Preparation and Properties of UHMWPE/SiO₂ Hybrid Hollow Fibre Membranes via Thermally Induced Phase Separation-stretching Method

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ABSTRACT

Ultrahigh molecular weight polyethylene (UHMWPE)/SiO₂ hybrid hollow fibre membranes were prepared by thermally induced phase separation-stretching (TIPS-S), using mineral oil as diluent and SiO₂ as additive. In this study, UHMWPE/SiO₂ blends were incompatible. Therefore, an interfacial microvoid was produced in the interface between UHMWPE and SiO₂ after stretching along fibre axis. Secondly, the stretching pore also appeared due to stretch. Moreover, UHMWPE/mineral oil was blended into a homogeneous phase at sufficiently high temperature and underwent phase separation when it was cooled. The TIPS pore was prepared by extracting mineral oil. Thereby, after stretching, multi-pore-structure (MPS) including interfacial microvoid, stretching pores, and pore by TIPS was built. The influential factors, including heat-treatment, draw ratio and drawing temperature were investigated. The results of this study indicated that the draw ratio had an optimum value in order to obtain the UHMWPE/SiO₂ hybrid hollow fibre membranes with good permeability. The permeability of membrane showed the best performance at the 5 folds draw ratio. The effects of heat-treatment and drawing temperature on pore structure have been mainly produced from the pores contraction and defect formation. Both the pore size and the pore number of HC₅ were the highest, those of C₅ took second place and those of HH₅ were the lowest. HC₅ showed the highest pure water flux compared to HH₅ and C₅. The mechanical properties of membranes were the result of a set of factors including crystallinity, degree of orientation, and defects in the membrane structure.

INTRODUCTION

Membrane material is an important part of the membrane separation technology. As a new type of engineering thermoplastic material, ultrahigh molecular weight polyethylene (UHMWPE) has incomparable properties, e.g., good impact resistance, abrasion performance, self-lubricating, solvent resistance and excellent low-temperature resistance compared to the other plastics [1-2]. However, UHMWPE presents rubbery state in melting due to its ultrahigh-molecular-weight (more than 1.0×10⁶ g/mol). Thus, UHMWPE does not almost exhibit a liquid state. Furthermore, it has small frictional coefficient and low critical shearing rate. All the above mentioned specifications make UHMWPE to be processed with difficulty. Thereby, it is seldom made into membranes with by
routine methods.

Generally speaking, there are two ways to prepare polyolefin membranes: thermally induced phase separation (TIPS) [3-5] and melt-spinning and stretching (MS-S) [6,7]. In TIPS process, polymer and diluent is blended into a homogeneous phase at sufficiently high temperature. The diluent is a low molecular weight, high-boiling chemical that is not a solvent for the polymer at room temperature, but acts as one at higher temperatures. The homogeneous solution undergoes phase separation when it is cooled and the diluent is then extracted. The voids left by the droplets are referred to as cells. Porous, flat membranes of UHMWPE were prepared via TIPS method by Ding Huaiyu [5]. For MS-S method, a pure polymer melt is spun, and the micropores of the membranes by MS-S process are formed by mechanical force acting on the membranes in the subsequent stretching step. The mechanism of microvoid formation is due to the stacked crystalline lamellae aligned normal to the fibre axis. When the fibre is stretched, the crystal lamellae are separated with the formation of a large amount of interconnected voids. Thus, the micropore structure is formed by the stress and then it is completed during annealing [8].

TIPS combined with MS-S (TIPS-S) can avoid the dense layer surface and obtain higher porosity [9-12]. Shipman [10] prepared PP membrane by TIPS with PP mass fraction of 70-80%. Compare with PP membrane without stretching, PP membrane cold-stretched in the length and cross directions has higher porosity and air permeability. Polypropylene/tallowamine (PP/TA) was melt-blended to form homogeneous mixtures and extruded as film by Kinze [11]. With increasing orientation, the film thickness and its resistance to flow is reduced, but the mechanical strength, porosity, and pores size increase. Gu B [12] prepared elastic PP hollow fibre using paraffin oil as diluents. Such fibres may have row-nucleated lamella superstructure and the paraffin oil remains in interlamellar regions. Hollow fibre membranes with good gas permeability can be obtained after the extraction of the paraffin oil and stretched to a small extension.

The porous polyolefin film made from resin and an inorganic particle (such as BaSO4, CaCO3, and TiO2) was prepared at least by uniaxial stretching. The sufficient porosity is achieved by the stretching at such a low ratio, which the rugged pattern on film surface becomes beneficial to stress concentration. The pore can be formed in the interface of resin and inorganic particles [13-15]. However, it is not common to prepare the UHMWPE/SiO2 hybrid hollow fibre membranes by TIPS-S. In this study, a proper amount of micron-sized SiO2 was dispersed in UHMWPE solution, as UHMWPE/SiO2 blends are incompatible. Therefore, the interfacial microvoid may be produced in the interface between UHMWPE and SiO2 after stretching along fibre axis.

The objective of this work was to build the multipore-structure (MPS) in UHMWPE/SiO2 hybrid membrane, enhancing pore formation by TIPS method, stretching pore and interfacial microvoid formation through TIPS-S method. The UHMWPE/SiO2 hybrid hollow fibre membranes with excellent permeability and tensile property were obtained. Finally the influential factors, including heat-treatment temperature, draw ratio, and drawing temperature were investigated.

**EXPERIMENTAL**

**Materials**

The UHMWPE (MIII) was purchased from Beijing No. 2 Reagent Plant (Beijing, China) with a weight-average molecular weight of 3.65×10^6 g/mol. The mineral oil (7 #) and gasoline were produced by Oil Refinery Plant of Daqing Petrochemical Co. China. The antioxidant (1076 #) is commercial products of Tianjin Lisheng Chemical Plant, China. The micro-size SiO2 (2-6 μm) was kindly provided by Tianjin Chemical Research Institute. The alcohol was analytically pure.

**Preparation of UHMWPE/SiO2 Hybrid Membranes**

The steps for preparing the porous, UHMWPE/SiO2 hybrid hollow fibre membranes are shown in Figure 1. First, mineral oil and SiO2 have been mixed well at 50°C and high rotating speed (45 rad/min) in a stirred autoclave for 1 h. Then, UHMWPE and antioxidant were dissolved in the mixture of mineral oil/SiO2 and heated to 140°C for 1 h (mass ratio of SiO2/UHMWPE=2/5; mass ratio of mineral oil/UHMWPE= 19/1). After sufficient swelling, the
solution was stirred strongly for 3-4 h at 175°C to prepare the homogeneous casting solution. All the above mentioned steps were run under vacuum in order to avoid bubble formation.

In spinning, a spinneret with the outer diameter of 10.5 mm and the inner tube diameter of 7.8 mm was used. The fibres were spun by the gel-spinning process (air-gap=15 cm) [16]. The temperature of the environment was 20°C and relative humidity was 65%. The take-up velocity was 11-12 m/min. The solution extrusion rate was in the range 35-36 mL/min and the internal cooling bath flow rate was in the range 3-3.5 mL/min. The gel-hollow-fibres were prepared by immersing in water at 20°C as a cooling medium, while mineral oil was used as internal cooling bath. The gel-hollow-fibres were put in gasoline for 48 h to extract the mineral oil. After gasoline volatilizing in air for 12 h, the residual gasoline was extracted with alcohol. The resulting membranes were washed with fresh water and then dried in air.

Subsequently, the hollow fibre membranes were drawn to various draw ratios in different drawing conditions as the followings. The sample, labeled as C, was cold-stretched directly in air; the sample which was cold-stretched in air after heat-treatment for 30 min in water below 100°C (cooling rate = 1°C /min) was labeled as HC; and the last sample which was hot-stretched in 100°C water after heat-treatment for 30 min in water below 100°C was labeled as HH. The draw ratio of 0, 2, 4, 5 and 6 folds are designated by the same number as subscript, respectively (for example, C5 means the membrane which was cold-stretched directly in air at 5 folds draw ratio). The time of stretch-set was 20 min.

**Pure Water Flux Experiment**

The membranes were kept in fresh water for at least 48 h. The pure water flux of UHMWPE/SiO2 hybrid membranes can be measured using the instrument as shown in Figure 2 and calculated by eqn (1) [17]:

\[ J = \frac{V}{S \times t} \]  

where \( V \), \( S \), and \( t \) are the total permeation (L), the total permeation area (m²), and the total permeation time (h), respectively. The operating pressure difference across the membrane is 0.1 MPa and the operating temperature is 25°C±1°C.

**Bubble Point Pore Diameter Measurement**

The bubble point pore diameter was measured using the gas permeation method. The membranes were put into the wetting fluid for 2 h, and then operated by increasing from 0 MPa to higher pressure in capillary flow porosimetry system (CFP-1100-A*, Laurel, India). The bubble point pore diameter (r) can be defined as Laplace eqn (2) [18]:

\[ r = \frac{2\sigma \cos \theta}{\Delta P} \]
where, 
\( \sigma \) : the coefficient of surface tension of the wetting fluid,
\( \theta \) : the contact angle between wetting fluid and the membrane, and
\( \Delta P \) : the operating pressure when the first bubble appears.

**Porosity Measurement**

The porosity of the blend membrane was determined by measuring the true density and the bulk density [19]. The sample was put into the density bottle (10 mL) filled with alcohol and the equation of cubage was expressed as follows:

\[
10 = \frac{M_a}{\rho_a} + \frac{M_m}{\rho_t}
\]

(3)

where \( M_a \) and \( M_m \) are the weights of residual alcohol in density bottle and dry membrane, respectively, \( \rho_a \) is the density of alcohol, and \( \rho_t \) is the true density of membrane. Therefore, the true density (\( \rho_t \)) is calculated according to eqn (4):

\[
\rho_t = \frac{M_m \times \rho_a}{10 \rho_a - M_a}
\]

(4)

To measure the bulk density, blend membrane was swollen at 20°C for 12 h and its wet weight (\( W_{wm} \)) was measured. The free liquid on the surface of the swollen membrane was padded dry with filter papers before weighing. The dry weight (\( W_{dm} \)) was measured after the sample was dried under vacuum. The bulk volume (\( V_b \)) was calculated by eqn (5):

\[
V_b = \frac{W_{wm} - W_{dm}}{\rho_a} + \frac{W_{dm}}{\rho_t}
\]

(5)

The bulk density (\( \rho_b \)) was calculated by eqn (6):

\[
\rho_b = \frac{M_{dm}}{V_b}
\]

(6)

The porosity (\( \varepsilon \)) of the sample was calculated by eqn (7):

\[
\varepsilon (\%) = (1 - \frac{\rho_b}{\rho_t}) \times 100
\]

(7)

**Morphology Examination**

The structure and morphology of the membranes were observed by SEM (Quanta 200, FEI, Netherlands). The cross-section of membranes was freeze-fractured under liquid nitrogen. The membrane samples were gold sputtered and analyzed by SEM technique.

**Differential Scanning Calorimetric Experiment**

Melting point, crystallization temperature, melting limit, and crystallinity were determined using the differential scanning calorimeter (DSC 200F3, NETZSCH, Germany). The samples were heated from 0°C to 200°C at a heating rate of 20°C/min under nitrogen atmosphere. After at least 5 min to ensure complete melting and equilibrium attainment, the samples were cooled at a cooling rate of 20°C/min. The sample approximately weighed 5 mg. The crystallinity of sample was calculated from heats of fusion taken through the thermograms, assuming a purely crystalline polyethylene has a heat of fusion of 289 J/g [20,21].

**Orientation Factor Measurement**

The sonic orientation factors were determined using the sonic velocity apparatus (SSY-1, Institute of Chemistry of Chinese Academy of Sciences, China). The sonic orientation factor (\( f_s \)) can be calculated by eqn (8) [22] as follows:

\[
f_s = 1 - \frac{C_u}{C}
\]

(8)

where \( C_u \) is the sonic velocity of fully oriented fibre and \( C \) the sonic velocity of the measured fibre.

**The Mechanical Properties**

The tensile strengths of dry and wet membranes were determined by a universal mechanical testing machine (3369, Instron, USA). The measurements were taken at 20°C with relative humidity of around 65% with the crosshead speed of 10 mm/min.

**RESULTS AND DISCUSSION**

For MS-S process, the crystal lamellae are separated with the formation of a large amount of interconnected voids when the fibre is stretched. This condition has also been observed in TIPS-S process. Thus, crystallization is the most important factor to be
considered for preparing UHMWPE membranes by the TIPS-S process. As shown in Table 1, HH0 has higher crystallinity compared to C0. Because the original crystal grains become more perfect and the new microcrystallites are produced by chain folding via heat-treatment [23]. The melting peak width of HH0 is smaller than that of C0, pointing to many microcrystallites which grow into perfect crystals in the latter case.

Figure 3 shows the SEM of the cross-sections of UHMWPE/SiO2 hybrid hollow fibre membrane with HC post-processing. As it is observed in Figures 3a and 3c all the outer diameters, inner diameters, and wall thicknesses decrease as draw ratio increases. In the cross-section of HC0 membrane, there are many cellular pores formed by TIPS, with the worse connectivity of pores (Figure 3b). The TIPS pore size increases and the connectivity is improved, as the draw ratio increases, pointing to the MPS including interfacial microvoids and stretching pores. However, the number of cellular pores decreases probably due

<table>
<thead>
<tr>
<th>Samples</th>
<th>Melting point of UHMWPE (°C)</th>
<th>Melting peak width (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>141.3</td>
<td>16.4</td>
<td>51.42</td>
</tr>
<tr>
<td>HH0</td>
<td>141.1</td>
<td>14.3</td>
<td>54.33</td>
</tr>
</tbody>
</table>

Table 1. Effect of heat-treatment and stretch on behaviours of melting and crystallization.

Figure 3. Cross-sectional SEM micrographs of UHMWPE/SiO2 hybrid hollow fibre membrane: (a) a panorama of HC0, (b) a high magnification image of HC0, (c) a panorama of HC5, and (d) a high magnification image of HC5.
to the pores closing along the drawing direction, as shown in Figure 3d.

Figure 4 displays the inner and outer skin layers of HC membranes at different draw ratios. As can be seen in Figures 4a and 4b, the outer skin layer and the inner skin layer of HC0 membranes are very dense, with no sign of pores. The interfacial microvoids, as triangle, are uniformly distributed in HC5 membrane, especially on the outer skin layer (Figure 4c). The size and the number of stretching pores formed by crystal lamellae separation increase with increasing draw ratios. At the same time, the UHMWPE phases are prolonged and show fibre morphology after drawing as it is evident in Figures 4b and 4d, while SiO2 acting as physical cross-linking [24].

As it may be seen in Figures 4d, 5a, and 5b, both the pore size and the pore number of HC5 are the largest, those of C5 take second place and those of HH5 are the lowest, respectively. The reason is that the defects in HH membranes are less likely due to easy slippage of macromolecular chains in stretching, resulting from the stronger movement ability of the chain segments in hot water. Furthermore, the HC membrane, stretched in air after heat-treatment, has many micro- crystallites acting as physical cross-linking [25]. These cross-linking points refrain from the slip of molecular chains and benefits in creating defects, which result from crystal lamellae separation in stretching. These defects can grow up to stretching pores by enough stretch operation. Therefore, the
effect of heat-treatment and drawing temperature on pore structure mainly results from pores contraction and defects formation.

Figure 6 displays the permeability of membranes with different post-treatments. The water flux is little and the porosity is small without stretch due to the dense outer skin layer, and increases with the draw ratio, reaching maximum at 5 folds draw ratio. This is mainly attributed to the interfacial microvoid being created and grown with draw ratio, especially in outer skin layer. The triangular area of interfacial microvoid grows to maxima at a certain ratio, and does not change when the draw ratio increases further, besides the long crack appears along the

Figure 6. Plots of (a) pure water flux, (b) bubble point diameter, and (c) porosity of membranes at different draw ratios and post-processing.
At the same time, the appearance of stretching pores increases the opened pore number. The MPS contributes to the improvement of connectivity. This is also beneficial to the improvement of pure water flux. However, beyond the high draw ratio, the TIPS pores were elongated and then changes to crevices which have large length and small radial size. Therefore, the pure water flux and porosity decrease as the draw ratio increases further. This is in agreement with the discussions extended for Figures 3 and 4.

Although the multi-pore-structure is built in the hybrid membrane, the shrinkage of membrane exists due to the low UHMWPE concentration. The stretching method can decrease the influence of the shrinkage along the fibre axis but has no effect on the shrinkage of the fibre vertical section. Thus, the pure water flux can reach 400 L.m⁻².h⁻¹. The pure water flux of UHMWPE membrane prepared by Zhang et al. [26] reaches 200 L.m⁻².h⁻¹. When compared with his finding, the UHMWPE/SiO₂ hybrid membrane with stretching shows better permeability. Therefore, we plan to increase the pure water flux in the future research. As the draw ratio increases, the bubble point diameter has the same trend as the pure water flux.

With regard to the effect of heat-treatment and drawing temperature, the pure water and the bubble point diameter of membrane without stretching somehow decrease after heat-treatment, pointing to the shrinkage of membrane in hot water. After drawing, pure water flux of HC membrane is the highest, that of C membrane takes second place and that of HH membrane is the lowest. These phenomena are attributed to the stretching pores varying in different drawing methods as can be seen in Figure 6. However, the bubble point diameter of HC membrane is less than that of C membrane, indicating that the bigger pore can be avoided by heat-treatment. The result of HC membrane has a lower bubble point diameter than C membrane, but a higher pure water flux which may be due to the higher porosity of HC membrane as evident in Figure 6c.

Figure 7 displays the effect of heat-treatment and stretch on sonic orientation factor. As can be seen, the sonic orientation is measured by the different propagation velocity of acoustic waves between, along, and perpendicular to the molecular chains. Thereby, the sonic orientation factor can basically reflect the overall degree of orientation, including crystalline orientation and amorphous orientation [27]. Comparing with C, the HC and HH have smaller sonic orientation factor, due to the disorientation of the samples in heat-treatment. Sonic orientation factor of HH is larger than that of HC at the same draw ratio. The reason is that the molecular chain obtains enough kinetic energy to move in hot water. The decrease of resistance in molecular chain is beneficial to the unfolding of molecular chain and the orientation of crystal grain. Moreover, sonic orientation factor increases with draw ratio of hollow fibre membrane, caused by the orientation of crystal grain and the unfolding of molecular chain along the drawing direction [28].

Figure 8 shows the tensile properties of membranes. As can be seen, the tensile strength increases while the elongation-at-break decreases with the increase of draw ratio for the same post-treatment, pointing to the degree of orientation increasing and the ability of molecular movement is being declined. Furthermore, for the membrane without stretching, the tensile strength decreases while the elongation-at-break increases after heat-treatment due to the disorientation of macromolecular chains.

After stretching, the tensile strength of HH membrane is higher than that of C membrane,
although the degree of orientation of C membrane is higher than that of HH membrane. The main reason is that more defects produced in the amorphous region of C membrane with stretching, whereas the defects are less in HH membrane with stretching, attributed to the stronger ability in the movement of macromolecular chains in hot water. Furthermore, the HC membrane stretched in air after heat-treatment has the poorest tensile strength due to the microcrystallite formed in heat-treatment which acts as physical cross-linking, refrains the slipping of chains, and benefits from creation of more defects in stretching. These observations are attributed to joint effects of crystallinity, degree of orientation, and defects.

CONCLUSION

UHMWPE/SiO₂ hybrid hollow fibre membranes are prepared by thermally induced phase separation-stretching (TIPS-S), using mineral oil as diluent and SiO₂ as additive. The results of this study indicate the draw ratio has a proper value in order to obtain the UHMWPE/SiO₂ hybrid hollow fibre membranes with good permeability. The area of interfacial microvoid and the pores connectivity increase with increasing draw ratios. The size and the number of stretching pores increase whereas TIPS pores close and draw ratio increases. The variety of MPS makes the permeability of membrane also in the best state at a proper draw ratio. The effect of heat-treatment and drawing temperature on pore structure mainly results from pores contraction and defects formation. The mechanical properties of the membrane are the result of a set of factors including crystallinity, degree of orientation and structural defects.

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SYMBOLS AND ABBREVIATIONS

- J : Pure water flux (L.m⁻².h⁻¹)
- V : Total permeation (L)
- S : Total permeation area (m²)
- t : Total permeation time (h)
- γ : Bubble point pore diameter (µm)
- σ : Coefficient of surface tension of the wetting fluid
- θ : Contact angle between wetting fluid and membrane (rad)
- ΔP : Operating pressure when the first bubble appears (MPa)
- C₀ : Sonic velocity of fully oriented fibre (m/s)
- C : Sonic velocity of measured fibre (m/s)
f_s : Sonic orientation factors
UHMWPE : Ultrahigh molecular weight polyethylene
TIPS-S : Thermally induced phase separation-stretching
MS-S : Melt-spinning and stretching
TIPS : Thermally induced phase separation

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