Competing effect of shear and β-nucleating agent on the crystallization of injection-molded iPP

Guoqiang Zheng,1,2 Xiaoqiong Hao,1 Yaming Wang,1 Chuntai Liu,1 Qinxing Zhang,1 Changyu Shen,1 Jingbo Chen,1 Xiangfang Peng2

1College of Materials Science and Engineering, National Engineering Research Center for Advanced Polymer Processing Technology, Zhengzhou University, Zhengzhou 450002, P.R. China; e-mail: gqzheng@zzu.edu.cn
2The Key Laboratory of Polymer Processing Engineering, Ministry of Education, South China University of Technology, Guang Zhou 510641, P.R. China; e-mail: pmxfpeng@scut.edu.cn

(Received: 28 January, 2009; published: 08 September, 2010)

Abstract: In this study, crystallization at different depth in the injection-molded iPP, filled with β-nucleating agent (β-NA), was investigated. According to WAXD result, one observes that the fraction of β-crystals unevenly distributes along the depth of the injection-molded parts. For iPP with lower content of β-NA, larger amount of β-crystals near the surface is shear induced; meanwhile, for the parts with higher content of β-NA, larger amount of β crystals away from the surface is β-NA induced. From the results, it could be suggested that the traditional role of nucleation agent, i.e., heterogeneous nucleation, under complex thermo-mechanical conditions during injection molding, might be suppressed.

Introduction

Injection molding is one of the common processing techniques for molding thermoplastics. In this process, the melt flow in the mold cavity is exposed to a complex thermo-mechanical environment, which is characterized by high cooling rate and strong stress field and has a significant effect on the microstructure of injection-molded parts [1, 2].

Nucleating agent (NA) is always used in semi-crystalline polymer processing since it can obviously increase the crystallization speed, reduce the cycle time, and improve the physical properties [3, 4]. And, the role of NA on crystallization is generally considered as heterogeneous nucleation. In case of injection molded iPP filled with α-NA, it is found that fraction of β-crystals increases dramatically to a maximum near the surface, and then decreases with the increase of depth till to the core, irrespective of the α-NA concentration. In addition, with an increase of α-NA content, the fraction of β-crystals decreases. This is because that the α-NA is capable of selectively nucleating the α-crystal [3]. With the presence of β-NA, the skin of injection-molded iPP is composed of nearly pure α-crystals, while the core consists of a higher amount of β-form [5]. However, what lead to the change of β-crystals content and how the β-crystal content changes across the depth were not discussed in detail.
The flow in injection molding is also an effective factor in promoting the formation of β-crystals. Actually, during injection molding, NA and the complex thermo-mechanical history might act simultaneously on the crystallization of iPP. Does this mean that flow and β-NA have a synergistic effect on the formation of β-crystals? Yet, up to now, their combined roles are scarcely studied. In this work, the roles of β-NA and flow on the crystallization of injection molded iPP were studied.

**Results and discussion**

Fig. 1 shows the WAXD result for the samples at different positions along the depth. As for the samples at 0 ~ 200μm of PP-0.0, a clear diffraction peak, corresponding to β-crystals, appears at 2θ = 16.1° [6].

![WAXD profiles](image)

**Fig. 1.** WAXD profiles versus distance from the surface (0 μm): (a) PP-0.0; (b) PP-0.05; (c) PP-0.2; (d) PP-0.4.

It also can be found that the intensity of β-crystal peak rises precipitously from 0 μm to 100 μm, and then decreases from 100 μm to 400 μm. For those at 800 μm and 1600 μm, the β-crystal peak vanishes completely. However, for iPP added with β-NA, a different trend of β-crystal development can be found. Generally, the intensity of β-crystal peak increases drastically from the surface (~ 0μm) to the core (~ 1600μm). Simultaneously, that of α- (110), (040) and (130) generally decreases, which indicates that β-crystal is dominant far from the surface. Employing the expression proposed by Turner-Jones [7], one can quantitatively evaluate $f_\beta$ as follows:

$$f_\beta = \frac{h_\beta(300)}{h_u(110) + h_u(040) + h_u(130) + h_\beta(300)}$$

where $h_i(hkl)$ represents the difference between the height of the reflection peak and the amorphous bottom. The $f_\beta$ values are plotted against different distance from the surface, as shown in Fig. 2. Apparently, not only for iPP but also for those containing β-NA, $f_\beta$ is unevenly distributed in the thickness direction, especially for those at 0 ~
400 μm away from the surface. For example, for iPP with lower content of β-NA (PP-0.0 and PP-0.05), \( f_\beta \) dramatically increases from 0 μm to 100 μm, and then it decreases rapidly from 100 μm to about 400 μm. Besides, for PP-0.05, from 200 μm, \( f_\beta \) increases gradually to 60% at 1600 μm, and for PP-0.0, it continues to decrease gradually to about 0% at 1600 μm. However, \( f_\beta \) of the iPP with higher content of β-NA (PP-0.2 and PP-0.4) dramatically increases from 0 μm to 200 μm and then continues to increase gently from 200 μm to 1600 μm. Additionally, near the surface, \( f_\beta \) of the iPP with higher contents of β-NA is generally smaller than that with lower contents of β-NA.

**Fig. 2.** Plot of \( f_\beta \) as a function of concentration of NA and the distance from surface.

![Graph](image)

**Fig. 3.** The exothermic traces of the samples by heating from room temperature to 200 °C at 10 °C/min and being held 200 °C for 3 min, subsequently cooled at 10 °C/min to room temperature and then heated to 200 °C at 10 °C/min: (a)PP-0.0; (b)PP-0.05; (c) PP-0.2; (d)PP-0.4.

To investigate the nucleation type of the samples in a specific part, samples were completely melt at 200 °C for 3 min, and then cooled to room temperature at 10 °C/min, after that, heated to 200°C at 10 °C/min. The melting curves of these
samples are shown in Fig. 3. It can be seen that there exists a single \( \alpha \)-melting peak, at around 165 °C for PP-0.0. However, for the iPP added with \( \beta \)-NA, there appears not only a larger peak at around 150 °C, but also another smaller one at around 167 °C. Obviously, the former corresponds to \( \beta \)-crystal and the latter attributes to \( \alpha \) one. Furthermore, for the samples from a specific part, their profile of melting curves is quite similar. In view of this, it is substantiated once again that, no matter the depth of the samples is in a specific part, crystallization is of the same type once the stress imposed during injection molding is fully eliminated. Thus, the uneven distribution of \( f_\beta \) should be ascribed to the stress imposed during injection molding.

It is well established that, upon applying the shear (flow), some polymer chains orient along the flow direction and then form the oriented \( \alpha \)-nuclei. This is crucial to induce \( \beta \)-crystals [6, 9, 10]. So, it is understandable that larger \( f_\beta \) for the iPP with lower content of \( \beta \)-NA is obtained at around 100μm, owing to the strong shear in this region. On the other hand, in this region, the higher the content of \( \beta \)-NA is, the smaller \( f_\beta \) is, which indicates that the \( \beta \)-NA is disabled in this region. This might be attributed to that, the more additives, the larger probability that \( \beta \)-NA disturbs the formation of the \( \alpha \)-row nuclei [4]. To prove this, the orientation degree was characterized by two-dimension wide-angle X-ray diffraction, which is shown in Fig.4. Clearly, near the surface (~ 200μm), the orientation degree is higher. And, it generally decreases with the increase of the content of \( \beta \)-NA. Therefore, near the surface, it causes the amount of oriented \( \alpha \)-nuclei in PP-0.0, PP-0.05, PP-0.2 and PP-0.4 to decrease one by one. To sum up, the imposed shear near the surface restrains the growth of \( \beta \)-crystals in the iPP with higher content of \( \beta \)-NA.

![Fig. 4. The orientation degree of iPP containing different concentration of \( \beta \)-NA at each layer calculated from \( \alpha \) (040) intensity distribution along the azimuthal angle.](image)

**Fig. 4.** The orientation degree of iPP containing different concentration of \( \beta \)-NA at each layer calculated from \( \alpha \) (040) intensity distribution along the azimuthal angle.

**Conclusions**

For iPP with lower content of \( \beta \)-NA (PP-0.05), near the surface, the formation mechanism of the \( \beta \)-crystals is almost the same as that of pure iPP (PP-0.0), viz., shear induced. However, in this region, for iPP with higher content of \( \beta \)-NA (PP-0.2, PP-0.4), strong shear rate near the surface suppresses the heterogeneous nucleation of \( \beta \)-NA and the formation of \( \beta \)-crystal. No matter what the content of \( \beta \)-NA is, for the samples that are far away from the surface, the formation mechanism of the \( \beta \) form as nucleating agent is heterogeneous nucleation.
Experimental part

iPP (T30S) used is a commercial product from Lanzhou Petroleum Chemical Co., China. Its melt flow index is 2.0 g/10 min (190 °C, 21.6 N). The β-NA (WGB-II), a kind of rare earth organic complexes, was kindly provided by Guangdong Winner Functional Materials, China. It was mixed with iPP in a twin-screw extruder, with a temperature profile of 150, 160, 170, 185, 195, and 190 °C from hopper to die, at a different concentration of β-NA. These specimens were named PP-0.0, PP-0.05, PP-0.2, and PP-0.4, corresponding to the β-NA concentrations of 0, 0.05, 0.2 and 0.4wt % respectively.

Materials were injected into a rectangular cavity of 170×10×4 mm³ with a single-end gate. A HT80T injection molding machine (HaiTian, China) was employed for the molding process, with a temperature profile of 150, 160, 185 and 180°C from hopper to die. Other molding parameters are as follows: mold temperature 40°C, injection pressure 80 MPa, cooling time 30s, holding pressure 40 MPa, holding time 4s.

Using a Leitz (Oberkochen, Germany) microtome, the injection-molded part was first cut at the midpoint and then sliced to 60 μm in thickness from skin to the core. 1D-WAXD patterns were obtained with a Philips X’Pert Graphics & Identify instrument (The Netherlands) operating at 50 kV and 30 mA with Ni-filtered Cu Kα radiation.

The DSC measurement was done using a MDSC-2920 (TA, USA).

2D-WAXD measurements were performed on a Bruker-Nonius D8 Discovery diffractometer with a Cu X-ray generator operating at 40 kV and 40 mA and equipped with a 2D gas filled multiwire detector.

Acknowledgements

The authors gratefully acknowledge the financial support of the National Nature Science Foundation (Grant No.50803060, 10590351, 10772164) and the Opening Project of The Key Laboratory of Polymer Processing Engineering (Grant No. 20071002), Ministry of Education of China. Thanks are also given to Prof. M.Fujiyama from Tokuyama Research Laboratory of Japan for his instructive suggestions.

References