



Shear induced shish–kebab structure in PP and its blends with LLDPE

Yong Wang^a, Bing Na^a, Qiang Fu^{a,*}, Yongfeng Men^b

^aCollege of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu 610065, People's Republic of China

^bBASF Aktiengesellschaft, Polymer Physics, Ludwigshafen 67056, Germany

Received 3 July 2003; received in revised form 7 October 2003; accepted 7 October 2003

Abstract

In order to better understand the effect of shear stress on the crystal morphology and orientation of polyolefins, dynamic packing injection molding was used to prepare oriented pure polypropylene (PP) and its blends with linear low density polyethylene (LLDPE). The obtained samples were characterized via 2d-SAXS, 2d-WAXD and AFM. Macroscopically, shear induced morphology with surface skin, central core and oriented layer between the skin and the core was observed in the cross-section areas of the samples. For pure PP, a highly oriented structure was seen in the sheared layer but much less oriented structure exists in the core. The orientation in the skin lies in between. The shish–kebab structure, composed of stretched chains (shish) and layered crystalline lamellae (kebabs), was found in the sheared layer. Shish structure exists mainly in the skin layer and oriented spherulites dominates in the core. For PP/LLDPE (50/50) blends, a change of phase morphology from less-phase-separated structure (homogeneous) in the skin, to co-continuous structure in the sheared layer and sea-island structure in the core was observed. PP formed a shish–kebab structure in all the three layers. And on the other hand, a very unique crystal morphology and lamellar orientation of LLDPE were obtained, with the lamellar stack oriented either perpendicularly or 45–50° away from the shear flow direction.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Shear; PP/LLDPE blend; Shish–kebab

1. Introduction

Shear-induced orientation and crystallization in semi-crystalline materials, which is very common in the industrial processing (e.g. extrusion, injection molding), has attracted more and more attentions due to the significant theoretical values and practical applications [1–7]. Many studies have been carried out to investigate the molecular orientation in the deformed melt and the resultant morphological changes during crystallization process. When polymers are crystallized from an oriented or strained melt, shish–kebab textures are usually a predominant feature of their morphology [8,9]. The shish–kebab structure in polyethylene has been intensively studied since it was first reported by Pennings in 1965, where he found a new kind of polymer crystallite in stirred polyethylene solutions [10]. The main effect of shear is to assist the formation of nuclei by the

alignment of polymer chains in the supercooled melt along shear direction. This alignment may act as a precursor for the formation of stable primary nuclei. Then, lamellae will be constrained to grow from the primary nuclei laterally due to their high aspect ratio, resulting in formation of a highly oriented, row-nucleated morphology. It has been concluded that the factors that is responsible for the alignment and relaxation of molecular chains can affect the formation of primary nuclei as well as the shish–kebab texture [11,12]. Observation of shish crystal growth of isotactic polystyrene (iPS) extending into non-strained polymer melt was also reported and explained by a model of an autocatalytically reproduced extensional flow field in the front of the grow tip [13]. Hsiao has recently carried out elegant experiment to study the shear-induced precursor (shish) in iPP melt by in situ Rheo-SAXS and Rheo-WAXD and concluded that the shish–kebab morphology was developed after applying a shear stress at 165°C, near the nominal melting point of iPP [14–17]. The shish-induced layered crystalline lamellae (kebabs) were found to be oriented perpendicularly to the

* Corresponding author. Tel.: +86-288-5460953; fax: +86-288-5405402.

E-mail address: fuqiang1963@yahoo.com (Q. Fu).

flow direction. Even more, for the first time, Hsiao has qualitatively described the shish–kebab morphology in iPP.

Recently, we have carried out intensive investigation on polyolefin blends achieved by dynamic packing injection molding [18–21], which relies on the application of shear stress fields to melt/solid interfaces during the packing stage by means of hydraulically actuated pistons. The main feature is that after the melt is injected into the mold the specimen is forced to move repeatedly in a chamber by two pistons that move reversibly with the same frequency as the solidification progressively occurs from the mold wall to the molding core part. Shear-induced morphology with core in the center and oriented zone surrounding the core was observed in the cross-section areas of the samples [20,21]. It was found that a shish–kebab structure is formed in oriented zone and the amount of shish crystal of HDPE can be promoted by adding second component, such as EVA [22]. In this work, the attention is focused on the shear-induced shish–kebab structure in iPP and its blends with linear low density polyethylene (LLDPE) to gain better understanding of formation of shish–kebab structure of iPP and LLDPE.

2. Experimental

2.1. Materials

The polypropylene (PP) and LLDPE used in the experiment are commercial products, PP (2401) was purchased from the Yan Shan Petroleum Chemical, China (melt flow index is 2.5 g/10 min); and LLDPE (7042) was purchased from the Ji Lin Petroleum Chemical, China (melt flow index is 2.0 g/10 min).

2.2. Samples preparation

Various binary blends were prepared by varying the LLDPE content in iPP matrix. Melt blending of a pair of polymers was conducted using twin-screw extruder (TSSJ-25 co-rotating twin-screw extruder). After making droplets, the blends were molded by dynamic packing injection molding technology. This technology can introduce the shear stress field as the solidification progressively occurs from the mold wall to the molding core part. A sample with highly oriented structure was obtained in this way and called dynamic sample. In this work, the melt temperature is 180 °C, the dynamic packing pressure is 35 MPa, and the packing frequency is 0.3 Hz, respectively. The detailed introduction and experiment procedure was described in Ref. [20]. As mentioned above, macroscopically the dynamic packing injection molded samples can be divided into three layers, namely, the skin, the sheared layer and the core. The three layers were separated manually before the following WAXD and SAXS experiments.

2.3. WAXD experiment

The 2d-wide-angle X-ray scattering experiments (WAXD) were conducted using a Rigaku Denki RAD-B diffractometer. The wavelength of the monochromated X-ray from Cu K α radiation was 0.154 nm and reflection mode was used. The samples were placed with the orientation (flow direction) perpendicular to the beams. The detector was placed about 15 cm from the sample holder. The scattering angles were calibrated using a α -alumina NIST standard. All the 2d-WAXD patterns given in this article have extracted the background thus a qualitative comparison between the 2d-WAXD patterns is made possible.

2.4. SAXD experiment

2d-SAXS measurements were carried out on Nanostar SAXS system, a commercial SAXS system of Bruker AXS GmbH, Karlsruhe, Germany. Typical collection time is 20 min. Calibration of q range is achieved by the scattering of silver behenate.

2.5. Atomic force microscopy (AFM)

AFM experiments were performed with a Nanoscope III scanning probe microscope. The height and phase images were obtained simultaneously while operating the instrument in the tapping mode under ambient conditions. Images were taken at the fundamental resonance frequency of the Si cantilevers, which was typically around 300 kHz. Typical scan speeds during recording were 0.3–1 line/s using scan heads with a maximum range of 16 \times 16 μ m. The phase images represent the variations of relative phase shifts (i.e. the phase angle of the interacting cantilever relative to the phase angle of the freely oscillating cantilever at the resonance frequency) and are thus able to distinguish materials by their material properties (e.g. amorphous and crystalline polymers). The flat surfaces of the samples which were examined, were obtained by cutting with a Diatome diamond knife at \approx -120 °C using an ultramicrotome (Ultracut E, Reichert and Jung) equipped with a cryo-chamber.

3. Results and discussion

3.1. 2d-WAXD result

As mentioned before, for a dynamic sample, shear induced morphology with core in the center and oriented zone surrounding the core was observed in the cross-section areas of the sample. One expects a highly oriented structure in the oriented layer and less oriented structure in the core. Showing as an example, Fig. 1 are the 2d-WAXD patterns of PP at different zone obtained perpendicular to the shear flow direction. For pure PP, in the skin, an intensity

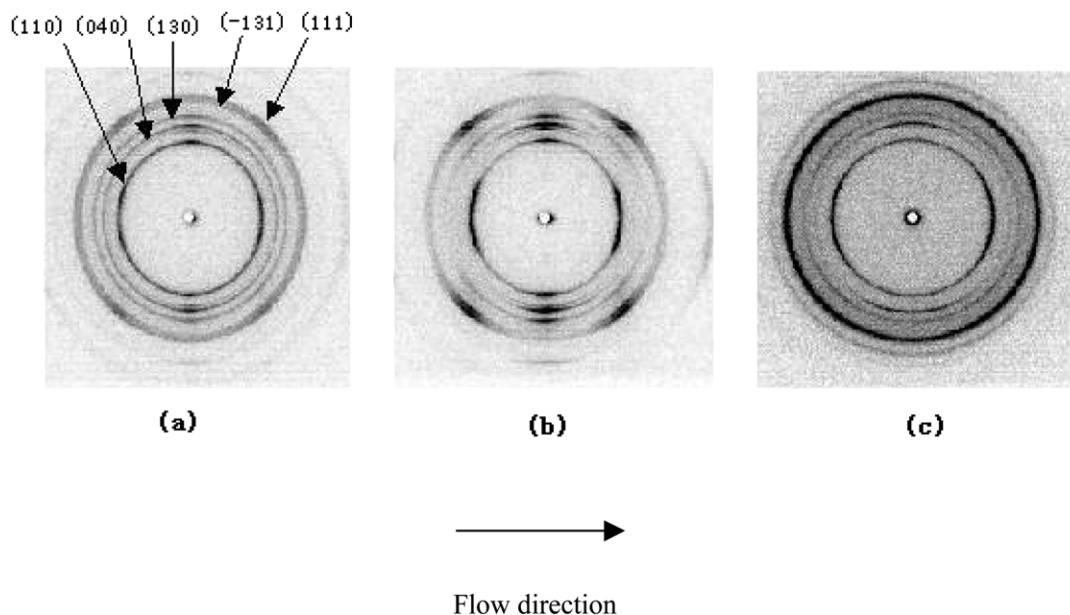


Fig. 1. 2d-WAXD patterns of PP at different zone obtained via the shear stress field. (a) The skin, (b) the shear layer and (c) the core.

distribution of PP is observed, which has five circles in WAXD patterns associated with different lattice planes of PP and there are some spots on the circle, which indicating some orientation of PP. The lattice planes observed are 110, 040, 130, -131 and 111, from inner to outside circles, respectively. It is known that the mode is elongated flow in the skin of the sample, and the molecules tend to orient along the flow direction. In the oriented layer, the circles are weakened and five very sharp dark spots are formed, indicating a highly oriented structure of the PP chain along the shear flow direction. In the core of the sample, only weak four-point arcs of (110) and two points of (040) lattice plane along the meridian can be observed, which suggests much less oriented structure than that in the oriented layer and the skin. The interesting result of 2d-WAXD is the change of orientation of PP as adding LLDPE in matrix PP. Fig. 2 shows 2d-WAXD patterns in the oriented layer of PP after adding LLDPE. One observes a dramatic enhancement of PP orientation by adding LLDPE up to 50 wt % content. The intensity of five distinct reflections become much stronger and reflection spots in the center part can also be seen. Furthermore, one observes two spots of 110 and 200 lattice planes of LLDPE in the blends but only two circles for pure LLDPE, which indicating an enhancement of LLDPE orientation in return by PP. To know the c axis of PP and LLDPE crystallite, we also carried out 2d-WAXD experiments along the flow direction. An isotropic orientation was always seen for all the samples when viewed along the flow direction. The appearance of 200 and 110 of LLDPE lattice planes on the meridian in Fig. 2 indicates that the c -axis is along the flow direction. However, the orientation of c -axis of PP lattice should be carefully examined. Since 040, 110 and 130 of PP lattice planes are observed on the meridian in Figs. 1 and 2, the c -axis should

be along the flow direction. However, a careful examination of the disposition of the inner iPP 110 diffraction arcs in the WAXD in Figs. 1 and 2, it may be due to the well known epitaxial growth in α form of PP with cross hatch crystallographic angle 80.67° [23,24]. The bimodal diffraction patterns in Figs. 1 and 2 are characteristic of the monoclinic crystalline unit cell of the α form. This 2d-WAXD pattern is typical to iPP and is believed due to the crystallographic branching of daughter lamellae growing epitaxially with their a - and c -axes parallel to the c - and a -axes of the parent lamellae, respectively, [25–27]. To know the detail about the degree of orientation and the possibility of epitaxial growth between crystal planes of PP and LLDPE the circularly averaged WAXD intensity profiles with proper crystalline reflections should be analyzed. This is present carrying out in our group.

3.2. 2d-SAXS and AFM results

The detailed crystal morphology can be deduced from 2d-SAXS data. The typical photographs of 2d-SAXS of dynamic sample for pure PP, including skin, oriented and core layers, are shown in Fig. 3. At the skin layer, only two weak spots are seen on the meridian, which indicating that a shish-like structure is formed in this layer. Due to the fast cooling at near the skin upon contact with the cold mold surface, the shish formed under extensional or shear stress can be easily fixed, but not much kebab is developed. On the other hand, two diffused spots are seen on the equatorial direction and less diffraction is seen on the meridian direction for the core, which suggesting that supermolecular structure with less orientation (most likely oriented spherulites) exists in the core layer. Interestingly, one observes two strong spots on the meridian and two weak

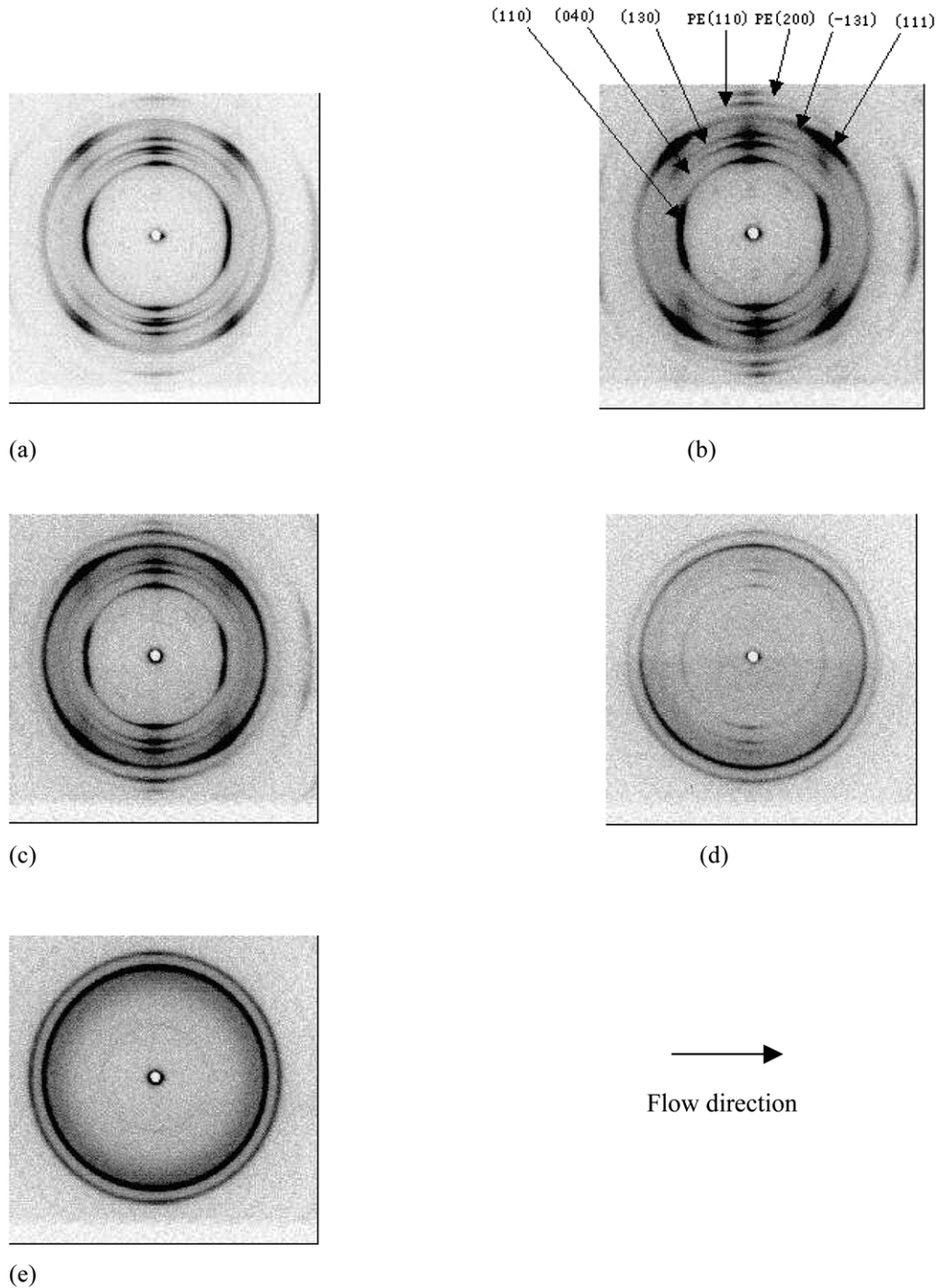


Fig. 2. 2d-WAXD patterns in the oriented layer of PP after adding different content of LLDPE. PP/LLDPE = (a) 100/0, (b) 80/20, (c) 50/50, (d) 20/80 and (e) 0/100.

spots on equatorial as well for the sheared layer, which indicates that a shish-kebab structure of PP is really induced under the effect of shear stress and can be fixed during cooling. The main effect of shear is to assist the formation of nuclei by the alignment of polymer chains in the supercooled melt along shear direction. This alignment acts as a precursor for the formation of stable primary nuclei. Then, lamellae will be constrained to grow from the primary nuclei laterally due to their high aspect ratio, a

process of formation of crystalline lamellae oriented perpendicularly to the flow direction, resulting in formation of a highly oriented, row-nucleated morphology, as in the case for the formation of shish-kebab structure in polyethylene under shear stress.

To understand the crystal morphology of PP/LLDPE blend, one must know the phase morphology first. For this reason, AFM experiment was carried out, and the AFM result for PP/LLDPE (50/50) is shown in Fig. 4. AFM

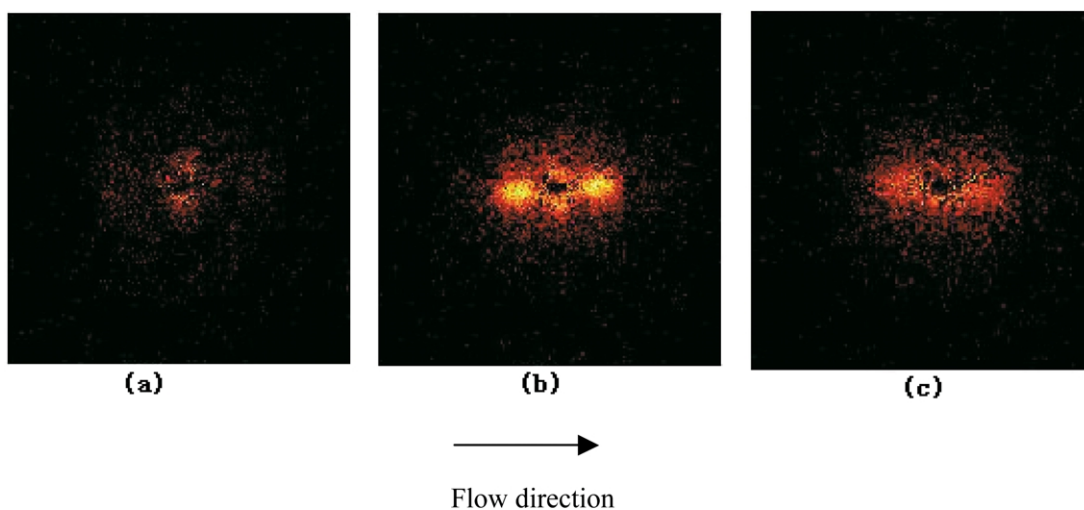


Fig. 3. The typical photographs of 2d-SAXD of dynamic sample for pure PP at different zone. (a) The skin, (b) the shear layer and (c) the core.

photographs were taken from different position from skin to center of the dynamic sample, the number of each picture represents the distance to the edge of sample (mm). From surface up to 0.4 mm is the skin region, from 1.6 to 1.9 mm represents the sheared layer and from 2.3 to 3.5 mm corresponds the core. Since the modulus of PP is much larger than that of LLDPE, the bright region is assigned to PP-rich phase and the dark region is assigned to the LLDPE-rich region. One observes a very homogeneous less phase-separated morphology at skin region. Due to the fast cooling of skin, applied shear has little effect on the morphology. A gradually change of co-continuous phase to island–sea structure under low shear rate is seen starting from 1.6 to 2.3 mm. A clear-cut island-sea structure with 2–3 μm domain is observed in the center (3.5 mm). The big domain size in the core can be explained by longer time cooling. Due to the heat released by the friction during shearing, a longer time is needed for cooling down the sample, which gives the sample more time for phase separation in the center.

Having the phase morphology of PP/LLDPE (50/50) blend, now let us check its crystal morphology and lamellar orientation. The 2d-SAXS patterns of PP/LLDPE (50/50) are shown in Fig. 5. One observes very beautiful but much complicated 2d-SAXS patterns with two sets of diffraction spots for all the three zones. The inner (bright) sets of diffraction spots should be due to the voids formed in the sample during the dynamic packing injection molding, which usually results in a strong diffraction. The out (weak) sets of diffraction comes from lamellae structure of the blend. Since we know from 2d-WAXD patterns that the c -axis for both PP and LLDPE is along flow direction, the diffraction spots on equatorial result from kebabs of PP and LLDPE, which oriented perpendicularly to the flow direction. So they look much diffuse compared with other four spots. Now how do we understand the four diffraction spots along 45–50° direction respect to shear flow direction, which indicating additional lamellar stacks in this direction.

It should be noted that the four diffraction spots are observed at all the three layers, regardless the phase morphology (less phase-separated or macroscopic phase-separated). In order to further emphasize the effect of shear stress on the formation the complicated structure, a corresponding static sample obtained via the conventional molding technology (no shear stress field) was also characterized through 2d-SAXS and the result is shown in Fig. 6. For the static sample, the pattern of 2d-SAXD shows circle-like scattering profile in the core, which is the result of the isotropic morphology, indicating the absence of any detectable structures and/or preferred orientation. But in the skin of the sample, the pattern of 2d-SAXD clearly shows the appearance of equatorial maximal, again due to elongated flow and fast cooling in this layer.

To verify the origin of the SAXS pattern of the blend, an annealing experiment was carried out. The dynamic sample PP/LLDPE (50/50) in the sheared layer was kept 140 °C for 15 min. At this experimental condition, LLDPE will melt and PP should maintain its initially state. The comparison of 2d-SAXD before and after annealing was shown in Fig. 7. It is clearly seen that after annealing, the inner diffraction of voids is completely disappeared. The out side diffraction spots on equatorial become more condensed, which indicating disappear of diffraction from LLDPE. However, the four diffraction spots along 45–50° direction respect to shear flow direction keeps unchanged. As the LLDPE was melted first, it would be very unlikely LLDPE to form a shish kebab structure upon cooling, especially under the presence of the iPP lamellar structure. SAXS patterns clearly indicate the persistence of a lamellar structure for PP and an interesting tilted lamellar structure for LLDPE. It is not clear at this moment why some LLDPE lamellar stacks are oriented 45–50° away from shear direction, and nothing to do with phase morphology. This worth to be further investigated.

For summary, the crystal morphology and orientation of pure PP and PP/LLDPE blend (50/50) can be schematically

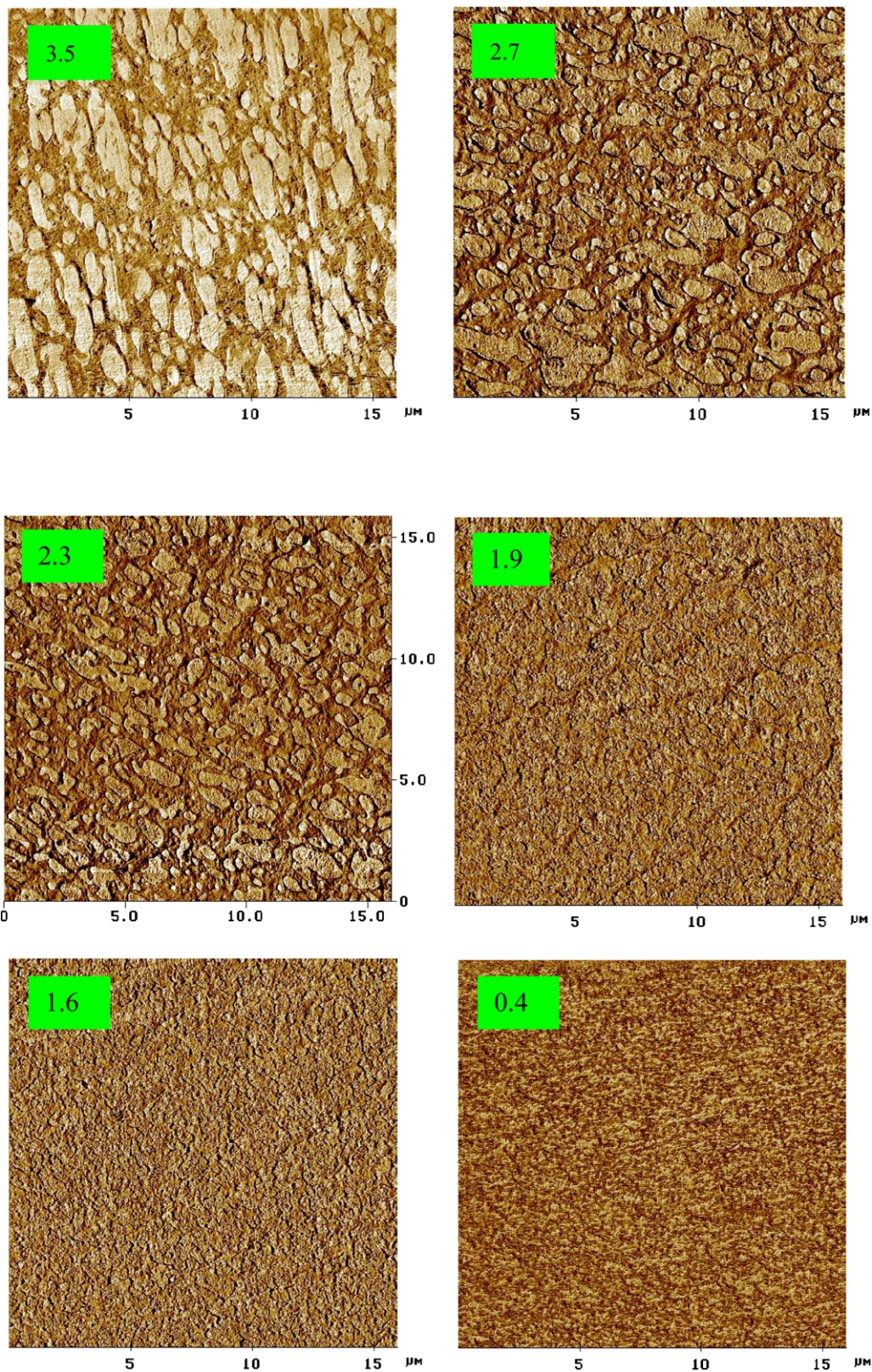


Fig. 4. AFM photographs for PP/LLDPE (50/50), the number of each picture represents the distance to the edge of sample (mm).

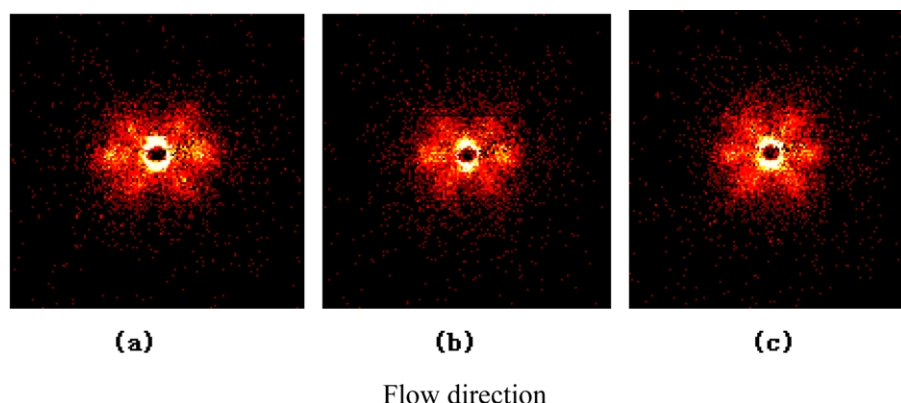


Fig. 5. The 2d-SAXD results of PP/LLDPE (50/50) blends obtained via the shear stress field at different zones. (a) The skin, (b) shear layer and (c) the core.

presented in Fig. 8. For the pure PP, according to the patterns of 2d-SAXD and 2d-WAXD, shish structure (extended chain) is a dominated feature in the skin and oriented lamellar stack (kebab structure) in the core. But in the sheared layer, because of the effect of shear stress along with the flow direction, the oriented lamellar stacks can grow perpendicular with the shish structure, and forms the typical shish–kebab structure. For PP/LLDPE (50/50) blend, a very interesting crystal morphology and lamellar orientation were obtained based on 2d-SAXS, 2d-WAXD and AFM. A separated lamellar stack of PP and LLDPE is formed either in less-phase-separated skin or in macroscopic phase-separated sheared layer or the core. For PP all the lamellar stacks oriented perpendicularly to the flow direction. For LLDPE part of its lamellar stacks is oriented perpendicularly to the flow direction, and part of the lamellar stacks is oriented $45\text{--}50^\circ$ away from shear flow direction. Future work, such as step heating 2d-WAXD or 2d-SAXS experiment from room temperature up to melting temperature of PP, is needed to interpret the lamellar

orientation of PP and LLDPE in the dynamic packing injection molded PP/LLDPE blends.

4. Conclusion

In summary, the oriented iPP and its blends with LLDPE were prepared via the dynamic packing injection molding technology, and the oriented samples were characterized through 2d-WAXD, 2d-SAXD and AFM. For the pure iPP, a strongly oriented structure could be obtained in the oriented layer and in the skin, and much less oriented structure in the core. Furthermore, the 2d-SAXD results suggested that the shish structure existed mainly in the skin, and shish–kebab structure mainly in the oriented layer, but kebab structure of iPP mainly in the core. For the blends of PP/LLDPE (50/50), a change of phase morphology from less-phase-separated structure (homogeneous) at skin, to co-continuous structure at sheared layer and sea–island structure at the core was observed by AFM. Besides the

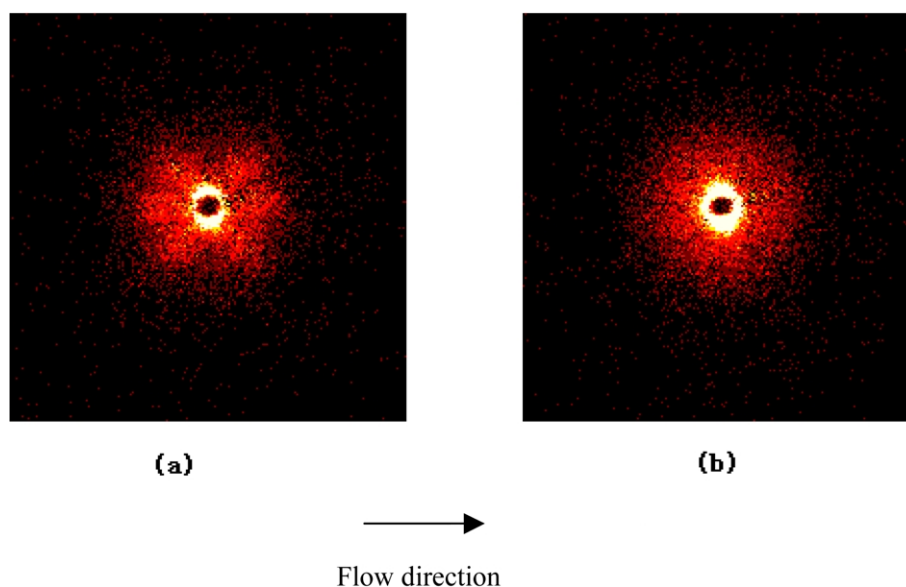


Fig. 6. The 2d-SAXD results of PP/LLDPE (50/50) blends obtained via the conventional molding technology at different zone. (a) The skin and (b) the core.

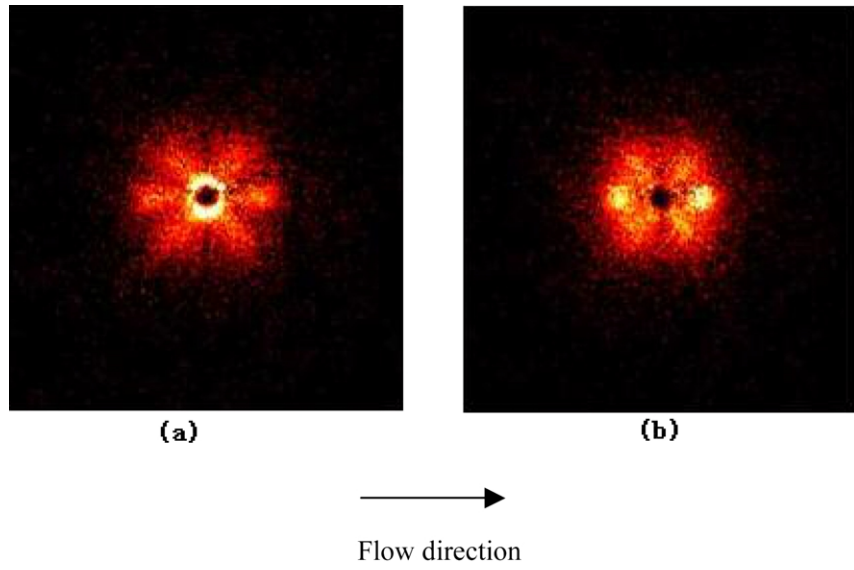


Fig. 7. The comparison of 2d-SAXD results in the core of PP/LLDPE (50/50) before and after annealing. (a) Before annealing and (b) after annealing.

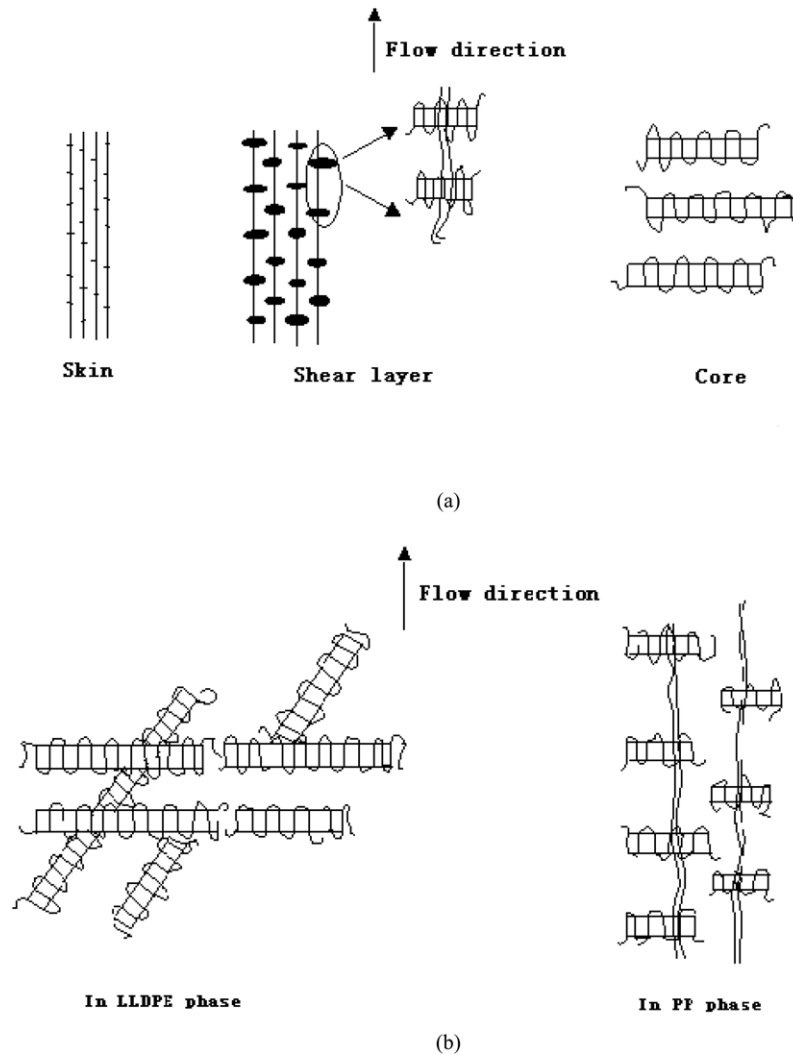


Fig. 8. The schematic representation of the crystal morphology of pure PP and PP/LLDPE blends obtained via the shear stress field. (a) Pure PP and (b) PP/LLDPE blends.

lamellar stack of PP and LLDPE oriented perpendicularly to the flow direction, and an interesting tilted lamellar structure of LLDPE was also found.

Acknowledgements

We would like to express our great thanks to the China National Distinguished Young Investigator Fund (29925413) and National Natural Science Foundation of China (20274028) for Financial Support. This work is also partly supported by Ministry of Education of China for Doctoral Degree (20020610004).

References

- [1] Kobayashi K, Nagasawa T. *J Macromol Sci (Phys)* 1970;B4:331.
- [2] Bushman AC, McHugh AJ. *J Appl Polym Sci* 1997;64:2165.
- [3] Okamoto M, Kubo H, Kotaka T. *Macromolecules* 1998;31:4223.
- [4] Ulcer Y, Cakmak M, Miao J. *J Appl Polym Sci* 1996;60:669.
- [5] Monasse B. *J Mater Sci* 1995;30:5002.
- [6] Duplay C, Monasse B, Haudi JM. *Polym Int* 1999;48:320.
- [7] Wolkowitz MD. *J Polym Sci, Polym Symp* 1978;63:365.
- [8] Odell JA, Grubb DT, Keller A. *Polymer* 1978;19:617.
- [9] Southern JH, Porter RS. *J Appl Polym Sci* 1970;14:2305.
- [10] Pennings AJ, Keil AM, Kolloid ZZ. *Polymer* 1965;205:160.
- [11] Somani RH, Hsiao BS, Nogales A, Srinivas S, Tsou AH, Sics I, Balta-Calleja FJ, Ezquerro TA. *Macromolecules* 2000;33:9385.
- [12] Hosier IL, Bassett DC. *Polymer* 1995;36:4197.
- [13] Peterlin A. *Pure Appl Chem* 1973;8:277.
- [14] Kumaraswamy G, Verma RK, Issaian AM, Wang P, Kornfield JA, Yeh F, Hsiao BS, Olley RH. *Polymer* 2000;41:8931.
- [15] Nogales A, Hsiao BS, Somani RH, Srinivas S, Tsou AH, Balta-Calleja FJ, Ezquerro TA. *Polymer* 2001;42:5247.
- [16] Kumaraswamy G, Kornfield JA, Yeh F, Hsiao BS. *Macromolecules* 2002;35:1762.
- [17] Seki M, Thurman DW, Oberhauser JP, Kornfield JA. *Macromolecules* 2002;35:2583.
- [18] Wang Y, Zou H, Fu Q, Zhang G, Shen KZ. *J Appl Polym Sci* 2002;85:236.
- [19] Fu Q, Wang Y, Li QJ, Zhang G. *Macromol Mater Eng* 2002;287:391.
- [20] Wang Y, Fu Q, Li QJ, Zhang G. *J Polym Sci, Part B: Polym Phys* 2002;40:2086.
- [21] Wang Y, Zou H, Fu Q, Zhang G, Shen KZ, Thomann R. *Macromol Rapid Commun* 2002;23:749.
- [22] Na B, Fu Q. *Polymer* 2002;43:7367.
- [23] Clark ES, Spruiell JE. *Polym Eng Sci* 1976;16:176.
- [24] Andersen PG, Carr SH. *J Mater Sci* 1975;10:870.
- [25] Lotz B, Wittmann JC. *J Polym Sci, Polym Phys* 1986;24:1541.
- [26] Norton DR, Keller A. *Polymer* 1985;26:704.
- [27] Kumaraswamy G, Verma RK, Issaian AM, Wang P, Kornfield JA, Yeh F, Hsiao BS, Olley RH. *Polymer* 2000;41:8931.