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# Notes

## Suppression of Skin−Core Structure in Injection-Molded Polymer Parts by in Situ Incorporation of a Microfibrillar Network

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### Introduction

The achievement of high performance in polymers, especially commodity polymers, such as polyethylene (PE), polypropylene (PP), etc., is still an important open research subject.[1] The mechanical properties of polymers can be enhanced through orientation of polymer chains during processing, such as spinning, hot stretch, and especially newly developed shear controlled orientation in injection molding (SCORIM).[2,3] For semicrystalline polymers, shear flow at the mold filling stage during injection molding may induce high molecular orientation. In the extreme case, the oriented crystals can form an interlocked shish-kebab structure, which results in dramatic enhancement of mechanical properties in the flow direction of injection-molded parts.[4,5] However, the parts usually exhibit an inhomogeneous structure, namely a skin−core structure. During injection molding, the hot polymer melt contacting cold mold walls experiences high strain, high stress and large cooling rate, and thus a skin layer with high orientation is formed near the walls. This indeed is an intrinsic problem of normal injection molding because these boundary conditions create large gradients of temperature, shear rate and stress fields.

This heterogeneous structure is not favorable to the improvement of mechanical properties due to the residual stress produced by different levels of crystal orientation in the thickness direction. Moreover, the different levels of crystal orientation may cause a deterioration of macroscopic properties.[6] From a practical point of view, elimination of the skin−core structure is expected to improve mechanical properties. One approach to deal with the problem, as has been previously reported,[7] is the use of a nucleating agent that can effectively suppress the crystal orientation. The presence of nucleating agent can eliminate the skin−core structure even with high shearing imposed on the polymer flow. However, in this case, the crystal orientation is generally low.[7−9] This is not always desirable since some level of orientation in the injection molded parts is of great benefit to the improvement of mechanical properties.

In isotactic polypropylene/poly(ethylene terephthalate) (iPP/PET) blends, PET microfibrils with diameter of 1−10 $\mu$m can be produced through in situ hot-stretch, which constructs a microfibrillar network in the iPP matrix.[10,11] It is expected that the iPP melt would flow through the microchannels or pores formed by the network during injection molding of such blends. In addition to the effect of redefining the flow field, microfibril networks also promote the nucleation of matrix polymers. In the in situ microfibrillar blend of iPP/PET, three origins for crystal nucleation in shear flow field were identified: (a) the shear induced row nucleation; (b) classical fibril nuclei; (c) nuclei induced by fibril-assisted alignment.[11] One can therefore speculate that the in situ microfibrillar network can suppress the formation of the skin−core structure of the injection-molded parts since the network can: (1) help to homogenize the flow rate of the fluid across the thickness of the part, (2) act as an efficient nucleating agent to generate a typical transcrystalline layers with the *c*-axis deflected from the flow direction, and (3) assist shear flow to form nuclei.

In this Note, the objective is to study the effect of an in situ microfibrillar network on the crystal orientation distribution of injection molded parts. Analyses of orientational parameters of different positions within the injection molded parts show that the presence of the microfibrillar network suppresses the skin−core structure effectively. Injection molded parts with high and homogeneous orientation were obtained with a combination of SCORIM and microfibrillar network.

### Experimental Section

The materials used in this study were poly(ethylene terephthalate) (PET) and isotactic polypropylene (iPP). The PET as the microfibrillar candidate was a commercial grade of textile polyester and was supplied in pellets by LuoYang Petroleum Chemical Co. (China) with $\bar{M}_n$ of about $2.3 \times 10^4$ g/mol. The iPP used as the matrix was F401, a commercial product of Lanzhou Petroleum Chemical Co. (China) with $\bar{M}_n$ of about $11.0 \times 10^4$ g/mol, and its melt flow index (MFI) was 2.5 g/10 min (190 °C, 21.6 N). To avoid hydrolysis, the PET was dried in a vacuum oven at 100 °C for at least 12 h prior to processing.

Preparation of in situ microfibrils had been reported in detail elsewhere.[11,12] The microfibrillar iPP/PET blend in this work consists of 15 wt % PET microfibrils of 1−10 $\mu$m in diameter, and iPP as the matrix. The representative structure of the PET microfibrils is shown in Figure 1, where the matrix iPP was etched away for clear observation. The neat iPP has also undergone the same processing for comparison purposes. The blend and neat iPP were injected into a mold using SZ 100 g injection molding machine at 200 °C and about 90 MPa. Then, SCORIM technology invented

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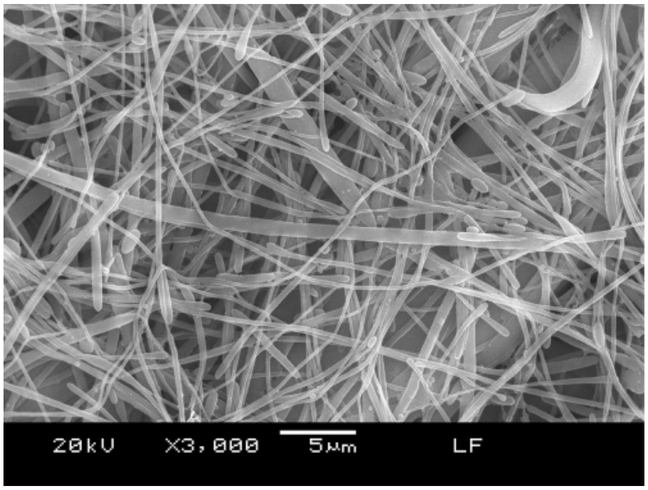

**Figure 1.** Representative SEM photograph of PET/iPP in situ microfibrillar blend

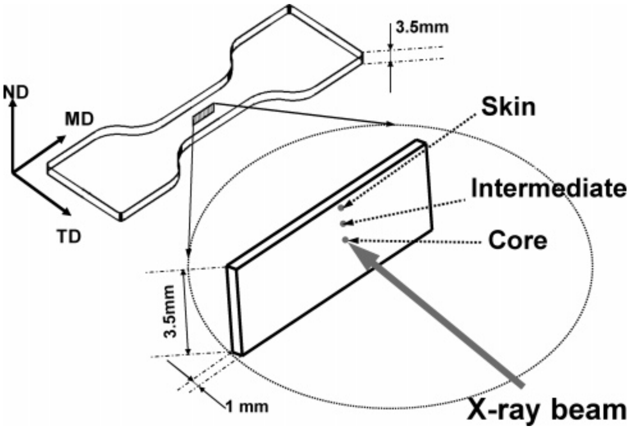

**Figure 2.** Schematic of the positions of the samples for WAXS measurement. Key: MD, the molding direction (i.e., flow direction); TD, the transverse direction; ND, the direction normal to the MD-TD plane.

by Bevis was applied with a frequency of 0.3 Hz and a pressure of 5 MPa.[2] The detailed introduction of this technology had been described elsewhere,[13] whose primary feature is that the hot melt was subjected to high shear stress in a chamber before frozen, which was given by two pistons moved reversibly with the same frequency.[2,13] The injection molding was also carried out under static packing (no vibration) under the same processing temperatures. The tensile tests were performed at room temperature using the dog-bone specimens with a crosshead speed of 50 mm/min, and their geometry was given in ref 13.

The orientation distributions in the thickness direction were characterized by the two-dimension small and wide-angle X-ray scattering (2D-SAXS or 2D-WAXS). The X-ray samples were machined from the 6 mm wide and 3.5 mm thick tensile bar to a 1 mm wide piece (the 3.5 mm thickness remains unchanged) as shown in Figure 2. The sample obtained is the middle section of the tensile bar. The direction normal to MD-TD (the molding direction-transverse direction) plane was defined as ND. The X-ray beam was perpendicular to MD-ND plane (along TD direction), and scanned three locations: skin, intermediate and core layers. The skin and intermediate layers are about 100 and 700 $\mu$m down from MD-TD surface, respectively. The core layer is in the center of the sample (about 1700 $\mu$m down from the MD-TD surface). 2D-WAXS measurements were performed on a Bruker-Nonius D8 Discovery diffractometer with a Cu X-ray generator operating at 40 kV and 40 mA and equipped with a 2D gas filled multiwire detector. The 2D-SAXS measurements were carried out on a home-built SAXS setup with 18 Kw Rigaku rotating anode and 2D gas filled detector.[14] All measurements were done in transmission geometry and the incident X-ray beam was set perpendicular to the flow direction.

The orientations of the crystals of iPP and PET were calculated using the Hermans orientation parameter, which is defined as

$$\langle P_2(\cos\phi)\rangle = (3\,\langle\cos^2\phi\rangle - 1)/2 \tag{1}$$

where $\langle \cos 2\Phi\rangle$ is an orientation factor defined as

$$\langle\cos^2\phi\rangle = \int_0^{\pi/2} I(\phi)\cos^2\phi \sin\phi\, d\phi \Big/ \int_0^{\pi/2} I(\phi)\sin\phi\, d\phi \tag{2}$$

where $I(\Phi)$ is the scattering intensity at $\Phi$. The orientation parameter has a value of unity when all the crystals are oriented with their c axes parallel to the reference direction (i.e., the flow direction), a value of $-0.5$ when all the c axes are perpendicular to the reference direction, and a value of 0 with totally random orientation. For our samples, the orientation parameter was calculated mathematically using Picken's method from both the first scattering peak of SAXS and the (040) reflection of WAXS for iPP.[15]

## Results

Parts a−d of Figure 3 show the 2D-WAXS patterns of the four samples at different distances from their skin. There exist some obvious reflections in all patterns, which can be indexed as the (110) at $2\theta = 14.1°$, (040) at 16.9°, (130) at 18.5°, and (111) and (131) at about 21.8° of α monoclinic form of iPP.[16] Parts a′−d′ of Figure 3 show the (040) intensity distribution along the azimuthal angle between 0 and 360°. Using eqs 1 and 2, the orientation parameters at different distances can be calculated from the (040) intensity distribution along the azimuthal angle, which are presented in Figure 3e. For the neat iPP sample, the typical skin−core structure in the direction of thickness exists in the conventional injection molded sample. The orientation parameter P2 is around 0.74 in the skin layer and around zero in the core region. For the microfibrillar PET/iPP blend, the hierarchy structure in the thickness direction does not appear. The difference of orientation parameters between the skin layer and core region is about 0.1, which is much smaller than the difference for the neat sample (0.7). Though the in situ PET microfibrillar network can homogenize the orientation along the thickness direction of the injection part, the overall orientation is relatively low.

To enhance the orientation of iPP crystals, the shear controlled orientation injection molding (SCORIM) is employed for both neat iPP and blend. Following the same analysis, the orientation parameters were extracted and are plotted in Figure 3e. For both neat iPP samples and PET/iPP microfibrillar blend samples, the degree of crystal orientation for the three layers have been enhanced due to the high dynamic shear force imposed on iPP melt during the injection molding. However, it cannot completely eliminate the hierarchical structure of neat iPP samples, though the difference of crystal orientation (ca. 0.3) between skin (ca. 0.96) and core (ca. 0.65) is less than conventional injection molding (ca. 0.7). In the microfibrillar blend parts, the orientation parameters at different distances from the skin are identically high. The negligible difference of orientation parameters (i.e., 0.02) between skin (ca. 0.86) and core (0.88) regions indicates the successful creation of an injection molded part with homogeneously high orientation. This homogenization of orientation does give better mechanical properties. The increment of tensile strength of iPP/PET blend is 34% from 37 MPa of conventional injection molded samples to 49 MPa of oscillation injection molded ones, which is higher than that of neat samples (27%), from 42 to 53 MPa. Evidently, articles of

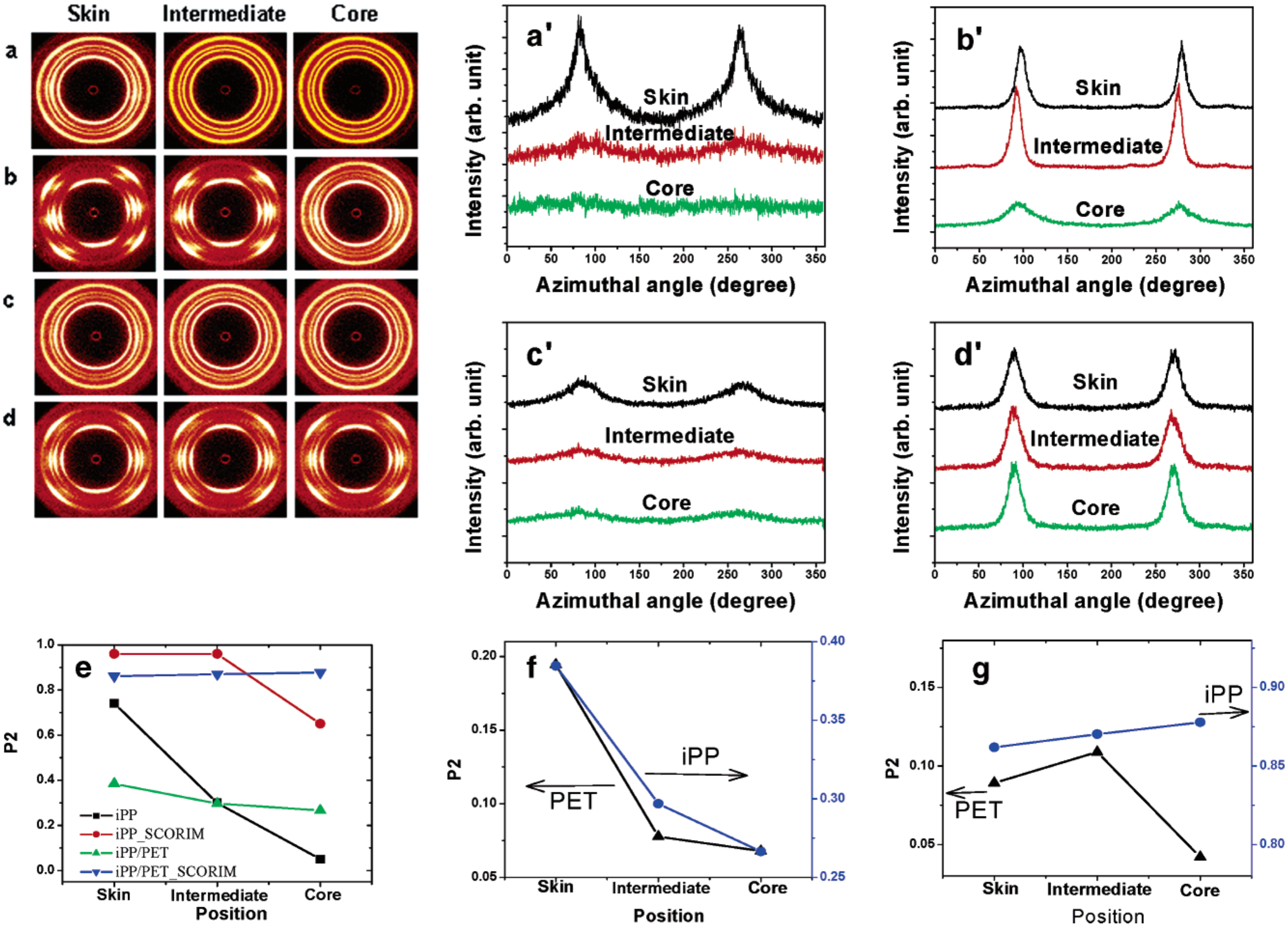

**Figure 3.** 2D-WAXS patterns (a−d) and intensity distribution of α (040) along azimuthal angle (a′-d′) as well as the orientational parameters P2 of moldings: (a and a′) the conventional injection molded sample of neat iPP; (b and b′) the oscillation injection molded sample of neat iPP; (c and c′) the conventional injection molded sample of micrifibrillar blend; (d and d′) the oscillation injection molded sample of microfibrillar blend; (e) the orientational parameters P2 of neat iPP and its in situ blends prepared through normal and shear controlled orientation injection molding at room temperature; (f) the P2 of iPP and PET in the normal injection molded in situ blend; (g) the P2 of iPP and PET in the shear controlled orientation injection molded in situ blend.

in situ microfibrillar blend with both high homogeneous orientation and high strength can be achieved in combination with SCORIM technology.

To understand the function of PET fibers, the orientation of microfibrils was checked with SAXS at 180 °C. At this temperature, iPP crystals were melted (confirmed with simultaneous WAXS measurements) and only PET crystals contributed to the scattering peak. The orientation parameters are plotted in Figure 3f and 3g for normal and oscillation injection molded parts, respectively. Ideally the lamella in the PET fibrils should completely follow the same direction as fiber axis. In this case the orientation of lamella is equivalent to the orientation of fibers. However, in practical cases, only a certain percentage of lamella follows exactly the fiber axis. A prefactor has to be multiplied on the orientation parameter of lamella to obtain the orientation of the microfibrils. Fortunately, the prefactor should be a constant for PET microfibrils prepared at the same condition. Thus, from the surface to the core of the injection parts, the trend of the orientation parameter of lamella and microfibrils is the same, which can be used without distinction. For comparison, the orientation parameters of iPP from the same samples are also presented in the same figures. In the normal injection molded part, a good correlation between the orientation of iPP and PET is found, while no correlation exists between the fibers and matrix in the shear controlled orientation injection molded one.

## Discussion

The above analysis of the orientation parameters of iPP/PET blends reveals that injection parts with high and homogeneous orientation in the thickness direction can be obtained through shear controlled orientation injection molding. However, the underlying mechanism is not so obvious. Injection molding of semicrystalline polymer essentially is a flow-induced nonisothermal crystallization process. Generally, a flow field can increase the crystallization rate and induce preferred orientation of crystals due to the formation of row nuclei or shish.[17−19] Under the nonisothermal condition, the enhancement of crystallization rate is reflected by an increase of the onset of crystallization temperature. The orientation of crystals is determined by the shear rate, shear stress and cooling rate. It is well-established that the orientation of polymer molecules is a result of the competition between shear-induced orientation and chain stretching and subsequent relaxations, which are defined by reptation time and Rouse time.[20] A higher shear rate and/or higher stress lead to a higher orientation of molecular chains, while a faster cooling rate slows down the relaxation or even freezes the orientation by the kick-in of crystallization. Bearing these general rules in mind, let us first look at the normal injection molding. When neat iPP melt was injected into mold, the skin layer was immediately cooled by cold mold wall, leading to a high shear stress. A combination of the high shear stress and low temperature generated a high orientation of crystals at skin layer (see Figure 3e). Because of temperature gradient from skin to core, a delay of crystallization is expected in the regions away from skin, which gives the different time windows for molecules to relax. This can explain the nearly linear decrease of orientation parameter from skin to core.

With the same injection pressure as for neat iPP, the iPP melt including PET microfibrils has a lower flow rate to fill the mold due to higher viscosity. Thus, a lower shear rate is imposed at the skin layer, which brings down the orientation parameter (see Figure 3e). In the core region, the situation is opposite. On one hand, the iPP matrix melt pushes PET microfibrils into the mold, which leads to some degree of preferred orientation of PET microfibrils (Figure 3f). The preferred orientation of PET microfibrils indicates a relative movement (different velocity $\vec{V}$) and stress between melt and solid microfibrils. Thus, the PET microfibril network plays effectively as a solid wall and redistributes the flow field. The network splits the space of iPP melt movement, and hence iPP molecules experience confined flow in the microchannels or pores in the microfibrillar networks. This is schematically shown in Figure 4. Compared to neat iPP melt, the local shear stress in the core region of iPP/PET blend is higher, which leads to higher orientation of molecular chains. On the other hand, PET microfibrils serve as nucleation agent and nucleation enhancer under flow condition, which increase both the onset temperature and crystallization rate of iPP. For example, at around 120 °C, the PET/iPP microfibrillar blend has almost finished crystallization, whereas the neat iPP is just in the onset during nonisothermal crystallization with a cooling rate of 10 °C/min, and the onset temperature and crystallization increased further under a step shear condition due to shear-induced crystallization.[21] The decrease of crystallization time is in favor of the retention of orientated segments. The above two mechanisms are supported by the correlation between the orientation parameters of PET and iPP, namely higher orientation of iPP corresponds to higher one of PET and vice versa (see Figure 3f). The redistribution of flow field and the nucleation effect from the PET microfibrillar network leads to a higher orientation for iPP/PET blend in the core region, and consequently reduces the difference of orientation parameter between skin and core.

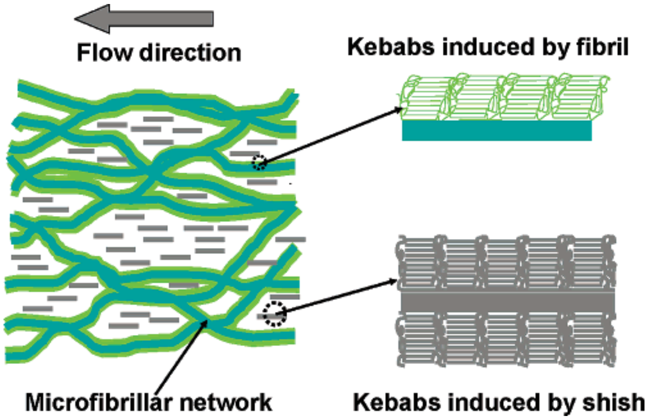

**Figure 4.** Schematic of kebabs induced both by shish and by microfibrillar network in injection molded parts.

The same mechanisms also happen during shear controlled orientation injection molding. During injection molding, the iPP melt suffers the shear force continuously until it finishes crystallization and solidification, which results in an increase of orientation parameters of iPP crystals in all regions. With the promotion from dynamic oscillation shear, the orientation parameters in the intermediate layer and core region of neat iPP experience a large increase, while a small increase occurs in the skin layer, which may be due to a high orientation parameter even at normal injection condition (Figure 3e). Nevertheless, even with the promotion from the dynamic oscillation shear, the orientation parameter in the core region is still lower than that at skin and intermediate layers, and a heterogeneous structure still exists.

The situation during shear controlled orientation injection-molding of in situ microfibrillar blend is much more complicated than that in pure iPP melt. There is no correlation between the orientation parameters of the matrix and the fibrils (see Figure

3g). Here not only does iPP melt experience a continuous oscillation flow during cooling, but also the PET microfibrilar network changes its configuration continuously. The overall orientation of PET microfibrils in the shear controlled orientation injection molded part is significantly lower than that in the normal injection molded one (about 41%) (Figure 3f and 3g). As the shear controlled orientation injection molding undergoes exactly the same first step as the normal injection molding, PET fibrils should also have the same orientation at the beginning of both cases. The decrease of orientation parameter by subsequent oscillation flow suggests that PET microfibrils do not experience a simple stretch movement, which would normally enhance the orientation. In fact, this decrease of orientation during continuous shear flow can be explained by a tumbling movement. During shear controlled orientation oscillation injection molding, PET transfers the stress not only back forth but also up and down, which effectively homogenizes the shear rates in the thickness direction.

Though there is no strong correlation between the orientation parameters of iPP and PET, the nucleation effect still exists as in the case of normal injection molding as well as in the quiescent condition. iPP melt suffers a shear force in the vicinity of PET microfibrils due to the relative flow rate of two components, which induces alignment of iPP molecules along the fibril axes and favors of the formation of a transcrystalline structure. The schematic illustration of crystalline morphologies of matrix in microfibrillar blend under a shear flow field is given in Figure 4. The shear amplification effect has been reported in a nanocomposite system of nylon-6, the nanoplatelets inducing high levels of orientation of the polymer matrix throughout the thickness of the molded part even at high mold temperatures.[22] In our case, the orientation of the network along the flow direction is not as easy as that of nanoplatelets due to the entanglement of microfibrils, therefore, the relative motion direction between the two phase will be not the same as the flow direction. This effect in local region may contribute to a little decrease of the average orientation parameter as shown in the skin region of injection molded microfibrillar parts.

## Conclusions

The presence of a three-dimension microfibrillar network in iPP melt during injection molding leads to polymer parts with a homogeneous orientation distribution across the thickness direction. This is attributed by the redefined flow field and nucleation effect of fibers. The analysis of the orientation of iPP crystals and PET fibers indicates the PET microfibrils acts as a stirring agent which transfers the stress not only back and forth but also up and down within the flow field. Consequently the gradient of shear stress is homogenized in the thickness direction. On the other hand, the nucleation effect of the microfibrils accelerates the crystallization process, which freezes more orientation induced by shear. The results demonstrate that polymer parts with a high and homogeneous orientation can be achieved with a combination of in situ microfibrils and dynamic oscillation shear.

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