In Situ Studies on the Temperature-Related Deformation Behavior of Isotactic Polypropylene Spherulites With Uniaxial Stretching: The Effect of Crystallization Conditions

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The deformation behavior of isotactic polypropylene (iPP) spherulites with uniaxial stretching was investigated at different drawing temperatures via in situ polarized optical microscope (POM) observation. The iPP spherulites were prepared by two procedures: cooled to the room temperature from melt and annealed at 135, 140, and 145 °C for 3 h. It was found that the crystallization conditions dominate the crystalline morphology and even the tensile properties of iPP. For iPP which crystallized during cooling progress, the spherulites were imperfect and the boundaries of the spherulites were diffuse, displaying good toughness at various drawing temperatures. For iPP annealed at high temperatures displayed the brittle fracture-modes and the crack happened between spherulites, which due to the large and perfective spherulites have thick lamellas and weak connection at interspherulitic boundary. The shape and size of the iPP spherulites formed at 140 and 145 °C are affected with uniaxial stretching till to the fracture of the samples at different drawing temperatures. The spherulites obtained at 135 °C are deformed along the drawing direction at 100 °C but not affected at low drawing temperatures, indicating the toughness increased with the increase of the drawing temperatures. POLYM. ENG. SCI., 53:125–133, 2013. © 2012 Society of Plastics Engineers

INTRODUCTION

Semicrystalline polymers have been drawn attention by the industry for their advantages such as enhanced mechanical and chemical properties as well as the ease of manufacturing and recycling. Toughness is one of the most important criteria for semicrystalline polymers as engineering materials. Several models have been proposed to deal with the relationship between the structure and toughness of polymers. A well-known model proposed by Wu claimed that the interparticle distance (ID, also called matrix ligament thickness) is the most important morphology parameter that dominates the brittle–tough transition of polymer blends [1, 2]. If ID is smaller than a critical value (IDc), the blend is tough, otherwise the blend is brittle. However, the toughening behavior of semicrystalline polymers was not consistent with this model [3–6]. For the multiscale polymer crystalline structures were not considered in Wu’s model. Most semicrystalline polymers are composing of hierarchical structures, such as a lamella, fibril (as a lamella bundle), and spherulite superstructures. The mechanical properties and the functional performance of the semicrystalline polymers are determined by the final crystalline structures. Therefore, the deformation of the polymer crystalline structures is an important factor in the mechanical properties of the polymers.

It is known that the deformation-induced structure transitions in semicrystalline polymers can allow the manipulation of mechanical properties. On deformation, the isotropic structure of polymer materials can be transformed into an anisotropic structure due to the orientation of polymer chains. Hence, the mechanism of such transitions and how they are related to the resulting morphology, structure, and physicomechanical properties are of great scientific interest and practical importance in polymer science. It is also understood that when crystalline polymers are in the molten state, chains are entangled in a dynamic manner. As the temperature is reduced, some chains can crystallize and the entanglement points are excluded from the crystalline domains and become concentrated in the interlamellar amorphous regions. Thus, the concentration and distribution of chain entanglements in interlamellar
amorphous regions would affect the final mechanical properties. The applicable properties of crystalline polymers are determined by their final formed structures and the process of structure formation. The mechanical properties of semicrystalline polymeric materials are also influenced by crystallinity, crystalline structure and morphology, amorphous chain orientation, distribution, and concentration of tie chains in the amorphous regions of interlamellae and interspherulite. The appearance of one or other crystalline modification depends on many factors. These include crystallization conditions (melt or solution temperature, rate of cooling, presence of specific nucleating agents, type of substrate, etc.) and mechanical treatment (drawing, pressing, and rate of treatment) [7, 8].

Comprehensive understanding of crystallization, orientation, and the deformation of crystals under a force field is essential to the performance of the semicrystalline polymer products. The related issues have attracted interests of many researchers [9–19]. Under static condition, the spherulites exist in most of the semicrystalline polymers. The morphology of spherulites can be modified by flow stretching due to the uncoiled polymer molecular chains, so that the extended-chain crystals are formed as well. Deformation of the polymer spherulite has been investigated extensively over more than four decades [20–23]. Kay and Keller observed the deformation behavior of spherulites by polarized optical microscope (POM) and found both homogenous and inhomogenous deformation pathways within and between the spherulites [24]. Samules quantitatively calculated the spherulite deformation of isotactic polypropylene (iPP) using small angle light scattering (SALS), they stated the deformation of iPP in hot drawing is the affine deformation [25]. Seguela and coworkers observed the spherulite deformation of polybutene with atomic force microscopy and found that the local deformation of the spherulites was very close to homogenous and obeyed an affine deformation law over the whole strain range and the interspherulitic boundaries displayed very high cohesion [26, 27]. Lee et al. investigated the deformation of isolated linear polyethylene spherulite with lamellar resolution in a dilute blend with branched polyethylene as matrix under different drawing temperatures [28]. A wealth of experiments has revealed the microdeformation processes that accompany the transformation of spherulitic lamellae into a microfibrillar structure. Under drawing the deformation of the spherulite and the rearrangement from a spherulite to a fibril structure has been widely observed [29–32]. The deformation process always involves structure changes like the dislocation and distortion of crystals, sliding and slipping, twisting and dissociation of lamellae, unfolding of molecular chains, cavitation and fibrillation, etc. [33–35]. However, the size of spherulite is in micrometer scale and can be conveniently observed by POM. It is well known that the semicrystalline polymers were brittle with large and perfect spherulite. To our knowledge, the influences of the crystalline morphology and crystallization procedure on the mechanical behavior of the semicrystalline polymers have not been well understood [36–38].

iPP was chosen as a model polymer in this work because of its hierarchical structure, consisting microscale spherulites, nanoscale crystalline lamellae, and atomic-scale crystal unit cells [39–41]. The relationship between deformation and structure evolution of iPP at different scales has been documented [32, 33, 42]. The in situ and ex situ studies of spherulite structural deformation and rearrangement during drawing have been performed by various measurement techniques, such as scanning electron microscopy (SEM) [43], SALS [44], small-angle X-ray scattering (SAXS) [45], wide-angle X-ray scattering (WAXD) [46], and POM [47] measurements. Although the deformation mechanisms have been proposed, the structure deformation in iPP still remains far from being well understood. In the present work, we emphasize on elucidating the uniaxial deformation of spherulite with different crystallization and testing conditions, that is changing annealing temperatures and drawing temperatures, by in situ POM-tensile measurement.

EXPERIMENTAL

Materials

The iPP used in this study is a commercial product of Aldrich Chemical Company. The \( M_w \) and \( M_n \) are \( 3.4 \times 10^5 \) g/mol and \( 7.4 \times 10^4 \) g/mol, respectively, measured by gel permeation chromatography. The melting point of iPP is around 165°C, measured by differential scanning calorimeter.

Sample Preparation for Uniaxial Drawing

The iPP pellets were compression-molded into less than 0.1-mm-thick sheets with erasing of heat and mechanical history at 220°C. Then cooled at a rate of 30°C/min down to the annealing temperatures: 135, 140, and 145°C and kept for 3 h. The prepared samples were designated as PP135, PP140, and PP145. The sample prepared at 25°C was cooled from 220°C and designated as PP25. Dumb-bell specimens were cut from the above special treated samples.

In Situ POM Observation During Uniaxial Drawing

Uniaxial tensile deformation was performed with a Linkam TST 350 Tensile Stress Testing System equipped with Linkam Polarizing Microscope and Q-imaging color video camera. The deformation measurements were performed at 25, 60, and 100°C with a tensile rate of 1 \( \mu \)m/s. The engineering stress–strain curves and cross polarized POM images related to the morphological change were obtained simultaneously from the Linkam Tensile Stress Testing System.
Small Angle X-Ray Scattering Measurements

SAXS measurements were conducted at the synchrotron X-ray beamline 4B9A at the Beijing Synchrotron Radiation Facility (China). The wavelength ($\lambda$) of the X-ray beam was 0.154 nm and the distance from detector to the sample position was 1750 mm. A MAR345 detector was used for data collection and all data were corrected for background scattering before analysis and treated with software Fit2D.

RESULTS AND DISCUSSION

Drawing at 25°C

The typical stress–strain curves and selected POM images during the drawing process obtained at 25°C are shown in Fig. 1. From the results in Fig. 1a, one can find that PP25 exhibited the ductility at low tensile speed. A yield point is at the strain lower than 10% after the beginning of deformation. With further drawing, the stress dropped rapidly at the beginning and after a critical point became stable with increasing strain. This phenomenon is referred to as strain softening, which was associated with the dislocation of the original crystals [37]. Generally, strain softening was related to the necking effect, which is a macroscopic effect. The corresponding POM pictures showed that PP25 formed imperfect spherulites during the cooling progress. The fast cooling rate and the low temperature led to the fast crystallization rate of PP25. It is known that the perfect spherulites develop at high crystallization temperature, the spherulites formed at low crystallization temperature have more defects such as little cavities [37, 38]. In this work, the spherulite size was small and the spherulite boundary was diffuse before drawing. The spherulite morphology changed little but the defects became obvious and the sample structures became loose after yield point, indicating the original spherulites began to dislocate. The samples were elongated and the distinct fibrillar structure emerged with further strain, which was aligned parallel to each other along the drawing direction. Finally, the original spherulites completely disappeared and fibrils formed before the sample fractured. For PP25, no regular spherulites formed, it was difficult to observe the initial deformation position of the sample. The crystal-
line morphology of iPP changed from spherulite to fibril during drawing has been widely observed and studied [33, 42, 43]. These findings suggested that the applied stress was quite localized in the spherulite, which might reflect the variation in the lamellar morphology.

The sample fractured at short elongation, indicating that PP135 was brittle when drawn at 25°C as shown in Fig. 1b. The related POM images showed typical spherulite morphology at the early stage of drawing. With the drawing proceeded, it was interesting to observe that the breakdown took place at the interspherulitic boundaries. Kay and Keller considered the films thinner along the spherulite boundaries than elsewhere, which would produce stress concentration and deformation between spherulites [24]. However, it was still not clear whether this particular effect reflected an intrinsic property and they found that the conditions for such interspherulitic deformation occurred only under conditions which favored inhomogeneous deformation of the spherulites themselves. To study whether the interspherulitic breakdown is the universal phenomenon of iPP, the other two iPP samples annealed at 140 and 145°C were drawn at 25°C, as shown in Fig. 1c and d. Similar to PP135, the typical spherulitic feature was formed and the boundaries between spherulites were sharp after annealing at high temperatures. Both PP140 and PP145 fractured in the brittle-mode with low elongation at break. At the late stage of drawing, the crack appeared along the spherulite boundary, and there were no any adhesive samples between the cracked spherulite boundaries, suggesting that the break was brittle. The above experiment result shows that the deformation at the interspherulitic boundary is common during iPP drawing.

**Drawing at 60°C**

Temperature is an important factor on the polymer processing and dramatically affects the mechanical properties of semicrystalline polymers. In this section, the uniaxial tensile deformation of iPP films was performed at 60°C. The engineering stress–strain curves of the samples are illustrated in Fig. 2. The observed stress–strain curve of PP25 was generally similar to that obtained at 25°C as shown in Fig. 2a. Interestingly, the distinct fibril structure appeared at higher strain than that drawn at 25°C. With drawing proceeded the voids and defects appeared and was elongated along the deformation direction. Fig. 2b shows the stress–strain curve obtained of PP135 drawing at 60°C. The sample fractured at a strain of 6.5%, also in brittle manner. However, comparing with that drawing at 25°C, the elongation at break was a little higher, which implied that iPP became more tenacious with the elevated temperature. The morphology changes of PP135 observed on the micrometer level by POM during deformation at 60°C were also similar as that obtained at 25°C with
cracking at the spherulite boundary. The spherulites at the fractured boundaries preserved original morphology, no elongated spherulites were observed during drawing. Amorphous region at the iPP spherulites boundaries acted as the interspherulitic connections. The amorphous iPP between the segregated boundaries were adhesive and elongated, suggested that PP135 turned tenaciously at higher temperature. Fig. 2c and d shows the stress–strain curves during drawing at 60°C of PP140 and PP145. PP140 and PP145 show the similar mechanical behaviors and morphology developments. There were no elongated amorphous samples appeared between the fractured interspherulitic boundaries and exhibited the interspherulitic damage during drawing at 60°C, indicated that the samples annealed at higher temperatures were much more brittle. The same as the observation of POM pictures at 25°C, the boundaries of the spherulites become sharper with the higher annealing temperature. It is feasible to deduce that if neighboring spherulites share sharper boundary, the amorphous connections at the boundaries are weaker, and the extensibility will be worse.

**Drawing at 100°C**

Fig. 3 presents the stress–strain curve and the POM images of the samples deformed with increasing strains at 100°C. A two-stage linear stress–strain response of PP25 was seen after yield from Fig. 3a. The initial stage exhibited that the stress changed little with the increased strain, which is related to strain softening. The final stage exhibited that the stress increased with strain, which could be attributed to the dominant process of strain-induced crystallization, sometimes termed as the strain-hardening stage [33]. The occurrence of strain hardening was accompanied with longer extension and higher stress. The morphology development of PP25 during drawing at 100°C was similar to that observed at low temperatures.

Fig. 3b shows the stress–strain curve and POM images obtained from PP135 drawing at 100°C. The fracture elongation of PP135 drawn at 100°C was about 10%, which was much higher than that obtained at low drawing temperatures. POM pictures showed that for PP135 the damage also happened at interspherulitic boundaries. More amorphous connections occurred between the boundaries and were prolonged by further drawing, which finally changed to fibrillar structure. Fig. 3c and d shows the stress–strain curves and the POM images during drawing at 100°C of PP140 and PP145. The samples were all cracked at interspherulitic boundaries and elongated amorphous connections appeared at the boundaries. However, the stress–strain curves show that the samples

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FIG. 3. The typical stress–strain curves and selected POM images during the drawing process obtained at 100°C: (a) PP25; (b) PP135; (c) PP140; and (d) PP145. Deformation direction is perpendicular.
fractured in a brittle manner, similar to that drawing at low temperatures.

The above results obtained at different drawing temperatures indicate that the interspherulitic deformation was the universal phenomenon of iPP, which has been annealed at the temperature higher than 135°C. The samples were much crisper with the increased annealed temperature.

DISCUSSION

The spherulites of PP25 grew fast and impinged on each other quickly, resulting in imperfect crystalline morphology with diffuse spherulite boundary and complex interspherulite structure during the process of sample preparation. Therefore, it is not so easier to be dislocated and rearranged for the imperfect spherulites under stretching with tensile deformation. It displays ductile fracture at different drawing temperatures.

For iPP annealed above 135°C from melt, the large and perfect spherulites formed with boundary defect. The obtained long period and lamellar thickness according to SAXS measurements and one dimension electron density correlation function indicated that both of the long period and lamellar thickness increase with the annealing temperatures as shown in Fig. 4. Combining the investigations of mechanical properties, it is obvious that the larger lamellar thickness makes the interlamellar connection weaker. The tie molecules, entanglement points and the macromolecular terminal groups would be aggregated in the amorphous region, which formed the interlamellae and interspherulites when the samples prepared at higher crystallization temperature. Therefore, they cannot sustain larger extensional deformation as reports [37, 38]. This suggests that the original crystalline structure plays an important role on the mechanical properties of semicrystalline polymers and determines the final morphology and property after drawing. The drawing of iPP which annealed at different temperatures showed that the samples cracked at the spherulite boundaries as shown in the related POM images. The spherulite diameters (parallel and perpendicular to the stretching direction) were recorded simultaneously with the increase of strain until the breakdown and showed in Figs. 5–7. As the spherulites grew freely and collide into each other during annealing progress, the spherulite diameters at the two directions were not equal. Figs. 5 and 6 show that the spherulite diameters of the three samples did not change with the increase of strain when stretched at 25 and 60°C. The results indicate that the spherulites were not deformed or deformed not in affine way during drawing, even though the crack occurred at the interspherulitic boundaries. To our knowledge the affine deformation often

FIG. 4. Long period and the lamellae thickness varied with annealing temperatures for iPP.

FIG. 5. The spherulite size varied with strain during drawing on 25°C: (a) PP135; (b) PP140; and (c) PP145. The measurement direction of the spherulite diameter is parallel and perpendicular to drawing direction, respectively.
occurred during the uniaxial drawing of polyolefin spherulites. Samules [25] and Erhardt and Stein [48] studied the affine deformation of iPP and LDPE using SALS. The experimental and calculated patterns were compared in terms of the shape of the clover leaf pattern and the intensity distribution along the radial angle and the azimuthal angle. They found excellent agreement between the macroscopic draw ratio and the extension of the spherulites and stated the deformation is affine deformation. In this work, we have not observed the affine deformation of iPP spherulites. The amorphous region in between the crystalline lamellae that composes iPP spherulite boundaries acted as the interspherulitic connections. It is known that the samples crystallized at higher temperature are composed of thicker crystalline lamellae and the amorphous region including more tie molecules, entanglement points and the macromolecular terminal groups. The crystallinity of iPP increased with the crystallization temperature, and accordingly, the amorphous fraction decreased with more defect [38]. The crystals with larger sizes and more perfect have less ability to rearrange themselves under stretching and therefore the brittle deformation occurs. From the observation of POM images, the boundaries of the iPP spherulites change from dull to sharp as the annealing temperature increases. It can be concluded that if neighboring spherulites share sharper boundary and

FIG. 6. The spherulite size changed with strain during drawing on 60°C: (a) PP135; (b) PP140; and (c) PP145. The measurement direction of the spherulite diameter is parallel and perpendicular to drawing direction, respectively.

FIG. 7. The spherulite size changed with strain during drawing on 100°C: (a) PP135; (b) PP140; and (c) PP145. The measurement direction of the spherulite diameter is parallel and perpendicular to drawing direction, respectively.
more defect in the amorphous region, extensibility will be worse, and fracture will be happened at the sharper boundary during stretching.

Fig. 7 shows the spherulite sizes of PP135, PP140, and PP145 changed with strains during drawing at 100°C. For PP140 and PP145, the spherulite sizes did not change with the strain, the same as that drawing at 25 and 60°C, indicating the spherulites would not be deformed until fracture happened and the samples were brittle. Pang et al. also observed the similar phenomenon with WAXD investigation [38]. They found that iPP specimen which isothermal crystallized at 130°C for 30 and 60 min exhibited unoriented structure when iPP fractured in ductile–brittle transition, indicating that the specimens fractured in brittle manner maintain nearly unchanged crystalline structure. In our experiment for PP135, an interesting phenomenon was observed as shown in Fig. 7a. The size of spherulites changed little at the strain below 1%, indicating the spherulite did not deform at the early stage of drawing. With the drawing proceeded the spherulite size increased in the direction parallel to the stretched direction with the strain. Meanwhile the spherulite size decreased in the direction perpendicular to the stretch direction simultaneously, indicating the deformation of spherulites. Then, the spherulite size decreased in the direction parallel to the stretched direction with further increase of the strain and finally recovered to its original value. At the same time, the size of the spherulite in the direction perpendicular to the strain direction reversed back to its original value as well. Theoretically, the mobility of the molecular chain was higher at high temperature so the molecules in the amorphous state gradually orient along the tensile direction and the dislocation and rearrangement of the crystalline lamellae in the spherulites will occur under the extensional stretching. Comparing to the tight structure of the spherulite, the interspherulitic forces are much lower, so that the samples are fractured with shorter elongation, which implies a brittle fracture. After breaking at the interspherulitic boundary, the tensile force applied on the spherulite was decreased, thus the lamellae together with the spherulite will reverse to the original size and morphology at higher temperature. The deformation of the lamellae and spherulite together with the orientation of the molecular chains gradually disappeared. This result also suggested the toughness of PP135 increased with the elevated drawing temperature. For PP140 and PP145 as shown in Fig. 7b and c, the spherulites are more perfect and the sizes of the spherulites are larger, the interspherulitic connections are weaker with more defect, and consequently they fractured in a brittle manner under drawing. The mechanical properties changed little with different drawing temperatures.

The aforementioned deformation mechanism of iPP is shown schematically in Fig. 8. The scheme of the drawing of the PP25 was the same as that proposed by Pang et al. [37], as shown in Fig. 8A. Small spherulites with low perfection formed by cooling progress, due to the crystallization was much faster with cooling. The spherulitic boundaries were diffuse and the amorphous connections between the iPP spherulites increased. These less perfect spherulites have higher ability to respond to extensional deformation, resulting in larger elongation. As the imposed stretching proceeds, the dissociation of lamellae and slipping of chains may occur, the molecules in the amorphous state orient along the tensile direction. Given further extension, the unfolding of molecular chains may occur, or even microfibrillation and cavitation. The perfect spherulites with sharp boundary are formed by annealing process at higher temperatures. The size of the spherulites increased with the increase of annealing temperatures, as shown as Fig. 8B (for PP135) and C (for PP140 and PP145). The larger spherulites comprise thicker crystalline lamellae with higher perfection and stability and thinner amorphous region with more defect and friability. For PP135, the amorphous connection is relatively stronger than that of PP140 and PP145. At low drawing temperature, the molecular chain has low mobility, the slipping and the unfolding of the chains is difficult to occur, so PP135 fractured without deformation of spherulites at interspherulitic boundaries, shown as Fig. 8b1 and b2. At high drawing temperature, the molecular mobility increases so that the dislocation, tilting and sliding of lamellae may occur under drawing and the amorphous molecules chain stretched along the drawing direction, the spherulites begin to deform and the samples fractured at the deformed interspherulitic boundaries with the further stretching, as shown in Fig. 8b3. After the crack happened between the spherulites, the size of the deformed spherulite recovered, as shown in Fig. 8b4. For PP140 and PP145, when stretched, it is difficult for the
thick lamellae to rearrange themselves to respond to tensile deformation, and the connections are weak, so that the samples are fractured with short elongation. It is concluded that the original crystalline structure governs the mechanical properties of iPP.

CONCLUSIONS

The uniaxial extensional deformation of iPP which were prepared with different crystallization methods has been investigated at different drawing temperatures. The crystallization mode (directly cooling to the room temperature and annealing at high temperatures) and the annealing temperatures dominated the crystalline structure and the consequent mechanical properties of iPP. The less perfect spherulites formed by cooling progress (PP25) increased the interspherulitic connections thus increased the toughness of iPP. These samples displayed typical stress–strain curves including yield, strain softening, and strain harden progress. The samples are fractured with short elongation. It is concluded that the original crystalline structure governs the mechanical properties of iPP.

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