Preparation of polyimide hollow fiber membrane

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Abstract. The polyimide hollow fiber membrane has the characteristics of high packing density, large specific surface area, simple membrane module structure, and good separation performance for CO₂/CH₄. Therefore, it has become a hotspot in the field of gas separation, while its preparation process needs further exploration. This study is aimed to prepare polyimide P84 hollow fiber membranes by the dry–wet phase transformation method and investigate the main influencing factors, such as spinning solution concentration, external coagulation bath selection, bore fluid selection, and air gap, in the preparation process. The results showed that the pore size of the dense layer of the hollow fiber membrane decreased with the spinning solution concentration. As the height of the air gap increased, the dense layer thickness on the outer surface also gradually rose. The external coagulation bath affected the internal finger holes of the hollow fiber membrane. As the external coagulation bath changed continuously from water, ethanol, and isopropanol to acetone, the finger pore structure decreased in turn. A mixed solution of water/isopropanol, water/ethanol, and water/acetone was used as the bore fluid. In the case of pure water application, the density of finger pores inside the film was remarkably reduced.

1. Introduction

The energy problem and clean energy development are getting very topical. In particular, clean and efficient separation of CO₂ and CH₄ from liquefied petroleum gas to obtain biogas has been explored by many scholars [1, 2]. Because a polymeric membrane has high gas separation performance [3, 4], it provides better processing ability and lower capital investment compared with the conventional technology. Therefore, it can replace the traditional separation method (such as absorption method, pressure transformation, and adsorption rectification method).

The polymeric gas separation membrane prepared from polyimide as a raw material has good gas separation performance for CO₂/CH₄. It is superior to other separation membrane materials (polysulfone, cellulose acetate, and so forth), and has gradually become a hot spot in the field of gas separation membranes [5, 6]. Polyimide P84 is synthesized from diphenyl-methane-diisocyanate, tolylene diisocyanate, and 3,3',4,4'-benzophenonetetracarboxylic dianhydride. P84 has excellent processability and outstanding gas separation performance, making it highly promising in the field of gas separation. The preparation methods for a hollow fiber membrane mainly include melt spinning method, thermal phase separation method, solution spinning method, and so forth [7-9]. The solution spinning method is a conventional method for preparing a hollow fiber membrane, and a dry–wet phase transformation method is a relatively common method. The spinning solution is solidified by the gas and liquid phases, the solvent and nonsolvent are diffused, and liquid–liquid or solid–liquid phase separation occurs. After separation, the enriched phase portion constitutes the main body of the
membrane, and the rest forms the finger-shaped pores of the support membrane. The hollow fiber membrane is prepared by a dry–wet method, and the polyimide solution is immersed in a nonsolvent coagulation bath through a certain height air gap. A pore structure is generated due to polymer precipitation via the exchange of a solvent and a nonsolvent.

However, to successfully apply gas separation membranes in the industry, their gas separation performance needs to be further improved. Due to the “upper-bound trade-off” effect of gas separation membranes, effectively improving their gas separation performance has always been the focus of research. Thus, Aik and Yu [10] found that by changing the preparation process of the polyimide gas separation flat membrane, the separation membrane structure could be adjusted to improve its gas separation performance. Also, polyimide gas separation membranes with dense structure tended to have better gas selectivity. The thin film was advantageous for achieving good gas separation performance. Some scholars found that adding a co-solvent to the polyimide casting solution at a certain ratio could increase the density and improve the gas separation performance of the gas separation membrane. Shi [11] and Chou [12] found that increasing the height of the air gap could increase the thickness of the dense surface layer of the hollow fiber gas separation membrane. Also, the permeability of the membrane was slightly lowered, but the selectivity increased.

A large number of studies indicated that the dense structure of the polyimide gas separation membrane could improve gas separation performance. However, the method of effectively improving the dense internal structure of the polyimide hollow fiber gas separation membrane during the preparation process is not comprehensive enough. The related literature and experiments indicated that during the preparation of the polyimide separation membrane, the composition ratio of the selected coagulation bath had a great influence on the structure of the membrane, and the solubility of the solvent and coagulant affected the spinning. Changes in the solubility of the solvent and coagulant could affect the rate at which the spinning solution solidified into a film, and this rate change affected the morphology of the film. By changing the composition and ratio of the inner and outer coagulation baths, the phase change process could be altered, and the structure and properties of the membrane were also adjusted. The inner and outer surfaces of P84 hollow fiber membrane were cured during the spinning process. Due to the influence of the internal bore fluid, the surface began to solidify when the spinning solution was extruded from the spinneret, and the outer surface also solidified. The preparation conditions, such as air gap, also affected the membrane structure. Studies on the preparation of hollow fiber gas separation membranes were conducted since the 1970s, but investigation is still required to achieve industrial gas separation.

In this study, the dry–wet phase conversion method was used to examine the preparation process of P84 hollow fiber membrane. The study also investigated the main influencing factors, such as spinning solution concentration, external coagulation bath composition, bore fluid, and air gap height, on the film preparation process of P84 hollow fiber membrane. The influence of morphology and the preparation process were optimized to prepare a dense hollow fiber membrane.

2. Experimental

2.1. Test materials
The test materials used in this study are listed in table 1.

| Name                  | Purity            | Manufacturer                              |
|-----------------------|-------------------|-------------------------------------------|
| Polyimide (P84)       | /                 | Self-made                                 |
| N,N-dimethylacetamide | Chemically Pure   | Beijing Chemical Reagent Company          |
| N-methylpyrrolidone   | Chemically Pure   | Beijing Chemical Reagent Company          |
| Ethanol               | Chemically Pure   | Beijing Chemical Reagent Company          |
| Isopropanol           | Chemically Pure   | Beijing Chemical Reagent Company          |
| Acetone               | Chemically Pure   | Beijing Chemical Reagent Company          |
2.2. Test equipment
The P84 polyimide hollow fiber membrane was prepared using the self-made equipment according to the flowchart depicted in figure 1. The equipment mainly included a liquid tank, a metering pump, a control cabinet, a spinneret, a bore fluid tank, a coagulation bath, and a collecting device.

![Figure 1. Schematic diagram of the preparation of hollow fiber membrane by dry–wet phase conversion.](image)

2.3. Test characterization
- Scanning electron microscope
  The hollow fiber membrane sample was vacuum dried at room temperature, and the cross-sectional morphology of the fiber membrane was observed using a JSM-7401F scanning electron microscope (Japan Electronics Co., Ltd., Japan). The surface of the sample was subjected to gold spray treatment at a voltage of 10 kV.
- Digital microscope
  The hollow fiber membrane sample was vacuum dried at room temperature, and the morphology of the polyimide hollow fiber membrane was observed at room temperature using a KH-8700 three-dimensional microscope (Hirox, Japan).

2.4. Preparation of P84 polyimide hollow fiber membrane
A certain amount of P84 was dissolved in N-methylpyrrolidone (NMP) to prepare a spinning solution of a certain concentration, and the mixture was added to a liquid kettle and stirred at 70°C. After sufficient dissolution, the mixture was allowed to stand, and the polymer solution was left in the liquid tank for more than 48 h to remove the bubbles. The hollow fiber membrane was prepared by a dry–wet phase conversion method, and the liquid tank was filled with a certain pressure of N₂. The spinning solution was introduced into the spinneret through a metering pump, and the amount of the bore fluid added was controlled with a metering pump. The spinning solution and bore fluid were extruded from the spinneret. After passing through a certain height of the air gap, the fiber membrane entered the coagulation bath, and was towed and rolled. The collected fiber membrane was solvent exchanged to remove excess solvent, dried, and collected.

3. Results and analysis
3.1. Effect of spinning solution concentration
First, the properties of different concentrations of polyimide solution in nonsolvent were verified. Figure 2 shows that when the polyimide spinning solution concentration was 5 wt%, the spinning solution entered the nonsolvent to form a sheet-like substance; it could not form a filamentous structure. When the spinning solution concentration was increased to 10 wt%, a filamentous substance was formed, but it was fine and cracking occurred. When the concentration reached 15 wt%, a complete continuous fiber filament was formed. As the concentration increased, the spinning effect
significantly improved.

![Figure 2](image2.png)

**Figure 2.** Properties of polyimide solutions with different viscosities in nonsolvent: (a) 5 wt%; (b) 10 wt%; (c) 15 wt%.

After the aforementioned concentration screening, three different concentrations of spinning solution (15 wt%, 20 wt%, and 25 wt%) were used in the hollow fiber membrane preparation; water was used as a coagulation bath for spinning. The sample obtained after spinning was dry and brittle. The morphology of the polyimide hollow fiber membrane was observed using a JSM-7401F electron microscope. Figure 3 shows that as the concentration increased, the pore diameter inside the dense layer of the prepared hollow fiber membrane gradually decreased. This was because lower concentrations of polymer solution increased the solvent and nonsolvent exchange rate and delayed phase stratification, thus increasing the internal pores of the dense layer.

![Figure 3](image3.png)

**Figure 3.** Hollow fiber membrane dense layer cross-section structure prepared with different spinning solution concentrations: (a) 15 wt%; (b) 20 wt%; (c) 25 wt%.

### 3.2. Effect of different external coagulation baths on hollow fiber membrane structure

After the nascent fibers entered the outer coagulation bath, the solvent in the film diffused into the coagulation bath, while the nonsolvent in the coagulation bath permeated into the film, causing solvent and nonsolvent exchange. This process resulted in a continuous decrease in the solvent content of the membrane surface, resulting in liquid–liquid phase separation. As the rate of diffusion of the solvent in the film to the outer coagulation bath was greater than the rate at which the nonsolvent in the coagulation bath penetrated into the membrane, the polymer that accumulated at the interface formed a relatively dense structure. However, the formation of such a structure in turn hindered the diffusion of the solvent into the coagulation bath, resulting in a decrease in the concentration of the polymer in the film to form a porous support layer. Water, ethanol, isopropanol, and acetone were selected as external coagulation baths to study the effect of the external coagulation bath on the morphology of the film. The cross-sectional structure of the obtained polyimide hollow fiber membrane is shown in figure 4.
Figure 4. Effect of different external coagulation baths on polyimide hollow fiber membranes: (a) water; (b) ethanol; (c) isopropanol; and (d) acetone.

The figure shows that the nonsolvent solidification medium had a significant effect on the thickness of the dense structure of the hollow fiber membrane. With the change in the external coagulation bath, the internal finger structure of the membrane significantly reduced, and the dense layer inside the membrane gradually increased. The extent of finger structure reduction from large to small was acetone > isopropanol > ethanol > water.

3.3. Effect of composition of bore fluid (internal coagulation bath)

Figure 5. Effect of bore fluid composition on polyimide hollow fiber membrane (external coagulation bath: water). Internal coagulation bath: (a) water; (b) $m_{\text{water}}/m_{\text{isopropanol}} = 20/80$; (c) $m_{\text{water}}/m_{\text{ethanol}} = 20/80$; and (d) $m_{\text{water}}/m_{\text{acetone}} = 20/80$. 
The remaining preparation process conditions were controlled, and the mixed solution of water, water/isopropanol, water/ethanol, and water/acetone was used as the bore fluid to study the effect of the internal coagulation bath on the film morphology. When water was used as the internal coagulation bath, the cross-sectional morphology of the hollow fiber membrane was as shown in figure 5(a), and the finger-like pore structure formed from the outer side of the fiber ran through the entire section. When water/isopropanol, water/ethanol, and water/acetone mixture was used as internal coagulation bath, the solidification ability of the inner coagulation bath gradually decreased with a gradual increase in the content of isopropanol, ethanol, and acetone. Also, the solidification speed of the inner spinning solution of the fiber was gradually lower than that of the outer coagulation bath. The spinning liquid phase separation on the inner side of the fiber was increasingly affected by the external coagulation bath. Figure 5(b) shows a structural view of a hollow fiber membrane prepared when the composition of the bore fluid was \( m_{\text{water}}/m_{\text{isopropanol}} = 20/80 \). Compared with water as the bore fluid under the same conditions, the phase transformation mode of the inner spinning solution of the fiber changed from instantaneous phase separation to delayed phase separation, and the finger pore structure on the inner side of the film significantly reduced. This phenomenon was also observed with a hollow fiber membrane prepared using \( m_{\text{water}}/m_{\text{ethanol}} = 20/80 \) or \( m_{\text{water}}/m_{\text{acetone}} = 20/80 \) as a bore fluid.

3.4. Effect of the air gap

When a hollow fiber is prepared by a dry–wet process, the distance between the spinneret and the coagulation bath is referred to as an air gap. After the hollow fiber membrane was extruded from the spinneret, it stayed in the air for a while and then entered the coagulation bath. Due to the high temperature during extrusion, the solvent on the outer surface of the membrane volatilized a lot, forming a dense skin layer on the outer surface. Therefore, the size of the air gap affected the structure of the outer surface of the film. The morphology of hollow fiber membranes prepared at different air distances (0, 10, 20, 30, and 40 cm) was examined. As shown in figure 6, as the air gap increased from 0 to 40 cm, the dense layer on the outer surface of the membrane increased. If the air gap distance continued to increase, the dense layer on the outer surface of the membrane did not increase significantly. However, an excessive air gap affected the spinning process, and the frequency of fiber membrane breakage increased significantly.

3.4. Effect of the air gap

Figure 6. Relationship between air gap height and thickness of the outer surface of the hollow fiber membrane.

4. Conclusions

In this study, polyimide hollow fiber membranes were prepared by dry–wet phase transformation method, and the main influencing factors (spinning solution concentration, external coagulation bath type, bore fluid, and air gap height) on hollow fiber were investigated. The major findings were as follows:
• When the concentration of the spinning solution was too low, the spinning could not be performed. As the concentration increased, the spinning effect improved, and the pore diameter inside the dense layer of the hollow fiber membrane gradually decreased. However, the concentration did not increase all the time, and when it was too high, the spinning difficulty was observed. When the concentration of the spinning solution was 25% by weight, a polyimide hollow fiber membrane having a small pore diameter inside the dense layer was obtained.

• The level of the air gap directly affected the outer surface structure of the membrane. With the increase in the air gap, the thickness of the outer surface skin layer increased. However, an excessive air gap caused the fiber membrane fracture frequency to increase, which made the spinning difficult. In general, the use of a 30-cm-high air gap was beneficial to the preparation of the dense structure of the hollow fiber membrane.

• The composition of different external coagulation baths had a great influence on the structure of hollow fiber membranes. The nonsolvent solidification medium had a significant effect on the thickness of the dense layer. With the change in the external coagulation bath, the internal finger structure of the membrane significantly reduced. The extent of reduction from large to small was acetone > isopropanol > ethanol > water.

• The type of the bore fluid affected the formation of the internal structure of the hollow fiber membrane. A mixed solution of water/isopropanol, water/ethanol, and water/acetone was used as the bore fluid phase. For water, the finger-hole structure on the inner side of the membrane remarkably reduced.

In summary, using a spinning solution concentration of 25 wt%, acetone as the external coagulation bath, a mixed solution of water and ethanol or isopropanol or acetone as the bore fluid, and a 30-cm-high air gap, relatively dense hollow fiber membranes were successfully produced.

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