

Fabrication of Microporous Membranes from Melt Extruded Polypropylene Precursor Films *via* Stretching: Effect of Annealing*

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Abstract In this work, the effects of annealing conditions on the microstructure of polypropylene (PP) precursor films and further on the porous structure and permeability of stretched membranes were investigated. Combinations of WAXD, FTIR, DSC and DMA results clearly showed the crystalline orientation and crystallinity of the precursor film increased with annealing temperature, while the molecular chain entanglements in the amorphous phase decreased. Changes in the deformation behavior suggested more lamellar separation occurred for the films annealed at higher temperatures. Surface morphologies of the membranes examined by SEM revealed more pore number and uniform porous structure as the annealing temperature increased. In accordance with the SEM results, the permeability of the membranes increased with annealing temperature. On the other hand, it was found that 10 min was almost enough for the annealing process to obtain the microporous membranes with an optimal permeability.

Keywords: Annealing; Microporous membrane; Polypropylene; Crystalline orientation; Deformation behavior.

INTRODUCTION

Microporous membranes made from polymeric materials have been increasingly employed for separation processes such as ultrafiltration and battery separators due to their good physical properties, low cost and easy fabrication. Generally, there are two main approaches for preparing microporous membranes. One is based on solution casting followed by phase separation^[1–3] and the other is uniaxially stretching a semicrystalline polymer film with a row nucleated lamellar structure^[4–8]. Compared with the phase separation method, the stretching method is relatively less expensive and has the advantage of limited environmental pollution. The fabrication of microporous membranes by stretching commonly consists of three major steps: (1) melt extrusion of a precursor film, (2) annealing of the precursor film and (3) cold and hot stretching of the annealed film followed by a thermo-fixation of the generated porous structure^[4–11].

It is well established that generation of a precursor film with an initial row nucleated lamellar structure plays a key role in determining the porous structure and permeability of the stretched membrane^[12]. Considerable efforts have been devoted to studying the factors influencing the crystalline structure and orientation state of the extruded films over the past decades^[6–18]. Sadeghi *et al.* compared the crystalline orientation of polypropylene

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(PP) films with different molecular variables but under the same processing conditions and the results suggested the molecular weight and molecular weight distribution of the resins were the main parameters controlling the crystalline structure^[8, 12, 13]. They also reported the crystalline orientation increased as the draw ratio increased^[8, 13]. Similar observations were made by Xu *et al.* in the case of poly(vinylidene fluoride) (PVDF) film^[6] and by Johnson *et al.* in the cases of polyoxymethylene (POM) and poly(4-methyl-1-pentene) (PMP) films^[14, 15]. Tabatabaei *et al.* examined the crystalline structure of PP films prepared under different cooling conditions and found that an air knife directed to the film surface right at the exit of the die contributed significantly to the uniformity of the row nucleated lamellar structure^[16].

However, production of a precursor film, with a suitable row nucleated lamellar structure, is essential but not necessarily a sufficient step for the microporous membrane formation^[19–21]. Annealing, as a second requirement, is also considered to be an indispensable procedure. Kim *et al.* illustrated that stretching without preheating spun polyethylene (PE) hollow fibers even failed to make a microporous structure^[19]. Johnson *et al.* found that the porous structure and permeability of the stretched POM and PMP membranes were largely dependent on the annealing process (temperature, time, as well as the tension applied during annealing)^[20, 21]. Consequently, it is suggested that the structure and properties of the finally obtained membranes were closely related to the crystalline structure of the precursor film prior to stretching, which could be further modified during the annealing process.

PP is a typical semicrystalline polymer with a high melting point, good mechanical properties and high chemical resistance. It has been widely employed for the production of microporous membranes such as those used as the battery separators^[22]. Compared to the efforts dedicated to the study of the optimum conditions fabricating a precursor film with an oriented lamellar structure, less attention was paid to the effect of the subsequent annealing process of the precursor film on microstructural changes and their influence on the structure and performance of the stretched membranes^[9, 23].

In this work, different annealing temperatures ranging from 100 °C to 155 °C, with a series of annealing intervals, were chosen and applied to a melt extruded PP precursor film having a row-nucleated lamellar structure. The changes in the microstructure as well as the deformation behavior of the PP precursor film upon annealing were explored. Then, these films were fabricated into microporous membranes *via* cold and hot stretching. The porous structure and permeability of the resulting membranes were compared.

EXPERIMENTAL

Material and Precursor Film Preparation

A commercial isotactic polypropylene (Pro-fax 6523) supplied by LyondellBasell Industries was used in this study. The resin had a density of 0.898 g/cm³ and a melt flow rate (MFR) value of 4.0 g/10 min (under ASTM conditions of 230 °C and 2.16 kg). The melting point, T_m , of the PP which was obtained using differential scanning calorimetry is 162 °C.

PP precursor film was melt extruded using a 45 mm diameter Killion single screw extruder with a slit die of 0.8 mm opening while die temperature was set at 220 °C. The distance between the die exit to the nip cast roll was around 15 cm, and the cast roll temperature was 50 °C. A draw ratio of 35 (ratio between final film speed and extrusion speed), as well as a certain amount of air flow was applied to the melts right at the exit of the die to produce an oriented precursor film having a thickness of around 23 μ m.

Annealing

The PP precursor films were placed in an oven to carry out the annealing procedures. Annealing temperatures ranging from 100 °C to 155 °C were chosen based on the range of temperatures encompassing the PP mechanical α_c relaxation, which ensures the molecular transitions in the crystalline phase, but avoiding lamellae melting on a large scale^[24]. Annealing times ranging from 1 min to 30 min were selected in light of feasible industrial processing times.

Microporous Membrane Fabrication

An Instron machine (Electroplus E3000, Instron Corp.) equipped with an environmental chamber was used to perform the cold and hot stretching. The films with a 70 mm by 80 mm rectangular shape were held between two grips separated by an initial length of 40 mm along the extrusion direction. Cold stretching was performed at room temperature with an extension ratio of 35% at a speed of 100 mm/min while hot stretching was carried out at 130 °C with an extension ratio of 60% at a speed of 50 mm/min. A subsequent heat setting of the stretched membranes at 130 °C for 90 s was used to fix the porous structure.

Characterization

Wide-angle X-ray diffraction (WAXD) patterns of the as-extruded and annealed films were recorded using a Bruker AXS X-ray goniometer equipped with a Hi-STAR two-dimensional area detector. The generator was set up at 40 kV and 40 mA and the Cu K α radiation ($\lambda = 0.154$ nm) was selected using a graphite crystal monochromator. To get the maximum diffraction intensity, several film layers were stacked together to obtain a total thickness of about 2 mm.

Fourier transform infrared spectroscopy (FTIR) was applied to the study of the molecular orientation in the precursor films. The measurements were performed on a Spectrum 65 FTIR Spectrometer (PerkinElmer Corp.) equipped with a wire grid polarizer. For each sample, two polarized spectra, namely parallel and perpendicular to the extrusion direction, were collected with 64 scans at a resolution of 4 cm⁻¹ in the wavenumber range from 4000 cm⁻¹ to 600 cm⁻¹. The orientation factor used (f) is defined as follows:

$$f = \frac{D - 1}{D + 2} \quad (1)$$

$$D = \frac{A_{//}}{A_{\perp}} \quad (2)$$

where $A_{//}$ and $A_{\perp}$ are the absorbance parallel and perpendicular to the extrusion direction, respectively. For PP, the crystalline orientation (f_c) could be calculated using the 998 cm⁻¹ band^[13].

Differential scanning calorimetric (DSC) measurements were carried out on a TA instrument DSC-Q2000 to analyze the thermal properties of the films. The samples were heated from 40 °C to 200 °C with a heating rate of 10 K/min. Crystallinity (X_c) of the sample was calculated using a heat fusion of 209 J/g for fully crystalline iPP^[25].

Dynamic mechanical thermal analysis (DMA) was applied to the films using a TA Q800 equipment (USA). Specimens cut parallel to the extrusion direction were subjected to the dynamical tensile deformation mode. The temperature ranging from -40 °C to 150 °C at a rate of 3 K/min and a frequency of 1 Hz were applied to the rectangular samples.

Tensile tests were carried out using an Instron 3365 machine at room temperature. The initial grip distance was set to 50 mm. Films with 25 mm width were stretched along the extrusion direction with a speed of 100 mm/min.

Scanning electron microscopy (SEM) was performed on a field emission scanning electron microscope (FESEM-Hitachi S4700) to examine the surface morphologies of the stretched membranes. All the samples were gold coated for 15 s before observations.

The water vapor transmission rate (WVTR) of the membranes was measured by using a MOCON PERMATERAN-W Model 101 K at 37.8 °C. Before measurement, calibration of the cell was performed with the relative humidity (RH%) in the lower chamber kept around 60%.

RESULTS AND DISCUSSION

Changes in the Microstructure of PP Precursor Film upon Annealing

Figures 1(a), 1(b) and 1(c) illustrate the 2D-WAXD patterns of the as-extruded PP precursor film and films

annealed at 120 °C and 155 °C for 30 min, respectively. The intense and sharp diffraction arcs instead of rings are seen for the as-extruded precursor film, implying the presence of oriented lamellar structure^[10, 16]. The arcs of the films become sharper and more concentrated after annealing treatment. It is suggested that crystalline orientation of the precursor film is further improved during the annealing process. This can be better shown in Fig. 1(d), where the intensity of the (110) crystalline plane (the first ring of the patterns in Figs. 1a–1c) is plotted as a function of the azimuthal angle. It is clear that the intensity of the equatorial peak increases while these two off-axis peaks decrease with increasing annealing temperature, implying *c*-axis orientation is enhanced while the *a*-axis orientation decreases^[16]. To reflect the changes in the crystallinity upon annealing, 2θ diffraction intensity profiles of the as-extruded and annealed films are shown in Fig. 1(e). It is found that the diffraction intensity increases with annealing temperature, suggesting the increased crystallinity upon annealing.

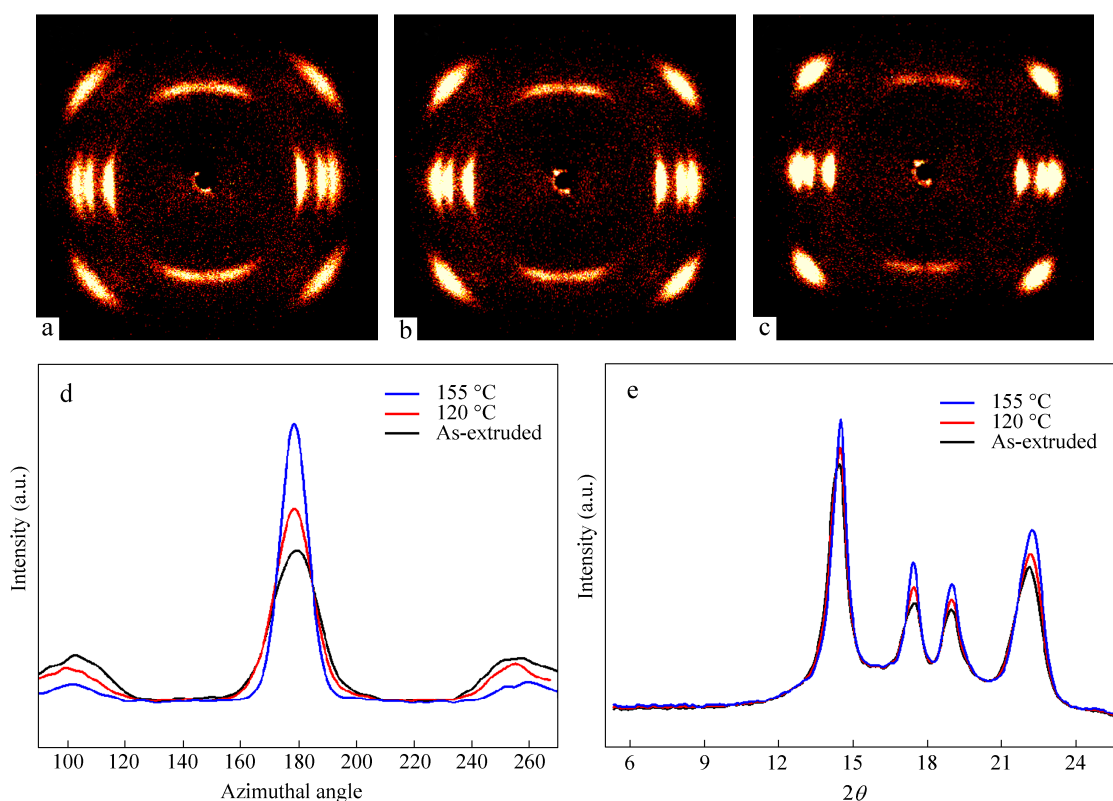


Fig. 1 2D-WAXD patterns of (a) the as-extruded PP precursor film and films annealed at (b) 120 °C and (c) 155 °C; (d) Intensity distribution of α (110) along azimuthal angle and (e) diffraction intensity profiles with integration through the circles

The effect of annealing on the crystalline orientation (f_c) and crystallinity (X_c) was further studied by FTIR and DSC methods, respectively, and the results are shown in Fig. 2. It can be observed that both f_c and X_c increase with annealing temperature. The change in f_c suggests that the possible lamellae twist resulted from the fast cooling during the cast extrusion process could reorient itself with its chain axis parallel to the extrusion direction. On the other hand, the change in X_c reveals that the secondary crystallization takes place during the annealing process, by which the molecular chains located nearby the lamellae could be reeled in, consequently leading to the increase in the crystallinity^[23, 26]. It is reasonably assumed that higher temperature renders the chain transition happen more easily, and thus results in larger crystalline orientation and crystallinity.

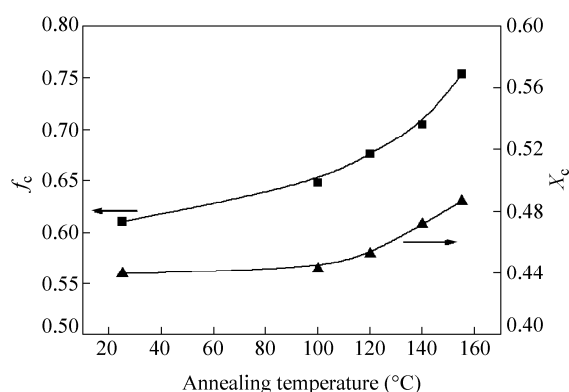


Fig. 2 Crystalline orientation (f_c) and crystallinity (X_c) of the PP precursor films as a function of annealing temperature

Figure 3 shows the DMA curves of the as-extruded PP precursor film and films annealed at different temperatures for 30 min. Two peaks located at around 15 °C and 85 °C could be observed, corresponding to the β and α relaxation of PP, respectively^[24]. The β relaxation is ascribed to the glass transition of unconstrained chains in the amorphous phase while the α relaxation is associated with the relaxation of constrained amorphous chains associated with crystals^[26]. As annealing temperature increases, the temperature of β relaxation decreases while its amplitude increases continuously, indicating a higher molecular mobility in the amorphous phase. It is suggested that annealing leads to a decrease in the molecular chain entanglements as some of the chains in the amorphous phase are rearranged into the crystalline phase owing to the secondary crystallization^[24, 26]. On the other hand, the amplitude of α relaxation decreases continuously with annealing temperature, suggesting more perfection of the crystalline structure as verified by the WAXD and DSC analysis above.

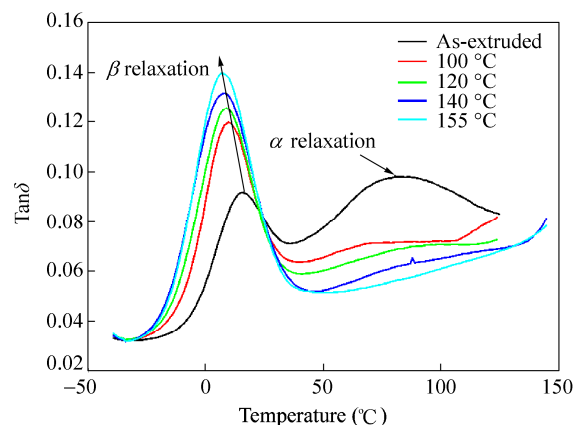


Fig. 3 DMA curves of the as-extruded PP precursor film and films annealed at different temperatures for 30 min

Changes in the Deformation Behavior of PP Precursor Film upon Annealing

It is known that the deformation behavior of the specimen depends largely on its microstructure and in turn determines the microstructural evolution during deformation process^[27, 28]. Since the porous structure of the PP membranes are created *via* stretching, it is necessary to study the effect of annealing on the deformation behavior of the precursor film. Figure 4 presents the stress-strain curves of the as-extruded PP precursor film and films annealed at different temperatures for 30 min. As expected, great difference can be observed among these films. Different from that of the as-extruded precursor film, two distinct yield points can be seen in the stress-strain curves for the annealed films. With increasing annealing temperature, the first yield stress and strain show decline while the second yield stress and strain keep increasing. Besides, the slope of the curves between the two points increases continuously as annealing temperature increases. According to Samules, the first and second

yield points correspond to the beginning of micropore formation in the amorphous region and disruption of the lamellar structure, respectively, and the lamellae are stretched apart along the tensile direction between these two yield points^[29]. Thus, the results indicate that creation of micropores happens more easily in the amorphous phase while the ability of the lamellae to resist damage become stronger for the films annealed at higher temperatures. It is reasonable because annealing leads to perfection of the lamellae as well as decrease of the molecular chain entanglements in the amorphous phase as revealed by the WAXD, DSC and DMA results above. Additionally, in view of the increased slopes of the curves upon annealing, it suggests more lamellar separation instead of interlamellar slippage happens during the stretching process^[13, 23].

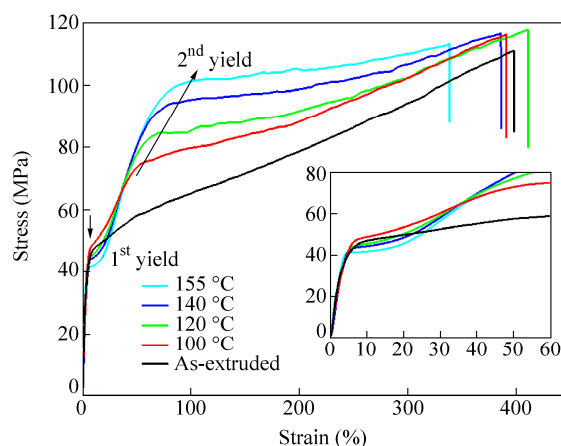


Fig. 4 Stress-strain curves of the as-extruded PP precursor film and films annealed at different temperatures for 30 min

To prove that annealing causes more lamellar separation, the surface morphologies of the stretched PP films with a strain of 35% were examined as shown in Fig. 5. As expected, little amount of micropores can be seen during stretching the non-annealed precursor film while a large amount of crazes oriented perpendicular to the extrusion direction are found for the annealed films. Increasing annealing temperature gives rise to more crazes in the stretched films, verifying that more lamellar separation takes place for the films annealed at higher temperatures.

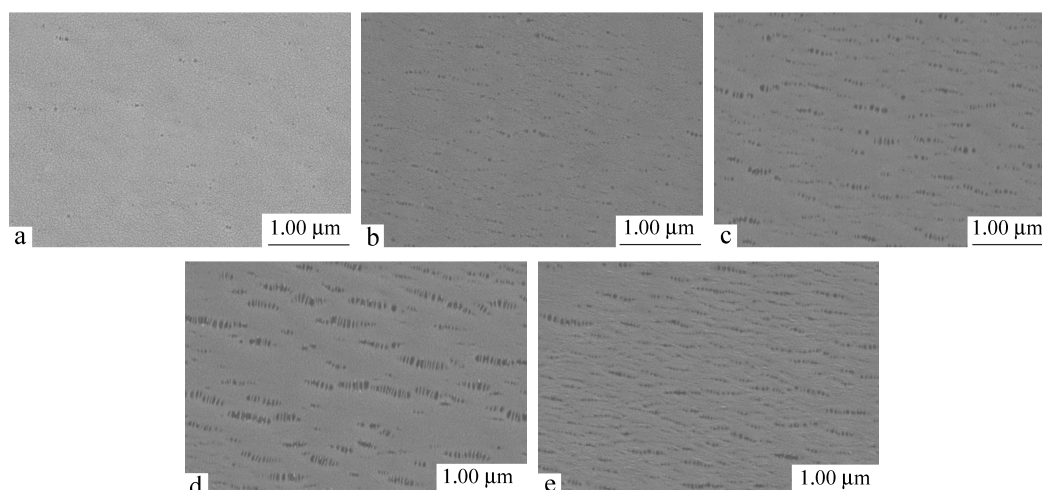


Fig. 5 Surface morphologies of the stretched films with a strain of 35% from (a) the as-extruded PP precursor film and films annealed at (b) 100 °C, (c) 120 °C, (d) 140 °C and (e) 155 °C

Morphology and Permeability of the PP Microporous Membranes

PP microporous membranes were fabricated from the precursor films following the optimum stretching conditions mentioned by Tabatabaei *et al.*^[9]. Figures 6(a)–6(e) display the surface morphologies of the microporous membranes obtained by cold and hot stretching of the as-extruded PP precursor film and films annealed at 100 °C, 120 °C, 140 °C and 155 °C, respectively. Obviously, significant differences can be observed between the micrographs in terms of the pore number per unit area as well as the porous structure among these stretched membranes. As shown in Fig. 6(a), there is a relatively few number of micropores distributed unevenly on the surface of the membrane fabricated from the non-annealed PP precursor film. In contrast, both the number and uniformity of the micropores are significantly improved by annealing the precursor. The pore number keeps increasing and its distribution gets more uniform with increasing annealing temperature as exhibited in Figs. 6(b)–6(e). As the micropores are originated from the lamellar separation, the increase in pore number indicates again that more lamellae are separated from each other along the stretching direction instead of slippage. This can be evidenced from the SEM images which show that the lamellar stacks (having several layers of lamellae) are more regularly arranged along the stretching direction and their thickness decreased as the annealing temperature increased. In addition, more microfibrils are generated in the interlamellar region of the membranes by using high temperature annealing for the film, consequently causing the pore shape to gradually evolve into a slit-like form, typical of the microporous membrane obtained by the dry process^[22].

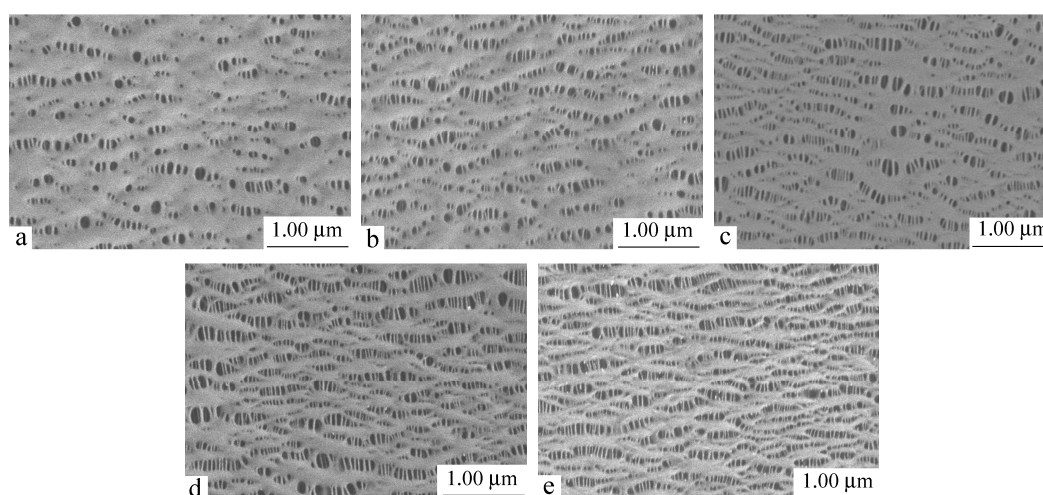


Fig. 6 Surface morphologies of the microporous membranes obtained by stretching (a) the as-extruded PP precursor film and films annealed at (b) 100 °C, (c) 120 °C, (d) 140 °C and (e) 155 °C

Permeability of the fabricated microporous membranes was evaluated by water vapor transmission rate (WVTR) under atmospheric conditions and the WVTR as a function of annealing temperature is displayed in Fig. 7. The permeability of a commercial battery separator (Celgard 2400) was also measured for comparison. It can be observed that thermal treatment of the PP precursor film improves greatly the permeability of the stretched membranes. The permeability increased with increasing annealing temperature. Higher permeability can be an indication of better interconnectivity between the pores in the microporous membranes as the tortuosity factor (*i.e.*, pore channel across the thickness) determines largely the WVTR^[8, 11]. The permeability results are also in accordance with the SEM results (Fig. 6), further confirming that higher annealing temperature causes more lamellae separation in the annealed precursor films. Annealing at 140 °C gives rise to a permeability of around 4.5×10^4 g/m²·day, which is comparable to that of the commercial membrane. Accordingly, it is preferable that annealing temperature of the PP precursor film should be 140 °C or more when fabricating PP microporous membranes used as battery separators.

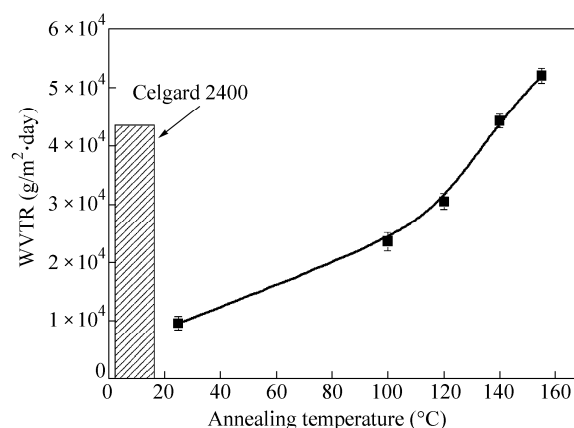


Fig. 7 Water vapor transmission rate (WVTR) of the PP microporous membranes as a function of annealing temperature

Based on the above discussion, it is clear that the microstructure and deformation behavior of the PP precursor films depend greatly on annealing temperature, consequently influencing the structure and properties of their stretched microporous membranes. Considering the structural evolution is also dependent on the duration of annealing, different annealing times at 140 °C were chosen to investigate its influence on the structure of the PP precursor films as well as the structure and properties of the microporous membranes in the following section.

Effect of Annealing Time

Figure 8 gives the crystalline orientation (f_c) as well as the crystallinity (X_c) as a function of annealing time for the PP films annealed at 140 °C. Both f_c and X_c show sharp increases as early as the first 5 min and then increase slowly to a plateau when the annealing time is around 10 min. Quick variations of the structural parameters upon annealing for PP have been reported by other researchers^[23, 30]. It is generally accepted that the structural variation with annealing time is involved with the secondary crystallization process, during which some new lamellae (*i.e.*, secondary lamellae) were formed between the primary lamellae^[23, 30, 31]. Thus, the results suggest 10 min is almost enough for completion of the secondary crystallization for the PP precursor films.

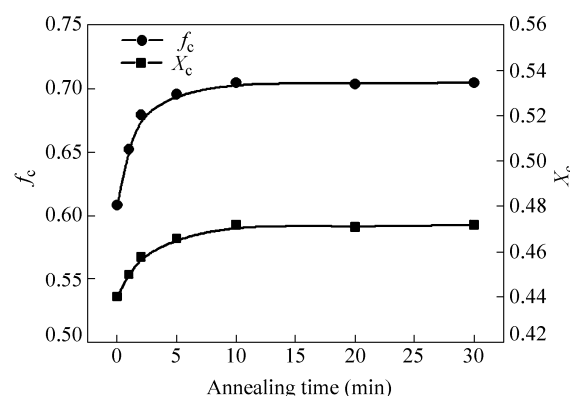


Fig. 8 Crystalline orientation (f_c) and crystallinity (X_c) and of the PP precursor films as a function of annealing time

Figure 9 presents the permeability of the stretched membranes obtained from the precursor films annealed at 140 °C for different times. It is observed that the permeability of the microporous membranes increases remarkably in the initial 5 min, and then attains slowly to an equilibrium value when the annealing time is up to 10 min. The surface morphologies of the membranes fabricated from the precursor films annealed at 140 °C for

0, 5, 10 and 30 min were examined as displayed in Figs. 10(a)–10(d), respectively. The pore number as well as its uniformity is greatly improved with increasing the annealing time from 0 min to 10 min. However, further annealing causes little change in the fabricated membranes. SEM results are in good agreement with the permeability results. Combining the results of Figs. 8, 9 and 10, it clearly demonstrates again the close relationship between the structure of the precursor films and the structure and the properties of their stretched membranes.

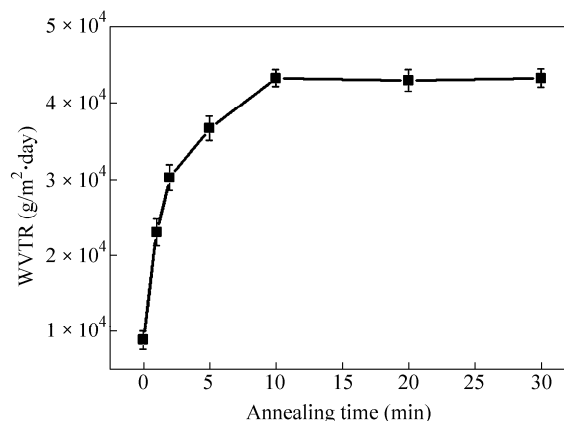


Fig. 9 Water vapor transmission rate (WVTR) of the PP microporous membranes as a function of annealing time ($T_{\text{an}} = 140\text{ }^{\circ}\text{C}$)

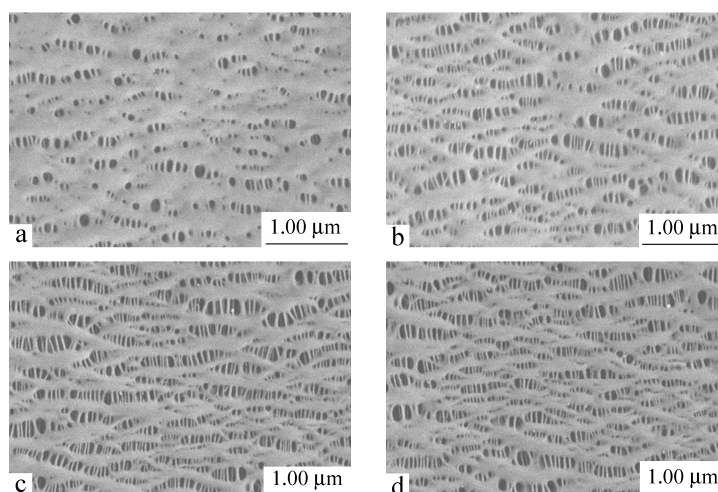


Fig. 10 Surface morphologies of the microporous membranes obtained by stretching the PP films annealed at $140\text{ }^{\circ}\text{C}$ for (a) 0 min, (b) 5 min, (c) 10 min and (d) 30 min

CONCLUSIONS

Combinations of WAXD, FTIR, DSC and DMA results clearly showed that the microstructure of the PP precursor film was further modified by the annealing process. Annealing led to more perfection of the crystalline region. Both the crystallinity and crystalline orientation of the precursor films increased with annealing temperature. Besides, annealing decreased the entanglements in the amorphous phase. Stretching the precursor films annealed at higher temperatures gave more lamellar separation instead of interlamellar slip as revealed by the changes in the deformation behavior. Examination of the surface morphologies by SEM showed more pore number and uniform porous structure were present in the stretched membranes annealed at higher temperatures. Water vapor permeability of the microporous membranes increased with annealing temperature. On the other

hand, variation of the crystalline orientation and crystallinity of the precursor film upon annealing took place rapidly and the most significant changes were almost completed within 10 min. Further, it is found that 10 min is almost enough for the annealing process to obtain microporous membranes with the optimal permeability.

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