The Study of Room-temperature stretching of Annealed Polypropylene Cast Film with Row-nucleated Crystalline Structure

Chen Xiande ^a, Xu Ruijie ^{a,*}, Xie Jiayi ^a, Lin Yuanfei ^b, Lei Caihong ^{a,*}, Li Liangbin ^b

a. Guangdong Provincial Key Laboratory of Functional Soft Condensed Matter, School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, PR China

b. National Synchrotron Radiation Lab and College of Nuclear Science and Technology, CAS Key Laboratory of Soft Matter Chemistry, University of Science and Technology of China, Hefei 230026, China

E-mail: lch528@gdut.edu.cn, xu565786@163.com

Abstract: The room-temperature stretching process of polypropylene annealed film with row-nucleated crystalline structure was studied by in-situ small-angle X-ray scattering (SAXS) setup and off-line wide-angle X-ray scattering (WAXS), temperature-modulated differential scanning calorimetry (TMDSC) and stress-strain curves testing. The formation process of initial connecting bridges and pores was clarified. For the annealed film, except for the initial lamellae structure, the recrystallized part formed by the melting and crystallization of imperfect crystals during annealing, tie chains connecting the lamellae structure among the amorphous region, secondary crystals from the crystallization of tie chains during annealing and daughter crystals from the special cross-hatched crystalline structure of PP coexist. It was found that 10 % stretching lead to the pronounced increase of long period and the appearance of a few initial connecting bridges. The stretching of daughter crystal and recrystallized part contributed to the formation of initial bridges. At stretching ratio of 30 %, uniform distributed connecting bridges were observed and the stretched film showed maximum structure periodicity. At this stretching ratio, except for the stretching of daughter crystal, the stretching of tie chains and secondary crystals within the amorphous region lead to the formation of more connecting bridges. At higher stretching ratios into the strain-hardening region and beyond the second yield point, except for the stretching of the above mentioned crystalline

and amorphous structure, the stretching of mother lamellae occurred and lamellae deformation was inevitable, resulting in lower structure periodicity. During room-temperature stretching, the pores were formed progressively and the stretching ratio of 30 %, situated at the transition point from plastic plateau to strain-hardening region in the stress-strain curves, was appropriate for the initiation of pores.

Keywords: melt-stretching mechanism, microporous formation, row-nucleated crystalline structure

1. Introduction

Based on melt-stretching mechanism ^[1], polypropylene (PP) microporous membrane has been successfully fabricated and used as a separator in the field of Lithium ion battery. The fabrication process mainly covers three stages: ^[2,3] (1) production of the precursor film with prerequisite row-nucleated lamellar crystalline structure, (2) annealing to thicken the lamellae and improve lamellae orientation and uniformity, (3) stretching of the film at room temperature for pores creation and then at high temperature to enlarge the pores. After these, the heat-setting is carried out to improve the dimensional stability of stretched microporous membrane. There have been detailed works about the influence of the physical properties of raw materials, applied cast processing conditions and annealing technology on the crystalline properties and stretched pore structures ^[4-13]. However, as to the pore initiation process during room-temperature stretching, few works have been carried out to clarify how the initial pores are formed.

In the works by Carreau group in the field of PP microporous membrane, the room-temperature stretching ratio was set at 35-40 % ^[7-11], based on the direct comparison of structure and properties of stretched microporous membrane. In our previous work ^[14-16], to follow the changes induced by room-temperature stretching, the room-temperature stretched films were heat-set at 145 °C for 10 minutes to decrease their shrinkage. This is since the

annealed films show higher elastic recovery and the stretched film by only room-temperature stretching will recover to its unstretched state after the stretching stress is relieved. Compared with that of precursor film, the pronounced changes after annealing were the appearance of plastic plateau region in the stress-strain curve and an endotherm plateau in the differential scanning calorimetry (DSC) curve, which were related to the occurrence of secondary crystallization behavior from tie chains during annealing. It was found that when the room-temperature stretching ratio was set around the transition point from the plastic plateau region to strain-hardening region in the stress-strain curve of annealed film, the endotherm plateau in the DSC curve and the plastic plateau in the stress-strain curve disappeared, and the corresponding microstructure showed initial pores among the separated lamellae. Then it was proposed that the secondary crystals formed during annealing were transformed to the initial pores during the stretching process. Sadeghi et al. ^[8] summarized that the following phenomena took place simultaneously during room temperature stretching: void formation as a result of short tie chain scission, crystal block slipping and their reorienting along the stretching direction, stretching of longer tie chains as shorter tie chains were broken apart and crystallization of highly stretched long tie chains. Here, the pore initialization was attributed to the stretching and scission of short tie chains. Matsui et al. ^[17] used time-resolved simultaneous wide- and small-angle X-ray scattering measurements to follow the cold stretching process. The result showed that the voids appeared after the amorphous region were stretched, at the same time, the lamellae crystals were deformed by bending. Lin et al. ^[18] believed that the orientation degree of lamellae crystals and thickness of amorphous region in the precursor film were the main reasons affecting pores formation.

Generally, annealing is carried out at temperature around 145°C. At this high temperature, some imperfect lamellae existing in the precursor film can be melted and recrystallized to more perfect crystals. At the same time, the tie chains among the amorphous region will crystallize through secondary crystallization. It is believed that the former

behavior stabilizes the initial lamellar structure. In addition, for PP, the mother-daughter crystal phenomenon (i.e. cross-hatched crystal structure) naturally occurs. For this unique mother-daughter crystal structure, the daughter lamellae grow epitaxially on the (010) plane of mother lamellae at approximately 80° ^[19]. This special mother-daughter assembly actually enriches the basic deformation mechanism^[20,21]. Nozue et al.^[22] pointed out that during the deformation process of spherulite, the amorphous chains were elongated at first and then disordering of parent lamella crystals along a-axis and rotation of daughter lamellae were followed by fragmentation along perpendicular direction, whereas along the parallel direction, at the initial stage disordering of crystals occurred along a-axis, subsequently rotation of parent lamellae were followed by rotation of daughter lamellae. It is obvious that the existing daughter crystals significantly affect PP properties.

In the annealed film with row-nucleated crystalline structure, initial main lamellae, recrystallized region from imperfect lamellae, secondary crystallization from tie chains, daughter crystal and tie chains in the amorphous region coexist. This will complicate the stretching behavior of annealed film and the pore initiation process during room temperature stretching. In addition to the above mentioned relationship among secondary crystallization, short tie chains and the initialed pores, we want to know what will happen to the recrystallized region from imperfect lamellae and the daughter crystals during room temperature stretching. Is there any relationship among them and the pore initialization? This paper monitors the stretching process of annealed PP films with row-nucleated crystalline structure under room temperature. The changes in crystalline structure and tie chains content were characterized. The pore formation process during room temperature stretching was discussed.

2. Experimental

2.1. Material

A homo-polypropylene resin with a melt flow rate value of 2.0 g/10min (under ASTM D 1238 conditions of 230 °C and 2.16 kg) from Yangzi petrochemical company, China, was used. The melting peak point (T_m) and crystallinity, obtained from differential scanning calorimetry (DSC; PerkinElmer DSC, Massachusetts, United States) at a rate of 10 °C/min, were 164.2 °C and 39.0 %, respectively. The reported crystallinity results were obtained using a heat of fusion of 209 J/g for fully crystalline PP [7]. The weight-average molecular weight and polydispersity index, measured using a GPC (Viscotek model 350) at 140 °C and 1,2,4-trichlorobenzene (TCB) as a solvent, were about 754 kg/mol and 6.29, respectively. The xylene soluble content at room temperature was less than 4 %.

2.2 Annealed and stretched film preparation

The precursor film was prepared by cast extrusion through a T-slot die followed by stretching and thermal-setting. During extrusion, the uniaxial (machine direction, MD) stretching was applied to PP melt, which resulted in the oriented crystalline structures. The die temperature was set at 210 °C and a draw ratio of 125 was applied. The draw ratio was determined by the take-up speed, since the extrude velocity at the exit of the die was constant. The films were produced at chill roll temperature of 80 °C. Then the prepared precursor film was annealed for 30 min at 145 °C in a hot oven to obtain the annealed film. The thickness of annealed film is 25 μm .

To follow the microstructure change during room-temperature stretching, the annealed film was also stretched using an Instron 5500R machine equipped with a heating chamber to different ratios at $50\mu\text{ms}^{-1}$ and then the stretched structure was kept by heat-setting the films at 145 °C for 10 min to avoid the shrinkage of the film. Figure 1 shows the stress-strain curve of annealed film during room temperature stretching. The stretching ratios were set at 10 %, 20 %, 30 %, 50 % and 110 %, respectively. The former two ratios were within the plastic plateau region. 30 % stretching ratio was around the transition point from plastic plateau

region to strain-hardening region. 50 % was within the strain-hardening region, whereas 110 % was beyond the second yielding point. The thickness of film stretched to 110% is around 22 μm .

Figure 1 The stress-strain curve of annealed film during room-temperature stretching

2.3 In-situ Small-angle X-ray scattering

The in-situ room-temperature stretching process was carried out in the stretching machine appended in the small-angle X-ray scattering (SAXS) setup. The SAXS measurements were made using an in-house setup with a 30 W micro x-ray source (Incoatec, GmbH), providing highly parallel beam (divergence about 1 mrad) of monochromatic Cu K_{α} radiation ($\lambda=0.154$ nm). The scattering intensity was collected by a multiwire proportional chamber detector (Bruker Hi-star) with a resolution of 1024×1024 pixels (pixel size of 105 μm). The distance between sample and detector was 2280 mm. The initial sample length was set at 10 mm and due to the limitation of stretching setup, the stretching rate was set at 50 $\mu\text{m s}^{-1}$. The scattering signal was collected every 10 s.

2.4 Wide angle x-ray scattering (WAXS)

WAXS was carried out on the X-ray-scattering station with Mar 345 image plate (3070×3070 pixels with pixel size 150 μm) as a detector and with a wavelength of 0.154 nm

in National Synchrotron Radiation Laboratory in Hefei (China). The sample-to-detector distance was calibrated to be 299 mm, and the data acquisition time for each frame was 300 s.

2.5 Temperature-modulated Differential scanning calorimetry (TMDSC)

A TA Instruments temperature modulated DSC Q2000 (TA, USA) was used for temperature-modulated differential scanning calorimetry (TMDSC) studies. The measurements were performed with a heating rate of 2 °C/min having a period of 60 s and amplitude of 0.5 °C. In order to maximize the signals, a specimen weights around 8 mg was used. All the measurements were performed under dry nitrogen atmosphere.

2.6 Scanning electron microscopy

The surface morphology was characterized by scanning electron microscopy (SEM; S3400N, Hitach, Japan). All the samples were sputtered with a platinum ion beam for 300 s before test.

2.7 Stress-strain curve

The engineering stress-strain curve of films that have been stretched to different ratios was tested using Instron 5500R machine at a deformation rate of 50 μms^{-1} . The original length of the sample between the Instron clamps was 50 mm.

2.8 Porosity

The porosity was measured using liquid absorption methods according to ASTM D-2873. The paraffin oil was used and the porosity was calculated based on the weight difference before and after immersion in the liquid.

Results and Discussion

3.1 Microstructure change during room-temperature stretching

Figure 2. SEM of annealed film stretched to different ratios at room temperature

Figure 2 shows the SEM of precursor film, annealed film, and stretched films to different ratios at room temperature. On the etched surface of precursor and annealed film, no spherulites could be observed and only row-nucleated lamellae structure appears. After annealing, the lamellae crystals are thickened obviously. At stretching ratio of 10 %, few pores are observed. More bridges connecting the separated lamellae and pores are initiated by stretching ratio to 30 %. Although higher stretching ratio initiates more connecting bridges, the deformation of separated lamellae is apparent. The SEM results prove that the initial connecting bridges are formed progressively and beyond the transition point from plastic plateau region to strain-hardening region in the stress-strain curves of annealed film, the deformation of separated lamellae is inevitable.

3.2 In-situ SAXS change during room-temperature stretching

Figure 3 SAXS patterns of precursor film, annealed film and stretched films under room-temperature, MD is the machine direction

Figure 4 The secondary signal intensity during room-temperature stretching.

To follow the structure change during stretching at room temperature, in-situ SAXS testing was carried out. Compared with the study of films that have been stretched to different ratios and heat-set to escape the shrinkage and to keep the stretched structure, during the in-situ SAXS testing, the heat-setting influence could be deleted. **Figure 3** gives the SAXS patterns of precursor film, annealed film and stretched films under room-temperature. For the

precursor film, only two teardrop shape patterns along equatorial direction can be observed. This means the existence of oriented crystalline structure in the precursor film ^[7]. After annealing, two equatorial scattering patterns move close to the beam, indicating the thickness increase of lamellae crystals. In addition, the second order scattering pattern along equatorial direction appears, indicating that the annealed film shows some higher periodicity ^[23]. In Figure 3, some weak scattering signals in the meridional direction emerge at the stretching ratio of 10 %, indicating that some new scattering structure perpendicular to the equatorial direction is formed during stretching, and these signals become strong with the increase of stretching ratios. The above SEM results show that some new connecting bridges and initial pores are formed during stretching. These structure contributes to the appearance of meridional signal. The improvement of meridional signal indicates that more connecting bridges and pores are formed.

Figure 4 gives the secondary signal intensity during room-temperature stretching. Here, the pore information is along the meridional direction. As mentioned in the experimental part, the thickness of stretched film is only decreased from 25 μm of precursor film to 22 μm after stretching to 110%. The second order scattering pattern is along equatorial direction. Hence, the effect of thickness and pore on the scattering intensity along equatorial direction can be neglected. The secondary signal is related to the structure periodicity. In Figure 4, it is surprising to find that with the increase of stretching ratio to 30 %, the secondary signal intensity increases. The stretched film shows higher signal compared with that of unstretched film. This indicates that small room-temperature stretching improves the structure periodicity, due to the occurrence of possible lamellae slipping. The similar situation was also reported by Matsui et al. ^[17] that the integrated intensity of SAXS profile along the stretching direction was increased at initial stretching stage. At stretching ratio of 30 %, the lamellar structure shows maximum periodicity. By further stretching to 130 %, the secondary signal decreases,

meaning that higher stretching ratio deteriorates the lamellae periodicity, in agreement with the above SEM results. Combined with the SEM results, it can be deduced that at the stretching ratio of 30 %, some connecting bridges appear and the possible lamellae slipping improves the periodicity, but at higher stretching ratio, although more connecting bridges are formed, the periodicity becomes worse.

Figure 5 the scattering intensity distribution curve along equatorial direction for films stretched to different ratios

Figure 5 gives the scattering intensity distribution curve along equatorial direction for films stretched to different ratios. The scattering intensity was integrated along the equatorial direction using sector integration. Before integration, the instrument background was subtracted considering sample absorption. In the one-dimensional scattering intensity distribution, no multiplication q^2 to $I(q)$ is performed because of the anisotropic orientation of the lamellae in the samples, where q is the scattering vector^[16],

$$q = 4\pi \sin \theta / \lambda$$

λ is the X-ray wavelength and 2θ is the scattering angle. The scattering peak moves to lower q value, indicating the increase of long period, which is estimated from the position of the

intensity maximum according to Bragg's law,

$$L = 2\pi / q$$

Table 1 lists the long period values. It can be seen that with the increase of stretching ratio, the long period increases. The above SEM results show that during stretching initial pores between the separated lamellae clusters within the amorphous region appear. The separated lamellae clusters are composed of 5-7 layers unseparated long period structure. [25] For crystalline polymers, the long period is the summation of crystalline thickness and amorphous thickness. The increase of long period can be used to reflect the pore formation process. 10 % stretching ratio induces pronounced increase of long period, indicating the appearance of initial connecting bridges and pores. However, within the stretching ratio of 10 % to 30 %, the increase percent of long period becomes small. Although here more connecting bridges are initiated, the average increase of long period is small.

Table 1 The long period (L) values during stretching

Stretching ratio [%]	0	10	15	20	30	40	50	70	90	110
L [nm]	15.83	20.01	20.48	20.68	21.4	22.32	24.18	26.96	29.21	30.37

3.3 2D-WAXS of stretched films to different ratios at room-temperature

Figure 6 The WAXS images for annealed film and stretched films to different ratios at room temperature

The above SEM and SAXS results both indicate that within the plastic plateau region the initial connecting bridges are initiated. The α crystal of PP shows specific mother-daughter crystalline structure. To clarify the relationship between the daughter crystal and initial connecting bridges, the WAXS testing of stretched films to different ratios was carried out. In the WAXS patterns shown in Figure 6, five lattice planes representing the α -crystals of PP from the inner to outer circles indexed as (110), (040), (130), (111), and (041) are clearly visible. As the most stable crystal form of PP, α -crystals exhibit a unique lamellar branching structure, as shown in Figure 6, in which the tangential (daughter) lamellae grow epitaxially on the (010) plane of parent lamellae at approximately 80° [19,26,27]. For the α (110) diffraction in the WAXS pattern, mother lamellae stacks scatter along the equator, while branched lamellae lie approximately $\pm 10^\circ$ off the meridian.

In an effort to clearly elucidate the intensity changes of main lamellar crystals, the azimuthal scan of (110) lattice plane as a function of azimuthal angle at different strains are displayed in Figure 7. The diffraction peak intensity change of mother and daughter crystal from lattice planes (110) are shown in Figure 8. The peaks of (110) lattice plane originating from mother lamellae locate at 0° and 180° , while those of (110) lattice plane from daughter lamellar crystals at about $\pm 10^\circ$ off 90° and 270° in the annealed film. The mother and daughter crystal diffraction intensity is decreased a little when stretching after yielding point. Within the plastic plateau zone, the mother crystal intensity does not show apparent change, but the daughter crystal intensity is obviously reduced. Within the strain-hardening zone, the mother and daughter crystals are simultaneously damaged. The crystal numbers affect the diffraction intensity [28]. Apparently, the number of daughter crystal is reduced earlier than mother crystal, in other words, the daughter crystals are destroyed before mother crystals.

Figure 7 The azimuthal-integrated intensity of 110 crystallographic plane of films stretched to different ratios at room temperature

Figure 8 The diffraction intensity change of mother crystal and daughter crystal and the stress-strain curve

To clearly characterize the daughter crystal change, its relative content was calculated based on Fujiyama's method ^[29]:

$$[A^*] = \left[\frac{A^*}{C + A^*} \right]$$

where C representing mother lamellae is taken as the area from azimuthal angle 45°-135° and A* representing daughter lamellar crystals is taken as the area from 135° to 225° in Figure 6

after subtraction of the baseline. The relative content of daughter crystal is shown in Figure 9 as a function of strain. The relative content of daughter crystal decreases from 45 % for annealed film to 29 % for the film stretched to 10 %. Within the stretching ratio from 10 % to 30 %, the relative content only decreases to 22 %. It can be seen that 10 % stretching induces pronounced decrease of daughter crystal content. As mentioned above, 10 % stretching ratio induces pronounced increase of amorphous region thickness, which is related with the formation of initial connecting bridges. Based on this, it can be deduced that the decrease of daughter crystal within stretching ratio of 10 % contributes to the formation of initial connecting bridges. Higher stretching ratio induces further decrease of daughter crystal content to be less than 10 %.

Figure 9 The relative content of daughter crystals at different stretching ratios

One-dimensional WAXS intensity will show more detailed information about crystal deformation during stretching. Thanks to the mask function of Fit2D software, 1D WAXS intensity can be displayed for mother crystal and daughter crystal separately in Figure 10. For the mother crystal (Figure 10(a)), the main diffractions are observed at 2θ of about 14.6° ,

16.9° and 18.6°, corresponding to crystallographic planes (110), (040) and (130), respectively. At the meridian, there is only one obvious diffraction peak of (110) lattice plane representing the daughter crystals, as shown in Figure 10(b). This difference is related to the highly perpendicular crystalline structure.

Figure 10 One-dimensional integrated WAXS curves for mother crystal (a) and daughter crystal (b)

To compare the structural evolution between mother and daughter crystal, Figure 11 displays the (110) d-spacing and the orientation of (110) scattering intensity of mother crystal. The (110) d-spacing of mother crystal slightly increases from 6.05 to 6.06 Å near yield strain, then declines and almost keeps constant. Meanwhile, different trend is found for the (110) d-spacing of daughter crystal. A pronounced decline at yielding point is observed and then keeps no change. The daughter crystal is directly stretched to be broken. This means that the daughter crystal is turned to small and misplaced ^[30]. The orientation change of mother crystal during stretching is calculated as Herman's orientation function and is given by ^[31]:

$$f = \frac{3\langle \cos^2 \phi_{hkl,z} \rangle - 1}{2}$$

where $\phi_{hkl,z}$ is the angle between the chain axis and a reference axis z, e.g. the MD.

$\langle \cos^2 \phi_{hkl,z} \rangle$ is defined as

$$\langle \cos^2 \phi_{hkl,z} \rangle = \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi}$$

where I is the intensity in photons and is defined as:

$$I(\phi) = \int_0^{2\pi} I(\phi, \beta) d\beta$$

where $I(\phi, \beta)$ represents the intensity distribution measured on the pole figure of the (hkl) plane as a function of the angle α ($\pi/2 \geq \alpha \geq 0$), where $\alpha = \pi/2 - \phi$, and β ($2\pi \geq \beta \geq 0$). The results show that during stretching the orientation degree of mother crystal is kept nearly constant at beginning and slightly increases at plastic deformation zone. Apparently, the increase of lattice dimension of mother crystal during stretching to 10 % is mainly due to the lamellae parallel slip [32]. Then crystals are broken step-by-step during further stretching.

Figure 11 The d-spacing and orientation degree of (110) crystallographic plane from mother crystal and daughter crystal

3.4 Stress-strain curves of stretched films to different ratios at room-temperature

In the annealed film, except for the mother-daughter crystal, tie chains in the amorphous region will show apparent influence on its structure and properties. Sadeghi [8] et al. attributed the pore initialization to the scission of short tie chains during stretching at room temperature, but up to now, no experimental results prove it. To clearly build the relationship between the pore formation and the tie chains, the tie chains content for the stretched films to different

ratios were calculated based on the test of stress-strain curves. **Figure 12** gives the stress-strain curve of annealed films and stretched films to different ratios at room temperature. For the annealed film, after the first yield point, a plastic plateau appears. The first yield point is combined with the transformation and rearrangement within the lamellae being oriented in the stretching direction without breaking. Then the curve goes into the strain-hardening region and later the second yield point appears. After the second yield point pronounced lamellae deformation will occur ^[33].

Figure 12 Stress-strain curves of stretched films to different ratios

Takayanagy^[34] et al. used the series model to explain the polymer mechanical properties, as shown in Figure 13. During stretching, the amorphous region and the tie chains bear the extension force in series with the crystalline phase. The elasticity modulus of the sample can be calculated as

$$\frac{1}{E} = \frac{X_c}{E_c} + \frac{1 - X_c}{(1 - \beta)E_a + \beta E_t}$$

where E is the elasticity modulus of the sample. E_c , E_a and E_t is the elastic modulus of crystalline region, amorphous region and tie chains, respectively. X_c is the crystallinity tested by DSC, β is the volume percent of tie chains. We assume that the amorphous region has no contribution to the sample elastic modulus during stretching, and the elastic modulus of extended tie chains equates to the crystalline phase. So the equation can be rewritten as,

$$\beta = \frac{(1 - X_c)E}{E_c - X_c E}$$

here the elastic modulus of crystalline phase in PP is 41 GPa^[35].

Figure 13 The schematic of Takayamagi model

The calculated results are shown in Figure 14. Compared with that of annealed film, 10 % stretching only induces the decrease of volume fraction of tie molecules from 0.79 % to 0.76 %. The porosity of sample at 10% stretching is 9%. Although this content of pores may affect the elastic modulus values, the small change of tie chains content indicates that tie chains show no pronounced change during initial stretching. Compared with the above change of daughter crystal content and the long period values, this decrease could almost be

neglected, indicating that within 10 % stretching, the tie chains almost show no contribution to the pore formation. But 30 % stretching results in the apparent decrease of tie molecules content to 0.32 %. Within this stretching region, the contribution of tie chains to pore formation is apparent. Of course, here, the contribution of pore to elastic modulus can't be neglected. After stretching to 30%, the porosity value is about 13.2%.

Figure 14 The volume fraction of tie molecules in the annealed film and stretched films to different ratios at room temperature

3.5 TMDSC of stretched films to different ratios at room-temperature

In our previous work, it has been proved that melting and recrystallization behavior of imperfect crystals and secondary crystallization of tie chains occur during annealing [36]. To build the relationship between these crystalline phenomena and pores formation, the TMDSC curve of annealed film and stretched films to different ratios were tested. As shown in **Figure 15**, similar to that in usual DSC testing [7,12-13], an endotherm plateau appears in the total heat flow curves. In the measurement, the obtained total heat flow, approximately equivalent to that from a conventional DSC, can be divided into a (capacity-related) reversible heat flow and a (kinetic) nonreversible heat flow [37]. Usually, crystallization and enthalpy relaxation (or recovery) appears only in the nonreversible signals, whereas melting occurs in both reversible

and nonreversible signals. For a simultaneous melting and recrystallization process, an endothermic peak in the reversing heat flow and an exothermic peak in the nonreversing heat flow are expected ^[38,39]. Here, for the annealed film, the existence of exothermic peak in the nonreversing heat flow curve indicates the occurrence of melting and recrystallization behavior during annealing. The area of exothermic peak in the nonreversing heat flow curve represents the contribution of recrystallized part. The endothermic peak in the reversing heat flow comes from the contribution of melting of recrystallized part and secondary crystallization part from tie chains. Figure 16 and 17 give the reversing and nonreversing curves of precursor film, annealed film and stretched film to different ratios at room temperature.

To follow the change of secondary crystallization from tie chains during stretching at room temperature, the area percent of melting enthalpy and recrystallized enthalpy were calculated using Peakfit software. In Figure 16, peak 1 represents the melting of recrystallized part from imperfect crystals and secondary crystallization of tie chains during annealing. Peak 2 represents the contribution of initial main lamellae. After stretching, the connecting bridge crystals appear, and these crystals show more perfect crystalline structure. The melting point of bridge crystals is 5 °C higher than that of main lamellae crystals.^[40] Thus, a small shoulder peak (Peak 3) near 170 °C is attributed to the connecting bridge crystals, as shown in **Figure 16**. The exothermic peak in the nonreversing curve in Figure 17 is related to the recrystallized part. Then, the contribution of secondary crystallization part to melting is simply calculated based on the subtraction of recrystallized enthalpy from P1 melting enthalpy.

Figure 15 TMDSC curves of annealed film

Figure 16 Reversible heat flow curves for annealed film and stretched films to different ratios at room temperature

Figure 17 Nonreversible heat flow curves for annealed film and stretched films to different ratios at room temperature

Table 2 lists the calculated melting enthalpy Peak 1 (including the contribution from recrystallized part and secondary crystallization), Peak 2 (mainly the contribution from main lamellae part), Peak 3 (mainly the contribution from connecting bridge part), recrystallized enthalpy, and secondary crystallization melting enthalpy. At the stretching ratio of 10 %, the recrystallized enthalpy is apparently decreased by 77.6 %, indicating the deterioration of recrystallized part, which is formed during annealing. At this time, the secondary crystallization melting enthalpy is a little increased. Combined with the above initial pore formation induced by stretching to 10 %, the disappearance of recrystallized part corresponds to the formation of initial connecting bridges. The increase of secondary crystallization melting enthalpy means that 10 % stretching does not deteriorate the secondary crystallization part, which is formed during annealing. The secondary crystals are situated within the amorphous region. Since the stretching is carried out at room temperature, the entanglement within the amorphous region limits the stretching of secondary crystals. At the stretching ratio of 20 %, the recrystallized enthalpy increases. Although the stretching is carried out at room temperature, stretching-induced thermal effect can't be neglected, which induces the melting

and recrystallization behavior^[41,42]. At higher stretching ratio, the enthalpy of recrystallized part and secondary crystallization melting decrease. Higher stretching ratio induces the deterioration of recrystallized part and secondary crystallization part. The melting enthalpy from connecting bridges is also included in Table 2. With the increase of stretching ratio to 30 %, the connecting bridges enthalpy increases, indicating that more connecting bridges are formed by stretching. Stretching high to 110 % induces small decrease of bridges enthalpy. This may be due to the disappearance or decrease of some connecting bridges, since at this higher stretching ratio, the deformation of main lamellae structure can't be escaped and some pores could be collapsed. In our recent work, we confirmed that the secondary crystallization during annealing occurred along (110) crystallographic plane, relating to the crystallization of tie molecular chains^[43]. The secondary crystallization is affected by the number of active tie molecules. During cold stretching, the content of secondary crystals does not change much below 20 % stretching and reduced by further stretching. This result agrees with the active tie molecule volume fraction changing during cold stretching. Apparently, the tie molecule fracture is related to the void increase.

Table 2 Reversible melting enthalpy, recrystallized enthalpy and secondary crystals enthalpy

Sample	Total heat flow enthalpy (J/g)	Connecting bridges enthalpy P3 (J/g)	Main lamellae enthalpy P2 (J/g)	(Recrystallized+ secondary crystals) enthalpy P1 (J/g)	Recrystallized enthalpy (J/g)	Secondary crystals enthalpy (J/g)
Annealed						
film	116.8	0	57.5	31.03	22.34	8.69
10%	119.7	5.41	58.32	13.84	5.01	8.83
20%	115.6	7.65	48.78	20.46	11.92	8.54
30%	121.5	12.78	48.76	22.85	15.35	7.50
50%	120.4	9.45	38.34	14.55	8.56	5.99
110%	119.9	8.85	39.63	10.82	6.28	4.54

In the annealed film with row-nucleated crystalline structure, initial main lamellae, daughter crystals, recrystallized part, secondary crystals and tie chains coexist, as shown in Figure 18(a). The former three parts are included in the crystalline part, whereas the latter two are within the amorphous region. During stretching at room temperature, initial connecting bridges are formed. When stretched to 10 % beyond the first yield point in the stress-strain curve, the daughter crystal and recrystallized part are decreased. At this time, the long period is apparently increased and initial connecting bridges can be observed by SEM. Figure 18(b) shows the initial pore formation stage. Then it can be deduced that the initial connecting bridges come from the decrease of daughter crystal and recrystallized part. It can be seen that the first structure destroyed by stretching at room temperature is in the crystalline part, not within the amorphous region. When stretched to 30 %, which is situated at the transition point from plastic plateau region to strain-hardening region in the stress-strain curve, except for the decrease of daughter crystals, the tie chains and secondary crystals within the amorphous region can be stretched. Figure 18(c) shows the schematic of stretching to 30% at room temperature. All these contribute to the formation of more connecting bridges. When stretched into the strain-hardening and beyond the second yield point, except for the change of above crystalline and amorphous structure, main mother lamellae will be destroyed. The lamellae structure periodicity is deteriorated. Therefore, for the fabrication of microporous membrane based on melt-stretching mechanism, the room-temperature stretching ratio should be set around the transition point from plastic plateau to strain-hardening region. The final microporous structure is shown in Figure 18(d).

Figure 18 Schematic of pores formation process during room temperature stretching

4. Conclusions

To clarify the pore initiation process and the appropriate stretching ratio during room-temperature stretching of PP film with row-nucleated crystalline structure, the room-temperature stretching process was studied. The initial bridges connecting the separated lamellae could be observed by 10 % stretching at room temperature. During stretching, the daughter crystal and recrystallized crystal within the crystalline region are stretched and converted to the initial bridges. At the stretching ratio of 30 %, which is situated at the transition point from plastic plateau to strain-hardening region in the stress-strain curve of annealed film, uniform initial connecting bridges and pores appear, at the same time showing maximum second order signal and higher structure periodicity. Here, except for the stretching of daughter crystal, the decrease of tie chains and secondary crystals within the amorphous region converts to the formation of more connecting bridges. Higher stretching ratio to 50 % lead to the stretching of mother lamellae and will induce lamellae deformation and lower structure periodicity.

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