Study on Crystallization Behavior of Polypropylene Induced by Nucleating Agent

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Abstract—The melting and recrystallization behavior of -iPP crystal induced by β-nucleating agent was studied. A new type of α-modification has been developed by self-seeding process. The growth process of these crystals is just like “photographic development process.” Crystalline phase transformation and the memory effect caused by local order was observed during the melting and annealing process. A high temperature is sufficient to destroy the local order and the β-nucleating agent efficiently induces formation of β-form.

1. Introduction

The isotactic polypropylene is a typical semicrystalline polymer with polycrystalline forms. Due to the different chemical properties of materials and processing techniques, the main crystal forms of the polypropylene are α-form and γ-form. The α-crystal and β-crystal are common forms[1-7], and there is an interesting and special growth transition between α and β-phases. The study of Varga showed that there was an obvious memory phenomenon in the melting process of β-polypropylene, that is, there were still some locally ordered molecular chain fragments in the melt when the melting temperature reached the melting point of β-form or α-form[8]. These ordered fragments would grow into α-crystals as nuclei through self-nucleation after cooling or recrystallizing process.

2. Experimental Section

2.1. Materials and Sample Preparation

The matrix material used in this work was commercial grade iPP, with Mw and Mn about 2.5×105 g mol⁻¹ and 6.7×104 g mol⁻¹ respectively. The melting temperature of this material was measured by DSC to be around 170 ℃. The granular iPP materials were used without any further treatment. The
β-nucleating agent was calcium heptanoate obtained from the acid-base neutralization reaction between heptanoic acid and calcium hydroxide. A small amount of β-nucleating agent and iPP granules were blended and extruded in a small internal mixer at 190 °C. IPP films about 10-20 µm thick were compression molded from iPP granules containing β-nucleating agent at 200°C at a pressure of 28 MPa.

The β-iPP film was heated to 200°C for 10 min to remove the thermal history, and then cooled to the crystallization temperature for isothermally crystallizing rapidly. The samples were isothermally crystallized from the melt at 135°C for 30 min and then cooled to room temperature. The influence of thermal history on the process of recrystallization was observed. The samples were isothermally crystallized at 135°C at a cooling rate of 60 °C/min.

In order to enhance the contrast and clarity of the sample under SEM, the sample was etched according to the method of Basstt et al. [9]. Firstly, 98% concentrated sulfuric acid and 85% phosphoric acid were mixed in a 2:1 volume ratio, and then 1% potassium permanganate was added under constant stirring to get the dark green etching solution. Secondly, the samples were etched in etching solution for 1-2 hours and then washed with a mixture of sulfuric acid, water and hydrogen peroxide according to the volume ratio of 2:7:1, and then washed with distilled water and acetone for about two minutes respectively. The samples were dried in a vacuum drying oven and a thin layer of gold is sputtered on its surface.

2.2. Experimental Apparatus
For optical microscopy observation, an Axioskop 40 A Pol Optical Microscope (Carl Zeiss) equipped with a Linkam LTS 350 hot stage was used. The temperature accuracy is to ±0.1 °C. The cooling rates were set at 60°C min⁻¹. All optical micrographs presented in this paper were taken under crossed polarizers. For electric microscopy observation, A JSM-6701F field emission scanning electron microscope (SEM) was used. The acceleration voltage is 5kV and emission current is 10μA.

3. Results and Discussions
Figure 1(a) shows a polarized optical micrograph of β-iPP spherulites, using a primary red filter (λ-plate). In our procedure, we first heated the iPP matrix to 200°C for 10 min to erase thermal history of the sample on subsequent crystallization and then isothermally crystallizing at 135°C for 60 min. It can be seen that there were obviously different between β-iPP spherulites and α-iPP spherulites, because the optical classification of β-iPP spherulites was related to the detail crystal plate microstructure [6,11]. The A-axis direction (according to hexagonal cell) of β-iPP spherulite and the radial spherulite growth direction were consistent [6,10,11]. The optical micrographs of β-spherulites usually appear brighter due to their strong negative refraction. There was a sag boundary between β-iPP and α-iPP crystals due to the higher linear growth rate of β-iPP spherulite. The α-iPP spherulites showed mixed spherulites with relatively weak birefringence. Figure 1(b) presents a scanning electron microscope image of the interface between β-iPP spherulite and α-iPP spherulite, isothermally crystallizing at 135°C. It can be seen that the β-iPP spherulites exhibited a hexagonal helical dislocation crystal plate structure [12]. The α-iPP crystals exhibited 'cross-hatched' morphology. In α-iPP crystals, there are radial banded lamellas and "cross projection" tangential lamella almost perpendicularly oriented along the radius exist. To enhance the contrast and clarity of the samples, the samples were etched and sputtered a layer of gold on the surface.
Fig. 1 Optical micrographs, using a primary red filter (λ-plate), presenting the α-iPP and β-iPP spherulities which were isothermally crystallized from the melt at 135 °C for 60 min (a); SEM micrographs of the α-iPP and β-iPP spherulities which were isothermally crystallized from the melt at 135 °C for 30 min and then cooled to room temperature(b).

Fig. 2 Optical micrographs, using a primary red filter (λ-plate), presenting the melting process of β-iPP spherulities: which were isothermally crystallized from the melt at 135 °C for 30 min and then cooled to room temperature. The pictures were taken at (a) RT, (b) 165 °C, (c) 135 °C for 10 sec, and (d) 20 min during the cooling process after melting at 165 °C.

Figure 2(a) presents a polarized optical micrograph of iPP film containing β-nucleating agent which were firstly heated to 200 °C to erase thermal history and subsequently reduced to room temperature after isothermal crystallization at 135 °C for 30 min. It can be observed that a small amount of β-iPP spherulites (as shown by the arrow) and α-iPP spherulites growing at 135 °C. Figure 2(b) shows β-iPP spherulites started to melt at about 165 °C and the birefringence disappears (as indicated by the arrow). At the same time, α-iPP spherulites still existed under melting point. Figure 2(c) indicated that the growth of β-crystals was different from that in Figure 2(a) after melting at 165 °C for 1 min and then cooled to 135 °C for isothermal crystallization. Crystals appeared immediately as photo-developing (about 30 sec). The surface of spherulites was more uniform with weak birefringence. There was no change for the newly formed crystals with the growth of crystallization time, as shown in Figure 2(d). This is because the crystals were not melted completely at the lower melting temperature. In the subsequent cooling crystallized process, these incomplete melting crystals can be used as nuclei to induce crystallization. This crystallization process is known as self-seeding.

Figure 3(a) shows a polarized optical micrograph of β-iPP spherulites with same thermal history as figure 2(a). Figure 3(b) shows β-iPP spherulites and α-iPP spherulites melted away in the visible range of optical microscope after heated to 173 °C for 1 min. Figure 3(c) presented that the phenomenon in the process of cooling recrystallization was similar to Figure 2(c) which crystals appeared immediately.
as photo-developing for memory effect (as shown by the arrow), and the birefringence of the crystals is relatively weak. Microcrystals appeared in the range of α-iPP spherulites and the crystallized process was very fast. With the increase of isothermally crystallizing time, the new crystals formed in the range of α-iPP spherulites continues to increase and showed positive birefringence as shown in figure 3(d).

![Fig. 3 Optical micrographs, using a primary red filter (λ-plate), presenting the melting process of β-iPP spherulities which were isothermally crystallized from the melt at 135 °C for 30 min and then cooled to room temperature. The pictures were taken at (a) RT, (b) 173 °C, (c) 135 °C for 10 sec and (d) 15 min during the cooling process after melting at 173 °C](image)

Figure 4 presents a polarized optical micrograph of a sample with the same thermal history with Figure 2, which was heated to 200 °C and then cooled to 135 °C for isothermally recrystallizing. Figure 4(b) presents that the crystals completely fused to a random state after heated to 200 °C. Crystal particles and the ordered molecular chain of melt were completely destroyed and the samples became to complete disorder anisotropic melt. The β -nucleating agent will play a leading role of inducing β-iPP spherulite crystals shown as in Figure 4(c).

![Fig. 4 Optical micrographs, using a primary red filter (λ-plate), presenting the melting process of β-iPP spherulities which were isothermally crystallized from the melt at 135 °C for 30 min and then cooled to room temperature. The pictures were taken at (a) RT, (b) 200 °C, and (C) 135 °C for 20min during the cooling process after melting at 200 °C](image)
In order to further observe the melting and recrystallizing characteristics of β-iPP crystal with the same thermal history of Figure 2, scanning electron microscope was used to study the phenomenon of β-iPP spherulite which was isothermally crystallizing at 165°C. Figure 5(a) shows that the original β-iPP spherulites have been replaced by a new "spherulite" with a smoother surface (as shown by the arrow). Figure 5(b) indicates that the internal structure of "spherulite" was very different from that of α-iPP spherulite prepared under normal conditions which homogeneous short edge-on wafers replaced the traditional cross-hatched structure. The morphology of the recrystallized samples after melting at 173°C was similar to that at 165°C.

![SEM micrographs](image)

Fig. 5 SEM micrographs of the β-iPP which were treated at 165 °C after isothermally crystallized from the melt at 135 °C for 30 min and then cooled to room temperature.

4. Conclusion

β-iPP crystal induced by β-nucleating agent is a good system for studying memory effect and self-nucleation during melt recrystallization. From the above results, it is clear that the crystals grown within the outline of the original spherulite immediately as photo-developing. With the crystallization time increasing, the growth of crystals were similar to the growth of the conventional α-iPP spherulite. During the melting process, there were still some ordered molecular chain segments in the melt, which would induce self-nucleation crystallization in the following recrystallizing process. Of course, the different melting temperature had a great influence on the phase transition of recrystallization process. There were more helical sequences in the melt at lower melting temperature, and the remaining ordered molecular chains played a leading role in the crystallizing process instead of β-nucleating agent. The β-nucleating agent will induced the formation of β-iPP crystals when the melting temperature was high enough, which can destroy the ordered molecular chains in melt.

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