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The hierarchy structure and orientation of high density polyethylene obtained via dynamic packing injection molding

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Abstract

The evaluation of microstructure and crystal morphology in injected-molded bar becomes much complicated because of the existence of a shear gradient and a temperature gradient from the skin to the core of the samples. To understand the relationship between shear rate-molecular weight and oriented structure of injection molded bar, in this work, the hierarchy structure and the effect of molecular weight on the formation of shish-kebab structure were investigated by examining the lamellar structure of injection molded samples of high density polyethylene (HDPE) with different melt flow index (MFI), layer by layer, along the sample thickness. To enhance the shear effect, so-called dynamic packing injection molding (DPIM), in which the melt is firstly injected into the mold and then 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, was used to obtain the molded bar. Furthermore, a small amount of ultra-high molecular weight polyethylene (UHMWPE) was added into HDPE to explore the effect of UHMWPE on the crystal morphology and orientation. Our results indicated (1) that the overall orientation in the molded bar increased with decreased MFI, and a small amount of UHMWPE could enhance substantially HDPE orientation; (2) at the skin, there existed intertwined lamellae constituting an interlocked lamellar assembly, a typical shish-kebab structure gradually developed from the subskin-layer to the core, with increased shish content toward the center, but in the core was a spherulite-like superstructure with randomly distributed lamellae; (3) UHMWPE played an important role not only in the formation of shish, but also in the transformation from spherulite to shish-kebab oriented structure for HDPE with a low molecular weight (high MFI).

Keywords: High density polyethylene; Shish; UHMWPE

1. Introduction

Shear-induced orientation and crystallization in semicrystalline polymer, which are very common in the industrial processing (e.g., extrusion, injection molding, spinning), have 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 and the resultant morphological changes during crystallization process under shear flow or in deformed melt. Shish-kebab texture, which was first found in stirred polyethylene solution by Pennings et al. [8], is usually a predominant morphological feature when polymers crystallize in shear flow. The main effect of shear is to assist the formation of nuclei by the alignment of the polymer chains in the super-cooled melt along the shear direction. This alignment may act as precursor for the formation of stable primary nuclei. Many primary nuclei can rapidly grow and forge connectivity along the flow direction to imprint the stress field. The growth of primary nuclei can be maintained or reinforced by a self-induced orientation of the molecules in front of the growing tip. The growth process is continued by the diffusion of new chain segments from the relaxed melt, which leads to orientation and assembly of the segments at the tip following an autocatalytic process [9]. These segments can come from any adjacent chains with both long and short chain lengths. If the growth rate of the tip is too

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slow with respect to the relaxation of the chain, both sides of the assembled segments can be absorbed into the surrounding melt, which eventually destroys the local orientation field and stops the growth process. It has been concluded that the factors that are responsible for the alignment and relaxation of molecular chains can affect the formation of the shish-kebab texture [10,11].

Since polymer crystallization is a kinetic event, variations in processing conditions (e.g., deformation rate, strain, temperature) and in molecular parameters (e.g., molecular weight, molecular weight distribution, chain branching and molecular architecture) of samples have great influence on final morphology and final mechanical properties. Some groups have recently carried out an elegant experiment to study the shear-induced precursor (shish) in iPP or PE melt by in situ Rheo-SAXS and Rheo-WAXD [12–15]. Their results showed that shish could be formed above a critical shear rate and molecular weight because long molecular chains have enough relaxation time to gain stable orientation state.

Recently, we have carried out intensive investigation on polyolefin blends achieved by dynamic packing injection molding [17–20], 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 the chamber by two pistons that move reversibly with the same frequency as the solidification progressively occurs from the wall to the molding core part, resulting in a multi-layer structure in final specimen [19]. Since for a given shear rate, there exists a critical orientation molecular weight (M^*), above which molecular chains could be oriented, in this work, our attention is focused on the molecular weight dependent-crystal morphologies of HDPE as obtained via dynamic packing injection molding to gain understanding of the relationship between shear rate-molecular weight and oriented structure, as part of long-term project aimed at super polyolefin materials. Furthermore, as the chain relaxation time of UHMWPE is extraordinarily long, it allows the retention of molecular orientation, at a significant degree, in the molten PE domain [16], thus small amount of UHMWPE was added into HDPE in our work to explore the effect of UHMWPE on the crystal morphology and orientation of HDPE.

2. Experimental

2.1. Materials

Three kinds of commercialized high density polyethylene (HDPE) with different melt index were introduced in this experiment. Since melt flow index (MFI) is widely used in industry to represent the average molecular weight of a polymer, MFI of each HDPE was measured at 190 °C under 2.16 kg load to characterize the average molecular weight. A higher MFI represents a lower average molecular weight and otherwise around. The detailed information of materials is listed in Table 1. HDPE F600 has the lowest MFI; HDPE 6070 has the highest MFI, and HDPE 5000S lies in between. UHMWPE was supplied by Beijing No. 2 Auxiliary Agent Factory with molecular weight of 200–300 × 10^4 g/mol.

Table 1
Materials

Materials	Brand	Supplier	T_m (°C)	T_c (°C)	ΔH_m (J/g)	MFI (g/10 min)
HDPE	F600	Korea Petrol. Co	130.4	116.9	164.4	0.058
	5000S	Lan zhou Petrol. Co	130.5	117.7	152.3	1.18
	6070	Du shanzi Petrol. Co	130.3	117.2	173.6	7.5

2.2. Samples preparation

Various HDPE samples were molded by dynamic packing injection molding (DPIM) technology using SZ100g injection molding machine. In this work, the melt temperature was 180 °C, the die temperature was controlled at room temperature (about 26 ± 2 °C), the dynamic packing pressure was 35 MPa, and the moving frequency of pistons was 0.3 Hz. The detailed introduction and experimental procedure can be found in Ref. [19]. The injection molding under static packing was also carried out by using the same processing parameters but without shearing, for the purpose of comparison. The specimen obtained by dynamic packing injection molding is called dynamic sample, and that obtained by static packing injection molding is called static one. The sample possesses a multi-layer structure due to the shear stress and thermal gradients. In the case of HDPE/UHMWPE blends, they were extruded and granulated on a twin-screw extruder (TSSJ-25 co-rotating twin-screw extruder). The temperature of the extruder was maintained at 160, 180, 200, 200 and 195 °C from hopper to die and the screw speed was about 120 r/min.

2.3. Two-dimensional wide-angle X-ray scattering (2D WAXS)

The 2D wide-angle X-ray scattering experiments were conducted using a Rigaku Denki RAD-B diffractometer. The wavelength of the monochromated X-ray from Cu Kα radiation was 0.154 nm and the reflection mode was used. The samples were placed with orientation (flow direction) perpendicular to the beams. All 2D WAXS patterns given in this article have extracted the background thus a qualitative comparison between the 2D WAXS patterns is made possible.

2.4. Ultrasonic detection

Ultrasonic technique as a non-invasion and non-destruction technique, could serve as a fast and easy way to determine the molecular orientation of a polymer [21]. The principle that ultrasonic wave could be used to determine the orientation is briefly summarized as follows. When propagating in the anisotropic media (uniaxial orientation) along y direction, shear wave has two characteristic velocities, depending on the direction of the particle displacement vector (Fig. 1). The shear

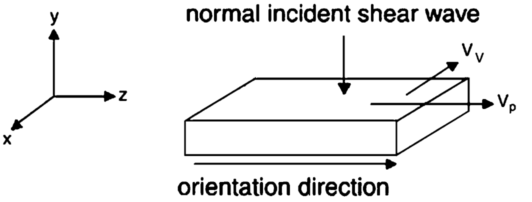


Fig. 1. Schematic diagram of normal incident shear wave propagation in unoriented media.

wave velocity is V_p when the particle displacement vector is in the z direction (parallel to the orientation direction), and V_v when in the x direction (vertical to the orientation direction). As far as the oriented sample is concerned, the shear stiffness is different. Generally, the higher the orientation, the greater is the difference in the shear stiffness, consequently, the velocity difference between V_p and V_v is much higher. Therefore, the velocity difference ($V_p - V_v$) can be utilized to characterize the degree of polymer chain orientation. Practically, the corresponding echo time is more convenient than velocity to reflect the orientation. It is easily inferred that higher velocity results in shorter echo time, therefore, the difference in echo time $\Delta T = (T_v - T_p)$ can also characterize the degree of anisotropy. Similarly, larger difference in echo time ΔT corresponds to higher orientation. When the particle displacement is 45° to orientation direction, shear wave can travel in both characteristic velocities, V_p and V_v simultaneously, so, the echo signal can also be divided into two echo times T_v and T_p. This property provides possibility in using shear wave to monitor at real time the variation of oriented structure during processing through observing the two echo times T_v and T_p from the same echo signal. In this work, as a complementary method to measure the molecular orientation quantitatively, the orientation of samples, particularly for those obtained via dynamic packing injection molding was estimated by measuring the echo time of each dynamic sample (Table 2). Shear wave transducer with a frequency of 5 MHz was purchased from Panametrics Inc., and the experimental detail was described elsewhere [22].

2.5. Scanning electron microscopy (SEM) observations

The evaluation of microstructure and crystal morphology in injected-molding bar becomes much complicated because of the existence of a shear gradient and a temperature gradient from the skin to the core of the samples. So a skin–core morphology with changed orientation and lamellar size along the thickness direction of molded bar is expected. To check the lamellar structure, the specimen obtained, was cryogenically fractured in the direction parallel to flow direction in liquid nitrogen, was etched by 1% solution of potassium permanganate in a mixture of sulphuric acid, 85% orthophosphoric acid and water [23], then the surface was coated with gold and examined from the skin to the core, layer by layer, by an X-650 Hitachi scanning electron microscope at 20 kV.

Table 2
Corresponding echo time of dynamic samples detected by ultrasonic technology

Blends	T_v (ms)	T_p (ms)	$\Delta T = T_v - T_p$ (ms)
HDPE F600	4.15	3.38	0.77
HDPE 5000S	4.02	3.34	0.68
HDPE 6070	4.05	3.5	0.55
HDPE 6070/UHMWPE (1%)	4.02	3.41	0.61
HDPE 6070/UHMWPE (5%)	4.14	3.43	0.71

2.6. Differential scanning calorimetry (DSC) measurements

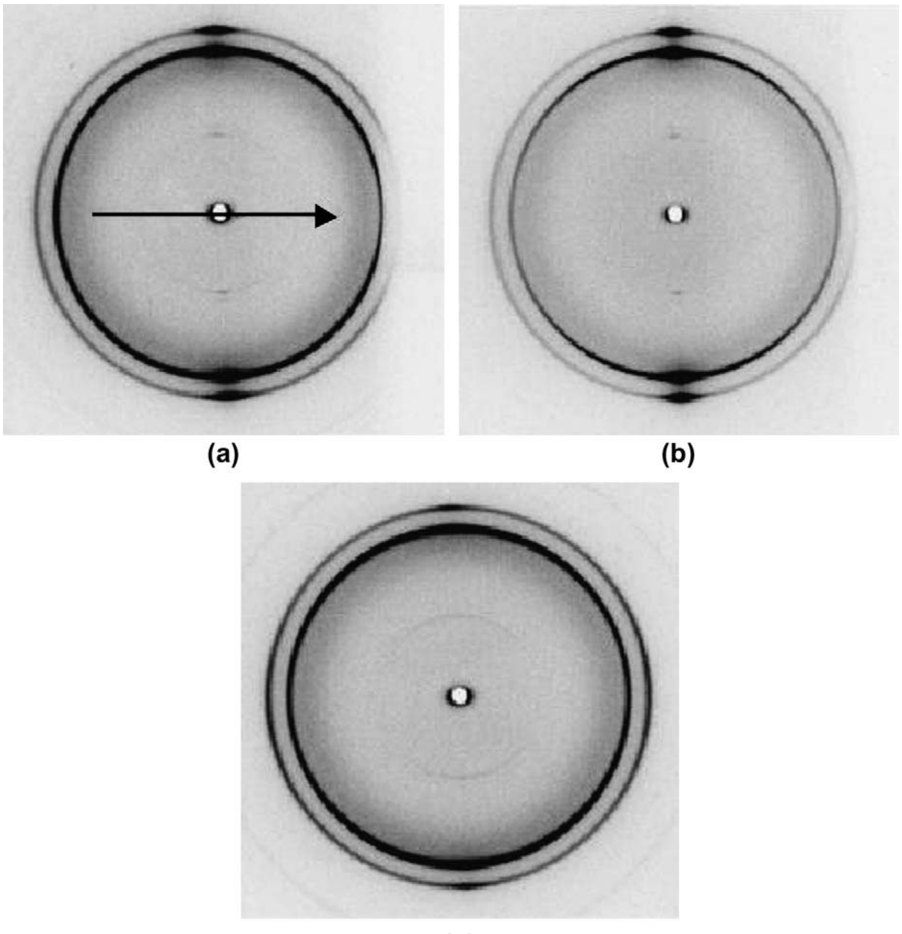
The thermal analysis of the homopolymer samples was conducted using a Perkin–Elmer DSC Pyris-1, which is indium calibrated. The slices were cut from the cross-section of static samples. The sample was heated to desired temperature (160 °C) at rate of 10 °C/min and held for a certain time, under the nitrogen flow. Then, the melt was cooled down at 10 °C/min to 50 °C.

3. Results and discussion

3.1. Shear-induced orientation

Fig. 2 is the 2D WAXS patterns of dynamic HDPE 6070 sample at different zones. One observes strong reflections of (110) and (200) planes at the meridian, indicating a preferential orientation along shear direction. However, the oriented structure exists only in the skin and shear layer even for dynamic samples. In the core, one observes two circles rather than arcs, indicating a random orientation. Due to the existence of a shear gradient and a temperature gradient, hierarchy structure exists from the skin to the core of the samples. For static samples, no preferentially oriented structure is observed, which is similar to Fig. 2(c). The orientation for all three HDPEs at shear layer was also characterized via 2D WAXS which appeared the same to HDPE 6070, independent to MFI. The similar result was also obtained for HDPE/UHMWPE blends (not shown here).

The oriented structure can be quantitatively estimated via ultrasonic method. When ultrasonic shear wave propagates in anisotropic media, there are two characteristic velocities — one is parallel to the orientation direction (V_p), another is vertical to the orientation direction (V_v) — as depicted in Section 2. Using corresponding echo times (T_p and T_v) to reflect the orientation, the discrepancy of echo time $\Delta T = T_v - T_p$ can characterize the degree of anisotropy. As listed in Table 2, the discrepancy of echo time (ΔT) for HDPE F600, HDPE 5000S and HDPE 6070 are 0.77, 0.68, and 0.55 ms, respectively. Thus HDPE with lowest MFI has the biggest discrepancy of corresponding echo time (ΔT), indicating the largest anisotropy among the samples, and other way around. As to HDPE/UHMWPE blends, the value of ΔT increased with the addition of UHMWPE, indicating an increased molecular orientation. Our result is in good agreement with literature, that is for a given shear rate, a higher orientation could be achieved for HDPE with a high molecular weight (a lower



(a) (b) (c)

Fig. 2. 2D WAXS patterns of dynamic HDPE 6070 sample at different zones, the arrow represents the flow direction: (a) the skin; (b) the shear layer; (c) the core.

MFI), and a small amount of UHMWPE could enhance substantially HDPE orientation [24]. It should be pointed out that the ultrasonic signal may be complicated if the blends are consisting of two different kinds of polymers. In this work, although the HDPE/UHMWPE blends consist of two categories of polyethylene, they have a similar constitutional unit except differing in molecular weight so that it could be regarded as one component system in this point of view and the ultrasonic method can be applied. It should be also noted that the degree of orientation measured by ultrasonic method represents an overall orientation including the contribution from skin layer, shear layer and core area.

3.2. Hierarchy structure observed by SEM

Macroscopically, the main feature of dynamic samples is the shear-induced morphologies with core in the center, oriented zone surrounding the core and the skin layer in the cross-sectional areas of the samples. SEM examination of the etched surface cut from the section parallel to flow direction provides important morphological information of static and dynamic samples. Static sample has two layer structures (skin and core layers) in final specimen. The typical crystal morphologies of the static samples of HDPE 5000S along the sample thickness are shown in Fig. 3. One observes the oriented lamellar structure in the skin and spherulite-like structure from the subskin to the core, with increased lamellae thickness, due to the fast cooling and freezing of the oriented structure in the skin, and increased temperature and relaxation time of molecular chains toward the core. The similar result was also observed for HDPE F600 and 6070 which was not shown here.

The hierarchy structure and the effect of molecular weight on the formation of shish-kebab structure can be clearly demonstrated by examining the lamellar structure of dynamic samples of HDPE with different MFI, layer by layer. Fig. 4 is the SEM result of HDPE F600 which has lowest MFI thus highest average molecular weight. At the skin, one observes intertwined lamellae constituting an interlocked lamellar assembly which aligns perpendicular to the flow direction, and some twisted growth is also seen. The morphological evolution from the subskin-layer to the core can be evident from 50 μm to 1.7 mm (the number represents the depth from the surface and the thickness of the specimen is 3.5 mm). From 50 to 1200 μm away from surface, a typical shish-kebab structure is seen gradually developed, with increased shish content toward the center. Very interestingly, some cluster-like crystallites are seen aligning parallel to the flow directions besides

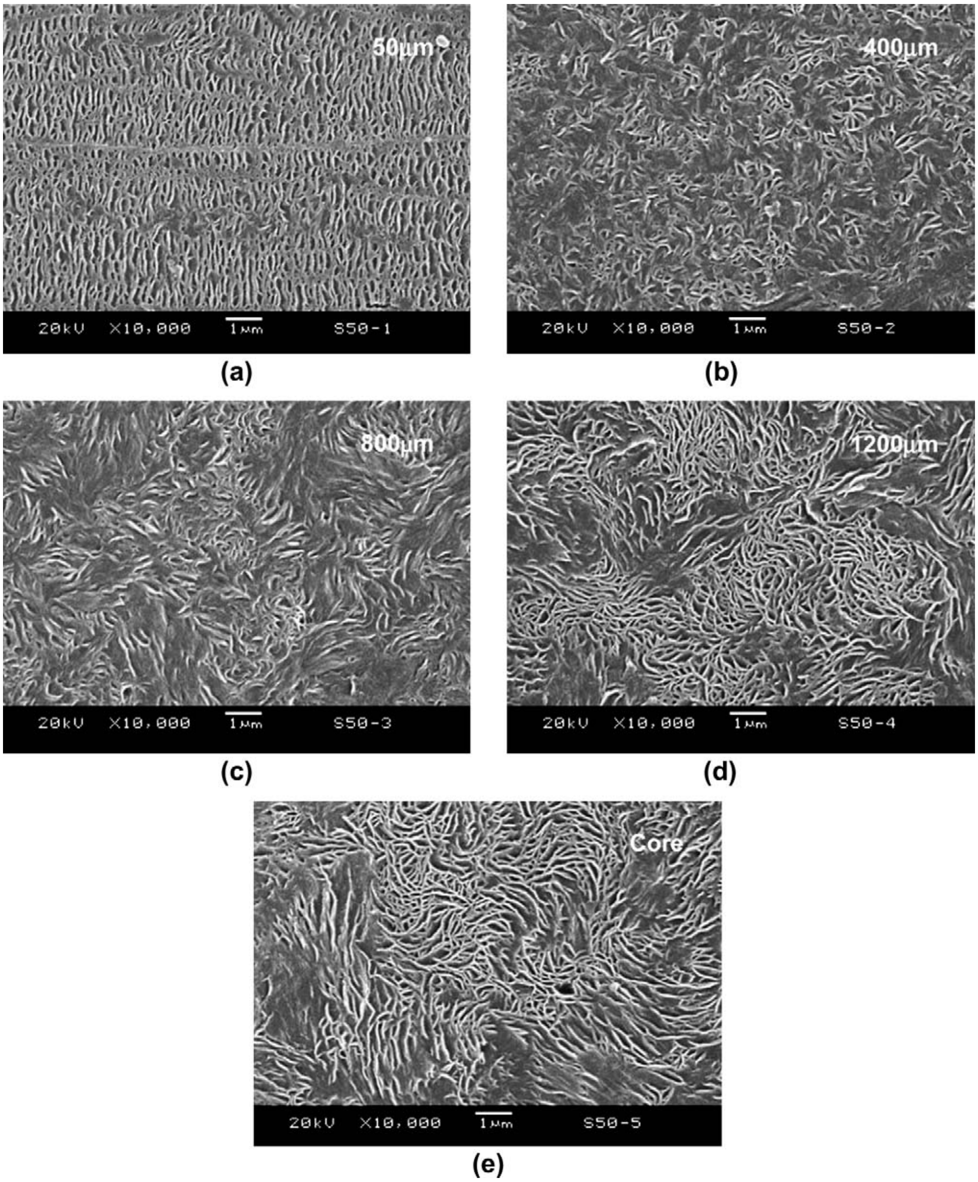


Fig. 3. SEM microphotographs of etched static HDPE 5000S sample at a magnification of 10,000 along the sample thickness: (a) at 50 µm; (b) at 400 µm; (c) at 800 µm; (d) at 1200 µm; (e) core area.

lamellar orientation along shear flow [Fig. 4(a)], similar to the results observed by Hobbs et al. using in situ atomic force microscopy (AFM) [25]. The specific structure of cluster-like crystallites is observed at higher magnification of the SEM image in Fig. 4 (a′) from which it is found that this crystallite is formed by blocks of segments and not by a bundle of extended chains. It is believed that the shish consists of defectively extended-chain crystals [25,26–28] other than blocks of segment. Unfortunately, the alignment of molecular chains in the segment is out of the resolution of SEM so that it is not discussed here in detail, but is worth to be further investigated.

It is also interesting that exactly at the center of the sample, a sudden change of crystal morphology from a dense shish-kebab structure to a spherulite-like superstructure (similar to Fig. 3(e)) is seen, due to a lower shear rate, higher temperature and longer relaxation time in the core. In this case (in the core) lamella has an irregular shape and no preferred orientation.

The similar crystal morphology of other two dynamic samples of HDPEs has been observed but with decreased density of cluster-like crystallite and degree of orientation at the same position. As shown in Figs. 5 and 6, at 50 µm, for instance, cluster-like crystallite in HDPE 5000S is much less and no shish is observed for HDPE 6070 which has the highest MFI thus lowest average molecular weight. At 1200 µm, shish-kebab structure disappears and spherulite-like superstructure is observed for HDPE 5000S and HDPE 6070 while a dense cluster-like crystallite remains for HDPE F600. Our result indeed suggests the importance of high molecular weight in the formation of shish structure. This can be further proved by adding small amount of UHMWPE into HDPE 6070 matrix. As shown in Figs. 7 and 8, compared with

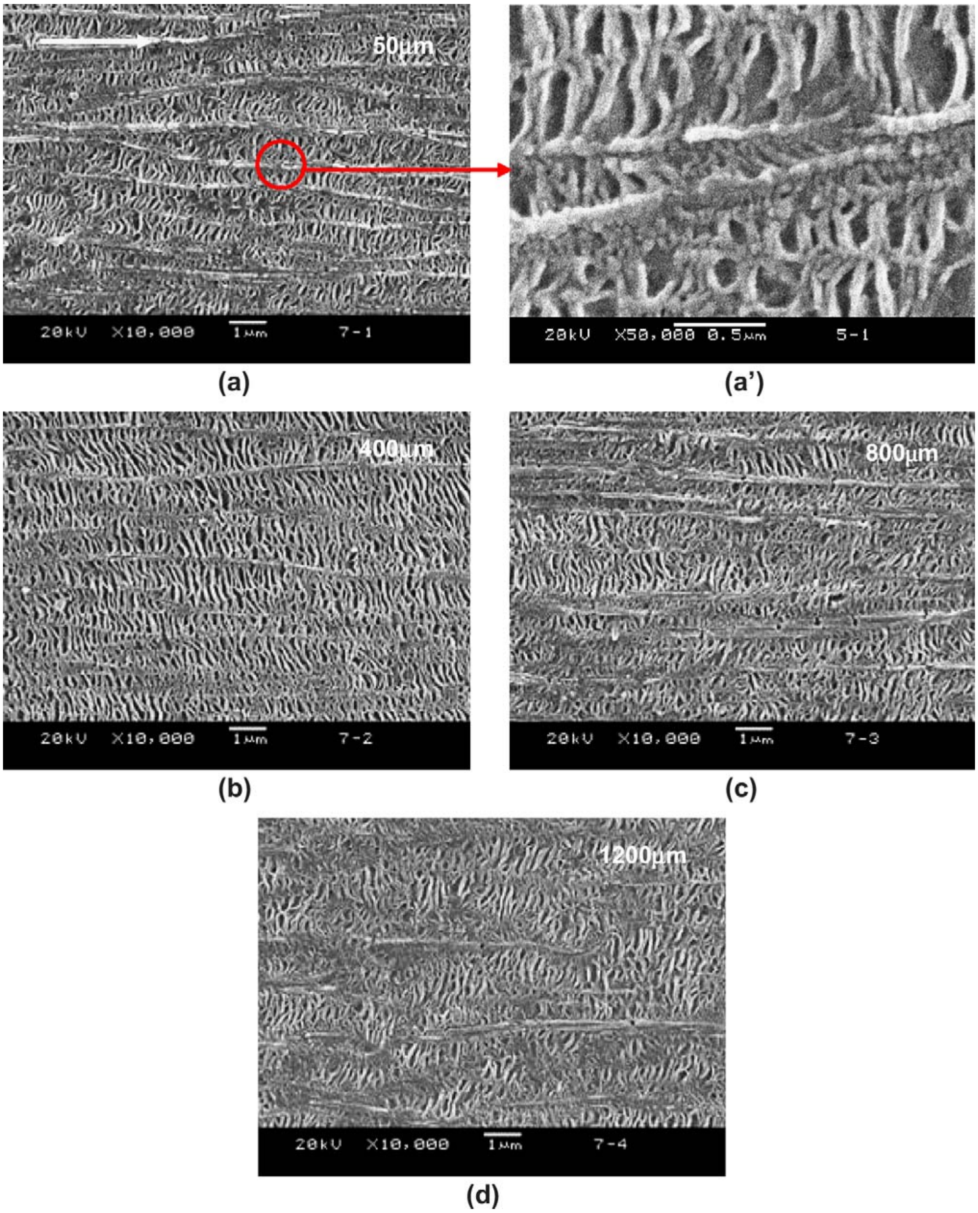


Fig. 4. SEM microphotographs of etched dynamic HDPE F600 sample along the sample thickness: (a) at 50 μm, ×10,000; (a′) cluster-like crystalline at high magnification, ×50,000; (b) at 400 μm, ×10,000; (c) at 800 μm, ×10,000; (d) at 1200 μm, ×10,000; arrow represents flow direction.

HDPE 6070 at the same depth along the sample thickness, the amount of cluster-like crystallite increased and the orientation degree enhanced with increasing content of UHMWPE in each layer.

A peculiar crystal morphology has been observed at low magnification for the dynamic sample HDPE 6070. As shown in Fig. 9(a), sphere particles with a size of 20–25 μm are seen dispersed in the matrix to form the island–sea morphology in the whole sample thickness. The sphere particles are actually spherulites composed of randomly distributed lamellae, as clearly seen at high magnification [Fig. 9(a′)]. The matrix is actually composed of oriented lamella, as shown at high magnification [Fig. 9(a″)]. Interestingly, the density of spherulite is seen to decrease and shish-kebab structure increases with the addition of UHMWPE. Especially at 5 wt% of UHMWPE, most of the spherulite is transferred into shish-kebab structure to form the matrix and only few spherulites remain to form the island [Fig. 9(c and c′)]. This result combined with the above observation, once again indicates clearly the importance of UHMWPE not only in the formation of shish but also in the transformation from spherulite to shish-kebab oriented structure. To the best of our knowledge, this observation has not been reported yet so far.

The cluster-like crystallite found in this work is similar to the so-called shish observed in some researches [17–20,26] (“shish” represents the cluster-like crystallite and “kebab” represents oriented lamellae for the moment in discussions below). The SEM images of the dynamic samples reveal that more and thicker shish could be formed in lower MFI matrix (Fig. 4). There exists a critical shear rate for the formation

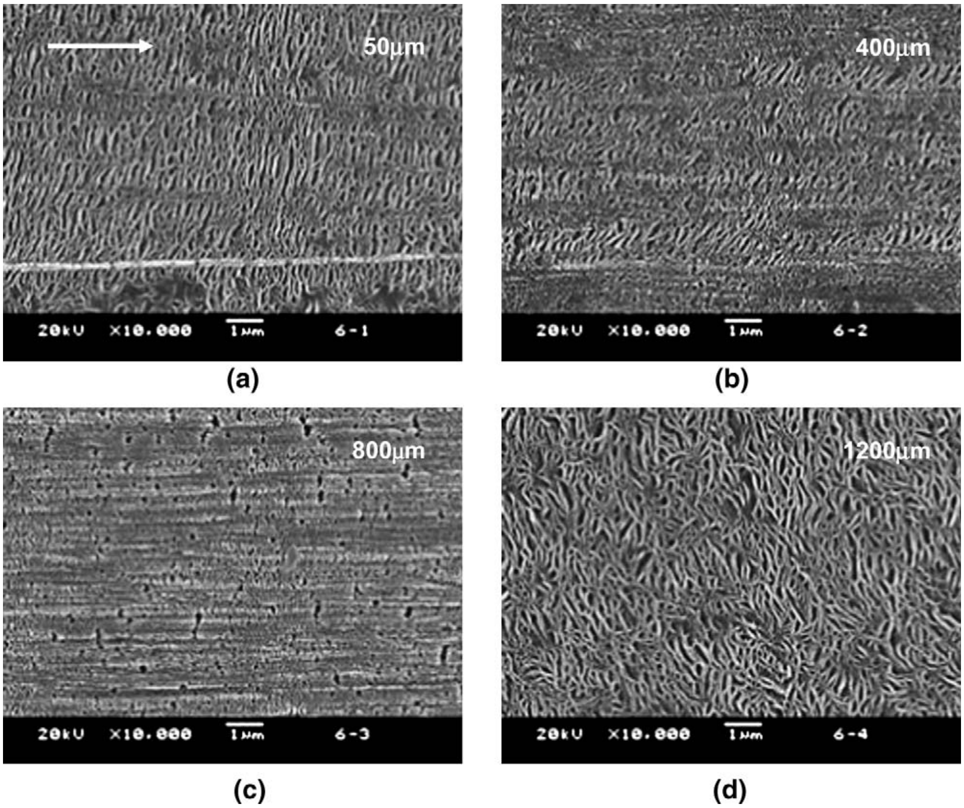


Fig. 5. SEM microphotographs of etched dynamic HDPE 5000S sample at a magnification of 10,000 along the sample thickness: (a) at 50 μm; (b) at 400 μm; (c) at 800 μm; (d) at 1200 μm; arrow represents flow direction.

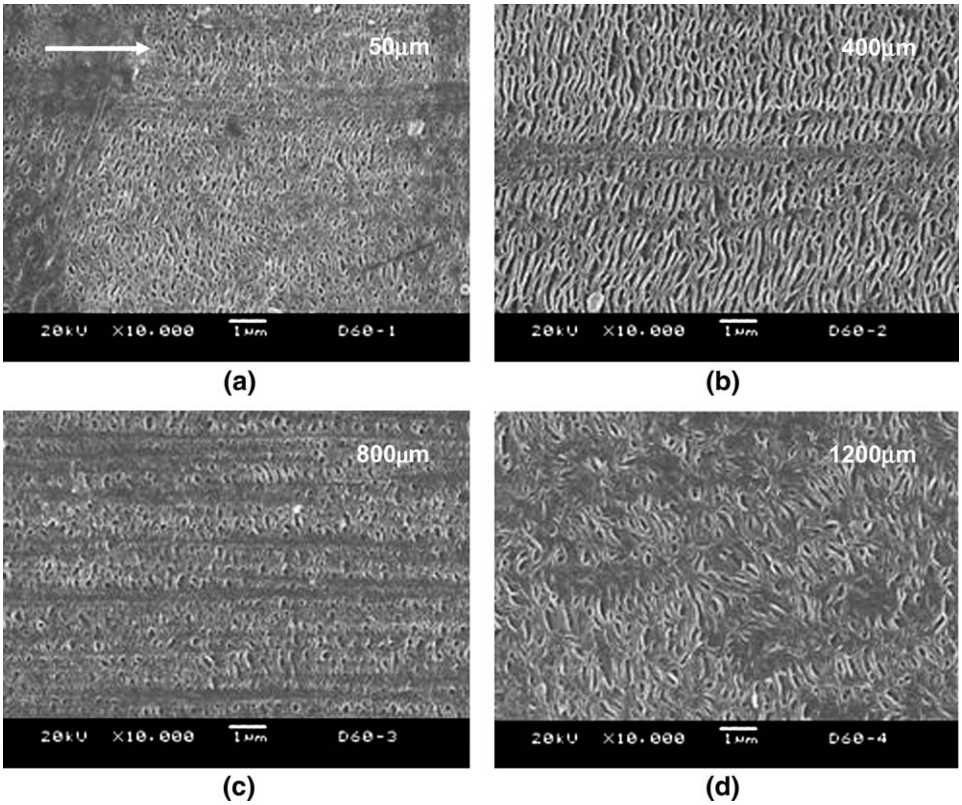


Fig. 6. SEM microphotographs of etched dynamic HDPE 6070 sample at a magnification of 10,000 along the sample thickness: (a) at 50 μm; (b) at 400 μm; (c) at 800 μm; (d) at 1200 μm; arrow represents flow direction.

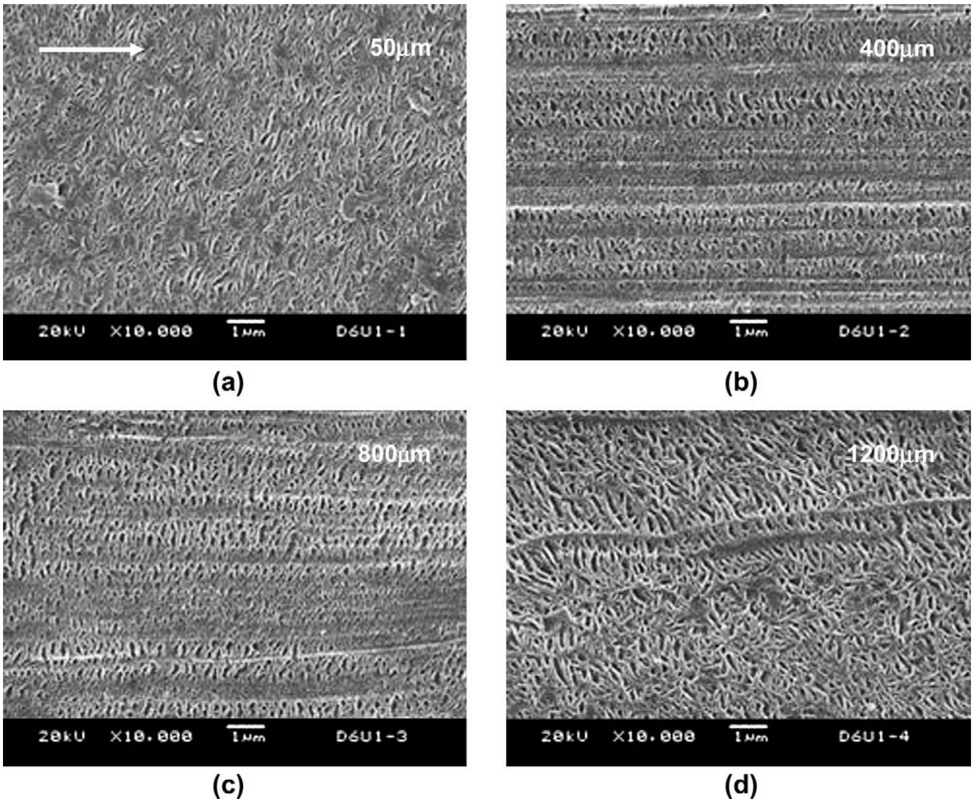


Fig. 7. SEM microphotographs of etched dynamic HDPE 6070/UHMWPE (1%) sample at a magnification of 10,000 along the sample thickness: (a) at 50 μm; (b) at 400 μm; (c) at 800 μm; (d) at 1200 μm; arrow represents flow direction.

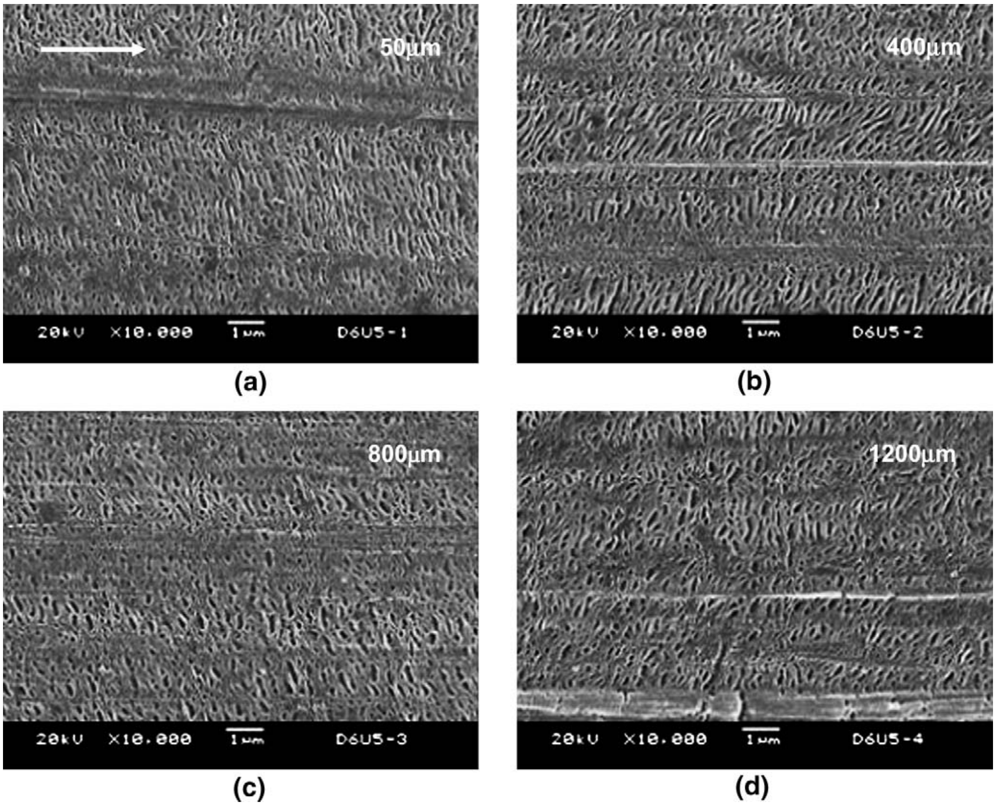


Fig. 8. SEM microphotographs of etched dynamic HDPE 6070/UHMWPE (5%) sample at a magnification of 10,000 along the sample thickness: (a) at 50 μm; (b) at 400 μm; (c) at 800 μm; (d) at 1200 μm; arrow represents flow direction.

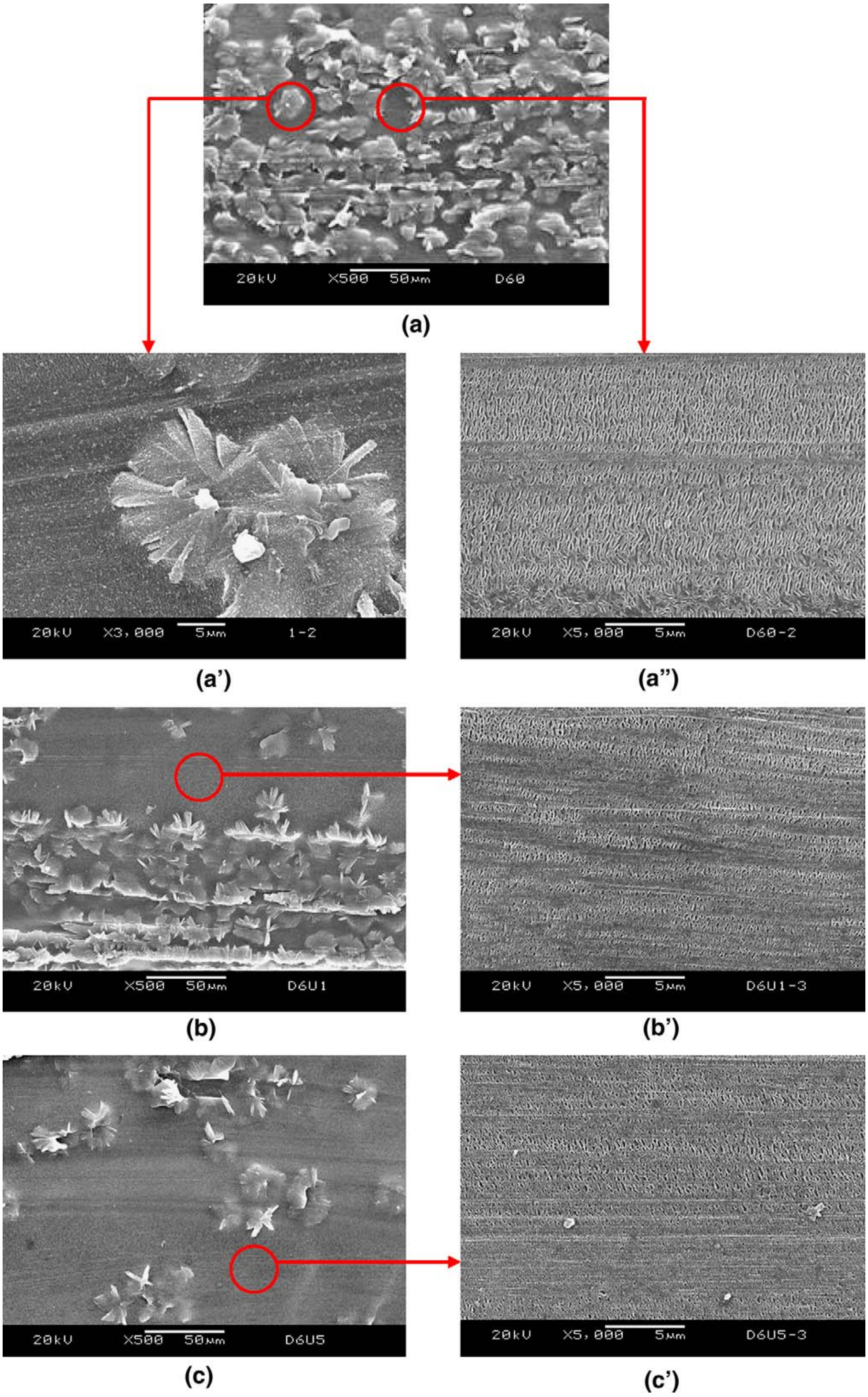


Fig. 9. SEM microphotographs of etched dynamic HDPE 6070 blends at 800 μm: (a) pure HDPE 6070, ×500; (a′) spherulite in HDPE 6070, ×3000; (a″) HDPE 6070, ×5000; (b) HDPE 6070/UHMWPE (1%), ×500; (b′) HDPE 6070/UHMWPE (1%), ×5000; (c) HDPE 6070/UHMWPE (5%), ×500; (c′) HDPE 6070/UHMWPE (5%), ×5000.

of shish [29]. Somani et al. [30] pointed out that a high shear rate is more effective in enhancing the molecular orientation. The morphology of each dynamic sample implies that the shear rate supplied in DPIM is sufficient for the formation of shish. Furthermore, given a certain shear rate, there is a critical orientation molecular weight (M^*). The critical orientation molecular weight is a very sensitive quantity at low shear rates and reaches a plateau above a certain shear rate. Polymer with higher molecular weight implies more fraction of molecular chain above M^*. And long chain has longer relaxation time, which is beneficial to hold the orientation state, resulting in a more stable shish structure. Therefore, the amount and size of shish are improved with decreasing MFI and with the addition of UHMWPE fraction to HDPE matrix, as shown in Figs. 4–8. The result illustrated in Fig. 4(a′) shows that the oriented lamellae grow parallel to each other and perpendicular to shish. This morphology can be best explained using the coil-stretch transition proposed by de Gennes [31] who predicted that a polymer, stretched from its equilibrium coiled state, follows an S-shaped diagram of chain extension versus deformation rate. Based on this theory, the stretched chains crystallize in shish and the coiled chains are subsequently absorbed onto the shish nucleating and growing to form kebabs [25,32], and eventually the integral degree of orientation is enhanced. If more shish is formed in matrix, there is larger nucleation density for coiled chains to form oriented lamellae and subsequently to decrease the amount of spherulite crystals (Fig. 9).

3.3. DSC measurement

The changed crystal structure and lamellar thickness in the injection molded samples along the sample thickness can also be demonstrated by DSC experiment. As an example, Fig. 10(a) shows the DSC heating curves at each layer of HDPE 5000S for both static and dynamic samples. One observes only one peak at the skin and in the core, but two peaks in between for both static and dynamic samples, indicating two crystal morphologies in the transition zone but one structure at the skin and in the core. This result is well consistent with the SEM observation that oriented lamellae at the skin and spherulite in the core, but shish-kebab structure in between for dynamic samples. By careful examination, it is found that for the dynamic samples, the lower melting peak located at 132.5 °C keeps constant along the sample thickness, but the high melting peak continuously increases along the sample thickness toward the center. This can be understood as due to the increased shish content as observed via SEM (see above Fig. 5). Since only spherulites are observed in the subskin-layer and transition zone for the static samples, two peaks in this region could be due to a shear-induced molecular segregation during injection molding. One also observes an increased melting point from the skin to the core for static one, but in this case, it is caused not due to the formation of shish-kebab structure but due to an increased lamellar thickness. This phenomenon is further evident by checking the DSC heating curves of the injection molded samples of HDPE 6070 which has the highest MFI. As shown in Fig. 10(b), two melting peaks are seen in a broad region for both dynamic and static samples, which represent two crystal morphologies for dynamic sample but shear-induced molecular segregation for the static sample. In this case one observes a constant low temperature peak along the sample thickness for the static sample, indicating a constant lamellar thickness. This is probably due to the peculiar molecular weight distribution in this sample.

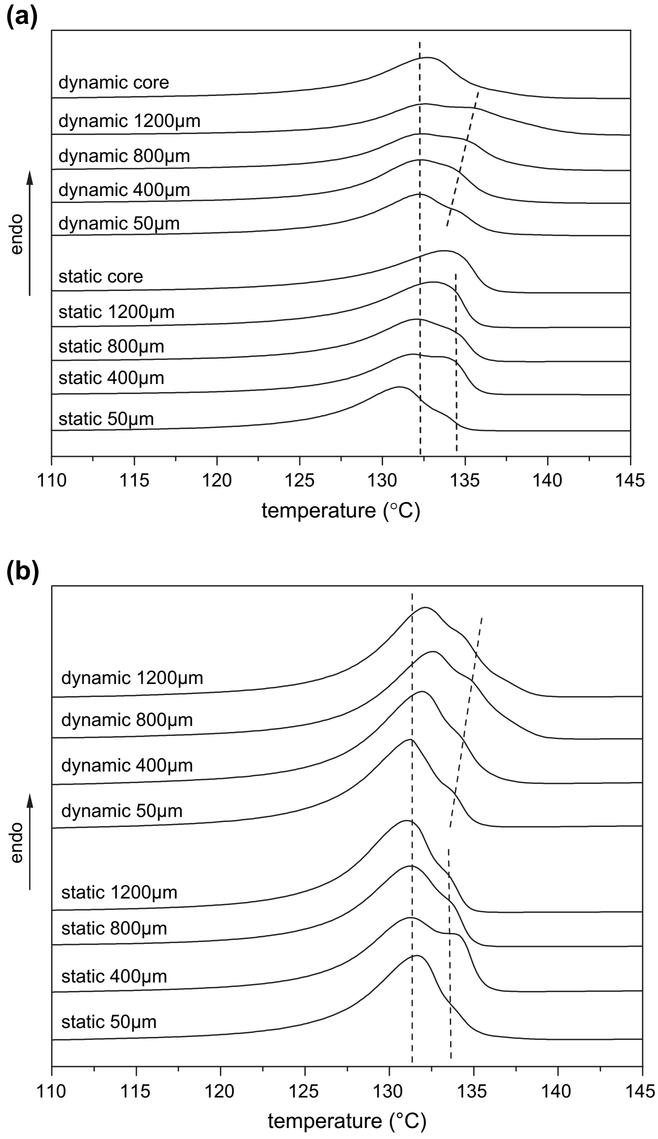


Fig. 10. DSC heating curves at each layer both for dynamic and static samples: (a) HDPE 5000S; (b) HDPE 6070.

4. Conclusions

The morphology and the effect of molecular weight on the formation of shish-kebab structure were investigated in detail by examining the lamellar structure of injection molded samples of high density polyethylene (HDPE) with different melt flow index (MFI), layer by layer, along the sample thickness. It was found that the overall orientation in the molded bar increased with decreased MFI, and a small amount of UHMWPE could enhance substantially HDPE orientation. A hierarchy structure with changed orientation and crystal structure along the thickness direction of molded bar existed due to the existence of a shear gradient and a temperature gradient from the skin to the core of the samples. At the skin, there existed intertwined lamellae constituting an interlocked lamellar assembly, a typical shish-kebab structure gradually developed from the subskin-layer to the core; with increased shish content toward the center, and in the core was a spherulite-like superstructure with randomly distributed lamellae. UHMWPE played an important role not only in the formation of shish, but also in the transformation from spherulite to shish-kebab oriented structure for HDPE with a low molecular weight (high MFI).

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