Notes

Distribution of Shish-Kebab Structure of Isotactic Polypropylene under Shear in the Presence of Nucleating Agent

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Introduction

The shish-kebab crystalline structure is a special kind of polymer chain assembly, which consists of the kebabs periodically held together by the shishes.[1−3] The formation of such a two-dimensional crystalline structure is considered to be a direct consequence of the conformational transition of polymer melts from coiled chains to stretched chains when the flow rate exceeds a critical value.[2,4] Longer coiled chains stretch to the shishes while shorter coiled chains epitaxially grow on the existing shishes into the kebabs at the same flow rate.[4−6] Although the flow is absolutely essential for the formation of the shish, computer simulations[4,7] and an experiment[8] have shown that the kebab can form by growing epitaxially on the shish in the absence of any flow. A few shishes can serve as nucleation sites for the kebab growth. Theoretically, a single shish is even predicted to induce a complete shish-kebab structure.[7]

Different morphologies in injection-molded isotactic polypropylene (iPP) plates have been found through the thickness direction.[9−12] The skin region is essentially characterized as amorphous. The broad core region has lower cooling rates that allow a complete relaxation of chains and growth of spherulites, and so the crystallization is generally considered to be quiescent. The skin and core regions are separated by a surface region or a shear zone. Compared with the elongational flow, the shear flow has much less effects on polymer melts, but nevertheless, the shear flow is still sufficient to induce locally the coil-to-stretch transition of polymer melts. This has been frequently evidenced by observations of the shish-kebab structure in the surface region of iPP.[9−12] It is believed that the shear flow induces the shish-kebab structure not only in the surface region but also over a broader range. Polymer chains can be modified in a way that some of them even in the core region align to a certain extent along the flow direction. Experimentally, however, to detect the shish structure is very challenging if its size and number are very small.

This paper reports on effects of a nucleating agent on the formation of the shish-kebab structure and the morphological distribution of injection-molded iPP plate. Nucleating agents enhance the crystallization by lowing the surface energy barrier for primary nucleation. However, nucleating agents cannot bring about the shish structure if there is no any flow at all. It will be seen that nucleating agents can act like a structure probe to trace a true range of the flow field at a position where the shish structure emerges.

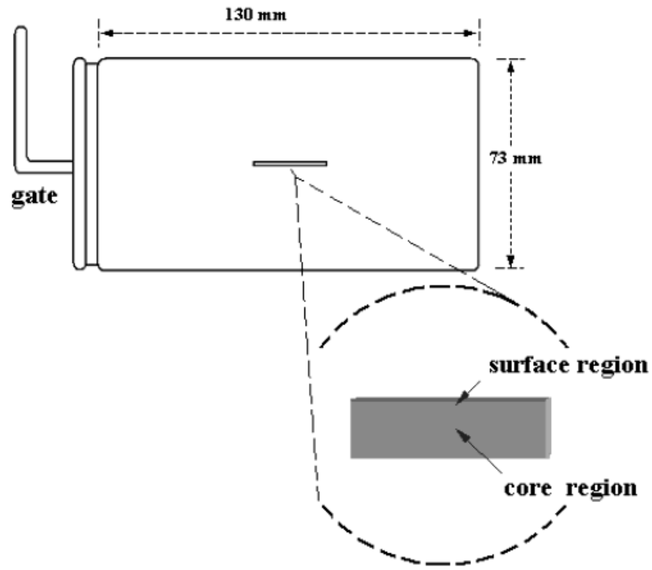

Figure 1. Schematic diagram of an injection-molded iPP plate and a specimen cut at a central position away from the gate. The plane of the specimen is parallel to the flow direction, and the X-ray beam is then perpendicular to the flow direction.

Experimental Section

Isotactic polypropylene (M_w = 260 000, M_n = 41 200) and sodium benzoate (SB) were obtained from Basell. SB was twice mixed with iPP at a SB concentration of 4.0 wt % using an extruder to produce a master batch. This was then mixed with further polymer in the extruder to produce different concentrations of SB before injection molding. The final concentration of SB in the injection molding is 1.2%. Rectangular plates of iPP with a length of 130 mm, width of 73 mm, and thickness of 2.6 mm were then injection molded with conditions as follows: melt temperature 220 °C, mold temperature 60 °C, holding pressure 40 MPa, holding time 3.8 s, and cooling time 40 s. The iPP specimens were cut at a central position away from the gate with a length of 10 mm, a depth of 1.0 mm, and a width of 2.6 mm, as shown in Figure 1. The plane of the specimen is parallel to the flow direction.

Small-angle X-ray scattering (SAXS) experiments were performed at the Australian National Beamline Facility (ANBF) in Tsukuba, Japan. The ANBF is installed on a bending magnet port and delivers monochromatic synchrotron X-rays in the energy range 4.5−20 keV. The instrument has a multiconfiguration vacuum diffractometer that uses image plates as its detector system. The square-shaped microbeam had a dimension of 200 × 200 μm^2. The wavelength of 2.0 Å was employed to record 2D SAXS image patterns. The specimen was mounted at the center of vacuum diffractometer at 570 mm from the image plate. The beam passed through the specimen, and the illuminated zone was changed with a vertical shift of the sample holder along the direction of specimen width. It was assumed that the morphologic distri-

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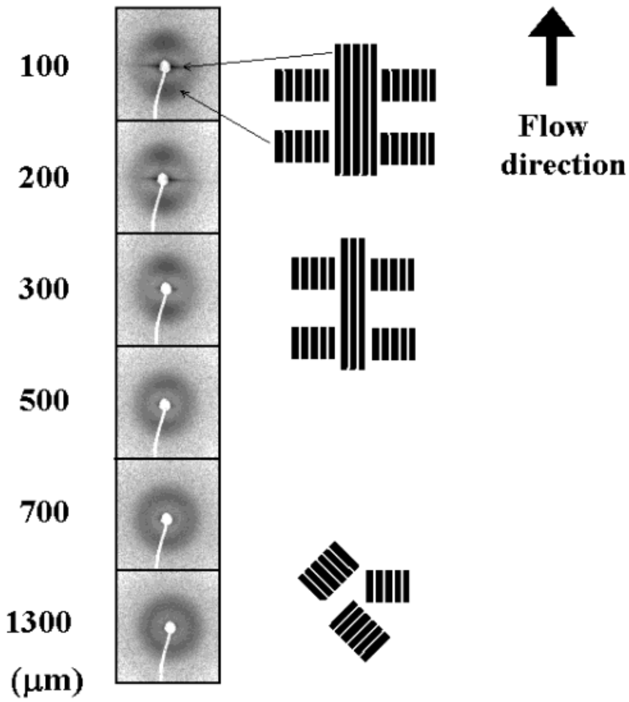

Figure 2. Two-dimensional SAXS image patterns at different distances from the surface in the absence of sodium benzoate.

bution was symmetrical, and only one half-width of a specimen was illuminated in the experiments.

Results and Discussion

Figure 2 shows 2D SAXS image patterns at different distances from the surface through the plate thickness. At 100 and 200 μm, two distinct maxima along equatorial and meridional directions are observed. The equatorial maximum at 300 μm decreases significantly, but the meridional maximum shows, qualitatively, not much change. The equatorial and meridional maxima at 500 μm, if they exist, are very weak. The image patterns show isotropic features with a further increase in the distance toward the plate center.

The equatorial maximum is attributed to a bundle of the shishes parallel to the flow direction whereas the meridional maximum is attributed to the kebab structure perpendicular to the flow direction.[3,13] Figure 2 reveals a distribution of the shish-kebab structure through the thickness of a iPP plate with no SB. The shishes induced by the flow at 100 and 200 μm are more than those at 300 μm simply due to the flow attenuation. However, the image pattern does not, visibly, show that the lower content of the shish at 300 μm has caused a significant change in the kebab. The shish-kebab structure at 500 μm is undecided, although the possibility may not be ruled out. With a further increase in the distance from the surface, the features of oriented images totally disappear. If it is postulated that there is absolutely no shear flow at 1300 μm (the plate center), the questions arises as to where the low limit of the shear flow field is and how the polymer melt is modified in weaker levels of the shear flow.

Figure 3 shows 2D SAXS image patterns at different distances in the presence of SB. As can be seen, the crystallization is remarkably enhanced. The equatorial and meridional maxima at 300 μm become much more distinct. Compared with the image patterns in Figure 2, the shish and kebab structures are clearly seen at 500 μm. Note that the scattering maxima are almost invisible without SB at the same position. The image patterns of 1300 μm remain the exactly same as those without SB. The absence of the shear flow at 1300 μm is therefore confirmed. The morphology of 1300 μm is expected to be the stacks of random crystalline lamellae.

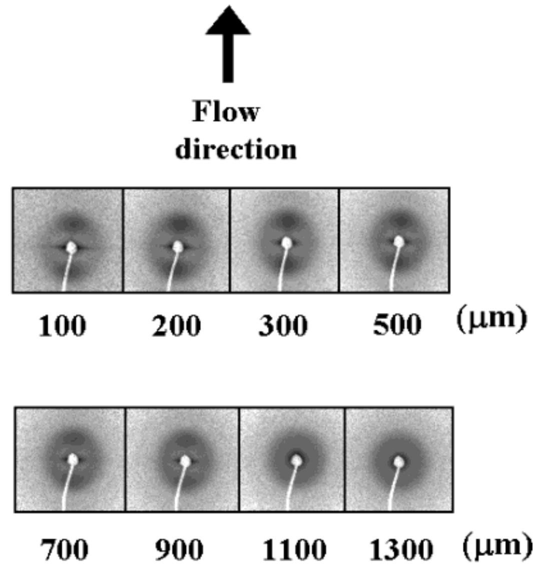

Figure 3. Two-dimensional SAXS image patterns at different distances from the surface in the presence of 1.2 wt % sodium benzoate.

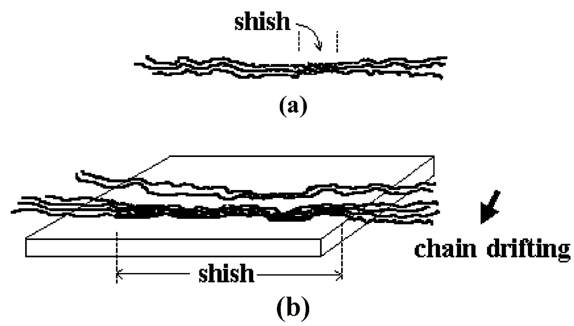

Figure 4. Possible shish sizes: (a) small shishes on the assumption that a few shishes can form in the absence of SB and (b) large shishes in the presence of SB.

It is interesting to see the emergence of the equatorial and meridional maxima at 700 and 900 μm from Figure 3. These two distances are actually beyond the normal range of the shear zone as observed by SAXS and optical microscopy. Since SB molecules cannot cause the formation of the shish-kebab structure, the observation of these oriented image patterns clearly indicates that in the presence of SB the shear flow not only exists at 700 and 900 μm but also is sufficient enough to induce the formation of the shish-kebab structure. The shear flow field is found to distribute over a much broader range than normally thought. For the present system, the limit of the flow field should not be lower than 900 μm. We do not have direct evidence to demonstrate whether a few shishes have already formed at 700 and 900 μm in the absence of SB. If so, the size and/or number of the shish are evidently so small that the shish structure cannot be detected using the current technique. Possible shish sizes are schematically shown in Figure 4. Another possibility that the shish structure does not exist at 700 and 900 μm in the absence of SB cannot be ruled out.

A detailed mechanism of shish crystallization in the flow fields remains open for debate. The addition of a nucleating agent into sheared polymer melts certainly complicates the crystallization process. To the best of our knowledge, the mechanism of shish crystallization in the presence of a nucleating agent is so far unknown. It is suggested that in the initial stage of shish crystallization the lower free energy barrier for the nucleation would allow iPP segments to prealign on the surfaces of SB molecules along the flow direction. These aligned segments can drift together, as suggested by Dukovski and Muthukumer,[4] to form an overlap region in the flow field. Once the overlap regions form, they can spread rapidly over the entire chains on the surfaces of SB to form a complete shish structure.[4]

Conclusions

The distribution of shish-kebab structure of the sheared iPP has been investigated using synchrotron small-angle X-ray scattering. It is found that the shish-kebab structure of iPP emerges in the presence of SB at the positions where this structure is not observed in the absence of SB. Since the SB molecules cannot cause the formation of oriented iPP chains, the addition of SB allows us to infer a true range of the flow field that is sufficient to induce the formation of the shish-kebab structure of iPP. The interesting findings indicate that the flow field actually distributes over a much broader range, and the shish crystallization of iPP can be significantly enhanced in the presence of SB in the shear flow.

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