	2.34	3.01

<sup>a</sup> CMPSF spinning casting solution concentration was 16%.

property of the CMPSF spinning casting solution on temperature is reduced, and so it is in favor of stable formation of the hollow fiber.

The CMPSF spinning casting solution is a transient crosslinking network structure and the change of the solution viscosity is the reflection of the network structure, that is the increase and decrease of the viscosity show the formation and destruction of this structure. The structuredness of the network structure could be characterized by the structural viscosity exponent  $\Delta\eta$ , and its definition is  $\Delta\eta = (-d\log\eta_a/dr^{1/2}) \times 10^2$ . The value of  $\Delta\eta$  can be calculated with the straight slope of the  $\log\eta_a-r^{1/2}$  plot. Based on the definition, the larger the  $\Delta\eta$  and the greater the structuredness, the poorer the solution's spinnability of the CMPSF hollow fiber matrix membrane. Table I shows that when temperature rises from 30 to 40°C, the  $\Delta\eta$  decreases and solution's spinnability increases, but when temperature rises to 50°C, the  $\Delta\eta$  increases instead. The reason is that when temperature rises to 50°C, the volatilization quantity of DMAC is the largest, the network structure in the solution is more compact, the density of the twisting points becomes larger, and then, the value of  $\Delta\eta$  increases. From Table I it can also be concluded that the shearing rate also affects the  $\Delta\eta$  value, and  $\Delta\eta$  decrease with the increase of the shearing rate. When the shearing was intensified, the association degree decreased, the intermolecular force is reduced, the molecular twisting points became less, and the structuredness of the solution decreased. Therefore, as far as the fiber spinning process of the CMPSF hollow fiber matrix membrane is concerned, selecting an appropriate spinning temperature and control of the shearing rate could improve the spinnability.

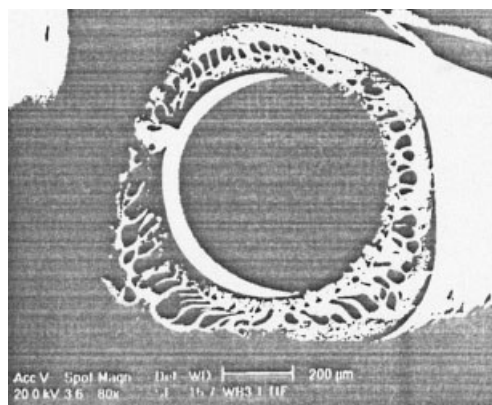
### Morphological structure of the CMPSF hollow fiber matrix membrane

Figure 6 is the environmental spinning electrical graph of the CMPSF hollow fiber matrix membrane. Figure 6 shows that there are thin skin layers on both the internal and external surface; the external surface is a little thicker and the internal surface is thinner relatively. The membrane structure close to the two

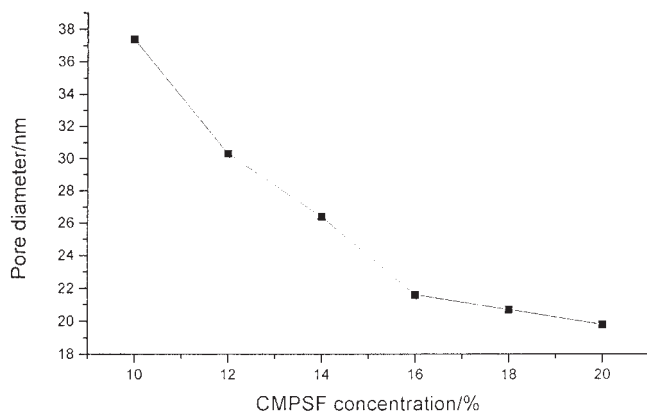
surfaces is the finger-like pore size structure, and there is a thin compact spongy structure in the finger-like pore sizes close to the external surface. Such a structure of the CMPSF hollow fiber matrix membrane is due to the different diffusivity of the solvent DMAC of the spinning dope in the dry and wet spinning process. In this study, the fiber spinning process adopted the dry-wet spinning technology. In the stage of dry spinning, the internal and external surfaces of the spinning dope were all in different mediums, and the external surface was in air. Although the solvent DMAC was easy to volatilize, the speed was a little slower, and the diffusing speed of the solvent from the spinning dope to external surface was much slower than that of the solvent to the internal surface. While the internal surface was fully contacted with the core liquid, the solvent DMAC on the internal surface was totally mixed up with water, and so the solvent in the spinning dope could only diffuse to the core liquid (only a little solvent diffused to the external surface), which resulted in the concentration of CMPSF close to the larger external surface and the external skin is thicker and more compact than internal one. In the wet spinning stage, the internal and external surfaces were all dipped in the coagulating bath, and therefore, the solvent in the spinning dope began to diffuse to the external coagulation bath and to the core liquid at the same time. No matter where the solvent in the center of the membrane diffused, the resistance was much more. This was the reason of the formation of rich phase of the polymer CMPSF in membrane and the appearance of the phase separation. To delay the liquid-liquid delamination, the membrane structure forming in the membrane was compact spongy structure.

### Effects of constitution of the spinning dope on structure of the hollow fiber matrix membrane

Figure 7 shows the effects of the concentration of CMPSF on the pores of the hollow fiber matrix mem-

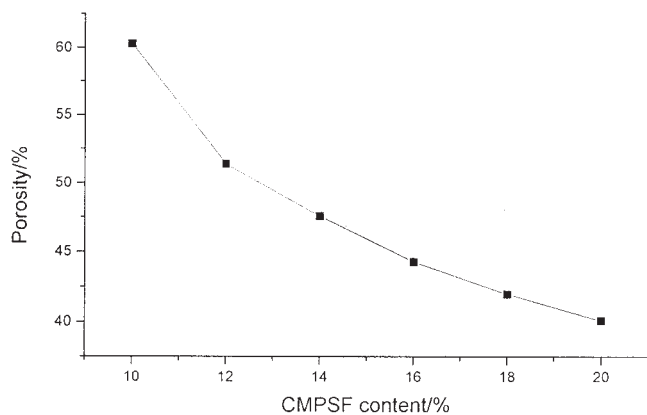


**Figure 6** The ESEM of the cross section of the CMPSF hollow fiber matrix membrane.



**Figure 7** The relationship between CMPSF content and pore diameters of hollow fiber matrix membrane (additive content, 0%; casting solution temperature, 25°C; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa).

brane, and Figure 8 shows the effect of the concentration of CMPSF on the porosity of the hollow fiber matrix membrane. The casting solution, that is the spinning dope, is one of the key factors that affect the pore structure of the hollow fiber matrix membrane. The concentration of CMPSF, which is the main material to compose the pore structure, affects the morphological structure of the hollow fiber matrix membrane directly. Figures 7 and 8 show that both the pore size and the porosity decrease with the increase of the CMPSF content in the spinning dope. It could be considered that with the increase of CMPSF content the liquid-liquid phase separation appeared under the skin layer in the process of preparation for the hollow fiber matrix membrane in the dry-wet spinning technology. Because the number of the crystal nucleus in the poor phase of CMPSF increased, the network



**Figure 8** The relationship between CMPSF content and porosities of hollow fiber matrix membrane (additive content, 0%; casting solution temperature, 25°C; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa).

**TABLE II**  
The Effect of Additive PEG Concentration on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>

PEG content (%)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
0	39.7	23.7	46.1
2	167.2	33.4	58.4
4	178.4	36.5	60.3
6	90.1	37.2	61.7
8	200.3	39.4	63.2
10	204.2	42.0	67.0

<sup>a</sup> Additive, PEG (molecular weight 10,000); casting solution temperature, 25°C; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa.

structure formed by the crystal nucleus after desolventizing got more compact and as the pore size became smaller, the porosity decreased and the flux was reduced. At the same time, the content of CMPSF affects the spinning dope directly, and depending on whether the viscosity of the spinning dope was too much or too little, both would result in the unstable spinning dope and affect the structure and performance of the hollow fiber matrix membrane.

In the process of preparation of the hollow fiber matrix membrane, the membrane structure came into being mainly in the inversion of phase of the as formed fiber. When the spinning liquid went off the spinning head and contacted with the coagulating bath, it first formed compact surface layers like spongy structure on both the internal and external surfaces of the membrane, that is, the double skin layers. But because the stress that was applied when the polymer desolventized and compacted could not completely disappear through the creep of the polymer, the compact surface layer would break at the stress rookery, and this breakpoint is the growing point of the finger-like pores. As soon as the finger-like pores appeared at the breaking point, they would grow up to the membrane matrix from this point. The exchange rate of the solvent and the coagulator could be changed by adjusting the content of the additive PEG (molecular weight is 10,000), that is, the stress state of the membrane surface in the gel process of the as formed fiber changed, thereby, the goal to control the membrane pore size and the degree of the growing in membrane matrix was obtained. Table II shows the effect of additive PEG (molecular weight is 10,000) concentration on the structure of CMPSF hollow fiber matrix membrane. From Table II it can be seen that the average pore size of membrane becomes larger, the porosity also shows the upward current with the increase of the content of the additive PEG (the molecular weight is 10,000), and the flux increases under the combined effects of pore size and porosity. When the content of PEG in the spinning liquid increased, the

**TABLE III**  
The Effect of Spinning Casting Solution Temperature on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>

Temperature (°C)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
20	138.2	41.0	65.1
25	133.1	39.2	63.8
30	128.7	37.3	62.1
35	121.0	35.4	61.7
40	117.1	36.3	60.3
45	120.4	39.4	60.8
50	133.9	40.3	65.0

<sup>a</sup> Additive, PEG (molecular weight 10,000); content 4%; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa.

exchange rate of the solvent and the precipitant was expedited for the strong hydrophilic effect, and much more finger-like pores formed. The increase of the proportion of the finger-like pores appeared as the increase of the porosity and the pore size. But too much additives would deduce the intensity of membrane, and so the viscosity of the spinning liquid is too high to spin.

The increase of temperature resulted in the decrease of the viscosity of the CMPSF spinning liquid, and when the spinning liquid immersed the coagulation bath, the double diffusion rate of the solvent and the coagulator increased, and consequently, the flux, the pore size, and the porosity of the hollow fiber matrix membrane increased. The results are shown in Table III. What need to be explained is the conclusion that the increase of the spinning liquid is favorable for the increase of membrane flux is only applicable within limits. Too high temperature will lead to the solvent volatilization promptly and the compact membrane is formed instead. Dry spinning is an extreme example in such a case. The hollow fiber matrix membrane with good water permeability can also be obtained at a lower spinning temperature and lower whole solid concentration. Thereby, the spinning temperature and concentration can be adjusted within limits.

### Effects of the extrusion rate on structure of the hollow fiber matrix membrane

In the spinning process of the hollow fiber membrane, the factors that affect the quality and structure of the hollow fiber can be divided into two parts. One is the effect of composition of the spinning dope, such as the composition and dosage of the additives and the content of the polymer. Another is the effect of the process conditions, such as the reeling velocity, the temperature of the spinning liquid, the pressure in the spinning process, the proportioning and the temperature of the core liquid, the temperature of the coagulating bath and the distance of the vaporizing part. Both the two factors have restriction and are related with each other in the experimental and product procedure. Table IV shows the effects of the volume flow rate of the extrusion on the membrane structure under other constant spinning conditions, such as dry spinning line, the reeling velocity, and the flow rate of the core liquid.

From Table IV it can be seen that when the volume flow rate increased, the external diameter, wall thickness, and the porosity of the CMPSF hollow fiber matrix membrane increased, while the pore size and flux decreased. The continuity condition of spinning process is as follows<sup>10</sup>:

$$\rho\pi(R^2 - r^2)V = \rho\pi(R_0^2 - r_0^2)V_0 \quad (10)$$

where  $R$  and  $r$  are the external and internal diameter of hollow fiber matrix membrane, respectively;  $R_0$  and  $r_0$  are the external and internal diameter of the spinning head, respectively;  $\rho$  is the density of the jetting spinning dope; and  $V_0$  and  $V$  are the extrusion rate and the movement velocity of the spinning dope, respectively. When the extrusion speed increases and the movement velocity of the spinning dope keeps invariable to meet the continuity condition, the left hand side term of the eq. (10)  $\pi(R^2 - r^2)$  increases, that is, the wall thickness of the hollow fiber membrane increases. Because the core liquid and the flow rate are constant, the internal diameter of the hollow fiber

**TABLE IV**  
The Effect of Extrusion Volume Outflow on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>

Extrusion volume outflow (mL/min)	External diameter (mm)	Wall thickness (mm)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
10.1	0.41	0.21	129.3	40.3	61.3
20.4	0.47	0.23	120.1	38.4	63.1
30.2	0.56	0.27	117.4	36.1	66.2
40.1	0.63	0.29	110.3	35.2	67.4

<sup>a</sup> Dry spinning distance, 10cm; additive, PEG (Molecular weight 10,000); PEG content 4%; coagulating bath temperature, 25°C; and ultrafiltration pressure 0.1 Mpa.



TABLE V  
The Effect of Dry Spinning Distance on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>

Dry spinning distance (cm)	External diameter (mm)	Wall thickness (mm)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
10	0.47	0.23	120.1	38.4	63.1
20	0.43	0.20	140.8	43.7	65.4
30	0.38	0.18	160.7	49.4	60.4

<sup>a</sup> Extrusion volume outflow, 20.4 mL; additive, PEG (molecular weight 10,000); PEG content 4%; coagulating bath temperature, 25°C; and Ultrafiltration pressure, 0.1 Mpa.

membrane remains unaltered and the external diameter of the hollow fiber matrix membrane increases. The change of the flux, pore size, and the porosity of the hollow fiber matrix membrane are consistent with the results in literature, that is, the flux decreases with the increase of the wall thickness of the hollow fiber matrix membrane. The reason for the pore size decrease was the increase of the shearing rate that caused the volume flow rate when the polymer CMPSF solution flows in the spinning head. The increase of the shearing stress could enhance the degree of orientation of the molecular chain of the CMPSF that makes the array more compact, and leads to the increase of the average pore size of the hollow fiber matrix membrane.

#### Effects of length of dry spinning line on structure of the CMPSF hollow fiber membrane

Table V shows the change of the structure of the CMPSF hollow fiber membrane with the change of the length of the dry spinning line at the constant reeling speed. From Table V it can be seen that the flux, pore size, and porosity of the CMPSF hollow fiber membrane increase with the increase of the dry spinning line, but the external diameter and the wall thickness decrease. The change of the dry spinning line affected the force on the spinning dope, thereby it resulted in the change of the shape of the spinning dope, and then in the change of the external diameter and wall thickness of the hollow fiber membrane. In the spinning process, the stresses applied on the spinning dope were mainly the following ones (1): the extensional force  $F_t$  forced by the collecting device on the spinning dope; (2) the deadweight of the spinning dope; (3) the inertia force  $F_{in}$  to render the spinning accelerating; (4) the friction force  $F_f$  caused by the spinning dope and surrounding medium; (5) the surface tension  $F_s$  of the spinning dope; and (6) the rheological resistance  $F_R$  of the intermolecular chains in the spinning dope. The acting forces of any point in the spinning dope satisfied the equilibrium of the aforementioned forces.

$$F_t + F_g = F_R + F_S + F_f + F_{in} \quad (11)$$

The exterior tension  $F_t$  caused by the winding equipment at  $L$  distance away from the spinning head could be expressed by the following equation<sup>11</sup>:

$$F_t = P_{xx}^0(L) \pi R_L^2 \quad (12)$$

where  $P_{xx}^0$  is the winding stress, and the equation of the gravity  $F_g$  is expressed as follows<sup>11</sup>:

$$F_g = (L - L_0) \pi R_L^2 g \left(1 - \frac{\rho^0}{\rho}\right) \cos \omega \quad (13)$$

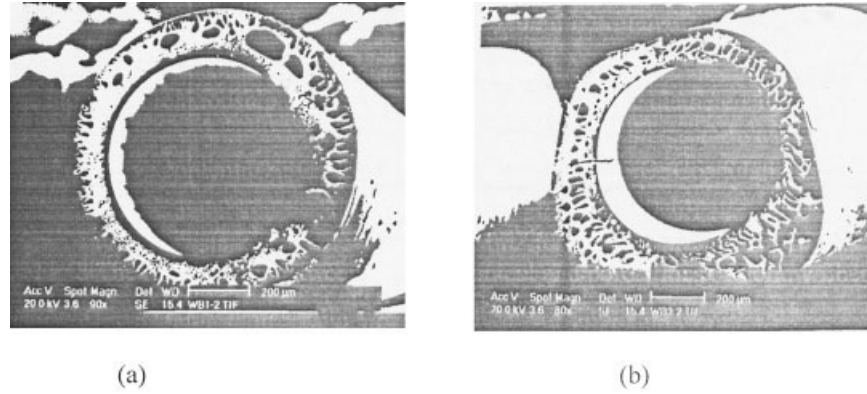
The  $\cos \omega$  value is related with the direction of motion. When the direction of spinning is upward vertically,  $\cos \omega = -1 = -1$ ; when horizontal,  $\cos \omega = 0$ ; and when downward vertically,  $\cos \omega = 1$ . In this study, the direction of the spinning in the dry spinning stage is downward vertically, and so  $\cos \omega = 1$ . Where  $\rho^0$  is the density of medium; and  $\rho$  is the density of the spinning dope. The inertia force  $F_{in}$  is to render the spinning accelerating. The work applied by the outside forces on the spinning dope equals to the increase of its kinetic energy, and it could be calculated by the following equation:

$$F_{in}(X_2 - X_1) = \frac{1}{2g}(mv_2^2 - mv_1^2) \quad (14)$$

$$F_{in} \Delta X = (mv_2^2 - v_1^2)/2g$$

where  $X_1, X_2$  are the distance of the two points on the nozzle plate, respectively;  $v_1, v_2$  represent the movement velocity when the spinning dope at  $X_1, X_2$ ; and  $F_{in}$  is independent with the degree of the spinning. Rheological resistance  $F_R$  appears in the shear flow of the pore passages in the spinning head and is caused by the viscoelasticity normal stress passed by the winding equipment. It was decided by the rheological behavior of the spinning liquid, the flowing condition when passing the spinning head, and the reeling velocity  $V_L$ .

$$F_R = \pi R_0^2 P_{xx,0}^0 \quad (15)$$



**Figure 9** The ESEM of the cross section of the CMPSF hollow fiber matrix membrane with different dry spinning distance (a) dry spinning distance, 10 cm; and (b) Dry spinning distance, 30 cm.

The fiction resistance  $F_f$  refers to the skin fiction force of the spinning dope and the surrounding medium and its expression is

$$F_f = 2\pi(L - L_0)v^2C_f/2g \quad (16)$$

where  $v$  is the velocity; and  $C_f$  is the coefficient of the friction resistance, which is related with Reynolds criterion.

$$C_f = 0.68 \times R_e^{-8} \quad (17)$$

$$R_e = Dv\rho^0/\mu$$

where  $D$  is the external diameter of the spinning dope;  $\rho^0$  and  $\mu$  is the medium density. The following eq. (18) was obtained when eq. (17) was substituted into eq. (16).

$$F_f = \frac{0.68}{2^{0.2}g}(L - L_0)\pi R_L^{0.2}\rho^{0-0.8}V_L^{1.2}\mu^{0.8} \quad (18)$$

The eq. (18) shows that the fiction resistance not only will increase to 1.2 power of the reeling velocity but also has relationship with the spinning line and the semidiameter of the spinning trick. The surface tension  $F_s$  on the spinning dope is so little that it could be ignored, and then the eq. (11) transmutes to the following expression when  $F_s$  ignored:

$$F_t = F_R + F_{in} + F_f - F_g \quad (19)$$

In the eq. (19), only the fiction resistance term and the gravity term have relation with the spinning line. Combining  $F_f$  with  $F_g$ , the following eq. (20) was obtained.

$$F_f - F_g = (L - L_0) \left[ \frac{0.68}{2^{0.2}} \pi R_L^{0.2} \rho^{0-0.8} V_L^{1.2} \mu^{0.8} - g \pi R_L^2 \left( 1 - \frac{\rho^0}{\rho} \right) \cos \omega \right] \quad (20)$$

Based on the eq. (20), when the fiction resistance is greater than the gravity, that is,

$$\left[ \frac{0.68}{2^{0.2}} \pi R_L^{0.2} \rho^{0-0.8} V_L^{1.2} \mu^{0.8} - g \pi R_L^2 \left( 1 - \frac{\rho^0}{\rho} \right) \cos \omega \right] > 0$$

the spinning rate is high, and with the increase of the dry spinning line, the distance ( $L [SCAP] - L_0$ ) between point  $L$  and the spinning head will increase, and the right hand side term of eq. (19) will increase. When the reeling velocity is constant, the left term  $F_t$  will be invariable. Thereby, to keep the stress balance of the spinning dope, that is, to set up the eq. (19), the inertia force and rheological resistance must be reduced. The eq. (14) shows that the decrease of the inertia force will result in the decrease of movement velocity of the spinning dope. From the equation of continuity we know that the decrease of the movement velocity of the spinning dope will enlarge the cross section of the spinning dope, that is, the wall thickness of the spinning dope will increase, and the internal diameter of the spinning dope will be invariable with the constant flux of the core liquid. Therefore, when the spinning rate is large, the movement velocity of the spinning dope will decrease and the semidiameter of the spinning dope will increase with the increase of the dry spinning line. When the friction resistance is less than the gravity, that is  $\left[ \frac{0.68}{2^{0.2}} \pi R_L^{0.2} \rho^{0-0.8} V_L^{1.2} \mu^{0.8} - g \pi R_L^2 \left( 1 - \frac{\rho^0}{\rho} \right) \cos \omega \right] < 0$ , the spinning rate is less at this point, and the left hand side term  $F_t$  of eq. (19) will decrease with the increase of the spinning line. When the reel-

**TABLE VI**  
**The Effect of Bore Liquid Outflow on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>**

Bore liquid outflow (L/h)	External diameter (mm)	Inner diameter (mm)	Wall thickness (mm)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
0.46	0.47	0.24	0.23	120.1	38.4	63.1
0.50	0.49	0.28	0.21	133.4	41.4	67.2
0.55	0.54	0.34	0.20	139.1	45.3	69.8
0.57	0.58	0.39	0.19	147.2	49.2	73.1

<sup>a</sup> Extrusion volume outflow, 20.4 mL; additive, PEG (molecular weight 10,000); PEG content 4%; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa.

ing velocity is constant,  $F_t$  will be invariable, that is, when the eq. (19) is set up, the inertia force and rheological resistance must be enlarged. The eq. (14) shows that the increase of the inertia force will result in the increase of the movement velocity of the spinning dope. Figure 9 is the ESEM images of the cross section of the hollow fiber matrix membrane in different dry spinning lines. Based on the condition of continuity, the increase of the movement velocity of the spinning dope will result in the decrease of the cross section of the spinning dope, that is, the external diameter of the spinning dope will decrease. Thus, when the reeling velocity is less, with the increase of the dry spinning line, the movement velocity will increase and the semidiameter of the spinning dope will decrease. In this study, with the increase of the dry spinning line, the velocity of the spinning dope increased, the diameter of the spinning dope decreased, the internal diameter was invariable, and the wall thickness decreased. These results accord with the second situation discussed earlier. Therefore, the spinning process in this study belongs to the low velocity spinning process. Because the wall thickness of the spinning dope became thinner with the increase of the dry spinning line, the diffusional resistance of the solvent decreased, the residence time of the spinning dope in air increased, and the solvent in the spinning dope diffused into the core liquid. This lead to the rich phase of CMPSF in the membrane center moving to the external surface, then, the thickness of the skin layer and density of the membrane increased. While because of the fast solvent diffusion and low polymer concentration, the membrane beneath the skin layer formed many big interconnected finger-like pores, the osmotic resistance was reduced greatly, and the porosity and pore size were elevated. In addition, the solvent volatilization can make the membrane surface compact, but DMAC easily absorb the moisture in air, thereby the coagulating concentration of the surface layer decreased and the coagulating course changed from the total wet double diffusion to gas phase coagulation partly. This resulted in the increase of the flux with the increase of the dry spinning line.

#### Effects of flow rate of the core liquid on the CMPSF hollow fiber matrix membrane

The insert tube type spinning head of the hollow fiber was adopted, and on one hand the core liquid was passed over the inset tube to offer a inside support for the fiber that just extruded, and on the other hand to operate the inside coagulation effect. The effect of the flow rate of the core liquid on the structure of the hollow fiber matrix membrane is shown in the Table VI. It shows that with the increase of the flow rate of the core liquid, the internal and external diameter both increase, but the increase of the internal diameter is faster and the wall thickness of the hollow fiber matrix decreases, and the flux, pore size, and the porosity increase. The reason is that with the increase of the flow rate of the core liquid, the acting force of the core liquid on the inner wall increases, and that results in the decrease of the wall thickness spinning dope; meanwhile, the increase of the flow rate of the core liquid increases the diffusion velocity of the solvent in the spinning dope to the core liquid, and also increases the differential concentration between the solvent and the coagulator on the interface of the membrane. Then, the rate of the membrane formation is quickened, and the porosity, the pore size, and the flux increase. But with the increase of the flow rate of the core liquid, the internal and the external of the membrane increase,

**TABLE VII**  
**The Effect of Internal Coagulant Composition on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>**

DMAC content (%)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
2	183.6	39.4	67.4
4	178.4	36.5	60.3
6	170.1	34.3	55.3
8	161.4	32.7	50.2
10	153.2	30.1	47.3

<sup>a</sup> Evaporation time, 10 s; additive, PEG (10,000) 4%; casting solution temperature, 25°C; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa.

**TABLE VIII**  
**The Effect of External Coagulant Composition on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>**

DMAC content (%)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
2	183.6	39.4	67.4
4	172.3	37.1	65.7
6	169.1	36.4	62.4
8	164.7	32.7	58.3
10	157.3	30.3	56.1
12	160.3	31.9	57.9

<sup>a</sup> Internal coagulant composition, DMAC 2%; evaporation time, 10 s; additive, PEG (10,000) 4%; casting solution temperature, 25°C; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa.

then the wall thickness decreases rapidly, and the bearing capacity of the membrane decreases suddenly.

#### Effects of coagulating conditions on the structure of CMPSF hollow fiber matrix membrane

The coagulation of the hollow fiber includes the two parts: one is the inner coagulation by the effect of the core liquid, and the other is the outer coagulation by the effect of the coagulation liquid. The inner coagulating liquid, namely the core liquid, is a mixed liquid of the solvent DMAC and the coagulator H<sub>2</sub>O. The effect of the content of the DMAC in the inner coagulator on the structure of the hollow fiber membrane is shown in Table VII.

At the same condition of the outer coagulating condition, with the increase of the content of the solvent DMAC in the inner coagulating liquor, the coagulating conditions were alleviated, the membrane structure became more compact, and the flux, the pore size, and the porosity decreased. The effect of the content of the DMAC in the outer coagulator on the structure of the hollow fiber membrane is shown in Table VIII. Table VIII shows that the flux, the pore size, and the porosity have a minimum change of the content of the DMAC in the coagulating liquid. The reason is that

when the content of the DMAC(solvent)in the outer coagulating liquid increases, the forming conditions are gradually alleviated, the rate of the double diffusion decreases, the membrane structure is more compact, and the flux, the pore size, and the porosity decrease. If the content of the solvent DMAC in the coagulating bath increases continually, the structure of membrane would become loose again for the swelling effect of the solvent DMAC on the CMPSF, and then, the flux, the pore size, and the porosity will increase a little.

#### Effects of heat drafting on the structure of CMPSF hollow fiber matrix membrane

The CMPSF hollow fiber matrix membrane needed to be heat drafted to obtain some mechanical property. The as formed CMPSF hollow fiber matrix membrane was dipped in a liquid bath at a given temperature, and was drafted by the tension that produced by the rate difference of the two lead rollers. Table IX shows the effects of the drafting multiple on the structure of the CMPSF hollow fiber matrix membrane. From Table IX it can be seen that with increase of the drafting multiple, the flux, the pore size, and the porosity of the CMPSF hollow fiber matrix membrane decrease. The reason is that when the hollow fiber matrix membrane is drafted above the second-order transition temperature, the random CMPSF macromolecule chains would be tropic in the axial direction of the hollow fiber, then the pore structure of the compact layer and the loose layer would be drafted slightly, the pore size and the porosity would decrease, and therefore, the flux would decrease. The drafting with too large drafting multiple is not appropriate to be operated to keep a necessary flux, pore size, and porosity of the hollow fiber matrix membrane. It is enough to make the CMPSF hollow fiber matrix membrane have enough mechanical strength when the drafting multiple is one to two. From Table X it can be seen that the effect of the drafting temperature on the structure of the CMPSF hollow fiber matrix membrane under a constant drafting condition. Table X shows that with the

**TABLE IX**  
**The Effect of Tensile Ratio on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>**

Tensile ratio	External diameter (mm)	Inner diameter (mm)	Wall thickness (mm)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
0.0	0.47	0.24	0.23	120.1	38.4	63.1
0.5	0.41	0.20	0.21	116.3	37.1	62.0
1.0	0.37	0.18	0.19	110.7	35.7	60.7
1.5	0.35	0.17	0.18	104.8	34.0	58.4
2.0	0.33	0.16	0.17	102.5	33.1	57.3

<sup>a</sup> Tensile temperature, 30°C; extrusion volume outflow, 20.4 mL; additive, PEG (molecular weight 10,000); PEG content 4%; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa.

**TABLE X**  
The Effect of Tensile Temperature on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>

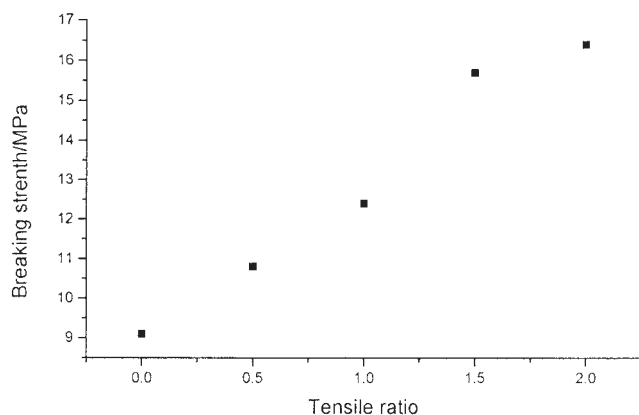
Tensile temperature (°C)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
30	110.7	35.7	60.7
40	103.2	32.1	57.8
50	94.5	30.2	51.2

<sup>a</sup> Tensile ratio, 1; additive, PEG (10,000) 4%; casting solution temperature, 25°C; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa.

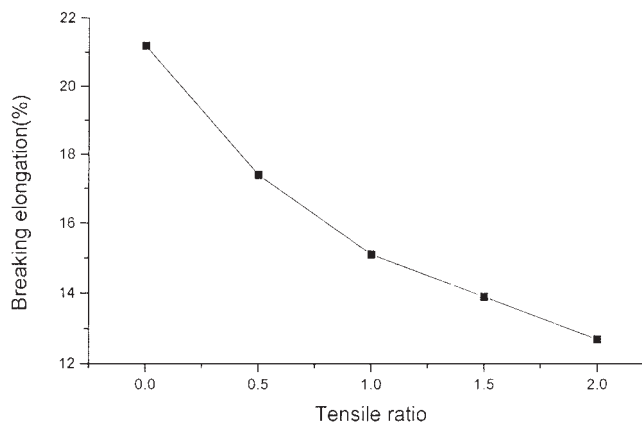
increase of the drafting temperature, the flux, the pore size, and the porosity of the CMPSF hollow fiber matrix membrane decrease. With the increase of the drafting temperature, the CMPSF macromolecule chains are easier to move and the moving ability of the macromolecule chains are stronger. In the drafting process of the hollow fiber matrix membrane at a higher temperature, the CMPSF macromolecules are easier to be tropic in the axial direction of the hollow fiber, then the pore structure of the compact layer and the loose layer would be drafted slightly, and the pore size and the porosity would decrease.

#### Effects of drafting on mechanical properties of the CMPSF hollow fiber matrix membrane

Figures 10 and 11 show the effect of the drafting multiple on the breaking strength and breaking elongation of the CMPSF hollow fiber matrix membrane, respectively. It can be seen from Figure 10 that with the increase of the drafting multiple, the breaking strength of CMPSF hollow fiber matrix membrane increases. The degree of orientation of the CMPSF macromolecule increases in the axial direction of the hollow fiber. The heat drafting can increase the break-



**Figure 10** The effect of tensile ratio on breaking strength of CMPSF hollow fiber matrix membrane (tensile temperature, 30°C).



**Figure 11** The effect of tensile ratio on breaking elongation of CMPSF hollow fiber matrix membrane (tensile temperature, 30°C).

ing strength in the axial direction of the hollow fiber. Figure 11 shows that with the increase of the drafting multiple, the breaking elongation of the CMPSF hollow fiber matrix membrane decreases correspondingly. In the drafting process, the degree of orientation of the CMPSF macromolecule increases in the axial direction of the hollow fiber with the increase of the drafting multiple, the array in the CMPSF macromolecule fiber becomes neater, and the texturing capacity of the macromolecular chain decreases. Therefore, the flexibility and the breaking elongation of the CMPSF hollow fiber matrix membrane decrease under the high power drafting.

The object of the heat treatment is to elevate the homogeneity and stability of structure of CMPSF hollow fiber matrix membrane. There are three factors that affect the membrane structure in the process of the heat treatment such as the temperature of the heat treatment, the medium of the heat treatment, and the time of the heat treatment. The effect of the temperature of the heat treatment on the membrane structure is the most appreciable. Table XI shows the heat treat-

**TABLE XI**  
The Effect of Thermal Treatment Temperature on the Structure of CMPSF Hollow Fiber Matrix Membrane<sup>a</sup>

Thermal treatment temperature (°C)	Water flux (L/m <sup>2</sup> h)	Pore diameter (nm)	Porosity (%)
30	108.4	34.1	58.4
40	101.7	31.1	56.3
50	92.7	28.3	50.7
40	49.8	21.7	41.8

<sup>a</sup> Thermal treatment medium, water; thermal treatment time, 5 h; additive, PEG (10,000) 4%; casting solution temperature, 25°C; coagulating bath temperature, 25°C; and ultrafiltration pressure, 0.1 Mpa.

ment of the CMPSF hollow fiber matrix membrane at different temperatures in the same medium and time of the heat treatment. From Table XI it can be seen that the flux, pore size, and porosity of CMPSF hollow fiber matrix membrane decrease with increase of the heat treatment temperature. With the increase of the heat treatment temperature, the fiber membrane became compact, and that resulted in the decrease of the flux. The pore size would compact too much such that the flux decreased if the temperature was over 60°C. Therefore, the temperature of the heat treatment should be controlled about room temperature to 40°C for the CMPSF hollow fiber matrix membrane.

### CONCLUSIONS

The CMPSF spinning casting solution belonged to the shearing force rarefying liquid; the liquid behavior was pseudoplastic and the flow rate accorded with the power law basically. With the increase of the CMPSF concentration in the spinning casting solution, the viscosity increased apparently. The higher the CMPSF concentration, the less the critical shearing rate when the shearing force rarefying appears. With the increase of the shearing rate, the flow-activation energy of the CMPSF spinning casting solution decreased. The flow-activation energy of the CMPSF spinning casting solution decreased especially under the high shearing rate, and the dependency of the flow-activation energy of the CMPSF spinning casting solution on temperature decreased at a high shearing rate and that is favorable for continuous spinning. Both temperature and the shearing rate have effect on the structural viscosity exponent of the CMPSF spinning casting solution, and therefore, the appropriate spinning temperature and shearing rate could control the structuredness of the CMPSF spinning casting solution, and then improve its spinnability. The CMPSF content, the additive content, and the temperature of the casting solution have significant effects on the structure of the CMPSF hollow fiber matrix membrane. The pore size, the porosity, and the flux of the hollow fiber matrix membrane decreased with the increase of the CMPSF content in the spinning dope, and increased with the increase of molecular weight and content of the additive PEG. The increase of the spinning temperature did favor to elevate the flux of the hollow fiber within a range of temperature. The viscosity of the spinning dope increased with the increase of the

CMPSF content and with the decrease of the solvent temperature. The asymmetric structure of the CMPSF hollow fiber matrix membrane had a close relationship with the diffusion difference of the solvent to in the dry and wet spinning line phase. In phase of the dry spinning line, the solvent DMAC only diffused to the core liquid, but in phase of the wet spinning line, the solvent diffused to both core liquid and outer coagulating bath. The external diameter, wall thickness, and porosity of the hollow fiber matrix membrane increased with the increase of the extrusion volume rate when other spinning parameters were constant, but the pore size and the flux decreased. The increase of the dry spinning line was favorable for promoting the properties of the hollow fiber matrix membrane; the increase of the flux of the core liquid would increase the membrane flux, but the supportability of the membrane decreased rapidly. Consequently, too high flux of the core liquid was adverse to improve the membrane performance. The CMPSF hollow fiber matrix membrane needed to heat drafting to obtain some mechanical strength. But the heat drafting would decrease the flux, pore size, and porosity of the hollow fiber matrix membrane. In general, the CMPSF hollow fiber matrix membrane can not only obtain enough mechanical strength but also keep an appropriate pore size, porosity, and flux when the drafting multiple is one to two. The CMPSF hollow fiber matrix membrane should have a tension heat set to increase the homogeneity and the stability of the structure. Too high temperature of the heat setting is inadvisable otherwise the pore size would compact too much and the flux decreased.

### References

1. Beeskow, T. C.; Kusharyoto, K.; Anspach, F. B. *J Chromatogr A* 1995, 715, 49.
2. Serfica, G. C.; Pimbley, J.; Belfort, G. *J Membr Sci* 1994, 88, 292.
3. Reif, O. W.; Volker, N.; Bahr, U. *J Chromatogr A* 1993, 654, 29.
4. Petsch, D.; Beeskow, T. C.; Anspach, F. B. *J Chromatogr B* 1997, 693, 79.
5. Li, J.; Che, H. L.; Chai, H. *Chem J Chin Univ* 1999, 20, 1322.
6. Bao, S. X.; Shi, G. J.; Jiang, W. *J Chem Ind Eng (Chinese)* 1995, 46, 15.
7. Wang, B.; Cui, Y. F.; Du, Q. Y. *J Appl Polym Sci* 2003, 87, 908.
8. Wang, B.; Huang, W.; Yang, X. *J Appl Polym Sci* 2005, 96, 2117.
9. Gao, Y. X.; Ye, L. B. *Base of Membrane Separation Technology*; Science Press: Beijing, 1989; p 173.
10. Hirose, S.; Shimizu, A.; Nose, T. *J Appl Polym Sci* 1979, 23, 3193.
11. Wang, G. H. *Principle of Forming and Processing of Polymer Materials*; Chemical Industry Press: Beijing, 1982; p 279.