Advantage of Preserving Bi-orientation Structure of Isotactic Polypropylene through Die Drawing

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INTRODUCTION

Isotactic polypropylene (iPP) is one of the most popular polymer materials that have been successfully commercialized due to its excellent mechanical properties and stability. Besides the crystalline polymorphism, another feature distinguishing iPP from other polymer materials is the cross-hatched structure, which is also noted as the parent-daughter lamellae structure often found in the α form of iPP. This structure was first recognized by Khoury as dendritic crystals. The dihedral angle between the parent lamellae and the affiliated daughter lamellae was suggested to be 80°, which is very close to the accurate value of 80°40′ further determined by Padden and Keith. After years of debating, the physical essence of this peculiar parent-daughter structure was ascribed to the molecular interaction originating from chain stems chirality. Lotz and Wittmann proposed that each molecular chain in the crystalline layer of α form iPP should be encircled by chain stems with different chirality. The subsequent molecular chain with the same chirality as the precursor chain in the crystallites would be pushed away, resulting in an unparallel chain arrangement in the affiliated daughter lamellae.

Attempts for inducing the oriented parent-daughter lamellae have been continually made because such structure is related to the product performance, in aspects of warpage tendency, thermodynamic properties, stability under shear, elasticity, etc. A theoretically facile method for obtaining biaxially oriented polypropylene (B OPP) could be proposed based on the cross-hatched structure of iPP, since the angle between parent and daughter lamellae is not much different from 90°. The introduction of α-nucleating agents into iPP was an efficient approach to produce the oriented parent-daughter lamellae structure under certain conditions. For example, the α-nucleating agents of dibenzylidene sorbitol (DBS) family as fibril structure could first align along the force direction when shearing the compounded iPP/DBS melts, and subsequently served as oriented nuclei for inducing the growth of oriented parent-daughter lamellae by consuming the iPP melt. However, compared to massive investigations on the adjustment of the daughter lamellae through modifying the polymer melt, only a few researches have been dedicated to the evolution mechanism or regulation of parent-daughter
lamellae structure during solid-state deformation.\cite{23,24}

Nozue et al.\cite{23} investigated the early deformation stage inside the spherulites and described the evolution of long periods for both parent and daughter lamellae during tensile stretching until slippage fragmentation. Li et al.\cite{24} investigated the fragmentation sequence of parent and daughter lamellae during deformation by stretching pre-oriented films at room temperature. It turned out that parent lamellae would always be destroyed first and were transformed into mesophase. In both cases, no desirable bi-oriented structure was preserved due to the rearrangement of lamellae orientation after fragmentation.\cite{23,24} That means it was difficult to achieve the bi-oriented structure during solid-state uniaxial deformation even though the initial iPP samples were with a well-established oriented cross-hatched structure.

Die-drawing is one of the most ideal solid-state polymer processing techniques.\cite{5,23–27} Simultaneously with the elongation, the material is shaped by a specially designed die which enables the materials to go through a moderate strain-stress field\cite{25,26}. The material is also processed by the force perpendicular to the elongation induced by the die wall rather than only the drawing force.\cite{27} Obviously, there are two forces along different directions controlling the die-drawing process. Such situation seems to be similar to the one presented in the two-step stretching process for inducing BOPP. The difference is that the two forces belong to the compression force and the pulling force in the former one while both of them are the tensile force in the latter case. Since the daughter lamellae are almost perpendicular to the corresponding parent lamellae, it is rational to expect different bi-oriented lamellae evolutions in samples processed by die-drawing.

In this work, we investigated the deformation of both neat and α-nucleated samples via die-drawing and tensile-stretching at different temperatures. The as-deformed samples were investigated by wide-angle X-ray diffraction (WAXD) technique to elucidate the different evolutions of oriented parent-daughter lamellar structures induced by the two distinct deformation processes. The physics behind the difference between samples deformed via different processes was deduced and the deformation scheme was illustrated.

**EXPERIMENTAL**

**Material Information and Sample Preparation**

A commercial homo isotactic polypropylene was employed as a base material. The molecular weight (\(M_w\)) was 1.589×10^5 g/mol and the polydispersity (\(M_w/M_n\)) was 3.8. One α-nucleating agents Millad 3988i (\(>96\%\) 1,3,2,4-bis(3,4-dimethylbenzylidene) Sorbitol (DMDBS, Miliken Inc.) and <4% confidential silica compound, per MSDS, version 1.3) was mixed into polymer melt along with two antioxidants, tris(2,4-di-tert-butylphenyl)phosphite and pentaerythritol tetraakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate). The weight ratio of the additives between the polymer melt (α-nucleating agents/two antioxidants/iPP) was 5/2/1000. Both the neat material and the α-nucleated polymer melt were further manufactured into standard injection molding bars with a length of 170 mm, a width of 10 mm, and a thickness of 4 mm. The melt temperature and mold temperature for injection molding were 200 and 80 °C, respectively. The purchase of α-nucleating agents and antioxidants, the compounding of iPP with α-nucleating agents, and the producing of injection molding bars were all carried out at ExxonMobil. All the injection molding bars were further cut into sample bars with a width of 5.3±0.3 mm to fit in the mini die-drawing setup.

**Differential Scanning Calorimetry (DSC)**

The crystallization temperature, melting points, and crystallinities of the iPP samples were measured by using DSC (DSC1 Star® System, Mettler Toledo, Swiss) technique at a cooling or heating rate of 10 K/min\(^{-1}\). For the compounded sample of iPP/α-nucleating agents, it showed a crystallization temperature of 131.5 °C which was much higher than the one of 112.4 °C observed in the neat iPP during cooling down from the melt state. For the injection-molded iPP samples, a larger crystallinity of 51% and a higher melting temperature of 167.1 °C could be found in the α-nucleated iPP than the values of 44% and 166.5 °C in the neat iPP. The crystallinities were determined by dividing integral area of endothermic peak by the theoretical heat fusion value of perfectly crystallized iPP.\cite{28} It confirmed that the low content of α-nucleating agents of DMDBS was efficient in promoting the crystallization of iPP.\cite{29}

**Polarized Optical Micrograph (POM)**

The optical micrographs were captured through Axio Imager A2m (Carl Zeiss, Germany) under the cross-polarized light. The morphologies of injection-molded iPP samples from the skin area to the core region are revealed in Fig. 1. The neat iPP showed the spherulitic structure, while the α-nucleated one presented the oriented structure at the skin and core regions as evidenced by the color stripes. In general, the core layer of injection-molded iPP normally showed the spherulitic structure.

![Fig. 1 POM images of the injection-molded neat iPP (top) and α-nucleated iPP (bottom). The arrows on the plot represent the direction perpendicular to the flow direction during injection.](https://doi.org/10.1007/s10118-020-2465-z)
due to the poor orientation of molecular chains. The well-developed oriented lamellae, however, had been observed in the core region of injection-molded iPP compounded with DMDBS in our case. It was clear that the DMDBS could encourage the growth of oriented lamellae, which was in line with the findings figured out by Lipp et al.

**Deformation Tests**

All the samples were deformed beyond necking with a drawing/stretching speed of 94 mm·min⁻¹ at 130, 140, and 150 °C via die-drawing and tensile-stretching processes, respectively. The die-drawing experiments were performed via a self-designed mini die-drawing setup, and the whole view of this setup could be found in our previous work. As schemed in Fig. 2, the die with a heating system was designed with a tilted angle of 15° to the deformation direction, which could provide the compression force (N) and the friction (f) to weaken the drawing force (F_d). In this simplified model (right of Fig. 2), the sample was controlled by both of the force parallel and the one perpendicular to the deformation direction inside the die. The major shaped area of sample during die-drawing was inside the die because the temperature out of the die was room temperature far below the deformation temperature inside the die. The pull-out region of die-drawn sample normally showed the similar macroscopic state, as highlighted by the black rectangle in the left of Fig. 2.

For the free tensile stretching tests, an electronic universal testing machine (Instron 5869, Instron, USA) equipped with heating oven was employed. Prior to deformation, all the samples were kept at the deformation temperature for 20 min to gain a homogeneous heat distribution. The intended deformation temperatures were 130, 140, and 150 °C, but it turned out the actual deformation temperatures were 130, 140, and 145 °C due to the temperature deviation at high temperature. Although the initial crystallinities of neat and iPP/DMDBS samples were different, the high temperature annealing could melt the disordered crystallites and these melts would recrystallize into more perfect crystallites. Thus, we found the crystallinity difference between the neat and spherulitically nucleated samples was approximately decreased from 7% to 3% before stretching due to the 20 min annealing effect. The deformation degree of the as-deformed samples was evaluated via actual deformation ratio, \( R_A \).

\[
R_A = \frac{\text{Original billet cross-sectional area}}{\text{Final product cross-sectional area}} \tag{1}
\]

Photos were taken before and after the sample deformation along with a steel ruler to record the variation of both the width and thickness of the samples. In addition, the cross-sectional area at the die exit was 2 mm (width) × 5 mm (thickness), so that the final \( R_A \) of die-drawn iPP samples mainly depended on the initial width since the initial thickness of sample was 4 mm.

**WAXD**

A customized micro-focus WAXD setup was employed to investigate the structure evolution of samples. This setup consists of a micro-focused Cu Kα X-ray source (GeniX³D, Xenocs SA, France) which was generated at 50 kV and 0.6 mA and a semiconductor detector with a resolution of 487 × 195 (pixel size = 172 µm × 172 µm) (Pilatus100 K, Dectris, Swiss). The sample-to-detector distance was around 50 mm and the size of the X-ray beam at the sample position was 40 µm × 60 µm. The acquisition time for each two-dimensional (2D) WAXD pattern was 60 s. The orientation degree of polymer chains and fractions of oriented parent lamellae were further calculated based on one-dimensional integrated curves obtained from 2D WAXD patterns.

The orientation parameter of polymer chains was calculated via Hermans equation:

\[
S_{hkl} = \frac{3 < \cos^2 \phi_{hkl} > - 1}{2} \tag{2}
\]

where \( \phi_{hkl} \) represents the angle between the deformation direction and the normal vector of the lattice plane (hkI).

Fig. 2 The details of the die of mini die-drawing setup (left) and a schematic representation of the force distribution inside the die along the width direction (right). \( F_d \), \( N \), and \( f \) refer to the drawing force, the compression force from the die wall, and the friction caused by the die wall. \( N \) and \( f \) can be orthogonally decomposed to \( N_h \), \( N_v \), \( f_h \), and \( f_v \) (right inset). These four forces are finally reconstructed to the force of \( F_d \) (parallel to the \( f_d \)) and \( f_h \) (perpendicular to the \( F_d \)) in order to simplify the force distribution inside the die.

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orientation parameter $\cos^2 \phi_{hkl}$ can be achieved from azimuthal scattering intensity distribution by the following equation:

$$
\cos^2 \phi_{hkl} = \frac{\int_{0}^{\pi/2} I_{hkl}(\phi) \cos^2 \phi \sin \phi d\phi}{\int_{0}^{\pi/2} I_{hkl} \sin \phi d\phi}
$$

where $I_{hkl}(\phi)$ describes the scattering intensity along the angle $\phi$. And $\phi$ can be obtained by using Polanyi equation:[32]

$$
\cos \phi_{hkl} = \cos \theta_{hkl} \cos \psi
$$

where $\theta_{hkl}$ denotes the Bragg scattering angle, $\psi$ is the azimuthal angle along the Dèbye circle. In this work, we chose the polymer chains in the (040)$_i$-lattice plane to evaluate the orientation degree of the system, which made $\theta_{hkl}$ $8.4^\circ$ according to the characteristic peak position of IPP (040)$_i$ lattice.[13] In the case of a perfect orientation of the lattice plane with its normal in the plane of equator, the order parameter $S$ is equal to −0.5. For an isotropic sample, the order parameter $S$ is usually 0. If the molecular chains are entirely oriented perpendicular to the polar direction, the value of $S$ is close to 1. However, in this work, the orientation parameter of $(h0l)$ planes can vary in the range from 0 to −0.5 since we only consider the alignment of molecular chains from its isotropic state to perfectly oriented along one along the polar direction, as the normal of such planes is generally perpendicular to chain direction. The closer the value of $S$ to −0.5, the higher the orientation level is achieved for the corresponding lattice plane.

As for evaluation on the fractions of parent lamellae ($f_{\text{parent}}$), the following equation[34] was employed after baseline subtraction:

$$
f_{\text{parent}} = \frac{A_{\text{parent}}}{A_{\text{parent}} + A_{\text{daughter}}}
$$

$A_{\text{parent}}$ represents the peak area of the parent lamellae diffraction peak which in this work was the peak around $90^\circ$, and $A_{\text{daughter}}$ represents the peak area of the daughter lamellae diffraction peaks around $-10^\circ$ and $10^\circ$ azimuthally. The crystallinity, the sum of parent and daughter lamellae, at different positions was calculated based on Gaussian fitting of both the crystallographic sharp diffraction peaks and the broad peak originated from amorphous region, as introduced in our previous work.[35]

Small Angle X-ray Scattering (SAXS)

In order to express the long spacing $d_{ac}$ of deformed IPP samples, the SAXS measurements were conducted with a modified Xeuss system of Xenocs, France, at a sample-to-detector distance of 1064 mm. The size of X-ray beam (Cu Kα X-ray source, $\lambda=0.154$ nm) was enlarged to 0.8 mm $\times$ 0.8 mm during exposure. For scanning the drawn IPP samples from the undeformed area to the deformed region, the stepwise scanning with an interval of 1 mm was employed. Each 2D SAXS pattern was collected within 30 min using the same detector mentioned in the WAXD technique. The 1D radial scattering intensity profiles were first obtained by integrating the background corrected 2D SAXS patterns within $\pm 20^\circ$ along the machine direction. The value of long spacing $d_{ac}$ was then computed by using the Bragg equation based on these 1D scattering curves.

$$
d_{ac} = \frac{2\pi}{q_{\text{max}}}
$$

RESULTS AND DISCUSSION

Orientation of Molecular Chains during Deformation

Selected 2D WAXD patterns of samples are presented in Fig. 3 and the corresponding characteristic a crystalline diffraction rings are indicated as well. Although the $\beta$ phase of IPP samples could be occasionally induced in the injection molding process,[36] no $\beta$ crystalline form could be traced in the current work. The 2D WAXD patterns of all the samples started from almost isotropic rings but were still accompanied by slight orientation which originated from the injection molding process.[37] The molecular chains in the IPP melt could be oriented along the flow direction during injection, which would act as the nucleation sites for inducing the crystallization of oriented lamellae. Moreover, the $\alpha$-nucleating agents would be also oriented along the flow direction together with the formation of oriented IPP molecular network, both of which accelerated the growth of anisotropic lamellae. With deformation ongoing, the strongly focused diffraction spots or arcs progressively appeared on each diffraction ring. Those intense diffraction spots or arcs manifested a preferential orientation of polymer chains within crystallites. Several 2D WAXD patterns of tensile-stretched samples were also born with a tilted feature ($e.g., R_s=2.08$ in Fig. 3c), which came from sample inclination and were corrected by positioning the maximum diffraction point of (040)$_i$-lattice plane at 90° before further calculation.

To quantify the orientation evolution of the deformed samples, the order parameter of (040)$_i$-lattice plane, $S_{(040)}$, was calculated as described in the experimental section and the results are presented in Fig. 4. The orientation degrees at the same $R_s$ of stretched samples through different deformation approaches are highlighted by the arrows in the figure. Firstly, the same as the results indicated by the 2D WAXD patterns, all the samples were oriented better than their original states after deformation. Secondly, tensile-stretching process could feature better orientation level than die-drawing process for all samples with or without nucleating agents. Thirdly, although the starting orientation degree was similar for the neat samples and the $\alpha$-nucleated samples, the former exhibited better orientation after die-drawing process ($S_{(040)}=-0.30$ and $-0.24$ at $R_s$ of 3.8). On the other hand, the difference between the neat and the $\alpha$-nucleated tensile-stretched samples was not evident ($S_{(040)}=-0.35$ and $-0.35$ at $R_s$ of 4.7). Fourthly, the free stretched IPP at a higher deformation temperature favored in obtaining a higher orientation at an earlier $R_s$. This behavior could be associated with the higher molecular chains mobility at a higher temperature, which strengthened the large scale of melting and recrystallization of lamellae in advance.[38] Such influence of deformation temperature on the orientation of die-drawn IPP samples was intensively reduced.

In a whole, the method of processing could affect the microstructure evolution of IPP during deformation and more importantly, the microstructure induced during deformation could also be influenced by the initial structure of IPP during die-drawing. One thing to be emphasized is that the $\alpha$-nucleated IPP samples presented a smaller value of final $R_s$ than the neat IPP samples, which was caused by the smaller initial width of the $\alpha$-nucleated samples.

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Evolution of Oriented Parent-Daughter Lamellae during Deformation

To calculate the content of oriented parent lamellae of different samples, ring integral was applied on the (110)\(\alpha\) lattice plane diffraction ring and the 1D curves of neat samples are depicted in Fig. 5. The integral azimuth ranged from −50° to 130° since the diffraction signal of the parent-daughter lamellae is symmetrical. The angle between a set of parent and daughter lamellae was around either 80° or 100°, bringing out different diffraction signal azimuth angles on the diffraction ring of (110)\(\alpha\) lattice plane. But at the isotropic state, the signal of parent lamellae and daughter lamellae would merge as the black curve in Fig. 5. The intensity distribution along the azimuth angle was approximately even making it impossible to distinguish the parent lamellae and daughter lamellae. Thus, we could exclude the isotropic cross-hatched structure by subtracting the baseline of these azimuthal integrated profiles in Fig. 5. The rest intensities of the subtracted profiles were predominantly devoted by the oriented lamellae and the fraction of oriented parent lamellae could be obtained through Eq. (5). The lamellae with normal parallel to the elongation direction were defined as parent lamellae.

Inspecting the intensity's azimuthal profiles, one finds a gradual reduction of the intensity with increasing RA, except for that at the azimuth angles perpendicular to the stretching direction, which is also the location of final parent lamellae. It should be made clear that only part of the lamellae with normal along the stretching direction belong to parent lamellae because most of the newly formed oriented lamellae due to stress induced melting and recrystallization do not show strong capability of inducing daughter lamellae. This is better seen from the data presented in azimuthal intensity distribution of (110)\(\alpha\) of the free stretched sample in the bottom chart.

Fig. 3 Selected 2D WAXD patterns of samples deformed at 130 °C via different processes. The top two rows are the patterns of die-drawn samples and the other two are for tensile-stretched samples. (a) and (c) represent the neat samples while (b) and (d) are for \(\alpha\)-nucleated samples. Deformation direction: horizontal.

Fig. 4 The (040)\(\alpha\)-order parameters of samples deformed at different temperatures via two processes. The top one represents the neat samples and the bottom one depicts the \(\alpha\)-nucleated samples.

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of Fig. 5. Globally, the free stretching intends to destroy all existing crystalline lamellae regardless parent or daughter ones along all directions and transforms all freed polymeric chain segments into highly oriented lamellae with normal along the stretching direction. As a result, to the extent of current deformation ratio, only a small fraction of diffraction originates from daughter lamellae adhered to the parent lamellae previously already possessing an orientation with the normal along stretching direction. Comparing data of the die-drawn and free stretched samples presented in Fig. 5, one immediately recognizes that a larger fraction of daughter lamellae can be observed in the die-drawn sample at the same deformation. This suggests strongly that a preferential preservation of the original parent and daughter lamellae already possessing such orientation has been realized via die drawing. In addition, the crystallinity almost stayed unchanged during all the deformation case, as included in Fig. S1 in the electronic supplementary information (ESI). Such a result could be assigned to the high deformation temperature favoring the formation of ordered crystallites, which would not decrease the crystallinity of sample initially featured with high crystallinity. $R_\alpha$ was not high enough to induce the disentanglement of the oriented amorphous network which can be recognized through the large strain cavitation,\cite{Lyu, D. et al. / Chinese J. Polym. Sci. 2021, 39, 91–101} so the crystallinity hardly increased.

Fig. 6 depicts the evolution of oriented parent lamellae fractions of samples deformed via different modes. The solid and hollow symbols represent the results of the die-drawn and tensile-stretched samples, respectively. These fractions are relative values instead of the absolute ones in the whole system since the randomly distributed lamellae have not been considered in accounting for the meaning of the baseline subtracted in Fig 5. However, the oriented lamellae increased with consuming the isotropic lamellae as the $R_\alpha$ increased, which means the fractions of oriented parent lamellae given in Fig. 6 became much closer to the absolute values in the whole system at the final deformation region. At the initial deformation stage, the $\alpha$-nucleated samples had an average value of 20% oriented parent lamellae, which is slightly higher than the neat $iPP$ samples with 12%. It confirms that the $\alpha$-nucleating agents DMDBS promoted the evolution of oriented lamellae during injection. With increasing $R_\alpha$, the oriented parent lamellae of all the neat $iPP$ samples kept increasing along with the draw ratio, indicating that the melting of original crystallites and recrystallization of new crystallites with normal parallel to the drawing direction took place. Although the fraction of oriented parent lamellae in the $\alpha$-nucleated samples first gave a slight decrease at the early deformation stage, the final fraction still increased. Considering that the $\alpha$-nucleated samples contained larger fraction of ori-

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With α-nucleating agents

The die-drawn sample, the main deformation area was inside the die. The oriented parent lamellae therefore increased slightly at $R_A$ larger than 2.61, where it was the region outside of the die. Furthermore, we also found that the final parent lamellae fractions of samples deformed via tensile-stretching were larger than the ones of die-drawn samples regardless of deformation temperature, indicating a less content of oriented cross-hatched structure was built in the former case.

The performance mentioned above could also be found in the α-nucleated samples. In the case of free stretched samples, both the neat and nucleated samples showed the same turning points around $R_A$ of 1.35. The final fractions of oriented parent lamellae in these two samples almost reached 90% notwithstanding the difference at the beginning. However, there were certain differences as comparing the neat and α-nucleated samples deformed through the die-drawing. It was clear that the final oriented parent lamellae fractions of the neat ones were larger than the α-nucleated ones during the whole deformation. The deformation temperature influenced the formation of the oriented parent lamellae of α-nucleated iPP as well. A higher stretching temperature preferred in forming a smaller fraction of oriented parent lamellae. In addition, the turning point at $R_A$ of 2.50 in the α-nucleated samples was slightly smaller than the one observed in the neat samples during die-drawing. Such result was attributed to the smaller $R_A$ of α-nucleated iPP samples at the out gate of die.

Combining the results given in Figs. 4 and 6, it could be concluded that the die-drawing process was in favor of the preservation of oriented parent-daughter lamellae and the existence of α-nucleating agents further enlarged the content of the oriented parent-daughter lamellae of die-drawn samples. A higher deformation temperature was also beneficial to obtaining an appropriate content of oriented cross-hatched structure in the die-drawn iPP. In contrast, the drawing temperature and the α-nucleating agents hardly affected the final fraction of oriented parent lamellae of iPP during free tensile stretching. All the iPP samples showed 90% oriented parent lamellae at the late deformation stage. Evidently, the die-drawing process had an advantage in obtaining the oriented cross-hatched structure, especially at high deformation temperature. In other words, it could be expected to achieve bi-orientation lamellae in iPP through die-drawing.

Another thing that should be emphasized is the turning points observed in Fig. 6 could also be found in Fig. 4, but the values of $R_A$ at the turning points in Fig. 4 were beyond the necking position for the free stretched samples. For example, the turning points of orientation parameter in the 140 and 145 °C free stretched cases were around $R_A$=1.7. It can be understood if we look deep into the calculation methods of the orientation parameter and the fraction of oriented parent fraction. In the case of orientation parameter (Fig. 4), it is a result of the arrangement of all molecular chains in the whole system. For the fraction of oriented parent lamellae (Fig. 6), only the oriented lamellae are considered and the fraction of randomly distributed lamellae has been excluded. Especially, the oriented lamellae only took a small fraction in the whole system at the early deformation stage. Therefore, we observed a later turning point in Fig. 4 since the large scale re-

Fig. 6  The evolution of oriented parent lamellae fractions of samples deformed at different temperatures via two deformation processes. The top one was the results of neat samples and the bottom depicted the results of samples with α-nucleating agents. (Error bar: within 4%)

tained parent lamellae after injection, these oriented lamellae could be regarded as the load-bearing subjects at the beginning of deformation. We thus observed an early decrease of the content of oriented parent lamellae in the α-nucleated samples due to the breakage of the original oriented parent lamellae. Besides, both deformation processes exhibited critical turning points which were used to reflect the rate for inducing oriented lamellae. Before these critical points, the oriented parent lamellae were born with a fast rate. Beyond these points, the growth of oriented lamellae suddenly slowed down. In a detailed analysis, the difference of the oriented parent-daughter lamellae developed during different deformation processes could be summarized as follows.

(I) In terms of the results of the neat samples shown in the top of Fig. 6, the turning points for obtaining a larger number of oriented parent lamellae in the tensile stretched iPP and the die-drawn samples were at $R_A$ around 1.35 and 2.61, respectively. $R_A$ of 1.35 was matched with the necking position of free stretched samples and the one of 2.61 was not far away from the corresponding die exit position on the die-drawn samples. Because the melting and recrystallization were mainly activated at the position of necking, the increase of the oriented parent lamellae in iPP samples became much slower at $R_A$ larger than 1.35 during free stretching. For
arrangement of molecular chains in the whole system could not be finished at the necking position. For the die-drawn iPP samples, the turning points for orientation parameter in Fig. 4 were similar to these found in Fig. 6. As discussed above, the factions given in Fig. 6 could represent the absolute values in the whole system at the large $R_A$. It means that both the orientation parameter and the fraction of oriented parent lamellae reflected their counterpart situations in the whole system at large $R_A$. Thus, the turning points for the orientation parameter and for the fraction of oriented parent lamellae in iPP during die drawing coincided with each other.

The Cause for a High Fraction of Bi-oriented Structure in Die-drawn iPP

As well known, the plastic deformation of semi-crystalline polymers was supposed to be controlled sequentially by two dominant mechanisms, the first one defined as crystalline slippage and the successive one noted as melting-recrystallization. At the early stage of deformation, i.e. around yield, the crystalline layers would slip to keep up with the macroscopic shape change. Beyond that, the melting and recrystallization of crystallites would take place. The stress imposed on the crystalline block progressively increased along with deformation and finally caused the mechanical melting. Crystalline layers or crystallites would be further degraded into smaller pieces so that molecular chains could relatively be freed and realign along the stretching direction to generate new crystallites.

For understanding the difference observed in samples deformed via two deformation modes, the relative optimal deformation path induced by the die in die-drawing process was primarily considered. During deformation the existence of die could contain the stress applied on the samples at a relatively low level comparing to tensile-stretching method. Clearly, the stress was the intrinsic reason of the adjustment of molecular chains and crystalline destruction. In our previous work the forces applied on the samples during die-drawing were resolved into parallel and perpendicular forces to the elongation direction, as illustrated in Fig. 2. In contrast, the stress was only applied along the machine direction in the tensile stretching process. The underlying reason that made the different results of samples prepared by these two methods should be the different forces applied on the samples.

Inspired by the work addressed by Aboulfaraj et al., the force applied on the lamellae at different positions inside the spherulite was analyzed in the case of die-drawing process. To gain a clearer look, the forces parallel and perpendicular to the drawing direction were further transformed into forces parallel and perpendicular to the normal of parent crystalline layers and the details are presented in Fig. 7. $F_\parallel$ and $F_\perp$ represent the force along the elongation direction and the one perpendicular to the drawing direction, respectively. The longer rectangles represent the original parent lamellae, while the shorter ones depict the affiliating daughter lamellae. Clearly, the forces along different directions had different effects on the lamellae at different positions ((a) equatorial region, (c) polar region, (b) and (d) diagonal region) of the spherulites.

**Fig. 7** The force applied on the lamellae during die-drawing process at four representative positions inside the spherulites. $F_\parallel$: force parallel to the elongation direction. $F_\perp$: force perpendicular to the elongation direction. Red arrows represent the resolved effect of either $F_\parallel$ or $F_\perp$ along and perpendicular to the normal of parent lamellae.

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As shown in Fig. 7, \( F_{\perp} \) tended to separate and subsequently destroy the adjacent parent lamellae at position (a), promoting the rearrangement of molecular chains along the deformation direction. At positions (b) and (d), the effect of the force was similar, tending to slide the lamellae against each other and successively destroy the lamellae at the same time. Then, the molecular chains recrystallized into the new lamellae with normal parallel to the \( F_{\perp} \) direction. At position (c) the force would stretch the parent lamellae along the direction perpendicular to the molecular chains, which was in favor of the crystalline destruction in the following melting-recrystallization process.

\( F_{\perp} \) by contrast could induce distinctively different influences on the lamellae at above-mentioned positions. Compressional force was supposed to be found in the lamellae at position (a), which could help keep the integrity of the parent lamellae. Although both \( F_{\parallel} \) and \( F_{\perp} \) would make the adjacent lamellae slide against each other at positions (b) and (d), the latter one would push them together instead of separating them. Such effect would make it harder for the adjacent parent lamellae to slip against each other and be mechanical melted, possibly leading to a bad reorientation along the force of \( F_{\perp} \). The lamellae at position (c) would be pressed together as well due to \( F_{\perp} \). In summary, it seemed that \( F_{\perp} \) could weaken the effect of \( F_{\parallel} \). As a consequence, the die-drawing process could not provide the efficient stress for melting the original lamellae and generating the new lamellae with normal along the \( F_{\parallel} \) direction.

As for the tensile-stretched samples, it is not difficult to deduce that similar but not the exactly same effect of \( F_{\perp} \) was achieved in the tensile-stretching process. Compared to the die-drawing process, larger stress was required during the tensile-stretching at high strains\(^{[25,26]} \). Because the stress should be strong enough, the melting of original lamellae and the recrystallization of new lamellae could proceed during deformation.\(^{[38]} \) The stress applied on the lamellae of iPP during free stretching was apparently larger than the one during die-drawing in account of the absence of \( F_{\perp} \). Hence, less original lamellae at any direction could be preserved and more new lamellae along the force direction were born in the iPP during the free tensile test. We thus observed a higher oriented parent lamellae fraction and a better orientation of molecular chains for the free drawn iPP at the final deformation stage, as shown in Figs. 4 and 6. The different behaviors found between samples deformed via different processes were supposed to be mainly originated from the \( F_{\perp} \) force perpendicular to the elongation direction.

With respect to the difference between the neat and the \( \alpha \)-nucleated samples deformed via the same process, the existence of \( \alpha \)-nucleating agents could elevate the crystallization temperature during injection molding\(^{[31]} \) as evidenced by the higher crystallinity and the larger long spacing displayed in Fig. 8. In the situation of free stretching, the stress exerted upon the lamellae was high enough for inducing the melting and recrystallization of original crystallities. It could be envisaged that most of the original lamellae could be melted and recrystallize into the new ones during free stretching. The initial microstructures, such as a high crystallinity and a large value of \( d_{ac} \), had no effects on the final content of oriented parent lamellae and the orientation of molecular chains. Accordingly, both the neat iPP and the \( \alpha \)-nucleated iPP presented the similar fractions of oriented parent lamellae and orientation degree of molecular chains at the later deformation region.

![Die-drawing](https://i.imgur.com/5zjR5.jpg)

![Tensile stretching](https://i.imgur.com/3yR5j.jpg)

Fig. 8 The evolution of long spacing \( d_{ac} \) against the deformation ratio \( R_{\lambda} \) in different deformation cases. (Error bar: within 0.9 nm.)

In the case of die-drawing, the melting and recrystallization of original lamellae had already become difficult due to the less sufficient force of \( F_{\perp} \) weakened by the one of \( F_{\perp} \). The breakage and recrystallization of thicker lamellae should require a larger stress, as being confirmed in our previous work.\(^{[38]} \) Therefore, the fragment and recrystallization of the \( \alpha \)-nucleated iPP born with thicker lamellae were limited during die-drawing. The number of newly-created lamellae with normal parallel to \( F_{\perp} \) in the \( \alpha \)-nucleated iPP became smaller, so that we observed a lower fraction of oriented parent lamellae after die-drawing.

Additionally, a higher deformation temperature could also increase the initial \( d_{ac} \) of iPP due to the annealing effect, as evidenced by the results in Fig. 8. The corresponding results further influenced the fraction of oriented parent lamellae in the \( \alpha \)-nucleated iPP during die-drawing. The distinct evolution of \( d_{ac} \) of iPP during free stretching and die drawing at the same temperature might be caused by the calculation error and that the initial thicker lamellae without melting during die-drawing also contributed a slight larger \( d_{ac} \) at final deformation stage. Such existing difference had certain influences on the structure evolution of iPP during stretching.

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while it did not affect the main discussion and conclusion in the current work. Although the α-nucleated iPP samples had distinct fractions of oriented parent lamellae at different temperatures during die-drawing, the orientation degrees of molecular chains of these samples registered in Fig. 4 were nearly constant. Such performances might be a result of the whole molecular chains of iPP deformed at different temperatures with a lower orientation degree. The slight increase of parent lamellae with normal parallel to the deformation direction could not lead to a significant change in the orientation degree of molecular chains.

CONCLUSIONS

The oriented cross-hatched structure evolution of die-drawn samples was revealed by employing the wide-angle X-ray technique and the tensile-stretched samples deformed at the same conditions were chosen as a reference. It turned out that not only the deformation mode, the existence of α-nucleating agents and the deformation temperature could also affect the final parent lamellae fractions of iPP after die drawing. The die-drawing process apparently had an advantage over the tensile stretching in preserving more oriented parent-daughter of iPP. The die-induced force $F_{\perp}$ which was perpendicular to the elongation direction was the main reason for causing the lower fractions of oriented parent lamellae with normal along the deformation direction in the die-drawn samples. This effect could be enlarged when the sample was with thicker initial lamellae. Thus, the final oriented parent lamellae of iPP during die-drawing was influenced by the addition of α-nucleating agents and the deformation temperature. Without $F_{\perp}$, the original lamellae could be mechanically melted and the molecular chains would realign along the elongation direction for forming the new lamellae due to the sufficient stress. Hence, the influence of α-nucleating agents and the deformation temperature on the development of oriented parent lamellae disappeared in the free stretched iPP samples. This work revealed the essence of the oriented parent-daughter lamellae evolution during the die-drawing process and provided a novel entrance for regulating the oriented cross-hatched structure at solid state iPP.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2465-z.

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