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Banded spherulites of HDPE molded by gas-assisted and conventional injection molding

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ABSTRACT

Crystal morphologies of high density polyethylene (HDPE) with low molecular weight obtained by gas-assisted injection molding (GAIM), conventional injection molding (CIM), and spontaneous cooling, respectively, were studied by scanning electronic microscopy (SEM). It is found that banded spherulites are generated in the inner zone of GAIM parts and the outer zone of CIM parts but are absent in quiescent parts. According to the results, the representative morphologies of crystal change with gradual increment of instantaneous flow field in crystallization from non-banded spherulite to banded spherulite and then to oriented lamellae. This morphological evolution indicates that banded spherulites could be induced by flow field with certain intensity, which is confined by both an upper critical value and a lower one.

1. Introduction

It is well known that polymer crystallization in processing could be influenced by the operating conditions such as flow rate and strain, due to the flow fields imposed on the polymer melt during molding process [1,2]. So far, great efforts have been dedicated to the studies of polymer crystallization in external flow field, and two typical crystal morphologies were reported as flow-induced oriented ones (e.g. shish–kebabs) and spherulites [3–6]. Even though non-banded spherulites are commonly observed in molding process, spherulites exhibiting bands are rarely reported in polymer processing. In fact, they could also be gained in flow field [7] but the intensive research on banded spherulites has been generally made in the quiescent state. Being characterized with alternating edge-on and flat-on lamellae, the presence of banding in polymer spherulites is generally attributable to a twisting of crystallographic orientation along the radial direction of the spherulites [8–11]. However, the effect of mechanical field on the banded spherulite formation and why crystalline lamellae twist in the banded spherulites are still unclear.

Recently, we have carried out intensive investigation on polyolefin achieved by gas-assisted injection molding (GAIM) [12,13]. The main feature of GAIM is that the mold cavity is partially filled with polymer melt, and then compressed gas penetrates the molten polymer and drives it further into the mold end until the cavity is completely occupied. The polymer melt in the GAIM process is confined by both the mold wall and the compressed gas, and is subjected to severe instantaneous flow field during the gas penetration stage, which is more complicated than conventional injection molding (CIM) process. In previous work we investigated the crystal morphology of high-molecular weight HDPE in GAIM, based on the consensus conclusion that polymers with higher molecular weight are more sensitive to flow field than the lower ones [14,15]. It was reported that the GAIM part is characterized with hierarchical crystalline morphologies through the thickness, including a highly oriented skin with parallel lamella stacks, a shish–kebab structured sub-skin, and a typically spherulitic core [13]. In order to systematically understand the relationship between shear intensity, molecular weight and flow induced microstructure in GAIM as a long-term project, research on HDPE with series of molecular weights is one of the necessary subjects. In this communication, the crystal morphology of low molecular weight HDPE obtained via GAIM is investigated based on the previous work. For comparison, the crystal morphologies of the same material obtained by CIM and quiescent melt-crystallization were also studied. Since banded spherulites in GAIM and CIM have never been reported up to now, our work represent the effect of instantaneous shear field on banded spherulite formation and provide a new opportunity to understand fundamental issues about the mechanism of lamellar twisting in banded spherulites.

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2. Experimental section

2.1. Materials

High density polyethylene (HDPE 2911) ($M_w = 1.4 \times 10^5$ g/mol) with a melt flow rate of 20 g/10 min(190 °C/2.16 kg, ASTM D1238) and a density of 0.960 g/cm^3, was supplied by Fushun Petrochemical Corp.

2.2. Sample preparation

The quiescent specimens were prepared by cooling the granular materials from 195 °C to 10 °C (the room temperature) spontaneously after 5 min of constant temperature melting.

A Grand 140–320 injection molding machine was employed for the dynamic specimens molded in the processing fields. During GAIM process, high pressure nitrogen was injected by a gas injection system (model MPC). In order to provide a routeway for gas penetration, the main bodies of both the GAIM and CIM parts were designed in a columned shape, as referred in literature [12]. The difference between them is that the CIM part exhibits a solid structure while the GAIM one shows a hollowed gas channel.

The highest temperature in the temperature profile of the injection molding machine was 195 °C. The mold temperature was about 30 °C. Other detailed experimental procedures and conditions in GAIM molding can be found in Ref. [13]. The CIM process was carried out by using the same processing parameters, except that the melt in CIM process was not exposed to gas penetration and gas-assisted packing process. Thus, it should be noted that the melt injection volume for CIM was as large as 100 vol%.

2.3. Scanning electron microscopy (SEM)

The specimens were characterized via SEM after selective permanganic etching. Before etching, the segments which are 5 mm long in the middle of GAIM and CIM parts were cut, then cryogenically fractured parallel to flow direction in liquid nitrogen. The selected regions in CIM and GAIM parts for observation are illustrated in Fig. 1. For the observation of crystal morphology, all specimens were etched by permanganic etching technique [16]. After the surfaces were covered with a thin layer of gold, the crystalline morphology in different zones of these parts was observed by a SEM instrument, JSM-5900LV, operating at 20 kV.

3. Results and discussion

3.1. The effect of gas penetration on crystal morphology

Fig. 2 shows representative SEM micrographs of crystal morphology in different zones of the etched HDPE molded by GAIM. They are quite different from the counterparts with higher macromolecular weight ($M_w = 5.28 \times 10^5$ g/mol) in previous work, which have, respectively, parallel lamella stacks and shish–kebab in the outer zones, and the common spherulites in the inner zones [13]. Without the appearance of shish–kebab structure, the outer zones of these GAIM parts sketched in Fig. 2(c) are dominated by parallel lamella stacks, perpendicular to the melt flow direction, as shown in (a). This is ascribed to a critical molecular weight that is needed for shish–kebab to be effectively induced at a given shear rate [17,18]. Only when the polymer macromolecular weight is larger than the critical value, the shish–kebab structure could be induced in certain flow field. The thickness of the outer zone is about 200 μm (Fig. 2(c)) along the residual thickness direction (the whole thickness of GAIM part is about 1500 μm. Crystal morphology has always hardly been observed in the 50 μm outer skin of both parts molded by CIM and GAIM, for the possible reasons of etching effect and small quantity of crystal. Therefore, the description in this paper has excluded this skin layer when referring to 'the outer zone' for the sake of brevity).

Most interestingly, one can observe a large number of well-developed banded spherulites going inwards from the interface which is about 200 μm from the outer skin to the inner skin close to gas channel (Fig. 2(b)). Meanwhile, it should be noted that the width of banded spherulite region could be influenced by the processing parameters. To the best of our knowledge, this morphology intensively reported in quiescent melt-crystallization process is observed in GAIM for the first time and seldom reported in other polymer processing methods. In the inner zone, the number and perfection of the banded spherulites vary in the radial direction, as shown in Fig. 3. As the distance from the inner skin close to gas channel decreased from1000 μm (Fig. 3(a)) to 500 μm (b) and then to 100 μm (c), the corresponding radiuses of banded spherulites are 55–85 μm, 35–60 μm and 25–40 μm. However, the distribution density of banded spherulites has an inverse relation with the radius along the residual thickness direction. The change in the radius and density of banded spherulites in the radial direction is the result of the complex thermo-mechanical field gradient [7], which was discussed in subsequent sections.

To obtain a detailed description of the fully grown banded spherulites, the banded spherulites in GAIM parts are investigated by SEM with high magnification, as shown in Fig. 4(a) and (b). Due to the easier dissolution of polymer chains at lamella edges and the different effects of etching between edge-on and flat-on lamellae [19–21], the flat-on lamellae can hardly be observed in the valley regions of the bands, while the edge-on ones are distinctly shown in the bright bands, i.e. the peak zones (Fig. 4(a)). Moreover, in the morphology shown in Fig. 4(b), the lamellae having S- or C-shaped profiles are observed as the pronounced dominant molecular architectures in bright bands, which is primely consistent with other reports [6,8]. These detailed profiles of the curved lamellae are well in line with the features that twisting occurs in the radially grown lamellae of banded spherulites.

Since lamellar twisting has seldom been reported in polymer molding process, the crystal morphologies in the CIM parts with the GAIM parts were compared to explore the effect of gas penetration on the banded spherulite formation. Fig. 5 shows the SEM micrographs of etched surface of HDPE molded by CIM. In Fig. 5(a), unlike the homogeneous distribution of banded spherulites in GAIM parts, banded spherulites in the outer zone of CIM parts are occasionally presented in the form of agglomerates. The thickness of banded spherulites rich zone in CIM parts is about 250 μm in the radial direction and the cross-section diameter of CIM part is about 8 mm, as shown in Fig. 5(c). As for the inner zone, typically common spherulites (non-banded) which have been universally observed as reported in large number of literatures randomly exist in the core of the CIM parts [1,2], with the diameters that ranged from 15 μm to 25 μm, as shown in Fig. 5(b). However, what attracted our very attention and interest is the location of banded spherulites in CIM parts (Fig. 5), combined with the crystal morphology evolution

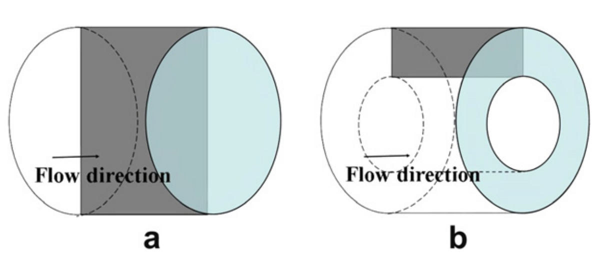

Fig. 1. SEM observation surface (in gray) of HDPE molded by CIM and GAIM. (a) CIM part; (b) GAIM part.