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Crystal morphology and tensile properties of LLDPE containing PP fibers as obtained via dynamic packing injection molding

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Abstract

The fibrillated linear low-density polyethylene (LLDPE)/isotactic polypropylene (iPP) fiber blends were subjected to dynamic packing injection molding (DPIM), in which the prolonged shear was exerted on the melt during solidification stage. Transcrystallization of LLDPE on PP fibers, with stacked lamellae parallel to each other and aligned approximately perpendicular to the long axial of the fibers, has been achieved for the first time in DPIM due to the prolonged shear. PP fibers were found to align parallel to the flow direction along thickness up to the oriented zone of sample prepared by DPIM. The presence of oriented PP fibers enhanced the orientation of LLDPE that developed row-nucleated type morphology. The molding temperatures were changed between 160 °C and 200 °C to investigate the effect of molding temperature on the crystalline microstructure of the blends. As increasing the molding temperature from 160 °C to 200 °C, the partial melting of PP fiber was changed to complete melting, resulting in a dramatic change of the crystal morphology and the mechanical properties as well.

Keywords: LLDPE/PP fiber blend; Shear-induced orientation; Transcrystallization

1. Introduction

Studies on the property and morphology of polyolefin blends have always received great academic interests, not only because of their wide application in industry and ease of re-cycling, but more importantly because of their diversiform and fascinated morphology depending on molecular structure, thermal history and external stress field. In order to modulate the morphology of blends and improve the property as much as possible, the key issue is to establish the relationship between property and morphology. The crystalline and phase morphologies of PP/PE blends have been extensively investigated [1–4]. Usually, semicrystalline polyolefin blends have specific interaction resulting in particular crystallization morphologies at the interface. Transcrystallization at interfaces, as a surface-induced crystallization, is an effective and economical method to improve the interfacial adhesion, and thus is attractive for many researchers in the past [5–8]. Transcrystallization is induced by the preferential heterogeneous nucleation at the interface between different components. The prerequisite for transcrystallization is the presence of a high density of active nuclei on the substrate/fiber surface. The closely packed nuclei hinder the full extension of spherulites, which are then forced to grow in one direction, namely perpendicular to the substrate/fiber [9,10]. To control transcrystallization, the modification of substrate/fiber or polymer matrix is equivalent due to the competition between interface nucleation and bulk nucleation. It has been found that shear plays an important role to induce the transcrystallization by enhancing the interface nucleation. An enhanced orientation and crystallization of iPP by using ultra-high molecular weight polyethylene (UHMWPE) short fiber have been reported by Hsiao et al. [2,11]. A cylindritic morphology in the iPP matrix with UHMWPE in the center was observed. Li and coworkers studied the formation of the shish-kebab morphologies together with transcrystallization of PP in a

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microfibrillar PET/PP blend [12]. Even more, twisted lamellae were reported in an iPP transcrystallinity induced by aramid fibers in Ref. [13]. The presence of transcrystallinity is expected to have a positive effect on the longitudinal properties of the composite materials, as measured in nylon66 composites [14] and as predicted for PP composites under stress [15].

Great interest is focused on the relationship between structure and morphology. However, most of the researches are in theory [16–19] and only few works concern with the practical processing field. In fact, no well-defined transcrystallization has been encountered in polymer composites subjected to conventional processing methods (such as extrusion and injection molding), although there are some indications in literature [12]. Achieving transcrystallization in polymer composites processed by conventional methods has not only significant theoretical value but also important practical applications.

As part of long-term project aimed at super polyolefin blends, we are seeking to establish a fundamental understanding of structure–property–processing relationships through the control of phase separation, molecular orientation and crystal morphology of polyolefin blends. In our previous papers [20], we reported the results of mechanical properties and structural studies of some polyolefin blends (such as HDPE/LDPE, HDPE/iPP, iPP/EPDM) obtained by dynamic packing injection molding. We have found that the molecular architecture, composition, temperature and shear stress field play important roles to determine the final morphology and mechanical properties. A well-defined epitaxial 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 [21].

In this work, the melt blends of linear low-density polyethylene (LLDPE) and isotactic polypropylene (iPP) fiber were prepared by twin-screw extruder set at a barrel temperature of 130–140 °C, which is well below the melting point of PP fibers. Then the fibrillated blends were subjected to 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. In our work, melt was forced to shear, which would induce oriented crystallization and macromolecular chain aligned parallel to the shear direction. Moreover, the morphology of PP can be kept by controlling the temperature lower than T_m of PP in cooling process. PP fiber is partially miscible with PE, which will avoid void and crack at the interface. All of this would be in favor of the transcrystalline growth. We will focus on crystal morphology and tensile properties of obtained blends. Our proposes are twofolds: one is to explore the possibility of transcrystallization of LLDPE containing fibers via injection molding under the effect of shear, and the other is to achieve super polyolefin blends with both high tensile strength and modulus and by controlling orientation and interfacial microstructure. LLDPE was chosen, instead of HDPE or LDPE, as the matrix, based on the consideration that LLDPE has higher melting temperature difference with PP compared with HDPE, and has higher crystallization ability compared with LDPE.

2. Experimental

2.1. Materials

A linear low-density polyethylene (LLDPE) with a melt flow index of 2.6 g/10 min (190 °C, 2.16 kg) was supplied by Maoming Petrochemical Corp. (trade marked as 7042). It has a melting point of 123 °C and a density of 0.92 g cm^{-3}. A commercially available polypropylene fiber (PP fiber) with a diameter of 20 μm was used in this study and has a melting point of 163 °C. According to the provider's data, the tensile strength and *E*-modulus of this PP fiber are approximated to 350 MPa and 3500 MPa, respectively.

2.2. Samples preparation

Melt blending of LLDPE/PP fiber composites was conducted using a co-rotating twin-screw extruder (TSSJ-25) set at a barrel temperature of 130–140 °C. After producing pellets, the composites were subjected to dynamic packing injection molding (DPIM) with molding temperature set at 160 °C, 170 °C, 180 °C and 200 °C. The shear rate is about 10 s^{-1} calculated from the geometry of mold. The schematic representation of this method and the processing parameters can be found somewhere [22]. The injection molding under static packing was also carried out by using the same processing parameters but without shearing for comparison purpose. The specimen obtained by dynamic packing injection molding is called dynamic sample, and the specimen obtained by static packing injection molding is called static sample. The structure of dynamic samples is different from that of static ones, with the appearance of oriented zone between skin and core zones, the characteristic of dynamic samples, caused by the shear stress. The detailed description can be found elsewhere [23].

2.3. Characterizations and measurements

The two dimensional wide-angle X-ray scattering experiments (2D-WAXS) 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 reflection mode was used. The samples were placed with the orientation (flow direction) perpendicular to the beams. The intensity was corrected by subtracting the background scattering.

The morphologies of the blends were studied by preferential etching of the amorphous phase in mixed acid for 1 h at the temperature of 60 °C. The samples were fractured in liquid nitrogen prior to etching. Then the surface was coated with gold and subsequently examined by an X-650 Hitachi scanning electron microscope with accelerated voltage 20 kV.

A Perkin–Elmer diamond-II differential scanning calorimetry (DSC) was used to determine the melting points of

LLDPE and LLDPE/PP fiber blend. The test samples (about 5 mg) were heated from 40 °C to 200 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

Polarizing light observations were performed using a Leica DMIP polarizing light microscopy (PLM) equipped with a Linkam THMS 600 hot stage under crossed polarizer. Thin slice was cut from the injection-molded sample, inserted between two microscope cover glasses, melted at 150 °C, which was upper the melting point of LLDPE and lower than that of PP, and then squeezed to obtain thin films.

An Instron Universal Testing Machine was used to get the tensile strength and modulus under a crosshead speed of 50 mm/min according to GB/T1040-92 standard, and the measured temperature was around 20 °C. In the mechanical testing, at least four samples have been measured and the average values were reported.

3. Results and discussion

3.1. Mechanical properties

Fig. 1(a) shows the trends of tensile strength vs. PP fiber content in LLDPE/PP fiber blends injection-molded at 160 °C. For static samples, one observes a very low tensile strength and almost unchanged value with increasing PP fiber content up to 20 wt% (the tensile strength is in-between 12 MPa and 14 MPa). This result indicates that PP fiber could not obviously improve the tensile strength via conventional injection molding in the investigated range of composition. In this case not much orientation is expected for both LLDPE matrix and PP fibers. For dynamic samples, however, an increase of tensile strength is seen even for pure LLDPE (from 12 MPa of static one to 19 MPa of dynamic one), as caused by molecular orientation under effect of shear. A further increase of tensile strength from 19 MPa to 29 MPa is achieved after the PP fiber content reaches to 10 wt%. This is certainly due to the reinforcement of PP fibers under the effect of shear. In this case much orientation is expected for both LLDPE and PP fibers as well, which has been confirmed by 2D-WAXS measurements. Tensile modulus presented in Fig. 1(b) shows a continuous increase with increasing PP fiber content for both static and dynamic samples. The tensile modulus of the dynamic ones is about 70–80 MPa higher than that for static ones, this is again due to the shear-induced orientation for both LLDPE and PP fibers.

Through comparing the tensile properties between static samples and dynamic samples, it can be concluded that the dependence of tensile properties on the PP fiber content is weak in the former, whereas the PP fiber is efficient for the enhancement of mechanical properties in the latter. In the static

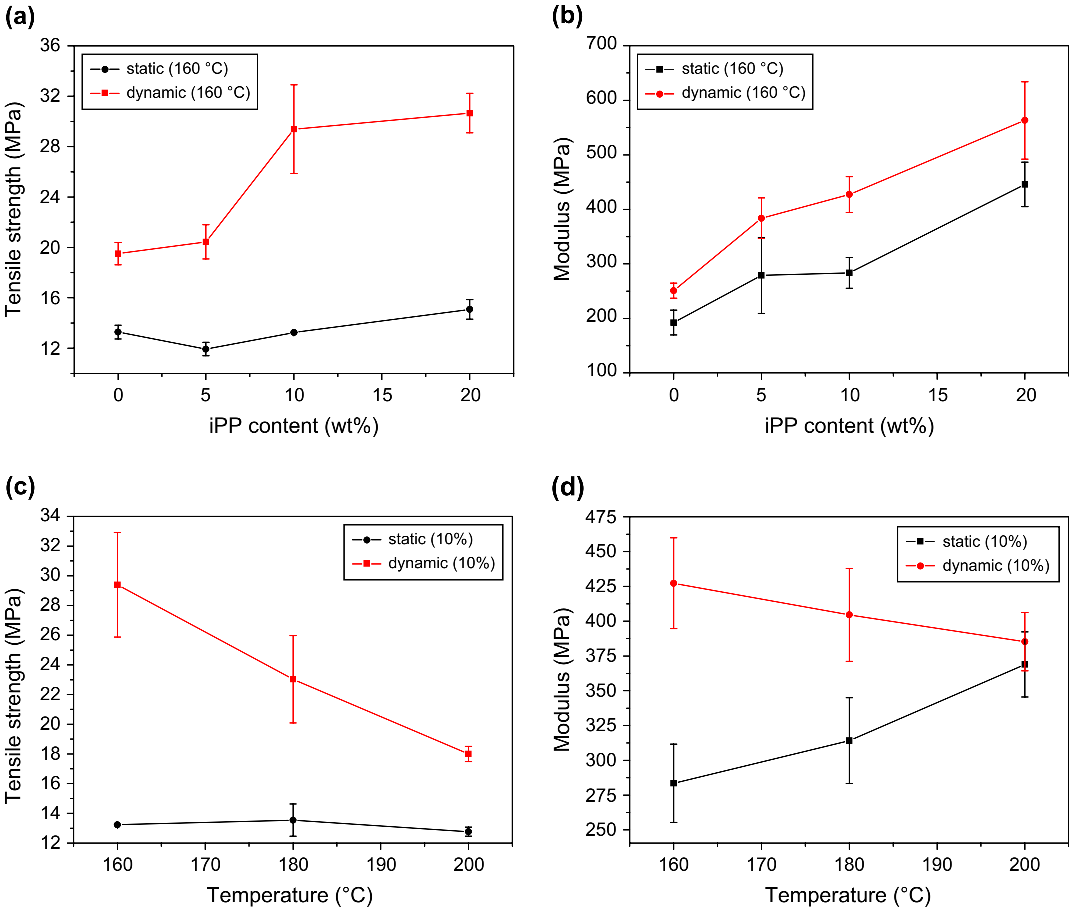

Fig. 1. Tensile strength and modulus of as-prepared LLDPE/PP fiber composites: (a) and (b) as a function of PP fiber content while (c) and (d) as a function of molding temperature.

samples, the polymer lamellae orient randomly, at the same time, the interconnection between PP fiber and PE matrix is very weak, resulting in the limited strengthening of properties by addition of PP fiber. As to the dynamic samples, the prolonged shear function causes the high level oriented structure and particularly promotes the interaction between PP phase and PE phase through tailoring the crystalline morphology at the interface, which will be experimentally proved in the following section.

As mentioned above, for polymer/polymer fiber blends, the molding temperature may play an important role to determine the mechanical properties. From the DSC heating diagram presented in Fig. 2, the melting temperatures (T_m) of LLDPE matrix and PP fiber are determined to be about 123 °C and 163 °C, respectively. Three processing temperatures, 160 °C, 180 °C and 200 °C, have been chosen to prepare injection-molding samples. The low temperature 160 °C is little lower than T_m of PP fiber and PP fiber will remain unmolten or only occur partly molten at the surface, whereas, PP fiber will be totally molten at other temperatures 180 °C and 200 °C. It can be anticipated that the reinforcement efficiency will decrease as the molding temperature increases due to the melting of polymer fibers. For example, the tensile properties of LLDPE containing 10 wt% PP fiber injection-molded at different temperatures are shown in Fig. 1(c) and (d). For static samples, the effect of molding temperature on tensile strength can be ignored because no significant change is seen as the molding temperature increases. Whereas a sharp decrease of tensile strength from 29 MPa to 18 MPa is observed for dynamic samples as the molding temperature increases from 160 °C to 200 °C. This can be understood as due to the melting of PP fibers and relaxation of LLDPE molecules (thus result in a less orientation) as molded at higher temperature. A similar trend of tensile modulus is seen. One also observes an increase in tensile modulus of static samples, as the molding temperature increases. This may be due to a higher crystallinity and a bigger crystal size as molded at high temperature, which will be further identified by DSC heating test and SEM observation.

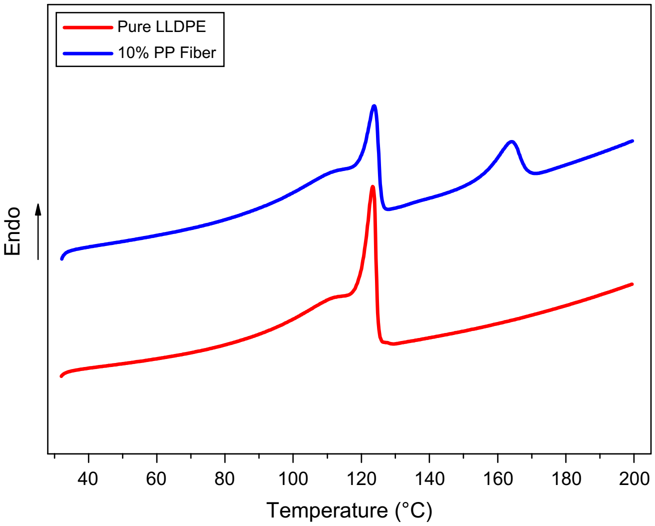

Fig. 2. DSC heating diagram of pure LLDPE and LLDPE/PP fiber blend prepared by extrusion.

3.2. Morphology and interphase structure

Macroscopically, contrasting to the static samples merely consisted of the skin and the core, the main feature of dynamic samples is the shear-induced morphologies with the core in the center, the oriented zone surrounding the core and the skin in the cross-section areas of the samples. The effect of prolonged shear on the orientation behavior of LLDPE/PP fiber blends has been illustrated through comparing 2D-WAXS patterns between static samples and dynamic samples, and only the core of static sample and the oriented zone of dynamic sample were investigated. For the static samples, as shown in Fig. 3(a) and (b), only isotropic circles of (110) plane ($2\theta = 21.6°$) and (200) plane ($2\theta = 23.6°$) of orthorhombic PE α-modification are observed even if the PP fiber has been incorporated, implying that there is no change in the orientation of LLDPE by merely adding PP fiber into LLDPE matrix. It should be noted that the reflections of PP crystal in Fig. 3 are very weak because of the quiet limited PP fiber content (~10 wt%). However, as shown in Fig. 3(c)–(e), two diffraction arcs of (110) plane are focused on the equatorial direction of 2D-WAXS patterns of dynamic samples including pure LLDPE and blends with 10% PP fiber. It means that the prolonged shear during DPIM has dramatically improved the orientation level of LLDPE matrix in both pure LLDPE and LLDPE/PP fiber blend. Meanwhile, such shear field can also induce a highly preferential orientation of PP fiber parallel to the shear flow direction along sample thickness up to the oriented zone, which is illustrated by the PLM image of Fig. 4. It is consistent well with the first supposition discussed above and explains why the dynamic samples have so higher mechanical properties than that of static samples. Although orientation of blends prepared at 160 °C is a little stronger than that of pure LLDPE and 180 °C sample, it is still difficult to explain the huge distinction of mechanical properties among them. The distinction may be interpreted by the second supposition namely interfacial coalescent effect, which can be reflected from the SEM image of Fig. 7(c) and the description about such morphology will be given.

As an overall review of PP fiber dispersion and orientation, the SEM fractured surfaces of the composites with low magnification were investigated. Three molding temperatures, 160 °C, 170 °C and 180 °C were used. For dynamic samples, through exerting 1.0 Hz repeatedly shear on the composites during melt solidification, the majority of fiber is aligned parallel to the flow direction along sample thickness up to the oriented zone. An isotropic morphology consisted with randomly oriented lamellae is observed in the core and the PP phase can’t be identified unambiguously from the basal PE phase, as shown in Fig. 5. On the other hand, instead of developing into spherulites, the lamellae form a highly ordered arrangement between the PP fibers at the skin and the oriented zone. They stacked together almost parallel to each other and are aligned approximately perpendicular to the shear

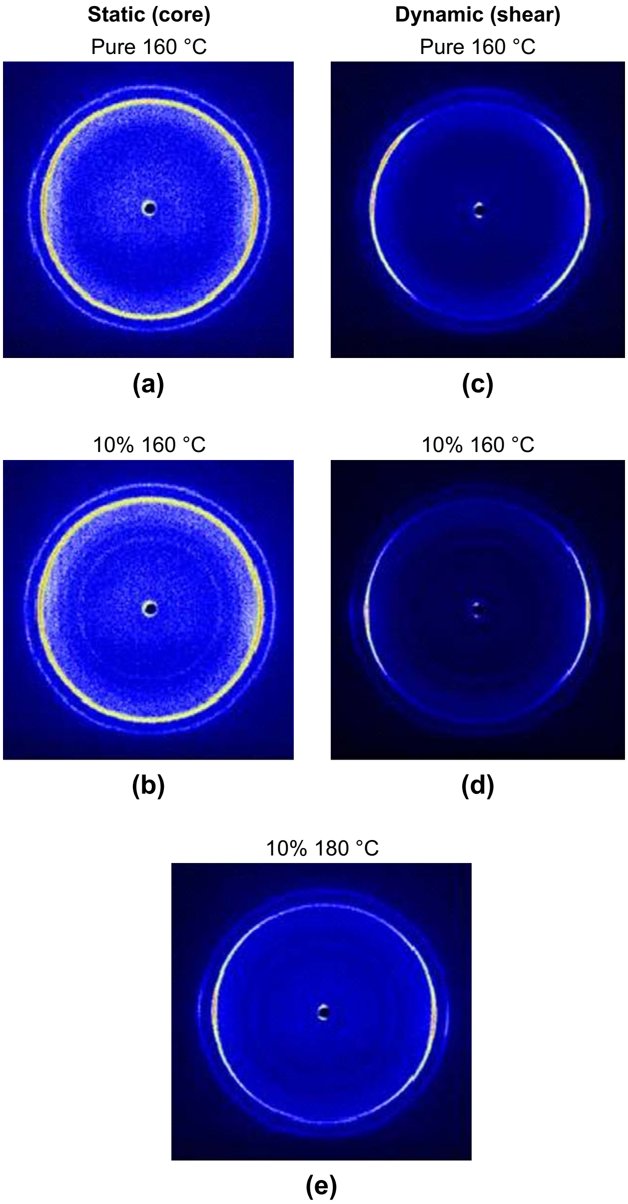

Fig. 3. WAXD patterns of the static samples (left) and the dynamic samples (right): (a) and (c) represent pure LLDPE, and (b), (d) and (e) contain 10% fiber. All the samples are prepared at 160 °C except (e) being prepared at 180 °C.

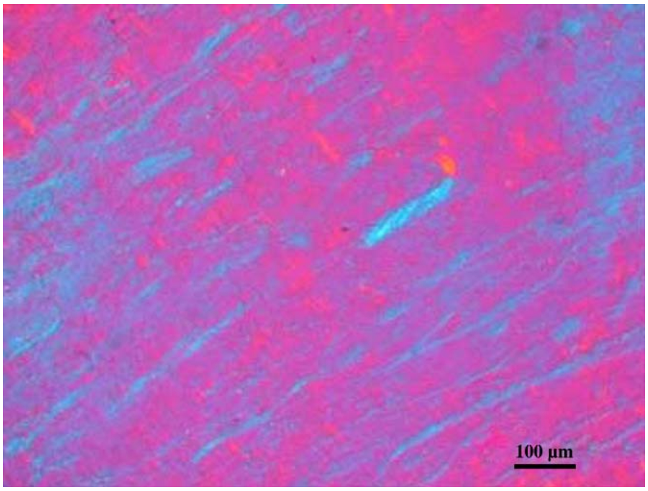

Fig. 4. PLM image of the oriented zone in the dynamic sample of blend containing 20% PP fiber (the sky-blue regions with high anisotropy represent PP fibers, whereas, the pink background is the LLDPE matrix) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

direction (also the fiber direction), forming a transcrystalline interphase. Towards the center, a spherulite-like superstructure is seen. Compared between Fig. 5(b) and (c), a obvious decrease of diameter of PP fiber is detected when the molding temperature is elevated from 160 °C to 170 °C. While a complete melting of PP fibers is seen as the molding temperature reaches to 180 °C, as shown in Fig. 5(d). In contrast, for static samples always a spherulite-like superstructure is seen along whole sample thickness, as shown in Fig. 6. Some oriented LLDPE lamellae and oriented PP fibers are expected at the skin even for static samples, due to the high shear rate at the nozzle. However, SEM result does not favor this phenomenon. Up to now, one argument is raised that is how to describe clearly the relationship of structure—property in the as-prepared LLDPE/PP fiber blends. There is a structural hierarchy in the injection-molded bars of dynamic samples, where a dramatic variety of orientation level and crystalline morphology along the thickness can be observed, whereas, the tensile properties represent the macroscopic behavior of whole bar. In both static sample and dynamic sample, the thickness of skin region is so thin that its effect on the macroscopic property could be neglected. For the static samples, the isotropic core region is dominant, which causes the limited improvement in tensile properties although the PP fiber was incorporated. But the mechanical properties of dynamic samples were determined by the anisotropic oriented zone [24]. The prolonged shear function has produced the thick oriented zone around the core and reduced the cross-section area of core region. We have roughly calculated the area percent of core region in the dynamic samples, which was only 4% [25]. So it can be expected that the effect of core region on the mechanical property is weak, while the strengthened tensile properties can be mainly ascribed to the formation of oriented zone. Another possibility that will affect the mechanical property is the heterogeneous dispersion of PP fiber along the thickness in the dynamic sample. The melt enthalpy of PP component in the various regions of dynamic samples containing 10 wt% PP has been calculated through DSC thermograms. The enthalpy values are 7.07, 7.22, and 7.86 J/g in the skin, oriented zone and core, respectively. One would note that the difference between these values is very small, thus the distribution of PP fiber along the whole thickness is uniform.

Since the effect of shear can be best demonstrated in the oriented zone, the crystal morphology and interface structure are highlighted at this zone and shown in Fig. 7. For pure LLDPE in Fig. 7(a), one observes intertwined lamellae constituting an interlocked lamellar assembly. Some twisted growth is also seen. For LLDPE containing PP fiber composites, an obvious transcrystallization of LLDPE lamellae on PP fibers is observed in Fig. 7(b). Although the acid treatment has

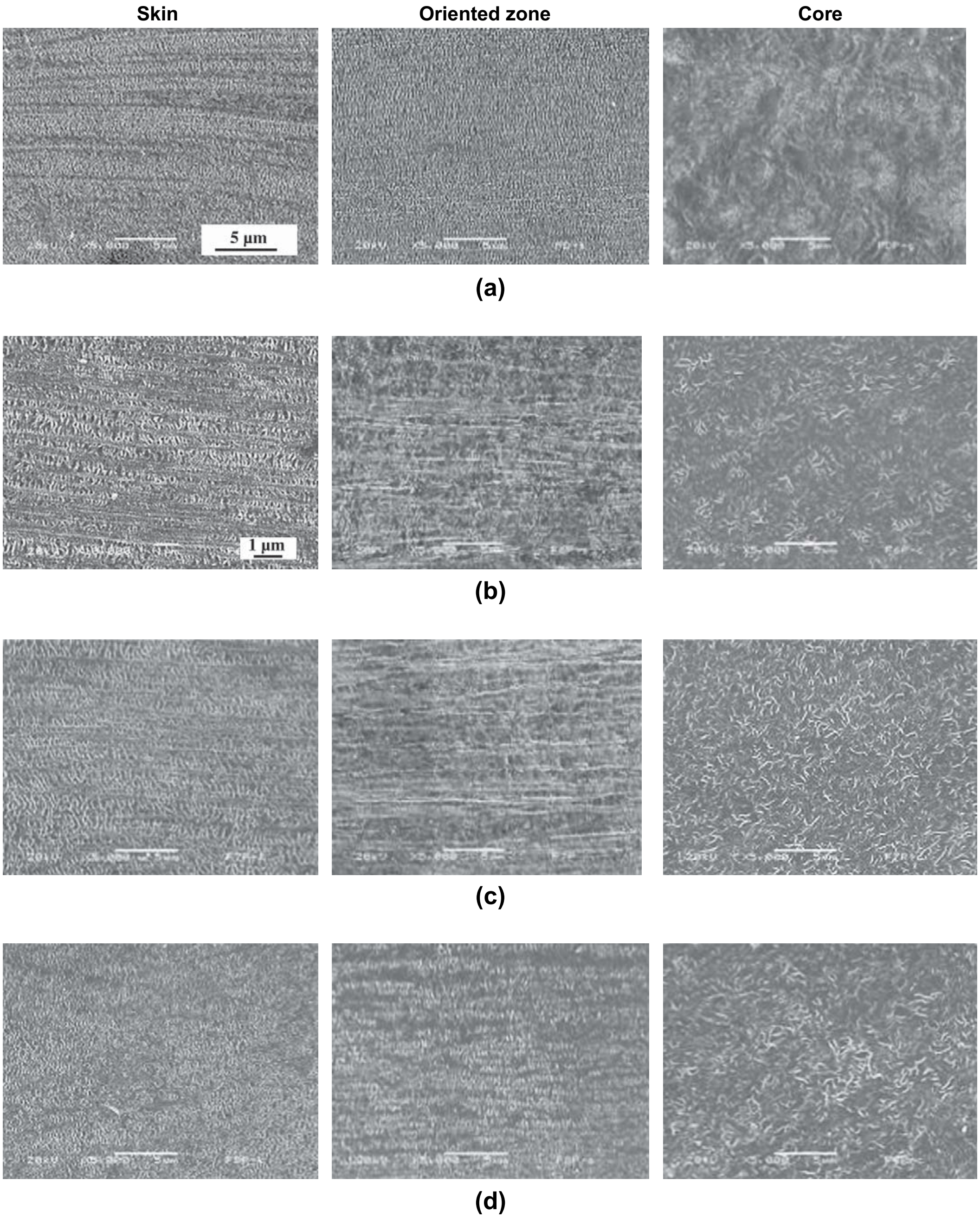

Fig. 5. Crystalline morphological development from the skin to the core in dynamic samples: (a) pure LLDPE at 160 °C, (b)–(d) are blends containing 10 wt% PP fiber at 160 °C, 170 °C and 180 °C, respectively.

etched the amorphous regions in both LLDPE and PP phases, one can still distinguish the crystalline structures of PE and PP in the SEM image (Fig. 7(b)). Inside the PP fiber, the alignment of PP lamella is compact and highly ordered because the fiber has experienced incomplete melting and the original structure could be adequately maintained. So the tightness of ribbon-like structures, indicated as signal A, could represent the PP fibers. Otherwise, in the domains between adjacent PP fibers, the alignment of lamella is loose and the regularity is low, which corresponded well to the crystalline morphology grew from molten LLDPE. These domains representing PE phase are indicated as signal B. This is a typical shish-kebab like structure with PP fiber forming the shish instead of PE and LLDPE lamellae forming the kebab. Between the PP fibers, parallel-stacked lamellae with smaller size are formed. As the molding temperature increases to 180 °C, a complete melting of PP fibers takes place. A striking change is observed at the interface between the fibers and matrix. Transcrystallization of LLDPE lamellae on PP fibers is observed anymore in Fig. 7(c). LLDPE lamellae extended from the matrix penetrate into the PP fibers. The boundary becomes rather diffuse. The change in the interfacial structure can be used to explain at least partially the change of tensile properties of the composites with increasing molding temperatures.

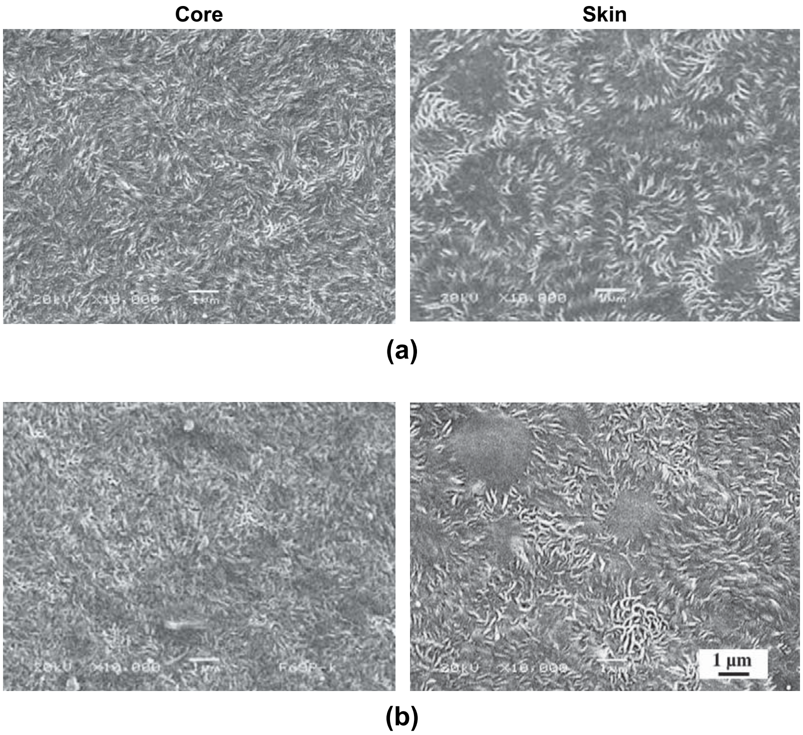

Fig. 6. Spherulitic morphologies observed in the whole static samples: (a) pure LLDPE (b) 10 wt% PP fiber. The injected molding temperature is 160 °C.

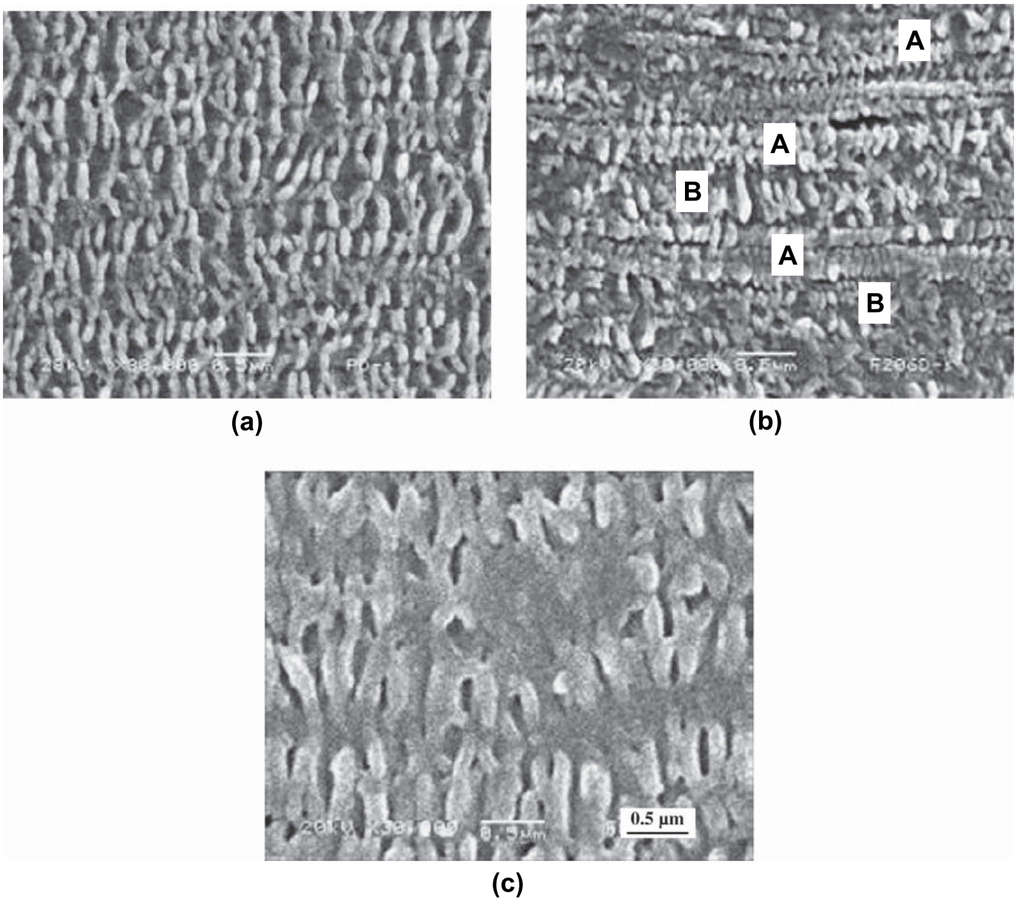

Fig. 7. SEM images with high magnification for highlighted the detail microstructures of oriented crystal in dynamic samples: (a) pure LLDPE molded at 160 °C; (b) blend contained 20 wt% PP fiber and molded at 160 °C; (c) blend contained 10 wt% PP fiber and molded at 180 °C. Meanwhile, **A** represents the microstructure of PP fiber and **B** indicates the PE domain in (b).

4. Conclusion

In summary, for dynamic samples, PP fibers are aligned parallel to the flow direction along sample thickness up to the oriented zone, in contrast to that obtained via conventional injection molding where a random orientation of fiber is observed along the whole sample thickness. The presence of oriented PP fibers could enhance the orientation of LLDPE, as caused by the transcrystallization of LLDPE lamellae on PP fibers under effect of shear. Molding temperature plays an important role to determine the crystal morphology and mechanical properties as well. As increasing the molding temperature from 160 °C to 200 °C, the partial melting of PP fiber is changed to complete melting, accordingly, the transcrystalline morphology changes to the interpenetration and diffused one, resulting in a dramatic decrease of the tensile strength and modulus.

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