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Effect of Annealing Temperature on PP Microporous Membranes Obtained by a Melt-Extrusion-Stretching Method

Isotactic polypropylene (iPP) precursor film with highly oriented lamellar structure was produced through a melt extrusion-annealing-uniaxial stretching (MAUS) process. The precursor films were annealed at various temperatures and the structure evolution of precursor films during various annealing temperatures and the pore formation of the annealed film during stretching were investigated. During annealing, recrystallized lamellar structure was formed to obtain “core-shell sandwich” structure. The thickness of newly formed lamellae increased with annealing temperature, which improved the ability of slipping resistance of the original lamellar structure during stretching. As the annealing temperature of precursor film increased, the micropore shape and diameter of the final membranes became more uniform. The porosity of the microporous membranes increased with increasing annealing temperature.

1 Introduction

Polymer-based microporous membranes are an important type of new functional materials which are widely used in water purification, battery separator (Arora and Zhang, 2004), biomedical separation (Cheng et al., 2018; Himma et al., 2016) and so on. After the first patent from Celanese in the 1970 s for the production of single-layer polypropylene microporous membranes by a melt extrusion-annealing-uniaxial stretching (MAUS) process (Bierenbaum et al., 1974), dry-stretching technique based on the stretching of polymer film or sheet containing row-nucleated lamellar structure has generally been industrialized and researched (Tabatabaei et al., 2008; Saffar et al., 2014; Li et al., 2018; Xiong et al., 2018). The effects of molecular weight and molecular weight distribution of resin, air cooling, chill roll temperature, and draw ratio on the row-nucleated lamellar structure and orientation of precursor film developed in PP cast films, and consequently on the micropore structure and mechanical properties of the resulting membranes after stretching stage, have been investigated (Tabatabaei et al., 2008; 2009;

Xu et al., 2018; Xu et al., 2015). Annealing the precursor film at temperatures near the melting point of the resin is the necessary and final stage of MAUS method for preparing polypropylene microporous films, where the orientation and the arrangement of row-nucleated lamella would be changed to improve the formation and uniformity of the micropores (Saffar et al. 2014; Lin et al., 2018; Wang et al., 2015).

Annealing time and annealing temperature are two important controlling factors. Mostly, 140 to 145 °C were selected by researchers to study the effect of annealing temperature on the microstructure of precursor film (Tabatabaei et al., 2008; 2009). During annealing the mobility of the chains in the interface of the crystal-amorphous regions and amorphous regions increases significantly. Incorporation of the segments of loose tie chains into the crystallites is probably induced, which results in an increase of lamellae thickness and an increase in the overall degree of crystallinity. Sadeghi et al. (2007) indicated that an efficient annealing time was 10 min at 140 °C; beyond 10 min the lamellar structure parameters (the thickness, orientation and the perfection of the lamellae) remained constant. In our previous report (Ding et al., 2013), the influence of annealing time at 135 °C on the orientation state, micropore formation and permeability was investigated. The results suggested that the orientation in the crystalline regions (f_c) and amorphous regions (f_{am}) and crystallinity (X_c) increased sharply with the annealing time mainly before 200 s, especially before 40 s. As the annealing time increased within 200 s, the f_c and f_{am} of precursor film increased, which is in favor of the increase of micropores number and pore size of the final membranes.

In the MAUS process, the annealing temperature is thought to be the most effective parameter in annealing to affect the lamellar structure and as well as f_c and/or f_{am} . Sadeghi et al. (2007) concluded that the annealing temperature highly improved the crystal phase orientation but had a much weaker effect on the amorphous phase. Rosova et al. (1996) suggested that the chain segments in the amorphous regions were drawn into the crystallites during annealing. The length of the polymer chains folds in the lamellae increased with the increase of annealing temperature, yielding a narrower length distribution of tie chains and larger number of stretched tie chains. Lee et al. (2006) proposed that the lamellar thickness tended to be larger and its distribution became broader as the annealing

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temperature increases. Lei et al. investigated the influence of annealing temperature on the row-nucleated lamellae and connecting bridge arrangement of PP membrane in the temperature range from 105 to 145 °C (Cai et al., 2015). They found that some weak secondary crystals were induced by annealing and the content of secondary crystals increased with the increase of annealing temperature. The secondary crystals induced by annealing converted to initial connecting bridges, which lead to the best connecting bridge arrangement for the membrane. Guo et al. (2015) reported that with the increase of annealing temperature the crystallinity and crystalline orientation of precursor films increased, accompanied by the decrease of the entanglements in the amorphous phase.

The research results have not summarized the law of the annealing-structure-property relationship of PP microporous membranes. From our previous studies of the optimum conditions (Liu et al., 2011) for preparing microporous membranes and the effect of the content of high molecular weight fractions on the porous structure and distribution (Ding et al. 2012), we have further studied the influence of annealing temperature on orientation of the lamellae and crystalline structure of the precursor films and, in turn, their effect on the membranes performance during the microporous membranes preparation. Then, a “core-shell sandwich” model was proposed to describe the annealing-structure-property relationship of PP microporous membranes.

2 Experimental

2.1 Material and Membrane Preparation

A commercially available isotactic polypropylene (iPP, PP5341E1) with melt flow rate of 0.5 g/10 min (230 °C/2.16 kg) and molecular mass $M_w = 680$ kg/mol ($M_w/M_n = 3.3$) was purchased from ExxonMobil (Irving, Texas, USA) and used as received. The molecular parameters were measured by gel permeation chromatography (GPC, PL-GPC200) at 150 °C, with 1,2,4-trichlorobenzene as a solvent.

The precursor films were prepared by cast film processing through a single screw extruder (SJ-20BX25, Shanghai Kechuang Rubber Plastic Machinery Set, Shanghai, PRC, $D = 30$ mm, $L/D = 34$, where D is the diameter of the screw and L is the length of the screw) equipped with a slit die (1.8~0.1 mm thick and 100 mm width), three roller traction machine and a drying oven. The temperatures of the three sections of the single-screw extruder and the die were 190 °C, 210 °C, 230 °C and 225 °C, respectively, and the screw speed of the extruder was 40 min⁻¹. To improve cooling, two fans were installed to supply air to the film surface right at the exit of the die. The gas flow rate of each fan was 3 l/s. Precursor films with the melt traction ratio of 90 ($DR = V_{draw}/V_{extrude} = 60$, where V_{draw} is the three-roll tractor drawing line speed and $V_{extrude}$ is the melt extrusion velocity) were obtained.

Following extrusion and drawing the precursor films were cut into rectangle-shape samples of 0.5 × 2 mm² and then the samples were annealed thermostatically in an oven at various temperatures (80, 90, 100, 120, 130 and 140 °C) for 30 min for the subsequent stretching process.

A universal testing machine (AGS-J, Shimadzu, Kyoto, Japan) equipped with a temperature control chamber was used

for stretching the annealed films. There were two steps of the stretching process: first of all, the annealed samples were cold stretched 40 % at 25 °C with a stretching speed of 200 mm/min; secondly, the samples were stretched again by 40 % with a stretching speed of 20 mm/min after the temperature was elevated to 120 °C. Cold stretching led to lamellar separation and pore creation, while the following hot stretching led to pore elongation. Finally, the microporous membranes were obtained by heat setting with clamping state at 120 °C for 20 min after the hot stretching.

2.2 Characterization

The infrared spectra were recorded on a Nicolet 6700 FTIR instrument (Thermo Electron Corp., Madison, USA) in the range 400–4000⁻¹ in the transmission mode, with a frequency resolution 4 cm⁻¹ and accumulation of 16 scans. If the films are oriented, the absorption of plane-polarized radiation by a vibration in two orthogonal directions, specifically parallel and perpendicular to a reference axis (machine direction), should be different (as shown in Fig. 1A). The dichroic ratio (D) is defined as $D = A_{//}/A_{\perp}$, where $A_{//}$ is the absorption parallel and $A_{\perp}$ is the absorption perpendicular to the specific reference axis (Tabatabaei et al., 2007; 2008; 2009). The Herman orientation function of this vibration is obtained according to $f = (D - 1)/(D + 2)$. For polypropylene, absorption at the wavenumber of 998 cm⁻¹ is attributed to the crystalline phase (c-axis) while that at 972 cm⁻¹ is due to the contribution of both crystalline and amorphous phases (Sadeghi et al., 2007). The absorption peak with wavenumber 998 cm⁻¹ was used to calculate f_c , along the MD, of the samples annealed at various temperatures.

The thermal properties of the specimens annealed at different temperatures for 30 min were analyzed using a differential scanning calorimeter (DSC TA Q20, Cranston, Rhode Island, USA) in a nitrogen gas atmosphere. Samples were heated from 50 to 220 °C at a heating rate of 10 °C/min.

A field emission scanning electron microscope (Inspect F, FEI Company, Cambridge, USA) was employed to examine the surface morphologies of the stretched samples. The accelerating voltage was 10 kV and the samples were gold coated before observations.

The liquid absorption method (ASTMD-2873) was used to detect the porosity (ϵ) of the microporous membranes based on three steps:

1. weighing the microporous membranes ($m_{\text{microporous membranes}}$);
2. dipping the microporous membranes in hexadecane for 1 h;
3. weighing the sample after wiping the surface by filter paper ($m_{\text{microporous membranes}} + m_{\text{hexadecane}}$).

The porosities (ϵ) of the microporous membranes were obtained according to:

$$E = (m_{\text{hexadecane}}/\rho_{\text{hexadecane}})/(m_{\text{microporous membranes}}/\rho_{\text{polymer}} + m_{\text{hexadecane}}/\rho_{\text{hexadecane}}) \quad (1)$$

where $\rho_{\text{hexadecane}}$ and ρ_{polymer} are the densities of hexadecane and polymer, respectively.

A Shimadzu AGS-J universal testing machine was used for the tension test. Strain rates of 30 mm/min were utilized during tensile tests. The samples were tested at 25 °C.

3 Results and Discussion

3.1 Effect of Annealing Temperature on the Lamellar Structure of the Precursor Films

Figure 1 shows the changes of the orientation parameter in the crystalline regions (f_c) of the precursor films annealed at various temperatures ranging from 80 to 140 °C. The inset image exhibits an enlarged view of the first 200 s of the curves. The orientation of the samples annealed at the various temperatures increased with the increasing annealing time up to ca. 1000 s. Especially, during the annealing time of 20 s to 200 s, the f_c of each sample increased with increasing annealing time and le-

veled off beyond 1000 s. It is notable that the growth rate and the stable values of f_c grew with the increase of the annealing temperature, especially for the samples annealed at 130 °C and 140 °C. Obviously, the annealing temperature had a greater positive effect on the final f_c of the annealed precursor film than the annealing time. When the annealing temperature increased, larger movement units in the iPP molecular chains would be triggered to obtain more perfect lamellar structure which contributed to the increase of orientation of the lamellae.

To detect the changes of the crystalline structure, the annealed films with the various annealing temperatures were investigated by DSC and the results were shown in Fig. 2. The inset is a vertical enlargement of the curves inside the dotted box.

Fig. 1. The decomposition of the band between 945 to 1030 cm^{-1} of iPP (A) and the changes of the orientation parameters (f_c) of the precursor films annealed at various temperatures (B)

Fig. 2. The DSC curves of the unannealed film and the films annealed at different annealing temperatures for 30 min

From Fig. 2, the positions of the main melting peak (T_m , about 165°C) of samples did not change with the increase of annealing temperature. Significantly, a slight shoulder appeared at lower temperature (T_m') for the annealed films, attributed to the formation of imperfect lamellae during annealing. The newly formed lamellae were thought to come from the arrangement of tie chains in the amorphous phase. With increasing annealing temperature, the shoulder peak at lower temperature became prominent, meaning the T_m' of newly formed lamellae increased as the annealing temperature increased.

The lamellar thickness (L) can be obtained from DSC data using the Thomson–Gibbs equation (Valles-Lluch et al., 2003; Włochowicz and Eder, 1984):

$$L = \frac{2\sigma_e}{\Delta H_m^0} \frac{T_m^0}{T_m^0 - T_m} \times 10^9. \quad (2)$$

For iPP the free fold surface energy σ_e and the equilibrium melting point of the 100% crystalline material T_m^0 are assumed to be 0.07 J/m^2 and 460.65 K , respectively (Clark et al., 1984). The heat of fusion per unit volume ΔH_m^0 was calculated from the heat of fusion of an ideally crystalline sample ($\Delta H_m^0 = 207 \text{ J/g}$) (Clark et al., 1984) on the basis of the density of perfectly crystalline iPP, $\rho_c = 936 \text{ kg/m}^3$ and T_m (or T_m') was the melting temperature as derived from the DSC experiments. The thickness of the original lamellae and the newly formed lamellae of the annealed films at different temperatures, based on Eq. 2 using the T_m and T_m' from Fig. 2, respectively, are listed in Table 1.

The total crystallinities (X_c) of iPP precursor films without and with annealing are calculated using the relationship:

$$\text{Crystallinity} = (\Delta H_m / \Delta H_m^0) \times 100\%, \quad (3)$$

where ΔH_m is the observed heat of fusion and ΔH_m^0 is 207 J/g . The X_c results were also listed in Table 1.

From Table 1, the original crystalline lamellae were not thickened and broadened after annealing. Also, with the increase of the annealing temperature, even annealing at 140°C , the thickness of the original lamellae and distribution of lamellae thickness remained the same. So, the increase of overall crystallinity of annealed film was assigned to the formation of imperfect lamellae during annealing. The thickness and the perfection of the newly formed lamellae continuously increased with the increase of the annealing temperature (Ta-

ble 1), which also induced a continuous increase of the overall crystallinity of the samples. At the annealing temperature (80 to 140°C), molecules in amorphous phase had enough energy to rearrange and fold, leading to the growth of imperfect lamellae. When the annealing temperature was higher, the movement of longer units of molecular chains was triggered. And enhancing movement units would result in the increasing and the thickening of newly formed lamellae.

3.2 Effect of Annealing Temperature on the Tensile Deformation Behavior of the Precursor Films

During the annealing process, the orientation, crystallinity and the thickness of the newly formed lamellae increased. Changes in the structure of the lamellae would have impacts on the mechanical properties of the specimens. From our previous discussion (Ding et al., 2013), during annealing at 135°C for different times, a significant decrease of the yield stress and elastic modulus of the annealed films took place during the first 40 s . After the uniform elastic deformation area, the slopes of each curve were significantly different, especially for the films annealed less than 40 s . Thus, our interest was in the effect of annealing temperature on the tensile deformation behavior of the precursor films. Figure 3 shows the typical stress-strain behavior of the original precursor film and the annealed films along MD direction. All samples showed the typical hard elastic stress-strain characteristics of films of a raw-lamellar morphology. For the unannealed film, an initial elastic response at low deformation followed by one strain hardening zone was obtained, and the stress ($\sigma_{y,u}$) was almost 90 MPa where the transition from elastic response to the strain hardening zone happened.

Obviously, the stresses at the transition point for the annealed samples and the elastic modulus gradually decrease with increasing annealing temperature. Comparing with the stress-strain curve of the unannealed sample which had only two evident stress increase stages (OA and AD), all the annealed films showed three significant stress increase stages. For example, the three significant stress increase stages for the film annealed at 140°C were OB, BC and CD, respectively. The different stress growth areas corresponded to the response

Annealing temperature $^\circ\text{C}$	Melting peak at lower temperature (T_m') $^\circ\text{C}$	Thickness of the newly formed lamellae μm	Thickness of the original lamellae μm	Crystallinity (X_c)
unannealed	—	—	18.88	43.74
80	91.1	3.57	18.62	43.90
90	103.8	3.92	18.41	44.09
100	111.1	4.61	18.66	46.09
110	112.8	4.73	19.43	49.76
120	125.6	5.81	18.96	50.53
130	135.2	6.91	18.67	51.44
140	147.2	8.65	18.92	51.72

Table 1. The crystallization properties of the precursor film and annealed films

of the different structural units. Thus the formation of the new lamellar structures and the changes of f_c in the annealing process were the reasons for the variation of the stress-strain curves of annealed samples, as described below.

The amorphous phase and the tie chains in the precursor film bear the main load during the elastic deformation process. After the majority of tie chains become incorporated in the new crystallites during annealing, the amorphous moiety of the sample appeared to be depleted. So, compared to the unannealed film, the σ_y and elastic modulus of the annealed films decreased and the decreasing of the σ_y became more obvious with the increase of the annealing temperature. Compared with the strain-stress curve of the unannealed precursor film, the strain-stress curves of the annealed films immediately switched into the region with a higher slope (BC). The significant difference for the precursor films annealed at different temperatures was caused by the deformation mode of the lamellar structure in the stretching process. A large number of perfect and thick newly formed lamellae could better toughen the original lamellae and fully protect the original lamellae from separation during stretching. In addition, the increasing

number and the thickness of the newly formed lamellae mean the reduction of the amorphous content. The decrease of amorphous content would weaken the mechanical strength of the amorphous regions which was also beneficial to the separation of lamellae and the formation of micropores. The improvement of f_c resulting from recrystallization could promote the deformation mode of lamellae to transform from twisting, bending, and slippage into separation which was beneficial for the pore formation during stretching.

3.3 Effect of Annealing on the Performance of the Microporous Membranes

After annealing at different temperatures for 30 min, the precursor films were stretched at 25 °C and 120 °C to create and enlarge pores, respectively. Then the microporous membranes were obtained by heat setting at clamping state at 120 °C for 20 min after the hot stretching. Figure 4 shows the photo of microporous membranes made from the precursor films which had experienced different annealing temperatures. Due to the

Fig. 3. Stress-strain curves of unannealed film and precursor films annealed at different annealing temperatures for 30 min

Fig. 4. Microporous membranes made from annealing films with different annealing temperatures (a) 80 °C, (b) 90 °C, (c) 100 °C, (d) 110 °C, (e) 120 °C, (f) 130 °C, (g) 140 °C for 30 min annealing time

scattering of natural light in the microporous structure of the membrane, the transparency of the samples can qualitatively describe the number of pores and porosity. The greater the number of micropores in the membranes the whiter it would be and, as a consequence, the larger the porosity and permeability of the microporous membranes. The microporous membranes prepared from precursor films annealed at low temperatures were translucent. With the increase of annealing temperature of the precursor films, the microporous membranes became more and more white, and the degree of necking of the samples reduced markedly. When the annealing temperature of the precursor films was higher than 110 °C, microporous membranes became completely opaque.

In order to detect the effect of annealing temperature on the pore structure of the microporous membranes, SEM was used to observe the surface morphology of each specimen, as shown in Fig. 5. The number of pores on the surface of the microporous membranes increased with increasing annealing temperature. Meanwhile, the pore size increased and the distribution of pore size narrowed down. The porosity of the microporous membranes, shown in Fig. 6, corresponds to the results of Figs. 4 and 5. The porosity of the microporous membrane increased with increasing annealing temperatures of the precursor films. When the annealing temperature was higher than 110 °C for the precursor film, the porosity of the resultant membranes exceeded 30%. When the annealing temperature varied from 110 °C to 140 °C, the growth rates of the porosity and pore size of the obtained membranes were slow down with the increasing annealing temperature. In addition, the uniformity of the micropores had a slight enhancement when the annealing temperature increased within the region of 110 °C to 140 °C.

Based on the discussion above, the micropores membrane obtained by the precursor film being annealed from 110 °C to 140 °C possessed superior performance. The improvement of the pore structure was the result of preventing a large degree of twisting, bending, and slippage of lamellae during stretching. It meant that the effective transformation of the lamellar deformation mode occurred at 110 °C. Meanwhile, the microporous membrane obtained by the precursor film being annealed at 140 °C possessed the most perfect micropores struc-

ture. This is why many researchers (Tabatabaei et al., 2008; 2009; Cai et al., 2015) choose 140 °C as their annealing temperature.

3.4 Discussion

The results in this study improved the “core-shell sandwich” structure model that we have previously described (Ding et al., 2013). As shown in Fig. 7, the unannealed precursor film is composed of stacked lamellae and amorphous regions. During annealing, the molecular chains (including tie chains, tail chains, and loop chains) in the interface between the amorphous regions and the lamellae were the most likely to crystallize. The newly formed lamellae were attached on both sides of the original lamellae to create a “core-shell sandwich” structure. When the annealing temperature increased, more chains in the amorphous regions folded into the crystal lattice, which

Fig. 6. The porosity (ϵ) of the microporous membranes made from annealed films with different annealing temperatures

Fig. 5. SEM images of microporous membranes made from annealing films with different annealing temperatures (a) 80 °C, (b) 90 °C, (c) 100 °C, (d) 110 °C, (e) 120 °C, (f) 130 °C, (g) 140 °C for 30 min annealing time

Fig. 7. Sketch of the structure of lamellae developing during annealing

induced higher content and thickening of newly recrystallized lamella. The newly recrystallized lamella became more perfect with the increase of the annealing temperature, especially in the temperature ranging from 110 °C to 140 °C. It can be concluded that the higher the annealing temperature was, the thicker the newly formed lamellae and the more perfect “core-shell sandwich” would be.

4 Conclusions

The precursor film was prepared by film extrusion and then annealed at various temperatures for various times. The growth rate of orientation of the annealed precursor film (f_c) increased with the increase of the annealing temperature, especially for the samples annealed at 130 °C and 140 °C. The thickness of original lamellae remained unchanged during annealing, while the thickness of the newly formed lamellae attached on both sides of the original lamellae, increased with increasing annealing temperature. When the annealing temperature was higher than 110 °C, the newly crystallized lamellae prevented a large degree of twisting, bending, and slippage, the lamellar structure mainly separated along the MD direction. Then, relatively perfect slit-like micropores formed between the separated lamellar structures, which could be proved by the increase of the number of pore structures, the pore size, and the porosity of the microporous membranes with the increasing initial annealing temperatures, especially from 110 °C to 140 °C. These results showed the effect of annealing temperature on the recrystallization and “core-shell sandwich” structure model, which could explain the microstructural changes of the precursor film during annealing and the pores formation in the samples under stretching.

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