

Hierarchical Crystalline Structures Induced by Temperature Profile in HDPE Bars during Melt Penetration Process*

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Abstract The hierarchical crystalline morphologies and orientation structures across the thickness direction in high-density polyethylene (HDPE) molded bars were investigated *via* a novel melt-penetrating processing method named multi-melt multi-injection molding (M³IM). The samples with various mold temperatures (20, 40 and 60 °C) were prepared, and the effects of the external temperature profile on the evolution of crystalline microstructures were studied. With scanning electron microscopy (SEM), the transition of crystalline morphology from ring-banded structure to oriented lamellae was observed with decreasing mold temperature, and the oriented lamellae were formed at the sub-skin layer of the samples at the lowest mold temperature, which was further testified by differential scanning calorimetry (DSC). With the decline of mold temperature, the degree of orientation, obtained from two-dimensional small angle X-ray scattering (2D-SAXS), was increased and long periods rose a little. Thus, decreasing mold temperature was beneficial to the formation of orientation structures because the relaxation of chains was weakened.

Keywords Hierarchical structures; Orientation; Multi-melt multi-injection molding; Mold temperature

INTRODUCTION

For semicrystalline polymers, the control of crystalline morphology plays a significant role in their final performance, because the properties of polymer materials are essentially dependent on their microstructures^[1]. Polyethylene can be processed into completely different products by diverse processing methods. The Young's modulus of the products may vary from 0.1 GPa to 200 GPa, corresponding to different microscopic morphologies including spherulite, oriented lamella and shish-kebab, *etc.* In recent years, some new processing molding technologies have been developed to satisfy the demand for high performance, such as dynamic packing injection molding (DPIM)^[2], layer multiplying co-extrusion (LMCOE)^[3], shear controlled orientation in injection molding (SCORIM)^[4] and vibration assisted injection molding (VAIM)^[5]. These methods are mainly based on shear-induced crystallization and orientation, which confirm that the rate of crystallization can be accelerated and crystalline morphologies can be influenced by shear flow^[6, 7].

Recently, our group has proposed a multi-fluid multi-injection molding (MFMIM), in accordance with the above-mentioned principles^[8–10]. MFMIM is a molding process involving two procedures: the first melt is injected into the mold cavity partially, followed by injection of a second (even a third and more) fluid as a penetrating medium after a delay time, which can push the first melt. When compressed gas or water acting as

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the second fluid, it is gas-assisted injection molding (GAIM)^[11] or water-assisted injection molding (WAIM)^[12]. In our previous work, the banded spherulites^[13], special transcrystallization^[11] and shish-kebabs^[14] have been observed due to the strong shear field *via* gas penetration. Among the MFMIM technology, there is a new one named multi-melt multi-injection molding (M³IM), in which polymer melt serves as the second penetrating fluid. Additionally, the intensive investigations have been conducted to find some special microstructures *via* manifold molecular parameters in our work. To be specific, the ring-banded spherulite and cylindrulite were formed in low molecular weight high-density polyethylene (LMW HDPE) system^[9, 15], while the shish-kebabs and oriented lamellae were observed in the middle high molecular weight HDPE system, which illustrated that the relaxation time of long molecular chains was longer than that of short molecular chains^[8, 16, 17]. Hence, the relaxation time of chains takes an essential part in governing stability of the oriented structures after secondary melt shear, especially under the condition of high temperature during M³IM process. The observation of shish-kebabs was available in the blend bars of LMW HDPE and ultra-high molecular weight polyethylene (UHMWPE) as well, due to the suppression of UHMWPE oriented chains during the intensive shear flow process^[15]. Besides, it was demonstrated that lightly cross-linked HDPE with longer relaxation time was beneficial to the transition from cylindrulites to shish-kebabs^[10].

The morphologies and structures of semicrystalline polymers are influenced by the coupling action of external fields (shear field and temperature field, *etc.*)^[18]. In our previous studies, it was manifested that the cooling curve in the gas channel zone expressed an obvious phase-change stage through an enthalpy transformation, and higher compressed nitrogen pressure retained a higher cooling rate of the polymer melt during GAIM process, generating a wider zone with close-knit orientation crystals and higher degree of orientation^[19, 20]. The sample with lower melt temperature had more compact and highly aligned oriented structures as well as wider oriented region due to increasing relaxation time^[21]. Moreover, stronger shear field could be introduced by the prolongation of gas delay time, and subsequently more row nuclei were formed along the flow direction. Finally, the amounts of shish-kebab structures and the degree of orientation increased in the samples with longer delay time, as well as macroscopic properties that there was a growth in both the dynamic storage modulus and loss modulus with a decline of the melt temperature^[22].

With respect to M³IM process, the practical thermal-mechanical fields are also complex. The shear field of M³IM process has been investigated and the results indicated a bimodal distribution along the thickness of samples^[23, 24]. The shear rate, estimated *via* the capillary number, reached a peak value at both the sub-skin layer and the position next to the core layer, which was consistent with the positions where cylindritic structures appeared. As for the temperature profile, HDPE samples with varied secondary melt temperatures were studied in M³IM process. It was found that the cylindritic structures were transformed gradually into irregularly-arranged spherulites at the core layer of LMW HDPE, resulting from the reduced motility for polymer chains with decreasing temperature of the second melt, which also led to the decline of orientation degree in LMW HDPE/UHMWPE blend^[9, 25]. Furthermore, mold temperature is also one of the most important processing parameters. The higher thermal conductivity of melt resulted in more nuclei and longer relaxation time of macromolecules near the mold wall, which would strongly affect the shrinkage of the product^[26]. On the contrary, the decrement of relaxation time at higher mold temperature was not conducive to the reserve of oriented crystalline structures. Yalcin *et al.* found that injection mold temperature had influence on the structure across the thickness of nylon 6, where oriented threads were formed at the surface but spherulites were formed in the interior^[27].

In this study, parts of LMW HDPE molded by M³IM process were prepared with a variety of mold temperatures to change the temperature profiles of each part measured by a real-time temperature instrument. The evolution of crystalline morphology and orientation structures at various mold temperatures were studied, characterized by combination of scanning electron microscope (SEM), two-dimensional small angle scattering (2D-SAXS) and differential scanning calorimetry (DSC). Valuable understanding was provided for the formation process of the hierarchical microstructures induced by temperature profile in M³IM samples.

EXPERIMENTAL

Materials

The high-density polyethylene (HDPE, model: 2911) provided by Fushun Petrochemical Inc., China, has a melt flow rate (MFR) of 20 g/10min (190 °C/2.16kg, ASTM D1238), a weight average molecular weight (M_w) of 1.42×10^5 and a molecular weight distribution (MWD) of 4.1 (Fig. 1). The molecular parameters were obtained by gel permeation chromatograph (model: PL-GPC 220, Agilent; the granules were dissolved in trichlorobenzene at 150 °C). The average molecular weight of high molecular ($M_{HMW} > 10^6$) portion is 1.44×10^6 and the value of low molecular weight ($M_{LMW} < 10^5$) portion is 5.96×10^4 .

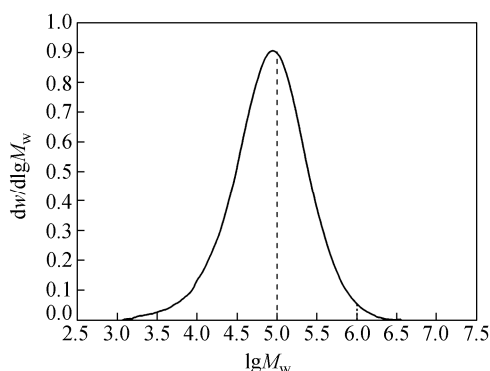


Fig. 1 Molecular weight distribution of the material obtained by GPC

Sample Preparation

M³IM instrument was constituted of a SM60HC injection molding machine and a SHJ20 micro-injection molding machine (see Ref. [8]). The two injection units worked independently so that the delay time between the onsets of them could be controlled. Samples were prepared in series by mold temperatures, named as T20, T40, T60, corresponding to 20, 40 and 60 °C, respectively, and the detailed processing parameters of M³IM are listed in Table 1.

Table 1 Processing parameters used in M³IM process

Parameters	Injection unit 1	Injection unit 2
Injection pressure (MPa)	50	~40
Mold temperature (°C)	20/40/60	
Melt temperature (°C)	210	210
Delay time (s)	1	
Cooling time (s)	150	150
Injection volume (%)	50	50

Rheological Tests

Rheological test for the polymer melt was carried out on a rheometer (Model AR2000-EX, TA Instruments Inc., USA) using a parallel plate geometry with diameter of 25.0 mm. Samples for this test were compressed into discs with a thickness of 1.50 mm and a diameter of 25.0 mm at 190 °C and 10 MPa. Frequency sweeps with a range of 0.01–100 Hz were conducted at different temperatures from 150 °C to 210 °C with a regular interval of 20 °C. All the tests were controlled by strain and a value of 0.1% was determined by the strain sweep to lie within the linear viscoelastic regime. In order to avoid the thermal degradation, the experiments were performed under nitrogen atmosphere.

Morphological Observation

Specimens for morphological observation by SEM were cut in the direction parallel to the flow direction (FD), shown in Fig. 2. First, the original M³IM samples with width of 20 mm and thickness of 5 mm were cut into parts with width of 5 mm at the position 30 mm away from the gate. Secondly, the slices of 60 μm thickness

were obtained by microtome, cut at the central zone of the parts along the flow direction. Then the slices were etched for 3.5 h and cleaned in diluted sulfuric acid and acetone separately under ultrasonic treatment. The slices were dried, covered with a thin layer of gold, the crystalline morphology was observed under SEM (FEI, INSPECT-F) at an accelerating voltage of 20 kV.

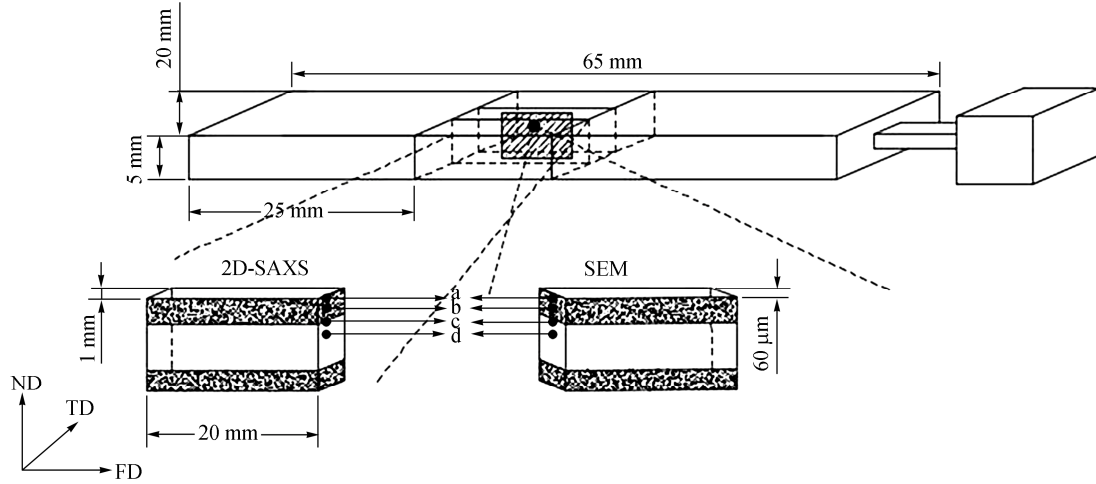


Fig. 2 Schematic representation of a specimen obtained for SEM and 2D-SAXS characterizations: (a) skin layer, (b) sub-skin layer, (c) intermediate layer and (d) core layer

Two-dimensional Small-angle X-ray Scattering (2D-SAXS)

As illustrated in Fig. 2, the specimens for 2D-SAXS observation were cut into 20 mm long and 1 mm wide at the central part of M³IM samples, 25 mm away from the gate. The surface was smooth. The measurement was conducted on an instrument BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). Wavelength of the monochromatic X-ray was 0.124 nm. The sample-to-detector distance was 2000 mm, and the size of the X-ray beam was 0.4 mm × 1.0 mm. Samples were placed with the flow direction perpendicular to the beams, and the detailed operations can be found elsewhere^[8, 10].

SAXS data were subtracted from background scattering during the data process and degree of crystal orientation could be calculated by Hermans' orientation function f as follows:

$$f = \frac{3\langle \cos \varphi \rangle^2 - 1}{2} \quad (1)$$

and $\langle \cos \varphi \rangle^2$ was defined as:

$$\langle \cos \varphi \rangle^2 = \frac{\int_0^{\pi/2} I(\varphi) \sin \varphi \langle \cos \varphi \rangle^2 d\varphi}{\int_0^{\pi/2} I(\varphi) \sin \varphi d\varphi} \quad (2)$$

where φ is azimuth angle and $I(\varphi)$ the diffraction intensity. For an ideal uniaxial orientation parallel to the orientation direction, the average azimuth angle $\varphi = 0^\circ$, namely $f = 1$. Conversely, when normal to the orientation direction, $\varphi = 90^\circ$, namely $f = -\frac{1}{2}$. While, if the molecular chains in samples are totally random orientation, $f = 0$.

Thermal Property Characterization

The specimens at different zones along the thickness direction were obtained; their thermal property was characterized by differential scanning calorimetry (DSC, TA-Q20). The sample was about 5 mg for each measurement. All the measurements were conducted under the nitrogen atmosphere and the heating rate was 40 K/min from 40 °C to 200 °C. The data were collected continuously and analyzed by Universal 2000 analysis package. The peak temperature of the main endotherm was detected as the melting temperature.

RESULTS AND DISCUSSION

Temperature Profile

Temperature during the actual processing was measured in order to see its effect on the microstructure of M³IM samples. Bimodal peaks were detected as characteristics of flow pattern in the M³IM. When the first melt was injected into the cavity, the first temperature peak (T1) was detected. After a certain delay time, a secondary melt penetrated the first one. The second temperature peak (T2) was detected and was mainly due to the secondary melt temperature. The whole cooling process was obtained at diverse positions from the mold wall (with $d = 0 \mu\text{m}$ and $d = 2500 \mu\text{m}$, representing the mold surface and the central zone, respectively). As shown in Fig. 3, a bimodal distribution was observed in all the real-time temperature monitoring curves. Moreover, the first and second temperature peaks, T1 and T2, were both increased with increasing the mold temperature at given positions, which could be clearly seen in Table 2. The amplification of T1 among adjacent samples varied from 14.3 and 22.2 °C (close to the mold wall) to 6.5 and 5.3 °C (in the center of samples), respectively. It could be explained that the cooling effects of the mold temperature became weaker with the position moved toward the central zone during the melt cooling stage. In addition, at the position $d = 200 \mu\text{m}$ (Fig. 3a), the curve of T60 was

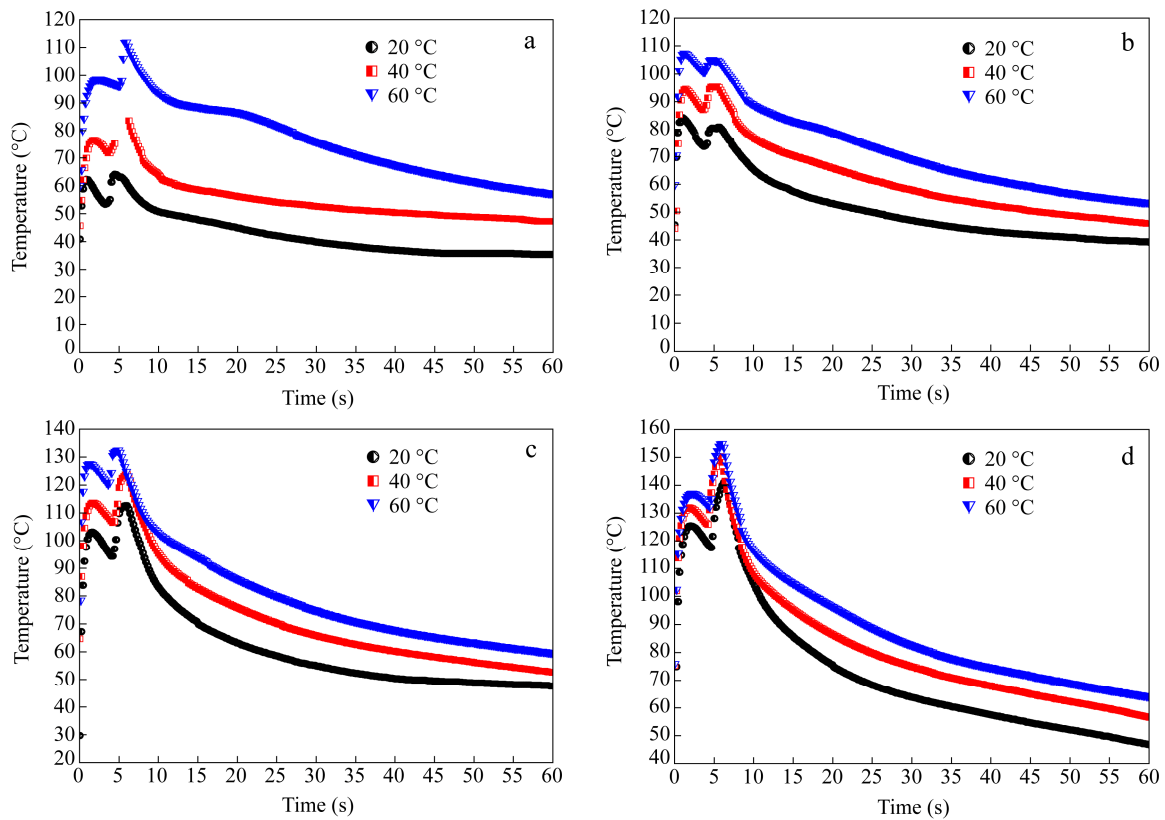


Fig. 3 Real-time temperature curves in M³IM parts with the different mold temperatures and the distances from the mold wall: (a) 200 μm , (b) 700 μm , (c) 1700 μm and (d) 2500 μm

shown as an isothermal platform regarded as the phase transformation platform (about 90 °C). However, the platforms of T40 and T20 samples were not displayed any more. It was widely accepted that a typical cooling process of the semicrystalline polymers underwent three different stages, namely the liquid phase cooling stage, phase-change plateau and solid phase cooling stage respectively. The existence of the phase-change plateau was mainly caused by the balance of the heat flow, where heat liberated from the crystalline process was the same as that taken away by the cold mold^[28]. Therefore, based on the observation of the plateau in T60 sample (Fig. 3a), the cooling heat loss could be compensated by the phase change heat enthalpy in this period, while the phase change heat enthalpies of T40 and T20 samples were less than the heat loss due to the rapid cooling rate.

Table 2 Values of T1 and T2 in M³IM parts with different distances from the mold wall

Sample	$d = 200 \mu\text{m}$		$d = 700 \mu\text{m}$		$d = 1700 \mu\text{m}$		$d = 2500 \mu\text{m}$	
	T1	T2	T1	T2	T1	T2	T1	T2
T20	62.2	64.0	84.2	80.7	103.0	112.6	125.4	141.4
T40	76.5	83.5	94.5	95.4	113.5	123.8	131.9	150.2
T60	98.7	111.9	107.4	105.1	127.7	132.6	137.2	155.0

For further comparison of the cooling rates among different mold temperatures, the statistical data of average cooling rates were computed from T2 to 50 °C (where the cooling curves began to be flat, and the solidification of molded bars was almost completed), the results are listed in Table 3. It was obvious that the cooling rate decreased with the increase of mold temperature, and the maximum decrement reached about 53 K/min from T20 to T40 at the skin layer (at position $d = 200 \mu\text{m}$ closed to the wall where the cooling rate was higher than at other positions). When the position moved toward the core layer, the cooling rate decreased on the whole. However, the values at position $d = 700 \mu\text{m}$ were even lower than those at the position $d = 1700 \mu\text{m}$ and $d = 2500 \mu\text{m}$, mainly due to the shear heat caused by the second melt penetrating the first melt. Moreover, the cooling rate of the sample T20 was the highest among the three samples, where the maximum value was up to 127.27 K/min and the minimum value was lowered to 94.94 K/min. As aforesaid, the cooling rate could be significantly promoted by decreasing the mold temperature, and the fastest cooling rate among the tested positions was as high as 127.27 K/min.

Table 3 Cooling rates of M³IM parts with different distances away from the mold wall

Sample	Cooling rates			
	$d = 200 \mu\text{m}$	$d = 700 \mu\text{m}$	$d = 1700 \mu\text{m}$	$d = 2500 \mu\text{m}$
T20	127.27	94.94	106.10	105.21
T40	73.89	63.24	73.06	70.27
T60	46.25	34.80	40.86	38.82

Rheological Time Scale

In view of rheology, the influence of flow on molecular conformation can be defined as Deborah numbers for chain orientation and stretch: $De_o = \tau_d \dot{\gamma}$ and $De_s = \tau_s \dot{\gamma}$, with τ_d , τ_s and $\dot{\gamma}$ being the disengagement and the stretch relaxation time and shear rate, respectively^[29]. When $De_o > 1$, molecules tend to orient and when $De_s > 1$, molecules tend to stretch. The magnitudes of τ_d and τ_s follow the relationships from the tube model of Doi and Edwards:

$$\tau_d = 3\tau_e (M/M_e)^3 \left(1 - 1.51/\sqrt{M/M_e}\right)^2 \quad (3)$$

$$\tau_s = \tau_e (M/M_e)^2 \quad (4)$$

where M_e is the average molecular weight between entanglements (828 g/mol for PE) and τ_e is the equilibration time and independent of the molecular weight of the chain (7×10^{-9} s at 190 °C). The relaxation time and critical shear rates for fibrillar nucleation hereby can be calculated (Table 4). Briefly, the symbols with superscripts of

HMW and LMW are used below representing when $M = M_{\text{HMW}}$ and $M = M_{\text{LMW}}$. It is found that the values of $\tau_{\text{D}}^{\text{HMW}}$ and $\tau_{\text{S}}^{\text{HMW}}$ are much larger than $\tau_{\text{D}}^{\text{LMW}}$ and $\tau_{\text{S}}^{\text{LMW}}$, indicating that fibrillar seeds can be formed more easily in HMW molecules, *via* entanglements promoting similar change of conformation in close-by molecules under flow^[30]. Moreover, the values of $\dot{\gamma}_{\text{D}}^{\text{crit}}$ at 190 °C, computed from Deborah numbers, are much smaller than the practical value during secondary flow penetration^[23]. According to the above results of temperature measurements, the temperatures (T2) were less than 190 °C when secondary melt penetrated by decreasing mold temperatures, meaning that the values of τ_{D} were higher and those of $\dot{\gamma}_{\text{D}}^{\text{crit}}$ were lower than those in Table 4. That is to say, the chains could be oriented under secondary shear flow and whether the precursors during crystallization could be preserved and finally formed into oriented structures depended on the cooling rates of polymer melt. In addition, the value of $\dot{\gamma}_{\text{S}}^{\text{crit}}$ was much larger than that of $\dot{\gamma}_{\text{D}}^{\text{crit}}$, suggesting shish precursors were difficult to be formed or very little for the HDPE used, though the $\dot{\gamma}_{\text{S}}^{\text{crit}}$ of HMW portion was within the range shear rate during M³IM process. Additionally, the concentration of HMW portion was very low (1.19%).

Table 4 Rheological parameters at 190 °C for HDPE

	τ_{D} (s)	τ_{S} (s)	$\dot{\gamma}_{\text{D}}^{\text{crit}}$ (s ⁻¹)	$\dot{\gamma}_{\text{S}}^{\text{crit}}$ (s ⁻¹)
M_{HMW}	102.61	2.12×10^{-2}	9.75×10^{-3}	47.23
M_{LMW}	5.36×10^{-3}	3.65×10^{-5}	1.86×10^2	2.74×10^4

On the other hand, when the polymer melt crystallizes under flow conditions, the orientation and relaxation of the molecular chains compete with each other. The chains may have longer relaxation times at lower temperature and here Carreau-A model is adopted to describe chain relaxation process by fitting the rheological data, which can be described as^[31, 32]:

$$|\eta^*| = \eta_0 \left[1 + (\lambda \dot{\gamma})^2 \right]^{(n-1)/2} \quad (5)$$

where $|\eta^*|$ is the complex viscosity, η_0 is the zero-shear viscosity, λ is the characteristic relaxation time, $\dot{\gamma}$ is the shear rate and n is the power-law index. As shown in Table 5, with lower temperature the values of n declined, suggesting an increase of the shear thinning phenomenon. The zero-shear viscosity was increased by double when the test temperature decreased from 210 °C to 150 °C, and the characteristic relaxation time was increased by 1.43 times, which demonstrated that the relaxation time of polymer chains could be really prolonged by reducing temperatures, in favor of the reservation of fibrillar precursors. Based on the above analysis, a fast cooling stage was very important for the formation of oriented structures, and the cooling rates were promoted indeed by reducing the mold temperatures.

Table 5 Molecular parameters in the Carreau-A model obtained by nonlinear fitting

Temperature (°C)	η_0 (Pa·s)	λ (s)	n
150	846.12	0.127	0.769
170	665.19	0.103	0.786
190	517.12	0.099	0.803
210	432.11	0.089	0.811

Crystalline Morphologies

The fine crystalline morphologies can be directly observed with SEM. The micrographs at the different positions across the thickness of T20 sample are shown in Fig. 4. There were banded spherulites observed in four positions except for the sub-skin layer where loose oriented lamellae were observed (Fig. 4b), which was scarcely found in LMW HDPE molded specimens in a previous work^[9]. This is due to the high shear rate at the sub-skin layer, where it was more advantageous to induce the orientation structures. It is clarified that flow field strength is important for banded spherulite formation^[14]. There existed critical intensities of the flow field; lamellae twisted

in the growth front of spherulites could be resulted from the local field when surpassing the lower critical value. The formation of oriented lamellae could be caused by higher intensity of local flow above the upper critical value. Meanwhile, the suppression of both the relaxation time and the reservation of oriented structure could be promoted by high cooling rate. Furthermore, a few cylindritic structures were also observed at the sub-skin layer, indicating that there were some local micro-flow patterns except for macro-flow of polymer melt during the melt penetration process. Besides, crystal size reduced but the number of grains gradually increased from the core layer to the skin layer, which was caused by the asymmetry temperature profile that the temperature close to the mold wall was much lower than that in the center as mentioned above^[33].

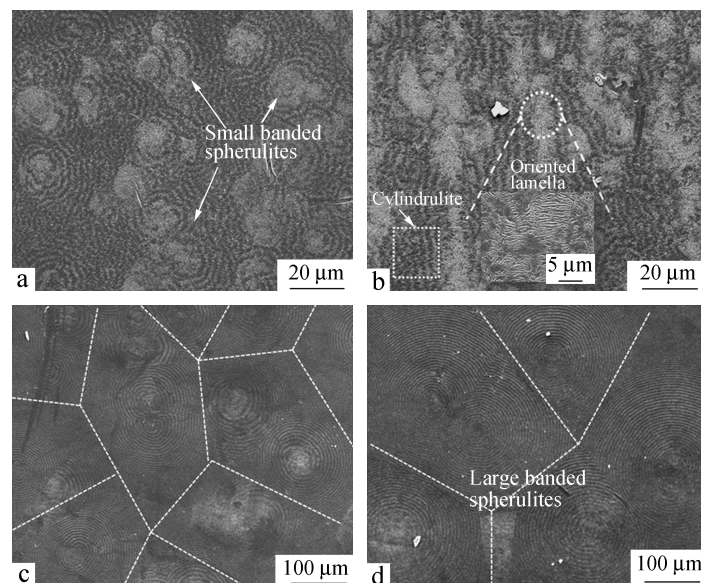


Fig. 4 SEM micrographs of the crystalline morphologies of T20 sample: (a) skin layer, (b) sub-skin layer, (c) intermediate layer and (d) core layer (The melt flow direction is vertical.)

In comparison with T20, more cylindrites and banded spherulites rather than oriented lamellae were formed in samples T40 and T60 (Figs. 5 and 6). So far, great efforts have been dedicated to study the banded spherulites. It is widely accepted that the formation of banded-spherulites is mainly due to twisting of crystallographic orientation along the radial direction of the spherulites with characteristics of alternating edge-on and flat-on lamellae, though the nature for lamellae twisting in the banded spherulites is not very clear^[34, 35]. Intensive works on banded spherulites have been generally taken under quiescent condition. Our group demonstrated that the banded spherulites and the cylindrites were introduced by certain flow field, as well as the degree and the size of crystallization zone were closely related to the processing parameters^[9, 14]. From Table 3, the maximal cooling rates in T40 and T60 samples were 73.89 K/min and 46.25 K/min, respectively, which was lower than that in T20 sample. Consequently, the oriented or stretched chains could be easily relaxed in T40 and T60 samples at higher temperature during melt penetration process. However, on the other hand, the viscosity of polymer melt decreased at high temperature so that the growth front was promoted to overcome the elastic resistance to induce lamellae twisting, therefore more cylindrites and banded spherulites were observed. In addition, the diameter of banded-spherulites in T60 sample was larger than that in T40 sample due to the slower cooling rate, and the molecular chains under higher temperature was prone to pile into the lamellae, leading to bigger crystals. The nucleation density of cylindrites in T60 sample was less than that in T40 (Figs. 5c and 6c). According to the theory of dormant nuclei, some partly arranged chains were acting as dormant nuclei during the quenching process of polymer melt, leading to a sharp increase in density of nuclei at low temperature. Thus, the nucleation was accelerated by faster cooling rate of T40 sample and more nuclei

could arrange along the flow direction.

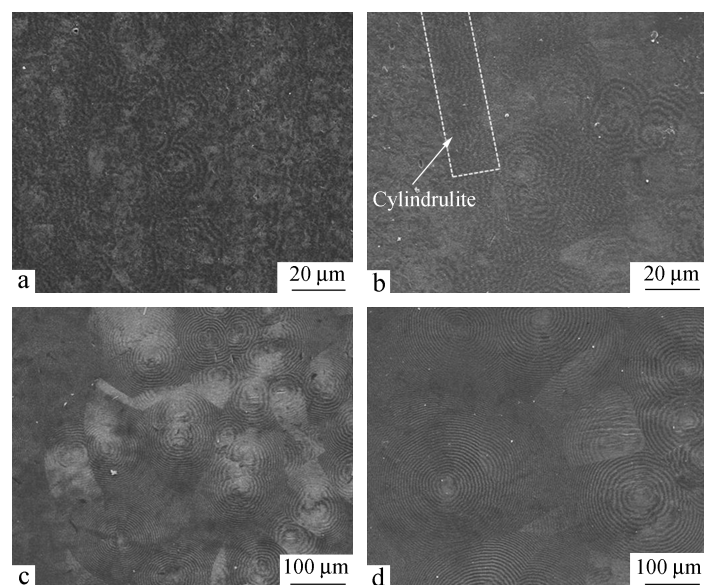


Fig. 5 SEM micrographs of the crystalline morphologies of T40 sample: (a) skin layer, (b) sub-skin layer, (c) intermediate layer and (d) core layer (The melt flow direction is vertical.)

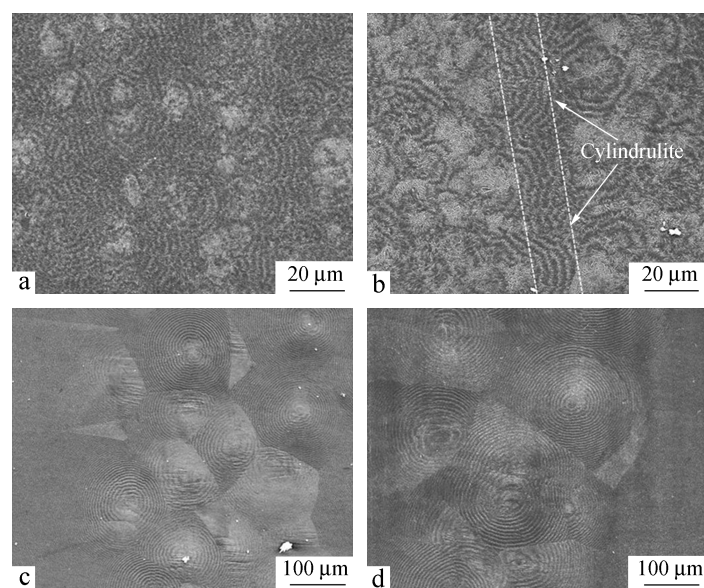


Fig. 6 SEM micrographs of the crystalline morphologies of T60 sample: (a) skin layer, (b) sub-skin layer, (c) intermediate layer and (d) core layer (The melt flow direction is vertical.)

2D-SAXS Measurement

2D-SAXS technology was used to characterize the molecular orientation of samples at different mold temperature as shown in Fig. 7. From the sub-skin layer to the core layer, the intensity maximum decreased on meridian direction and increased on equatorial direction, illustrating that the signal was transformed from the oriented into isotropic-like scattering pattern. At the sub-skin layer of T20 sample, the scattering intensity maximum was concentrated on both sides of meridian direction, and scattering streak signal did not appear along

the equatorial direction. According to previous literatures, appearance of scattering light in the meridian direction suggested that there were oriented lamellae perpendicular to the flow direction, the streak scattering in the equatorial direction was attributed to the shish, and the isotropic ring indicated random crystalline structure in the specimens^[36, 37]. In this work, the equatorial scattering streak was not seen (Fig. 7), in line with SEM results, indicating that the content of shish formed in the samples was too low to be detected by 2D-SAXS or SEM instrument, which was caused by the number of long chains that the critical molecular weight for shish formation was not enough^[38]. The orientation of all samples reached the maximum value at sub-skin layers, where the shear and cooling rates were both high throughout the thickness of molded bars.

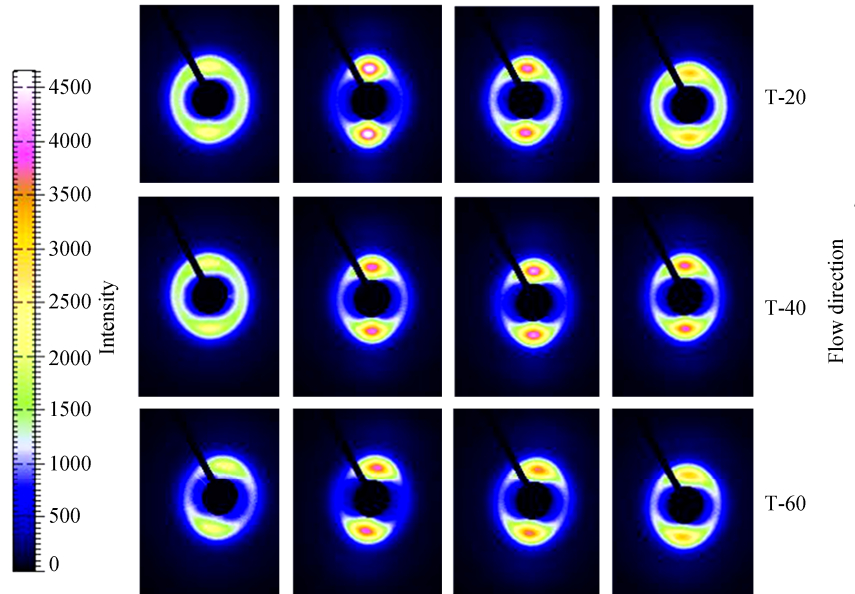


Fig. 7 2D-SAXS patterns of specimens at various positions: skin layer, sub-skin layer, intermediate layer and core layer, from left to right

In order to quantitatively compare the orientation degree at different layers, Herman's orientation factor, f , which was widely used to characterize the orientation degree quantitatively, was calculated by Eqs. (1) and (2). The results are collected in Table 6. It can be seen that the value of f increased first from the skin layer to the sub-skin layer, and reached a maximum value, and then gradually decreased from the sub-skin layer to the core layer. Moreover, the orientation degree of each layer was reduced with increasing the mold temperature, arising from the cooling rate decreased during cooling stage (Table 3). Thus, oriented or stretched chains could be relaxed to some extent at high temperature. The maximum orientation factor in T20 samples was 0.75 as the result of the existence of oriented lamellae, which was grown from the fibrillar precursors due to significantly high cooling rate, in accordance with the SEM morphological observation.

Table 6 The orientation factor f calculated by 2D-SAXS of specimens at different layers

Sample	f			
	Skin layer	Sub-skin layer	Intermediate	Core layer
T20	0.51	0.75	0.68	0.50
T40	0.50	0.64	0.61	0.52
T60	0.49	0.53	0.51	0.48

The periodic interval (length) between lamellae in polymer crystal is called long period (L), which is related to the thickness of crystal and amorphous regions in the lamellar structure^[39]. To expound the evolution of the long period, 2D SAXS radially integrated intensities $I(q)$ ($q = 4\pi(\sin\theta)/\lambda$, where 2θ is the scattering angle and λ

is the wavelength) were obtained for integration in the azimuthal angular range of $-180^\circ \leq \varphi \leq 0^\circ$ (such as Fig. 8a). The peak value of $q_{\max}$ is related to the long period (L) and the specific values of long period can be obtained *via* Bragg equation:

$$L = \frac{2\pi}{q_{\max}} \quad (6)$$

As shown in Fig. 8(b), with the position moving toward core layers, the values of long period monotonically increased. The long period could be influenced significantly by temperature: below initial melting temperature, the long period was improved with the increment of thermal treatment temperature, mainly due to the rearrangement of defective lamellae; above initial melting temperature, the melting process became a dominating factor for the increase of long period, due to the transition from compact lamellae into loose amorphous interlayers^[40–42]. Even the long period along the shear direction can be promoted with increasing shear strength^[43], but the values of long period at sub-skin layers were even smaller than those at core layers, which illustrated that the temperature profiles had dominating effect on the long period in this work. Hence, when the position moved to the core layer, the increase of long period could be explained by an increase in crystallization integrity and crystal size promoted by annealing effect with lower cooling rate. However, the increment was slight. There was approximately 1 nm variation from the skin layer to the core layer of all three samples, which could be caused by the fast cooling rate during M³IM process. And this result agreed well with the reported study that the change of long periods was not significant for PET crystallization at different temperature^[41]. Additionally, the increment of long period probably arises from the transition of crystalline morphology from random spherulites to oriented lamellae. However, the oriented microstructures were loose and not necessarily to form well ordered structures at nanoscale according to the morphological observation. Hence, we still believe that the increment of long period was resulted from mold temperature rather than the transition of crystalline morphology^[44]. Besides, the long periods were also slightly promoted with increasing the mold temperatures at the same position. The reason was similar to that by decreasing cooling rates when the mold temperatures rose, resulting in better crystallization.

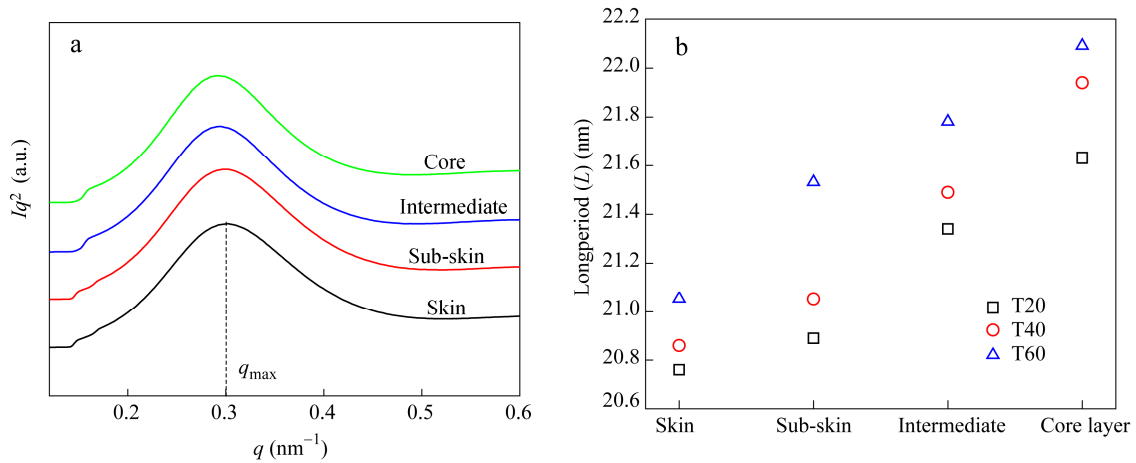


Fig. 8 (a) 1D-SAXS intensity profiles (Iq^2 versus q) along the meridian at different layers of the specimen T20; (b) Long period (L) at different layers of three samples

Thermal Properties

DSC can also be used to measure the variation of crystalline structure and lamellar thickness in the M³IM samples. The melting curves of the three samples were obtained at different mold temperatures, as shown in Fig. 9. Interestingly, it was seen that a shoulder melting peak appeared in the DSC curves of T20 at the sub-skin layer, indicating that another crystalline morphology (most likely orientated structure) was formed^[45], in

accordance with the SEM observation. The shoulder peak value at 141.91 °C was higher than the main melting value at 134.08 °C, demonstrating that the melting stability of the oriented lamellae was higher than that of the twisted lamellae. Also, it can be interpreted that during the heating stage, the random twisted lamellae were closer to their final configuration in melt and had, therefore, less energy barrier to overcome than relatively closely arranged oriented lamellae to melt, in contrast with the crystallization process where stretched chains had less kinetic barrier to conquer than random chains^[46]. However, there was only one melting peak in the melting curves at the sub-skin layer for both samples T40 and T60, due to lack of oriented lamellae based on SEM observation. Otherwise, it also suggested from Fig. 9 that the melting temperatures increased steadily from the skin toward the core for all three samples. This was due to the decrease of cooling rates along the thickness, *i.e.*, the position close to the core relatively possessed long time and high temperature for crystallization, and thereby some lamellae with high thickness were formed at core layers. In summary, the results of DSC were consistent with the analysis of SEM and 2D-SAXS, and the existence of oriented lamellae was further certified.

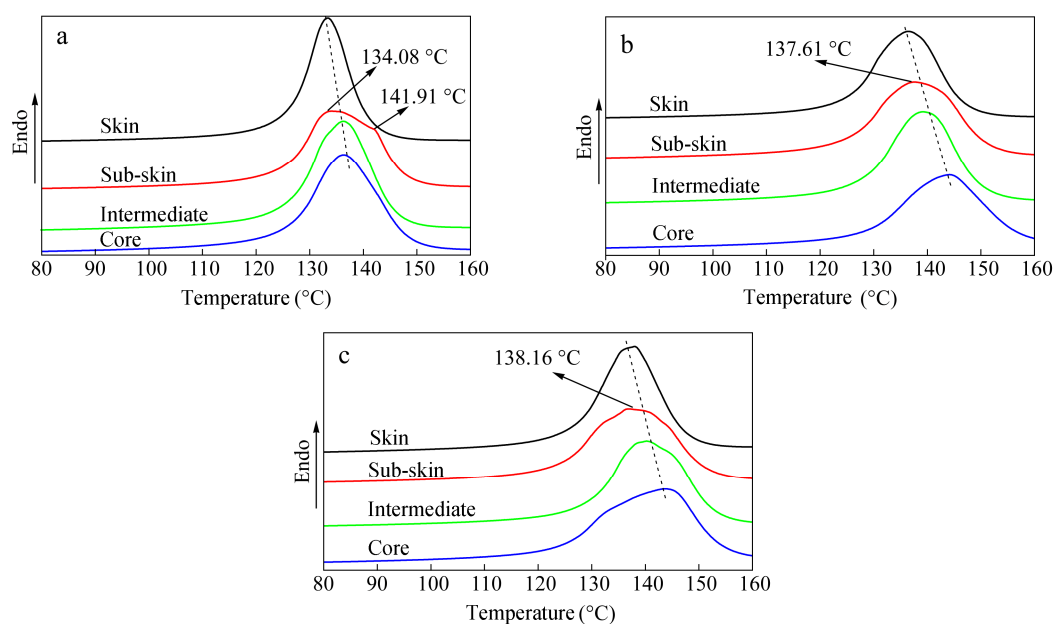


Fig. 9 Melting curves at different layers acquired by DSC: (a) sample T20, (b) sample T40 and (c) sample T60

To logically explain the effect of the mold temperature on the microstructures of LMW HDPE M³IM samples, a schematic picture was drawn in Fig. 10. Combining with our previous work, the cylindritic structures were composed of some precursors domains impinging against each other closely along the flow direction^[9]. Initially, the molecular chains in the melt were random coils. When imposed on shear and elongational flow, these macromolecular chains could be stretched and oriented, similar to the dormant nuclei activated from a large amount of ordered chains during the quenching process of melt^[47]. For the sample with high mold temperature, the cooling rate was low, so the oriented precursors could be easily relaxed due to high temperature and banded spherulites were finally formed (Fig. 10a). Meanwhile, the local shear flow was relatively intense due to low viscosity of polymer melt at high temperature, leading to good arrangement of the precursors and compacted in line along the flow direction. Additionally the stress could be easily accumulated in the incipient lamellae due to shear flow, so the growth of lamellae was prone to release the surface stress by twisting. The stacks of twisted lamellae were grown perpendicular to flow direction due to the restriction of adjacent nuclei. Finally, the cylindritic structures composed of banded-structures were formed in the sample T60 at the sub-skin layer (Fig. 6b), where both the cooling rate and shear rate were relatively high throughout the thickness

direction. With decreasing mold temperature, the viscosity of polymer melt increased instantly. The local ordered domains were difficult to arrange along the flow direction, therefore, there were less cylindrites and more random spherulites as observed at the sub-skin layers of sample T40 (Fig. 5b).

However, when the mold temperature was very low, the precursors were more stable because of longer relaxation time at high cooling rate, and the shear rates above $\dot{\gamma}_D^{\text{crit}}$ were easier to achieve during M³IM process; then the molecular alignments turned into the fibrillar nuclei along the flow direction and crystal growth began by absorbing the random chains through self-diffusion. In case of closely-spaced nuclei, the crystal growth could only take place perpendicularly to the flow direction. The final result was the formation of oriented lamellae, performed at the sub-skin layer of sample T20 (Fig. 4b). With low cooling rate in the zone close to center, the oriented fibrillar nuclei were tough to be reserved but form point-like row nuclei and grow into random banded spherulites (Fig. 10b), even though the change of crystalline morphologies was observed mainly at sub-skin layers in this work due to the pressure limitation of secondary injection. It is certainly demonstrated that the decreasing the mold temperature can induce fascinating crystalline morphologies and achieve the transition from cylindrites into oriented lamellae.

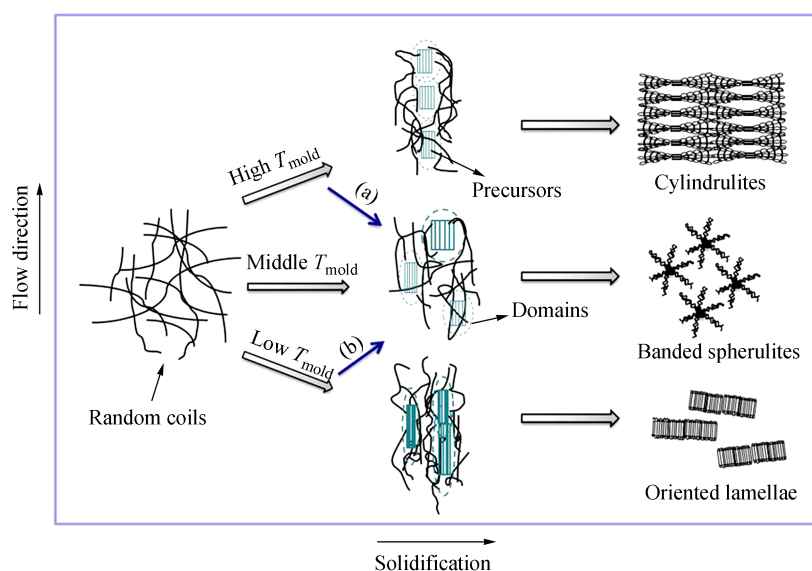


Fig. 10 Schematic evolution of different crystalline structures at various mold temperatures (abbreviated as T_{mold} for convenience) during M³IM process

CONCLUSIONS

It was demonstrated that the mold temperature was vital for the formation of microstructures in the M³IM parts. It was revealed that the cooling rate could be significantly promoted by decreasing the mold temperature according to results of real-time temperature measurement. In consequence, the oriented lamellae can also be observed at sub-skin layers at low mold temperature even for LMW HDPE, though cylindritic structures were observed at high mold temperature. Except for sub-skin layers, there were mainly well-developed banded spherulites in other zones throughout the injected bar. Therefore, the hierarchical structures and orientation behavior were closely related to the temperature profile. A model was illustrated for better analysis of the role of mold temperature in the evolution of different crystalline morphologies.

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