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Lamellar orientation in the blends of linear low density polyethylene and isotactic polypropylene induced by dynamic packing injection molding

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In this work, we have carried out 2 dimensional small and wide angle X-ray scattering experiments on the blends of linear low-density polyethylene (LLDPE) and isotactic polypropylene (iPP) obtained by dynamic packing injection molding in which the melt was firstly injected into the mold then forced to move repeatedly in a chamber by two pistons that moved reversibly with the same frequency as the solidification progressively occurred from the mold wall to the molding core part. iPP was found to form a shish-kebab structure with its lamellar stack oriented perpendicularly to the shear flow direction. Very interestingly, the lamellae of LLDPE were found tilted away from shear flow direction with molecular chain still along flow direction, and the tilted angle increases from the skin to the core part. This can be only understood if the intra-lamellar block slip in the chain direction is generally activated during shearing process achieved by dynamic packing injection molding. Our finding is important and seems to provide further support for the idea that the structure of the crystalline lamellae is not continuous but constructed of small building units with thin boundary in between. © *2005 Springer-Science + Business-Media, Inc.*

Polymer crystallization and crystal structure have been long time important issues in polymer physics. Melt crystallized polymeric systems represent a semi-crystalline lamellar structure. In the recent years, some more evidences have been found which show that the structure of the crystalline lamellae are not continuous but constructed of small building units with thin boundary in between [1, 2]. Actually, the idea of "blocky" structure for polymer crystals was pioneered by Hosemann (he referred to it as a "mosaic block" structure) [3]. Even more, this special blocky feature of lamellae has been found theoretical explanation which suggests that the crystallization of an entangled polymer melt is a multi-step process passing over intermediate states. Before the formation of lamellar crystallites the system creates a mesomorphic layer, which then solidifies through a cooperative structure transition to produce a granular crystalline layer before finally transforms into a homogeneous lamellar crystallites which are built up by blocks with thin boundary in between [4]. The direct evidence of block structure of lamellae can be found from TEM or AFM observations which showing that the lamellar crystals split into an array of blocks [5, 6]. Recently, a high temperature mechanical relaxation due to the block slip motions has been suggested for melt crystallized polymers [7].

In recent years, dynamic packing injection molding has been found a very important way to control polymer morphology and mechanical properties. The pioneered work on dynamic packing injection molding went back to 1986, when Prof. Bevis reported such technology and owned the patent [8]. As a long-term project aimed at engineering polyolefin blends, we have carried out intensively experiments on polyolefin blends obtained by dynamic packing injection molding in which the melt is firstly injected into the mold then forced to move repeatedly in a chamber by two pistons that moved reversibly with the same frequency as the solidification progressively occurred from the mold wall to the molding core part [9–13]. We are seeking to establish a fundamental understanding of structure-property-processing relationships through the control of phase morphology (phase separation and phase inversion), molecular orientation and

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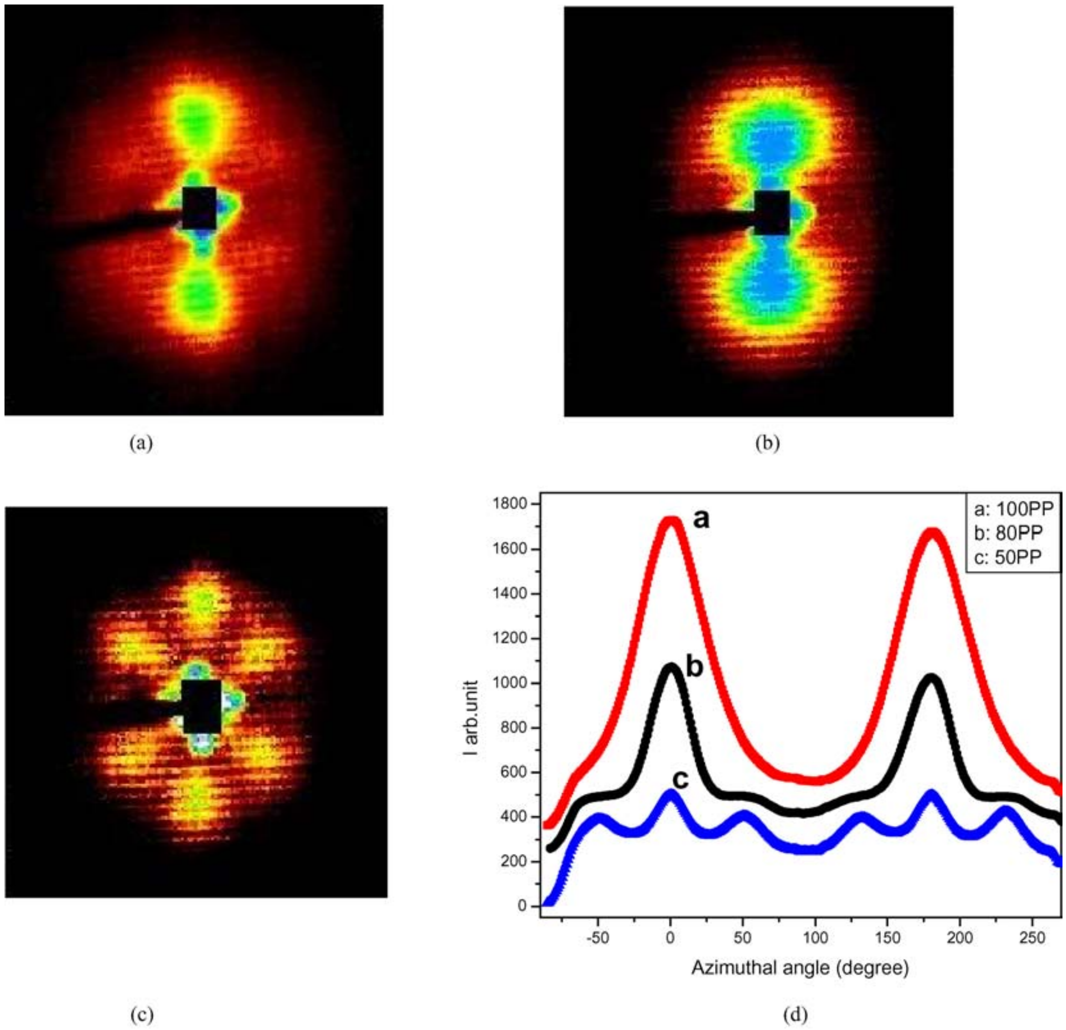
crystal morphology(epitaxy and transcrystalline growth, lamellae interlock) of polyolefin blends. In most cases, shear induced shish-kebab structure has been evident in isotactic polypropylene (iPP), polyethylene (PE) and their blends [14, 15]. More interestingly, a well-defined heteroepitaxial growth of high-density polyethylene (HDPE) on the lamellae of isotactic polypropylene (iPP) has been achieved for the first time in their blends via dynamic packing injection molding, depending on the composition and sequence of crystallization between iPP and HDPE [16]. In this report, we present the results on the blends of iPP and linear low density polyethylene (LLDPE). A tilted lamellae of LLDPE was found away from shear flow direction with molecular chain still along flow direction. In contrast to the epitaxial growth in iPP/HDPE blends, intralamellar block slip along chain direction of LLDPE has been suggested based on the 2d-saxs and 2d-waxs characterization. The coupling between the blocks and lamellae provides the physical basis to understand the observed phenomenon.

The iPP 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). 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 200°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 reference [10]. Macroscopically, the dynamic packing injection molded samples can be divided into three layers, namely, the skin, the sheared layer and the core. The blends are labeled by the weight percentage of iPP, For instance, 100PP and 50PP represent dynamic samples consisting of 100% iPP and 50% iPP by weight, respectively. Two dimensional small angle X-ray scattering (2D SAXS) measurements were carried out on the dynamic packing injection molded samples using an in-house setup with a rotating anode X-ray generator (Rigaku RU-H300, 18 kW) equipped with two parabolic multilayer



(a) (b) (c) (d)

Figure 1 Scattering patterns of 2D SAXS at 25°C of (a) 100PP, (b) 80PP, (c) 50PP and (d) corresponding azimuthal scans of 2D SAXS. Shear direction is along meridian.

mirrors (Bruker, Karlsruhe), giving a highly parallel beam (divergence about 0.012°) of monochromatic CuK* radiation (=0.154 nm). The SAXS intensity was colleted with a two-dimensional gas-filled wire detector (Bruker Hi-Star). A semitransparent beamstop placed in front of the area detector allowed monitoring the intensity of the direct beam. Azimuthal scan of 2D SAXS were made at a step of 1° from −90 to 270 deg. The 2 dimensional wide-angle X-ray scattering (2D WAXS) experiments were conducted using a Rigaku Denki RAD-B diffractometer. The wavelength of the monochromated X-ray from CuK* radiation was 0.154 nm. The samples were placed with the orientation (flow direction) perpendicular to the beams. Azimuthal scan of 2D WAXS were made for selected crystal plans of both polyethylene and polypropylene at a step of 1° from 0 to 360 degree.

Fig. 1a–c is the 2D SAXS patterns at 25°C of 100PP, 80PP and 50PP, respectively. Corresponding azimuthal scans of 2D SAXS are also included in Fig. 1d. One observes very beautiful but much complicated 2D SAXS patterns with two sets of diffraction spots for 50PP. From the corresponding azimuthal scans, it can be found that not only for 50PP but for 80PP, two sets of diffraction spots exist. To distinguish attribution of lamellae between LLDPE and iPP in scattering patterns, similar measurements at 135°C have been carried out for 50PP. At 135°C the lamellae of LLDPE will be melted and only PP lamellae are remained. The result is shown in Fig. 2. Combination of Figs 1 and 2, it is clear that for pure iPP(100PP) only two strong scattering spots in the meridianal direction, indicating that preferential growth of all lamellae is perpendicular to the shear direction. While for both 80PP and 50PP, the two scattering spots along meridian are caused by orientation of iPP lamellae perpendicular to shear direction and other four spots, attributed to that of LLDPE, are about 50° apart from meridian. SAXS result clearly indicates a preferential growth of PP lamellae (shish-kebab structure) and an interesting tilted lamellar structure for LLDPE. The shear induced shish kebab structure of polymer has been documented in literature and can be well understood. However, for tilted lamellar of LLDPE, there are two possibilities. One is due to the epitaxial growth of LLDPE on iPP lamellar, just like the case in iPP/HDPE blends [16]. Another possibility is due to the intralamellar slip of LLDPE under the effect of shear, just like the case of deformation by drawing and shearing of HDPE [17, 18].

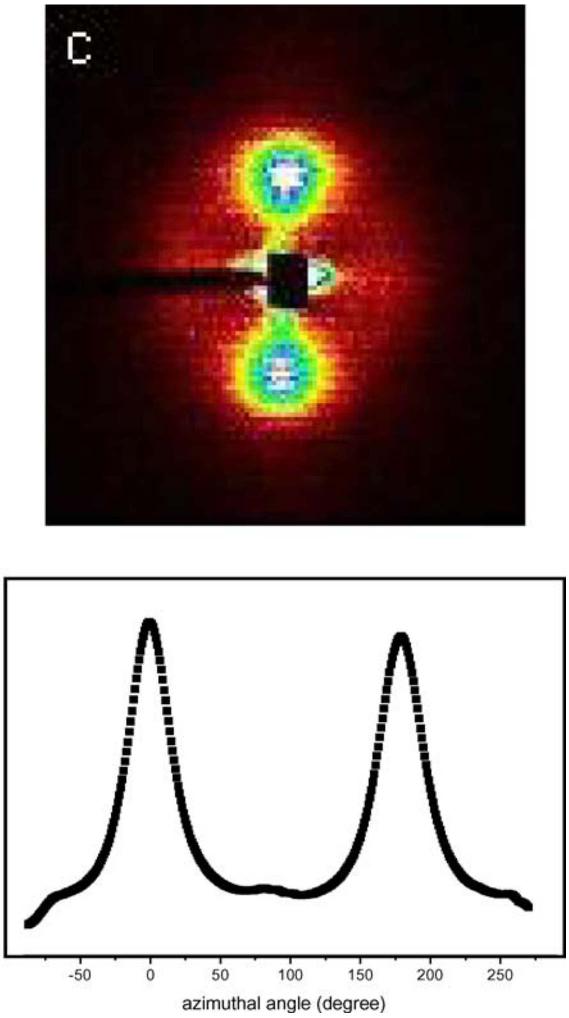
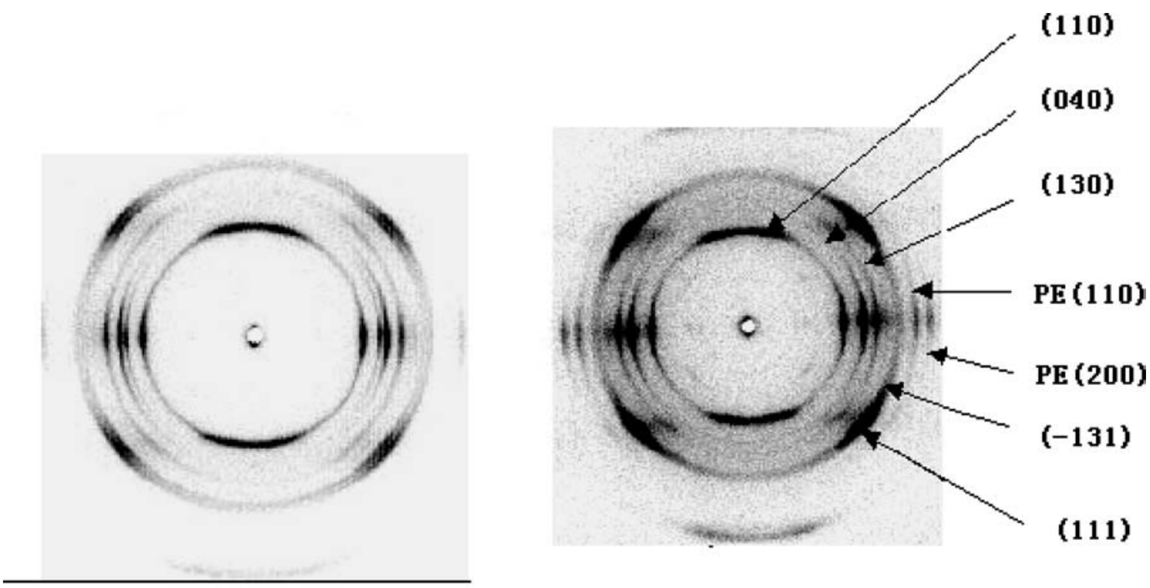
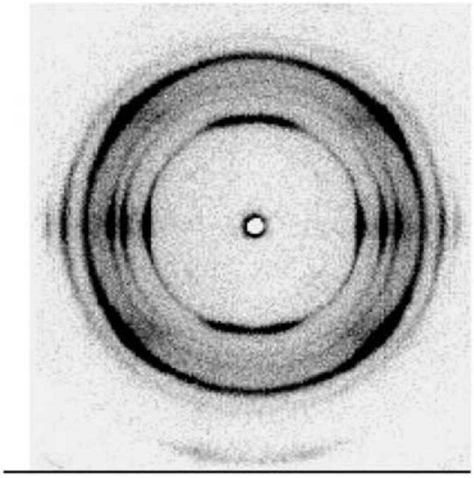


Figure 2 Scattering patterns of 2D SAXS at 135°C of 50PP corresponding azimuthal scans of 2D SAXS. Shear direction is along meridian.

To verify the origin of the tilted lamellarstructure for LLDPE, 2D WAXS experiment was carried out to check the molecular orientation of iPP and LLDPE. Fig. 3 is the 2D WAXS patterns obtained perpendicular to the shear flow direction of 100PP, 80PP and 50PP, respectively. For the orientation of iPP, one observes for the three compositions a highly oriented structure as indicated by the sharp dark spots on the five circles in WAXS pattern. The lattice planes are 110, 040, 130, −131 and 111 of iPP and (110), (200) of LLDPE, from inner to outside circles. Strong reflections of (hk0) plane in iPP and LLDPE along the equatorial direction indicate that molecular chains are preferentially oriented along shear direction, independent of compositions. Four reflections around the meridian also emerge in the (110) plane of iPP, indication of lamellar branching through homoepitaxy between-crystals themselves [19, 20]. These arise from the iPP component daughter regions which, are related (a-axis parallel to the meridional direction) to the parent component iPP regions (*c*-axis parallel to the meridian) epitaxially in an orientational relationship first established in α-spherulite quadratic precursors some years ago and later explained on a molecular basis by Lotz *et al.* [19]. The first factor concerns the relative amounts of the epitaxially related iPP components having their *c*-axis (parent) and *a*-axis (daughter) respectively parallel to the meridian in the PP and PP/LLDPE sampleswhose WAXDs are shown in Fig. 3 a–c. It is evident even from visual comparison of the equatorial and first layer line (near meridional) 110 iPP reflections that the relative amounts of the two epitaxially related iPP orientations are comparable. To see more clearly the molecular chain orientation, the corresponding azimuthal scans of all the planes for LLDPE and iPP have been carried out and indeed the reflections of (hk0) plane in iPP and LLDPE along the equatorial direction. Shown as an example, the selected azimuthal scans of (110)



(a) 100PP (b) 80PP

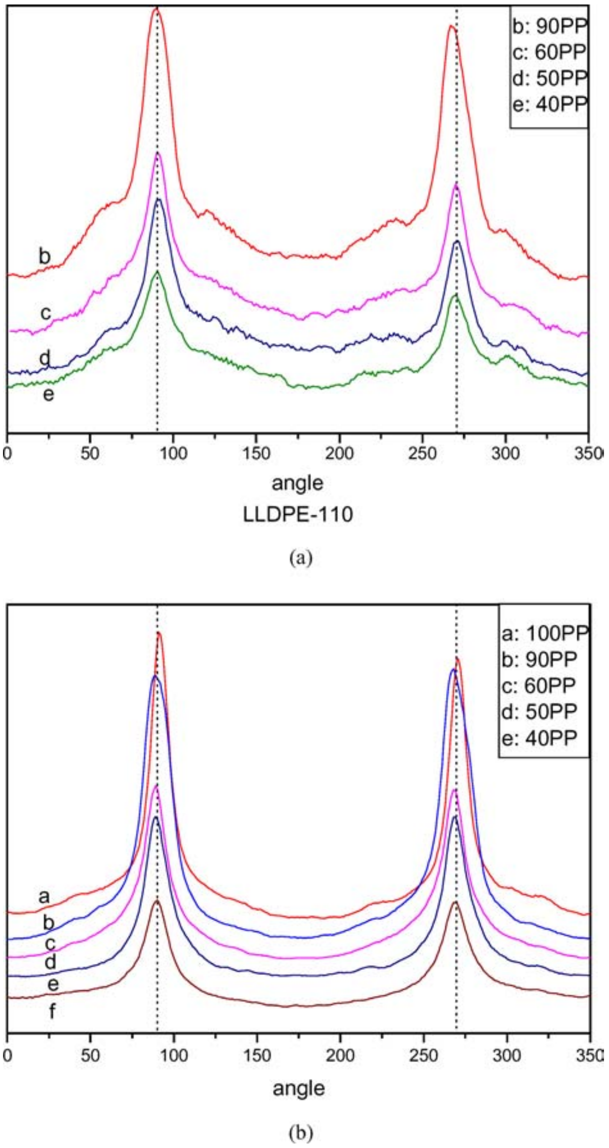


(c) 50PP

Figure 3 Scattering patterns of 2D WAXS at 25°C of (a) 100PP, (b) 80PP, (c) 50PP. Shear direction is along meridian.

plane for LLDPE and (040) plane for iPP are shown in Fig. 4. It should also be noted that the azimuthal scans of the iPP 040 reflections of all the samples given in Fig. 4b which exhibit a predominant equatorial orientation of the *b*-axis cannot be used as an orientational criterion for differentiating between the relative contents of the two epitaxially related iPP populations since they both share the same *b*-axis orientation. Combination of above results of 2D SAXS and 2D WAXS, it is evident that for iPP part of molecular chains is along shear flow direction (the meridian) and part of molecular chains is along the equatorial direction. For LLDPE majority of molecular chains are along shear flow direction. However, orientations of lamellae are totally different for LLDPE and iPP. For iPP the lamellae grow perpendicular to shear direction, resulting in shish-kebab like structure. However, with regard to SAXS of the substantial iPP epitaxial component in which the *a*-axis is oriented meridionally (i.e. the *c*-axis is correspondingly nearly equatorially oriented), based on the two references mentioned above as well as other studies the latter iPP regions would be expected to be lamellar. Given that their c-axis is near-equatorial, they would be expected to give rise to diffraction spots which are correspondingly near-equatorial. This latter feature is clearly not manifested in Fig. 1, which gives rise to the question of what is the nature of the morphological details of these regions and how they are related to or play a role if at all, in the evolution of the LLDPE orientations and morphology.

For LLDPE the lamellae are tilted away from shear flow direction with molecular chain still along flow direction. This can be only understood if the intralmaellar block slip is generally activated during shearing process achieved by dynamic packing injection molding. The schematically representation is shown in Fig. 5. The slip by layer like shearing and interlamellar sliding is also included in Fig. 5. For interlamellar sliding, the molecular chain is tilted away from shear flow direction [21] and should be excluded out in our model. The



(a)

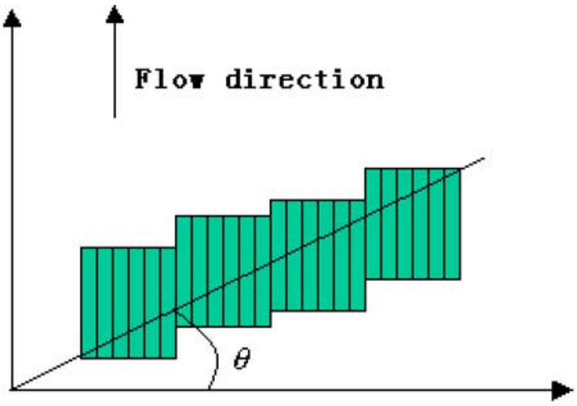
(b)

Figure 4 The corresponding azimuthal scans of (110) and plane polyethylene (a) and (040) for polypropylene (b).

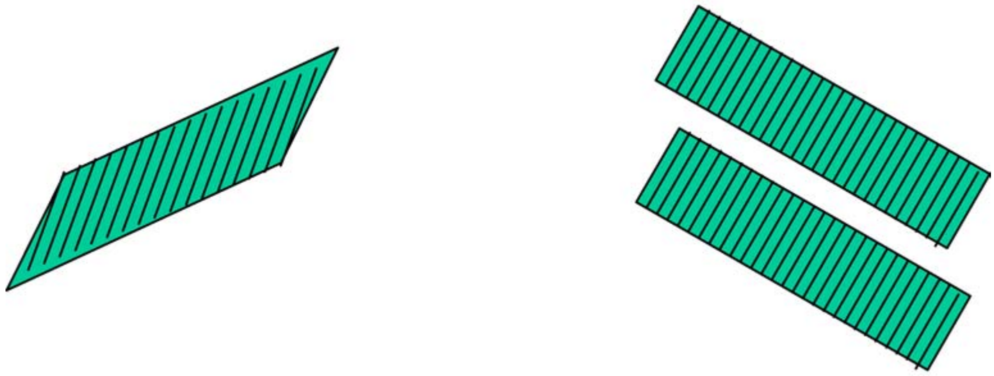
slip by layer like shearing should in principle produces the same chain orientation as block slip does. However, layer like shearing cannot be the general mechanism in our system (see discussion below).

The deformation mechanism in semi-crystalline polymers has been well established in which the intralamellar block slop is the main deformation mechanism [21–27]. The true stress-strain curves together with detailed studies on the recovery properties yields a surprisingly simple scheme for the process of tensile deformation in semicrystalline polymers where at least three critical points can be defined. These critical points could be explained as (1) the onset of isolated inter- and intra-lamellar slip process after the initial purely Hookean elastic range (point A), (2) change into a collective activity of lip motions at the yield (point B), and (3) the beginning of destruction of crystal blocks followed by the formation of fibrils (point C). Intralamellar block slip mechanisms provide sufficient degrees of freedom to accomplish a homogeneous strain distribution between crystalline and amorphous. The idea of intralamellar block slop obtained by tensile deformation is very helpful to understand the tilted lamellae of LLDPE in our system. Due to the effect of co-units content, the crystallization rate of LLDPE is highly slowed down compared with linear polyethylene. The development of lamellar structure will be hindered thus remains more likely its blocky structure. When they are subjected to external shear force, a shish-kebab structure with lamellae perpendicular to shear direction may be formed first. Then as the solidification progressively occurred from the mold wall to the molding core part, there exist a gradient of flow velocity with increasing from the skin to the core. The push and pull shear force provided by dynamic packing injection molding will cause the intralamellar block slip along the shear flow direction, resulting in the formation of tilted lamellae. One expects a change of tilted angle as change of shear force. This was indeed true when samples in different zone were checked. The tilted angle is 35°, 50°, 55° for the skin, sheared layer and the core of 50PP, respectively. The epitaxial growth of LLDPE on the lamellae of iPP may also play certain role to determine the lamellar orientation of LLDPE, as indicated by the small shoulder in 2D WAXS (Fig. 4). However, it is definitely less important in this case. The investigation on the change of the crystallites during deformation also convinces an interlamellar sliding and a crystallographic intralamellar slip of type (110) [001], as discovered by X-ray scattering experiments [28–31] and by the transmission electron microscopy (TEM) experiments [32]. More evidence come from DMA measurements on PE where it is shown that the block slips will be activated at lower temperature than that of chain sliding diffusion even in HDPE [33]. In case of LLDPE, the sliding of single chain is strongly blocked by the high amount of side chains. Thus it leaves mainly the block slip mechanism. One may expect even a larger block slip of LLDPE in the pure state than in the blends with iPP. However, we failed to obtain highly oriented lamellae for pure LLDPE by the dynamic packing injection molding. It is interesting that the tilted lamellae of LLDPE are only evident after it blended with iPP at this moment. This can be explained the relatively high viscosity of LLDPE. Since the shear stress, τ, keeps unchanged, shear rate is related to the viscosity, η, of blends, expressed by $\dot{\gamma} = \frac{\tau}{\eta}$. It is clear that shear rate is inverse proportional to the viscosity. The viscosity of homopolymer and their selective blends has been measured by using a high-pressure capillary rheometer Rheograph 2002 (Gottfert) with a 1 mm die and *L*/*D* ratio of 30 at 200°C over a shear rate range, $\dot{\gamma}$, from 10^1 to 10^4 s^{-1}, indeed showing that the viscosity of blends increases with increasing iPP content in whole range. We have not found either the tilted lamellae for pure iPP and for its blends with LLDPE or HDPE, which indicating that the slip of PP crystallites is much difficult compared with LLDPE.

In conclusion, 2D SAXS and 2D WAXS data suggest that iPP forms a shish-kebab structure with its lamellar stack oriented perpendicularly to the shear flow direction. This is well documented and easily understood. However, LLDPE forms lamellae tilted away from shear flow direction with molecular chains still along flow direction. This is unusual and can be only



(a) intralamellar block slip along chain direction



(b)Lay like shearing

(c) Interlamellar sliding

Figure 5 The schematically representation of slips of crystallites during dynamic packing injection molding.

understood if the intralmaellar block slip in the chain direction is generally activated during shearing process achieved by dynamic packing injection molding. Our finding seems to support the idea that the structure of the crystalline lamellae is not continuous but constructed of small building units with thin boundary in between. However, a further work is needed from morphological point of view via AFM, TEM to really prove the occurrence of intralmaellar block slip.

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