Microporous hollow fiber membranes formed from blends of isotactic and atactic polypropylene

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Abstract

A novel process to prepare microporous hollow fiber membranes is proposed. Fibers of blends of isotactic polypropylene (i-PP) and atactic polypropylene (a-PP) spun under high take-up draw ratio are found to be elastic. Small angle X-ray scattering (SAXS) observation indicates that fibers have row-nucleated lamella structure normal to the fiber direction. Microporous polypropylene hollow fiber membranes were obtained from the fibers by extraction of atactic polypropylene and cool-stretching. The membranes have smaller pore size and higher permeability than those of traditional stretch method. The mechanism of micropore formation is discussed. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Microporous membranes; Hollow fiber; Lamella; Atactic polypropylene; Small angle X-ray scattering

1. Introduction

Microporous polypropylene hollow fiber membranes have a wide variety of applications as an efficient material for separation. They are used in oxygenators [1], gas separation [2], blood purification [3] and other aspects.

So far two methods have been developed for the preparation of microporous hollow fiber membranes. The traditional way is the stretch method [4]. In 1970s, it was found that several crystalline polymers were capable of being processed into a highly oriented morphological state which showed increased modulus and tenacity, an unexpectedly large extensibility and high elastic recovery from large extensions [5–7]. The structural characteristic of these polymers is the row-nucleated lamella structure normal to the fiber direction, and the lamellae are linked by the tie molecules. Microvoids will form upon stretching of these polymers because of the separation of the lamellae. After heat-setting microporous membranes are obtained [8]. The membrane structure is influenced by melt-draw ratio, spinning temperature and annealing temperature [9]. This process is simple and easy to perform, but the distribution of membrane pore size is not easy to be controlled. membranes thus prepared have been used in oxygenators. During extracorporeal circulation the pore walls of the hydrophobic polypropylene membrane will be gradually wetted by the protein in blood. Plasma leakage will occur through the relatively bigger pores and cause subsequent decay of gas exchange. The membranes used in oxygenators, therefore, should have relatively smaller pore size with higher gas permeability.
Another method to prepare microporous hollow fiber membranes is through the process of thermally induced phase separation (TIPS) [10]. A homogeneous solution is formed at an elevated temperature by dissolving the polymer in a solvent with high-boiling point and low molecular weight. The solution is spun into the shape of hollow fiber, then cooled at a controlled rate or quenched to induce phase separation. After the diluent is removed (typically by solvent extraction) microporous hollow fiber membranes can be obtained. The structure of membranes prepared by the TIPS process is greatly influenced by thermodynamic interactions between polymer and diluent, the composition of the coexisting phases, temperature, cooling conditions and other factors that affect the kinetics of phase growth once phase separation has taken place. By modifying these factors, pore structure can be controlled [11–14]. However, membranes formed via TIPS are somewhat fragile and a dense skin is easy to form during TIPS process. Therefore, if the porosity is the same, the permeability of the membranes formed via TIPS seems lower than those obtained via the stretch method. For the reduction of plasma leakage of TIPS membranes used in oxygenators, research has been done for higher tortuosity and smaller size of the pores [15–16].

The purpose of this work is to develop a new process to prepare microporous hollow fiber membranes with smaller pore size and higher permeability than that of the stretch method. The properties of the membranes prepared are compared with those of the traditional stretch method. The mechanism of micropore formation is discussed.

2. Experimental

2.1. Materials

Isotactic PP (T30S) with melt index 3 g/10 min, $M_w = 4.46 \times 10^5$, $M_w/M_n = 4.03$, was purchased from Shanghai Jinshan Petroleum Chemical.

Atactic PP was obtained from Lanzhou Petroleum Chemical, and its average molecular weight was determined to be $3.4 \times 10^4$ by viscometry in cyclohexane, assuming $K_o$ and $\alpha$ to be $1.6 \times 10^{-5}$ m$^3$/kg and 0.80, respectively [17].

Celgard® X30 240 microporous polypropylene hollow fiber membrane was purchased from Hoechst Celanese Corporation.

2.2. Blending and spinning

Blends of isotactic and atactic polypropylene were prepared in a twin-screw extruder (SHL-35, $D$: 35 mm, $L/D$ ratio: 28). The fibers for studying crystalline structures were spun in a capillary rheometer (CSS-153), with a-PP contents 10%, 20%, 30%, 40%. Hollow fibers were spun using a single-screw extruder ($D$: 20 mm, $L/D$ ratio: 25) equipped with a gear pump at the spinneret temperature of 210°C. The outer diameter of the spinneret was 23 mm and the width of the orifice was 2 mm.

2.3. Preparation of membranes

The hollow fiber thus obtained was annealed at 130°C for 30 min, extracted with xylene at 30°C, stretched at room temperature and then heat-set at 140°C for 20 min.

2.4. Characterization of structure and properties

The stress–strain curves of fibers were obtained at 20°C on an Instron Modal 1121 (strain rate: 100% elongation/min). The long period of fibers were determined by a Rigaku Dmax/rB X-ray diffraction device. The melting temperature, crystallization temperature of the raw materials and the melting temperature of the fibers were measured by Netzsch DSC-200 at a heating rate of 10 K/min. The density of each fiber was measured at 25°C using a density gradient column filled with an ethanol–water mixture.

The fluxes of nitrogen gases through a hollow fiber module were measured by employing a soap bubble meter at a transmembrane pressure of 0.01 MPa. The bubble point pressure was measured in an ethanol–water mixture (45 vol% ethanol). Permeability coefficient was calculated according to [18]. Porosity was calculated from the density of the hollow fibers.

The average pore size was measured by nitrogen adsorption method on Micrometrics ASAP 2010. The morphology of the surface of the hollow fiber mem-
Table 1
Characteristics of the blends

<table>
<thead>
<tr>
<th>a-PP content (%)</th>
<th>Melting temperature (°C)</th>
<th>Crystallization temperature (°C)</th>
<th>Crystallinity (%)</th>
<th>Bulk viscosity (N min/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>168.0</td>
<td>128.5</td>
<td>41.0</td>
<td>0.28</td>
</tr>
<tr>
<td>10</td>
<td>164.6</td>
<td>111.8</td>
<td>39.1</td>
<td>0.22</td>
</tr>
<tr>
<td>20</td>
<td>163.6</td>
<td>111.6</td>
<td>37.6</td>
<td>0.20</td>
</tr>
<tr>
<td>30</td>
<td>161.9</td>
<td>111.4</td>
<td>34.1</td>
<td>0.14</td>
</tr>
<tr>
<td>40</td>
<td>161.6</td>
<td>109.8</td>
<td>29.4</td>
<td>0.10</td>
</tr>
</tbody>
</table>

branes was examined using a scanning electron microscope (Hitachi S-250).

3. Results and discussion

Table 1 summarizes the properties of the blend samples, where crystallinity was calculated on the basis of heat of fusion.

One notes that the melting temperature, crystallization temperature and crystallinity decreases with the increase in a-PP content. Bulk viscosity also becomes smaller with the addition of a-PP having lower molecular weight. Eq. (1) describes the melting point depression of the crystalline polymer due to the mixing with an amorphous polymeric diluent [19]:

\[
1/T_m - 1/T_m^0 = -R V_2/\Delta H_2 V_1 [\ln \phi_2/m_2 \\
+ (1/m_2 - 1/m_1)(1 - \phi_2) \\
+ \chi_{12}(1 - \phi_2)^2]
\]

where \( T_m^0 \) is the equilibrium melting point of the crystalline polymer, \( T_m \) the experimental melting point of the blend, \( \Delta H_2 \) the heat of fusion of 100% crystalline polymer per mole of repeating units, \( V_1, V_2 \) the molar volume of the amorphous polymer and the crystalline polymer repeating units, \( \phi_2 \) the volume fraction of crystalline polymer, \( m_1, m_2 \) are the degree of polymerization of the amorphous polymer and the crystalline polymer, and \( \chi_{12} \) the Flory–Huggins interaction parameter. In the case of the blend of i-PP and a-PP of this work, \( \chi_{12} \) can be expected to be very small, \( m_2 \) is much greater than \( m_1 \), therefore, Eq. (1) can be simplified as:

\[
1/T_m - 1/T_m^0 = - R V_2(1 - \phi_2 + \ln \phi_2)/\Delta H_2 V_1/m_2 \quad (2)
\]

It can be seen from Eq. (2) that the increase in \( \phi_2 \) will lead to the decrease in \( T_m \). Therefore, the decrease of \( T_m \) in Table 1 can be considered as an effect of the content increment in the amorphous polymeric diluent.

In the traditional stretch method of preparing microporous hollow fiber membranes, the precursor is typically hard elastic isotactic polypropylene [4,20–21]. In our experiment it was found that after blending isotactic polypropylene (i-PP) with atactic polypropylene (a-PP), high elastic fibers can be still obtained at a relatively higher draw ratio. A clear relationship between elastic recovery after 100% elongation and take-up draw ratio is shown in Fig. 1. The draw ratio is calculated approximately from the ratio of the area of the spinneret outlet to that of the fiber cross-section. As shown in Fig. 1, at relatively higher draw ratio, elastic recovery is higher correspondingly.

The stress–strain curve is shown in Fig. 2 for the blend having different a-PP contents. With the increase of a-PP content, the yield point becomes lower. It can be inferred that a-PP exists between i-PP lamellae. A typical curve of cyclic loading was shown in
Fig. 2. Stress–strain curve of the fibers with different a-PP contents (a-PP content: (●): 0, (▲): 10%, (◆): 20%, (■): 30%).

Fig. 3. Two loading-unloading cycles for fiber with 20% a-PP to 50% elongation at a strain rate of 100% elongation/min: (—) first cycle, (-----) second cycle.

Fig. 3, which confirms that the fibers prepared in present work are hard elastic.

Figs. 4, 5 show the small angle scattering curve of i-PP and its blends with a-PP, respectively. One notes that there is no Bragg diffraction peak in the equatorial direction, whereas in the meridional direction such a diffraction maximum exists, which is consistent with the SAXS curves of typical hard elastic materials reported [5]. It is clear from the SAXS curves that the fiber containing a-PP have row-nucleated lamella structure normal to the fiber direction, which further proves that blended fibers are also hard elastic. Long period of fiber samples is given in Table 2.

The lamella thickness of the fibers (Table 2) are estimated on the basis of density, assuming $\rho_c = 0.936$ and $\rho_a = 0.850$, respectively [22].

During crystallization the a-PP in the blend will be expelled into the interlamella regions and the crystallization of molecules of i-PP in the blend will be restricted by the existence of amorphous a-PP. Compared with i-PP, the crystallization of its blend with a-PP when spun under the same cooling conditions will take place on the filature line at a farther distance from the spinneret. Therefore, the depression of crystallization temperature and the increase in the degree of undercooling results in the decrease of lamella thickness.
Table 2
Characteristics of fibers from the blends

<table>
<thead>
<tr>
<th>a-PP content (%)</th>
<th>Melting temperature (°C)</th>
<th>Long period (Å)</th>
<th>Lamella thickness (Å)</th>
<th>Fiber density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>166.3</td>
<td>199.7</td>
<td>109</td>
<td>0.897</td>
</tr>
<tr>
<td>10</td>
<td>165.5</td>
<td>195.7</td>
<td>91</td>
<td>0.890</td>
</tr>
<tr>
<td>20</td>
<td>165.4</td>
<td>194.0</td>
<td>88</td>
<td>0.889</td>
</tr>
<tr>
<td>30</td>
<td>164.1</td>
<td>191.1</td>
<td>79</td>
<td>0.886</td>
</tr>
<tr>
<td>40</td>
<td>163.1</td>
<td>188.6</td>
<td>62</td>
<td>0.879</td>
</tr>
</tbody>
</table>

Fig. 5. SAXS curve of PP fiber with 40% a-PP: (a) meridional, (b) equatorial.

The properties of membranes prepared are listed in Table 3. Those of i-PP hollow fiber membranes prepared under the same conditions and commercial fiber are also listed as a comparison. The porosity and the average pore diameter of Celgard® X30 240 are quoted from its specifications.

From the data of bubble point pressure, which is an indication of the maximum pore size, it can be seen that the maximum pore size of the membrane prepared from the blend of i-PP and a-PP is smaller than the one prepared directly from i-PP and Celgard® X30 240, and the permeability of the membrane from the blend is higher, while the average pore size is smaller, the scanning electron micrographs of the membranes prepared from the blend of i-PP and a-PP and i-PP are given in Fig. 6(a, b), which also shows smaller pore size of the membrane obtained from the blend.

It is generally accepted in all of the structural models of hard elastic fiber deformation that the separation of lamellae leads to microvoid formation. In the traditional stretch method, when the precursor elastic fiber is extended beyond 10% extension microvoids open up. Drawing the precursor elastic fiber to high extensions (100–200%) will cause the breakage of lamella which result in the extensive formation of relatively bigger pores [5]. Blending of low molecular weight a-PP reduced the chain entanglement density of polypropylene. According to the theory of craze formation and growth [23], craze will be easier to form when chain entanglement density becomes lower. The formation of uniform craze becomes easier. On the other hand, a-PP is expelled into the interlamellar region upon crystallization of i-PP, the number of tie molecules linking the lamellae reduced, therefore, lower stress is needed for the separation of lamellae, which can be seen from the stress–strain curve in Fig. 2. It can be believed that there will be less lamellae breakage in the blend of i-PP and a-PP when stretched and the chances of the production of macrovoids is reduced. The membranes with such pore structure are preferred in oxygenators where high permeability and small pore size are desired.
Table 3
Characteristics of microporous hollow fiber membranes

<table>
<thead>
<tr>
<th>Material</th>
<th>Blend of i-PP and a-PP</th>
<th>i-PP</th>
<th>Celgard® X30 240</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability coefficient (10^{-5}) cm(^3) (STP) cm/cm(^2) s cmHg)</td>
<td>9.7</td>
<td>2.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Bubble point pressure (MPa)</td>
<td>0.068</td>
<td>0.035</td>
<td>0.015</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>42</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>Average pore diameter (micron)</td>
<td>0.017</td>
<td>0.021</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Fig. 6. Scanning electron micrograph of the microporous hollow fiber membranes prepared from (a) blend with a-PP 40% (b) i-PP (fiber direction as the arrow indicated).

After a-PP was extracted, it was found that if there was no stretch, the permeability of the membrane was rather low, \(6.1 \times 10^{-7}\) cm\(^3\) (STP) cm/cm\(^2\) s cmHg. During extraction the lamellae might retract to lower the surface energy, thus filling the pores left by the extraction of the atactic phase, which results in the low permeability of the membrane thus formed. After stretching, the lamellae are drawn apart and pores formed again.

4. Conclusions

The blends of i-PP and a-PP still demonstrate hard elastic properties when spun under high take-up draw ratio. SAXS results show fibers containing a-PP have row-nucleated lamella structure normal to the fiber direction. Lamella thickness is reduced by the addition of a-PP. After melt spinning in a stress field and appropriate treatments, microporous hollow fiber membranes can be obtained. The addition of a-PP decreases the chain entanglement and reduces the interlamella tie molecules, which may account for the easier formation of uniform micropores in the method proposed. Microporous hollow fiber membranes prepared from the blend of i-PP and a-PP have small pore size and high permeability.

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References