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Journal Name

ARTICLE

Influences of Melt-draw Ratio and Annealing on the Crystalline Structure and Orientation of Poly(4-methyl-1-pentene) Casting Films

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The poly(4-methyl-1-pentene) casting films with row-nucleated lamellar structure were extruded through a slit die followed by stretching using a chill roll. The influences of melt draw ratio, annealing temperature, annealing time and supplied strain level on the crystalline morphology and orientation of the poly(4-methyl-1-pentene) casting films were carefully investigated by means of scanning electron microscopy, differential scanning calorimetry, Fourier transform infrared spectrometer and X-ray diffraction. It was found that the crystalline morphology and the degree of orientation greatly influenced by melt draw ratio. In addition, both the changes of crystallinity and orientation degree exhibited similar tendency (firstly increased and then decreased) as the heightening free annealing temperature and time. It was for the reason that appropriate temperature and time greatly contribute to molecular chains of amorphous region rearranged into crystal lattice and defects remove, while excessive annealing temperature and time might lead to partial imperfect crystals melting and recrystallization or even disorientation phenomenon. In contrast to free annealing method, it was surprisingly discovered that annealing under supplied strain was really helpful to improve crystalline structure and orientation of casting films.

Introduction

Poly(4-methyl-1-pentene), trade name called TPX, is an important semi-crystalline polyolefin material with many understanding properties^{1, 2}. Compared with conventional polyolefin materials, TPX exhibits high degree of transparency, favorable heat resisting property and excellent permeability, which has been widely used in various industrial fields, such as fibers^{3, 4} and microporous membranes⁵⁻⁷. With the advantages of environmental protection and lower cost, melt extrusion/annealing/uniaxial stretching (MAUS) way (dry process) is widely used to prepare microporous membranes with a row nucleated lamellar structure^{8,9}. Normally, the main issues in this process are the generation of an appropriate initial row nucleated structure and subsequent heat treating¹⁰. As we know, extrusion lead to planar extensional flow along the machine direction (MD), this promoted crystallization and uniaxial orientation behavior with respect to the MD axis. The properties of casting films were greatly influence by the initial crystalline morphology¹¹⁻¹³. Annealing plays an important role in improving performances by eliminating the internal stress and defects of products. After processing, a portion of the polymer chains in the crystalline region and amorphous could adjust their energy state to the equilibrium state as the mobility of chains increase during annealing procedure.

At present, there have been many researchers^{7, 14-19} to study the fabrication process of microporous membranes. A precursor film with the lamellar morphology is believed to be obtained by crystallization of the chains during melt stretching, which in literatures is called stress induced crystallization^{14, 20}. Some papers²¹⁻²³ reveal that the elongation induced morphology is strongly dependent on the effective stretching flow expressed in terms of melt draw ratio. With the increase of melt draw ratio, the crystalline orientation and crystalline morphology transformation from spherulite to parallel lamellae perpendicular to the extrusion direction²³. Zhi-tian Ding et al²⁴ studied the effect of annealing on structure and deformation mechanism of isotactic PP film with row-nucleated lamellar structure, he found that the recrystallized lamellar structure attribute to annealing improved the ability of slipping resistance of original lamellar structure during stretching, which explain the unique tensile property and the microstructure changes of the annealed films.

There is no doubt that the crystalline morphology of precursor films is profoundly influenced by intensive stretching (elongation) flow fields during extrusion stage. Moreover, the development of oriented lamellar structure during annealing often have important effect on properties or performance of annealed films in the next usage or application²⁵. Therefore, the quantitative analysis about the relationship between structure changes (crystallinity, orientation) and accurate annealing conditions (temperature, time and etc.) become necessary and important. In this work, the Poly(4-methyl-1-pentene) was selected as the raw material for our research. The effect of melt draw ratio on crystalline morphology and orientation structure was detailed studied. Compared with the

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abundant research literatures on temperature and time during annealing stage, the study of the annealing under external force is relatively scarce. Aside from Seyed H. Tabatabaei et al.²⁶ and Ta-Hua Yu¹⁴, few paper was published to mention the effect of annealing under external force and both of their conclusion was that this annealing method has no benefit to crystalline morphology and orientation. Therefore, skeptical attitude towards above results was still shown because they did not give too much experimental data or detailed explanation for the results. This motivated us to conduct an intensive study on this problem as well as the relationship between the strain level and crystallinity and orientation changes of the TPX films. Finally, different results obtained from experimental data, which indicating that annealing under strain was helpful to improve crystalline structure and orientation degree.

Experimental

Material and Precursor Film Preparation

An extrusion grade of TPX (RT18 XB), melt flow rate 8 g/10min (250°C, 3.8kg), which purchased from Mitsui Chemicals America, Inc. was used. The schematic diagram for processing precursor films was presented in Fig. 1. The precursor films were extruded through a single screw extruder (D=20 mm, L/D=25, where D is the diameter of the screw and L is the length of the screw) equipped with a slit die which thickness 1.2 mm thick. The temperature of the extruder along the barrel from hopper to die were 180°C, 245°C, 245°C, 250°C, and the rotation speed of the screw was 15 rpm. To improve cooling, an air knife was installed to supply compressed gas to the film surface at the exit of the die. The air temperature was kept at room temperature about 25 °C and the cooling rate was controlled through cooling air blower. There has been published paper²⁷ to discuss the influence of the air flow rate on the crystalline orientation, morphology, mechanical and tear properties of the PP casting films. They concluded that the use of a low air cooling rate contributed significantly to the perfection of the crystalline phase, while further increasing of air cooling did not noticeably affect the crystal structure. The row-nucleated lamellar crystalline structures of precursor films would be formed by applying elongation stress and intensive cooling on the film surface at the exit of the die²⁴. The degree of melt extension was described as draw ratio (DR), the ratio of die thickness to precursor films. The precursor films of DR from 15 to 55 were prepared, whose thickness were vary from 80 μm to 22 μm. The samples used for thermal annealing and subsequent characterization were obtained from the middle of the precursor films.

Thermal Annealing

The precursor films of DR=40 were selected to be free annealed in a temperature-controlled chamber for 30 min at temperature of 110, 170, 190, 200 and 210°C, respectively. The annealing times employed were 5, 10, 20, 30, 40 min under consideration of in light of feasible industrial processing times. Then come to annealing under a specified level of extension, the levels of strain were 3, 6, 9, 12, 15 percent, respectively. The specific levels of strain utilized for the present study are, in part, based upon the previous work of Yu on HDPE films¹⁴. The effect of external force during annealing is

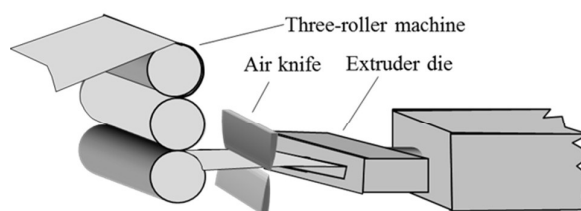


Fig. 1 The schematic diagram for processing precursor films.

important to the industrial scale process, where a certain amount of strain is applied to keep the film taut while it proceeds through the annealing oven in a continuous process. The level of strain may alter the film morphology and crystalline orientation prior to stretching, which in turn can affect the microporosity and the morphology of the microporous film.

Film Characterization

Scanning Electron Microscopy (SEM)

The observations for the surface morphology of the etched films were carried out using a SEM instrument (model JSM-5900LV, JEOL Inc., Japan) operating at 20 kV. All samples were coated with a thin layer of gold before the tests.

Differential Scanning Calorimetry (DSC)

The crystallization behaviors of the specimens before and after annealing were analyzed using TA Q20 differential scanning calorimeter under a nitrogen atmosphere. The samples were heated from 40°C to 260°C at a heating rate of 20°C/min. The degree of crystallinity was calculated from enthalpy change values obtained in the heating curve, supposing a heat of fusion of 62.16 J/g for fully crystalline Poly(4-methyl-1-pentene).

Orientation Degree Characterization

For the measurements of orientation degree, a Nicolet 6700 Fourier transform infrared spectrometer (FT-IR) instrument from Thermo Electron Corp. was used. The beam was polarized through a Spectra-Tech zinc selenide wire grid polarizer from Thermo Electron Corp. The measurement is based on the absorption of infrared light at certain frequencies corresponding to the vibration modes of atomic groups present within the molecule. In addition, if a specific vibration is attributed to a specific phase, the orientation within that phase can be determined^{8, 18, 26, 28}. 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 (MD), should be unequal. The ratio of these two absorption values is defined as the dichroic ratio, D. So the value of D can be obtained from the equation $D = A_{\parallel} / A_{\perp}$, where A_{\parallel} is the absorption parallel and A_{\perp} is the absorption perpendicular to MD. For uniaxial orientation, the dichroic ratio is related to the Hermans' orientation function (f_H) by the relationship $f_H = \frac{(D+2)}{(D-1)} \left[\frac{(D-1)}{(D+2)} \right]$, where $D_0 = 2\cot^2\alpha$, and the value for α is the angle between the chromophore transition moment and the chain axis²⁹. For TPX, a vibration specific to a single phase is not known. He and Porter³⁰, however, have used the dichroism of the 918 cm⁻¹ band, a rocking mode vibration from two methyl groups³¹, to follow sample orientation as a function of extension. We have also utilized this absorption band in this study.

X-ray Diffraction (XRD)

All samples were characterized using a DX-100 automatic X-ray diffractometer with Cu K α radiation ($\lambda=1.54 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 40 mA operating at a step size of 0.06° from 5° to 25° .

Two-dimensional wide angle X-ray diffraction (2D-WAXD) is based on the diffraction of a monochromatic X-ray beam by the crystallographic planes (hkl) of the polymer crystalline phase. Using a pole figure accessory, the intensity of the diffracted radiation for a given hkl plane is measured as the sample is rotated through all possible spherical angles with respect to the beam. This gives the probability distribution of the orientation of the normal to hkl plane with respect to the directions of the sample. The orientation function utilized was the Hermans' orientation function (f_H), $f_H = \frac{(3 \cdot \cos^2 \theta - 1)}{2}$, where θ is the angle between the chain or specific unit cell axis and a chosen reference axis, which is the MD in our case.

Results and Discussion

Effects of Melt Draw Ratios on Crystalline Morphology and Orientation Structure of Casting Films

In order to characterize the crystal structure of TPX, the XRD profile of casting films prepared at different DR values was shown in Fig. 2. In the present report, TPX displays five crystalline modifications with X-ray diffraction profiles. According to Daniel³² and Tao³³, the most stable TPX crystalline structure of Form I could be obtained through molten state under cooling and as evidenced by the reflections at $2\theta=9.5^\circ$, 13.4° , 16.6° , 18.5° , 20.6° and 21.5° , which belong to (200), (220), (212), (321), (113) and (322/203) crystal plane diffraction peak, respectively. All the above six diffraction peaks of precursor films appear at relative lower DR. With the increase of DR, 16.6° , 18.5° and 20.6° diffraction peaks, which belong to the (212), (321) and (113) crystal plane gradually weakened. At relative higher DR, the above three crystal plane peaks even disappeared under the effect of high speed stretching. It could be confirmed that the crystal form of TPX casting films is not changed under the effect of traction-roller. The weakening and even disappearance of above three diffraction peaks might be owing to the increasing crystalline orientation along the flow direction. The growth of (212), (321) and (113) crystal plane was gradually restrained because of uniaxial stretching, which resulted in the diffraction peaks are not presented in our results. What is more, the crystallinity also improved due to the effect of stress induced crystallization. Therefore, it could be qualitative conclude that higher draw ratio is beneficial to form the more orderly crystal structure^{22, 23, 34}.

To better characterize the crystalline morphology under different DR values, etched surface morphology of SEM photographs were presented in Fig. 3. It was apparent that some twisted lamellae and even random arrangement lamellae can be seen clearly under lower DR values (15 and 20), whereas with the increase of DR values, regular lamellae structures which arrange perpendicular to the machine direction were exhibited in our result. The degree of orderly crystal gradually increased with the increase of DR values. It was again well established that external stress condition has profoundly influence on crystalline morphology of casting films: lower stress result in lower oriented and twisted lamellae structures, and yet higher stress produce highly oriented lamellae structures.

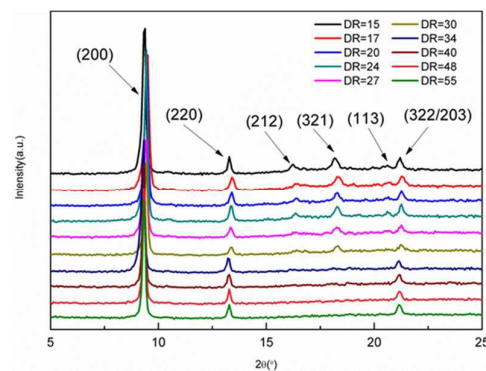


Fig. 2 XRD curve of casting films prepared at different DR values.

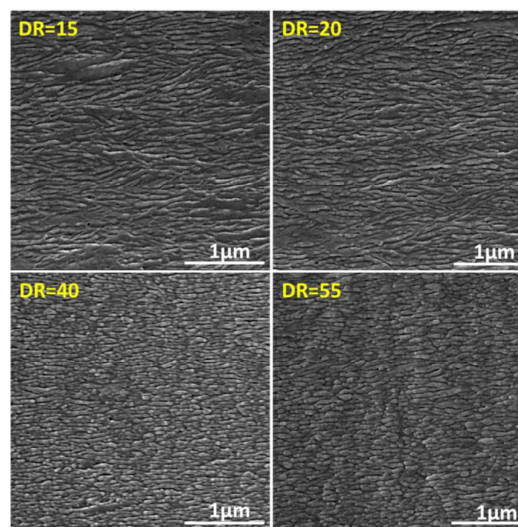


Fig. 3 SEM photographs of casting films prepared at different DR values (The flow direction is vertical).

To detect the changes of the crystalline structure, precursor films with different melt draw ratios were tested by DSC, and the results were shown in Fig. 4. As the DR increased, the position of main peak of precursor films was nearly unchanged as the melting point at about 232°C , suggesting that the crystal lamellar thickness did not change much with the increasing draw ratio. The significant changes were that the low-temperature shoulder peak on the left of the main melting peak gradually weakened or disappeared with the increasing draw ratio. We believed the shoulder peak at lower temperature reveals the crystal with smaller crystal thickness. Looking carefully at the temperature range of the melting processes with various DR values allows us to find that the temperature range for melting is almost independent of DR values. Furthermore, the FWHM (full width at half maximum) of the melting peak with lower DR value is much narrower than that with higher DR values. These results suggest that the crystal with lower DR value has more uniform crystal thickness, revealing a more "perfect crystal".

As shown in Fig. 5, there is absorbance difference between the parallel and perpendicular spectroscopy on 918cm^{-1} in infrared polarization spectra. By following the formula mentioned above, we chose 918cm^{-1} as the representative of the crystalline area and calculated the crystalline orientation degree of casting films prepared at different DR values. According to the degree of crystallinity and crystalline orientation values shown in Tab. 1, although the melting point have no obvious change as increasing

Tab. 1 Degree of crystallinity (X_c) and crystalline orientation (f_c) of casting films prepared at different DR values.

DR	15	17	20	24	27	30	34	40	48	55
X_c (%)	61.79	62.19	62.61	63.34	63.92	64.25	64.85	65.72	65.74	64.92
f_c	0.286	0.285	0.296	0.290	0.300	0.308	0.341	0.363	0.394	0.393

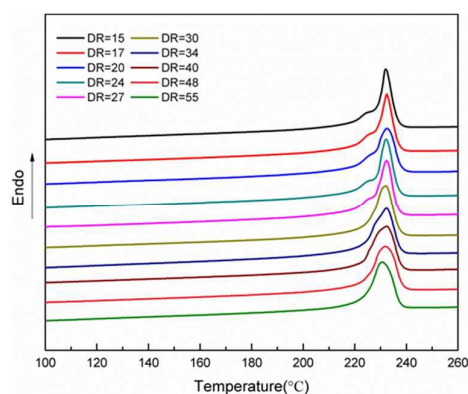


Fig. 4 DSC curve of casting films prepared at different DR values.

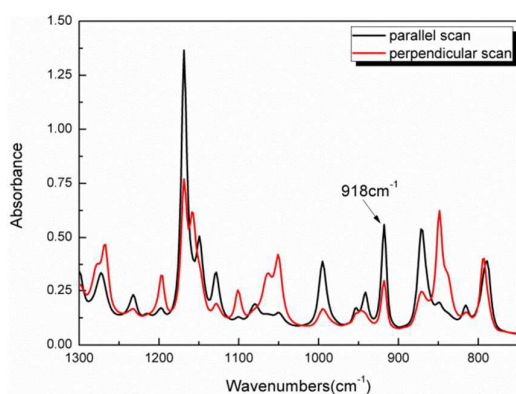


Fig. 5 The FTIR spectrum of TPX casting film with parallel(0°) and perpendicular(90°) to extrusion direction.

melt draw ratio, the crystallinity and crystalline orientation increased gradually and become stability until at DR value of 40. It could be concluded that the crystal with higher DR value has higher crystallinity and orientation degree.

Effects of Free Annealing on Crystalline Morphology and Orientation Structure of Casting Films

Free annealing of precursor films of DR=40 were performed at different temperature for 30 min in a temperature-controlled

chamber. After DSC test, the main melting peak position showed nearly no apparent change with the annealing temperature increased, and no endotherm plateau was observed on the left side of main melting peak after heat treatment (Fig. 6). If a crystal population with a different morphology or secondary crystals are formed during annealing, the endotherm plateau should be found in the heat flow curve for the melting process^{35, 36}. Therefore, we could come to the conclusion that no new crystal morphology was formed in our result. In addition, no obvious change of melting point indicating the lamellar thickness was hardly any change at all, which was not match very well to the thickening of lamellar after annealing by other researchers^{24, 37}. This unusual phenomenon was probably owing to that the small changes of melting point were covered up by experimental and test error.

The crystallinity and the orientation changes with the increasing of annealing temperature were presented in Fig. 7, both curves showed a similar trend. In the first stage, the movement ability of TPX molecular chains was enhanced significantly during the heightening of temperature, which is helpful to promote the molecular chains of amorphous region arranged into lattice, resulting in further perfect crystallization and the rise of crystallinity. While the temperature exceed 200 °C, the overhigh annealing temperature also lead to molecular chain disentanglement and melting of metastable crystalline structure (the appearance of the molten bimodal peaks of DSC curve of Fig. 6). Similarly, more regular and orderly chains arrangement resulted from polymer segments movement supply an explanation of orientation improvement. So 200 °C was selected as an optimal temperature during heat treatment stage.

Precursor films of DR=40 annealed at 200 °C for various times were characterized by DSC and FT-IR methods. From the changes presented in Fig. 8, it was obvious that the rapid increases of X_c and f_c with the annealing time mainly took place in 20 min and reduced gradually after that. In the first 20 min, X_c and f_c of annealed films were 6% and 13% higher than the precursor films, which well verified the promotion effect of small-scale structural modification on crystalline structure during annealing stage.

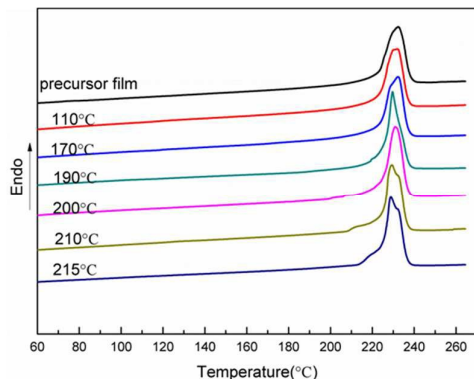


Fig. 6 DSC curves of casting films annealed at different temperature.

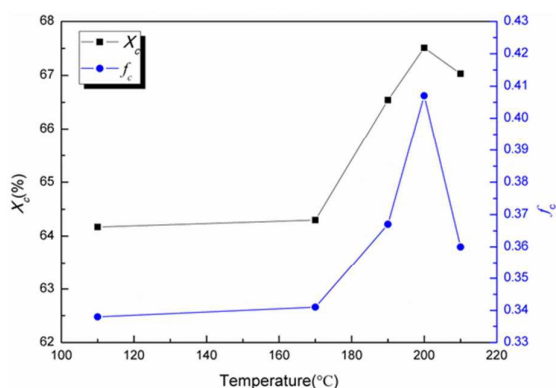


Fig. 7 Changes of the crystallinity (X_c) and the orientation with the increase of annealing temperature.

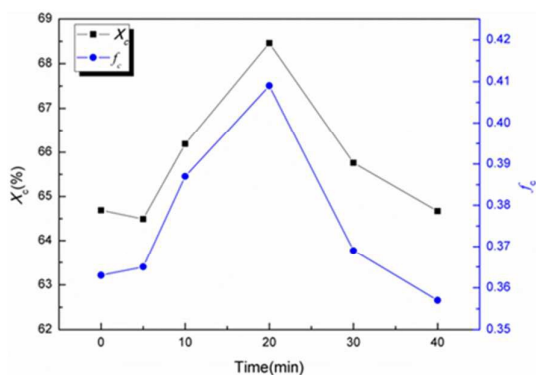


Fig. 8 Changes of the crystallinity (X_c) and the crystalline Orientation with the increase of annealing time.

Through the research of free annealing process, there is no doubt that annealing procedure will partially removes the defects in the

crystalline phase and finally improves lamellae orientation and uniformity. Nevertheless, it should be noted that overhigh temperature and overlong time during annealing might deteriorate the initial lamellar structure through local partial melting and recrystallization, which is coordinate with preceding results of Fig. 7 and Fig. 8.

Effects of Annealing under external force on Crystalline Morphology and Orientation Structure of Casting Films

Compared with abundant literatures on free annealing procedure^{24, 26, 37}, the study of annealing under extension is relatively rarely reported. However, the special annealing procedure might alter the crystalline structure of precursor films under the effect of external force, which is of great significance for subsequent stage of microporous formation. Therefore, this work was fully conducted in our experiments.

After DSC test of precursor films annealed under a specific strain level (0, 3, 6, 9, 12 and 15%), no obvious change of melting peak position was found, revealing lamellae thickness have not been apparently altered in this process. Nonetheless, according to the degree of crystallinity variation which presented in Fig. 9, the degree of crystallinity was improved significantly under increasing strain level, indicating great dependency relationship between crystallinity and strain levels from the graph. It is somewhat due to the fact that appropriate external force is helpful to motivating molecular chains straighten and stretch under the supplied strain levels, and then attain the aim of promoting the amorphous zone molecular chains rearrange into crystal lattice and boosting the degree of crystalline. However, when the strain level exceeds 9%, excessive tensile force may bring about fracture and even structural break in crystalline phase, resulting in the falling off of crystallinity finally.

To better understand the effect of external force on the orientation of crystal, sequences of 2D-WAXD patterns annealed at various strain levels were presented in Fig. 10. It could be observed clearly that strong reflection of the (200) plane was seen in diffraction pattern, suggesting obvious orientation phenomenon. Under the 9% strain level of annealing, the reflections of the (200) plane were stronger than others, indicating a better orientation in this condition.

To study the 2D-WAXD patterns in detail, (200) reflections were analyzed using the FIT-2D software and plotted against the azimuth angle from 0° to 360° (as shown in Fig. 11). With the augment of supplied strain level, we could see an increase of diffraction intensity of the (200) plane from 0% to 9% and then decreased from the 9% to 15%. Furthermore, the corresponding diffraction intensity of the (200) plane of the 9% level sample was more conspicuous than other samples, implying higher degree of orientation of the annealing under 9% strain level.

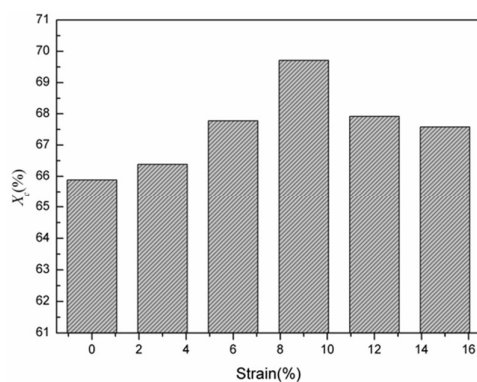
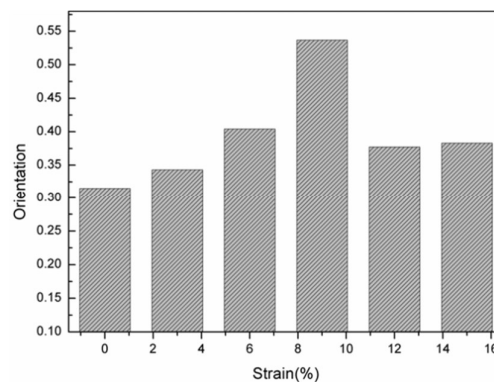
Fig. 9 Changes of the crystallinity (X_c) under increasing strain level.

Fig. 12 The orientation of (200) plane at different strain level.

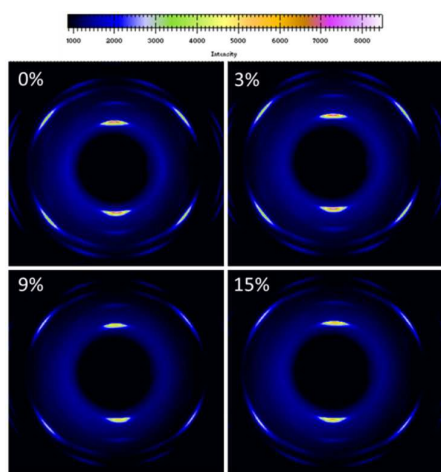


Fig. 10 2D-WAXD patterns of annealing under different strain level.

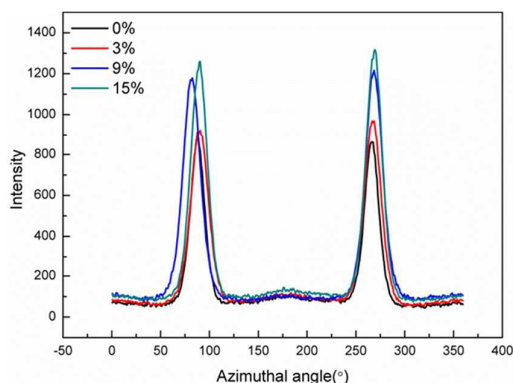


Fig. 11 The intensity of (200) plane at different azimuthal angles.

The values of order parameters at various strain levels, which can give a half-quantitative comparison of the degrees of lamellae orientation among different samples, were shown in Fig. 12. It could be seen obviously that annealing under external force improves the orientation of casting films significantly. Moreover, compared with free annealing, there was 70% increase for the degree of orientation at 9% strain level. This can be greatly attributed to the effect of external force induced orientation. The molecular chains become easier to arrange into crystal lattice

orderly under the supplied force, which resulted in more uniform oriented lamellae structure. However, consistent with the crystallinity change tendency, the degree of orientation started to descend when the strain reaches to 9%. It seems due to the fact that excessive force might lead to lamellae distortion or even destruction and finally resulted in the drop of orientation.

Conclusions

In this study, the TPX melt was extruded through a slit die followed by stretching using a chill roll. The influence of melt draw ratio, annealing temperature, time and supplied strain level on the crystalline morphology and orientation of casting films was carefully investigated. These above experiments revealed that the morphological character and the degree of orientation have obvious draw ratio dependence. Row nucleated lamellar structure which perpendicular to machine direction was gradually formed under the higher stress condition. In addition, both the crystallinity and orientation degree changes exhibited similar tendency (firstly increased and then decreased) as the heightening free annealing temperature and time. This was somewhat due to the fact that appropriate temperature and time greatly contribute to molecular chains of amorphous region rearranged into crystal lattice and defects remove while excessive temperature and time might lead to partial imperfect crystals melting and recrystallization or even disorientation phenomenon. With regard to annealing under specified strain level, we found that in contrast to free annealing method, supplied external force during annealing procedure was really helpful to the improvement of crystalline structure and orientation.

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