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Suppressing the skin-core structure in injection-molded HDPE parts via the combination of pre-shear and UHMWPE

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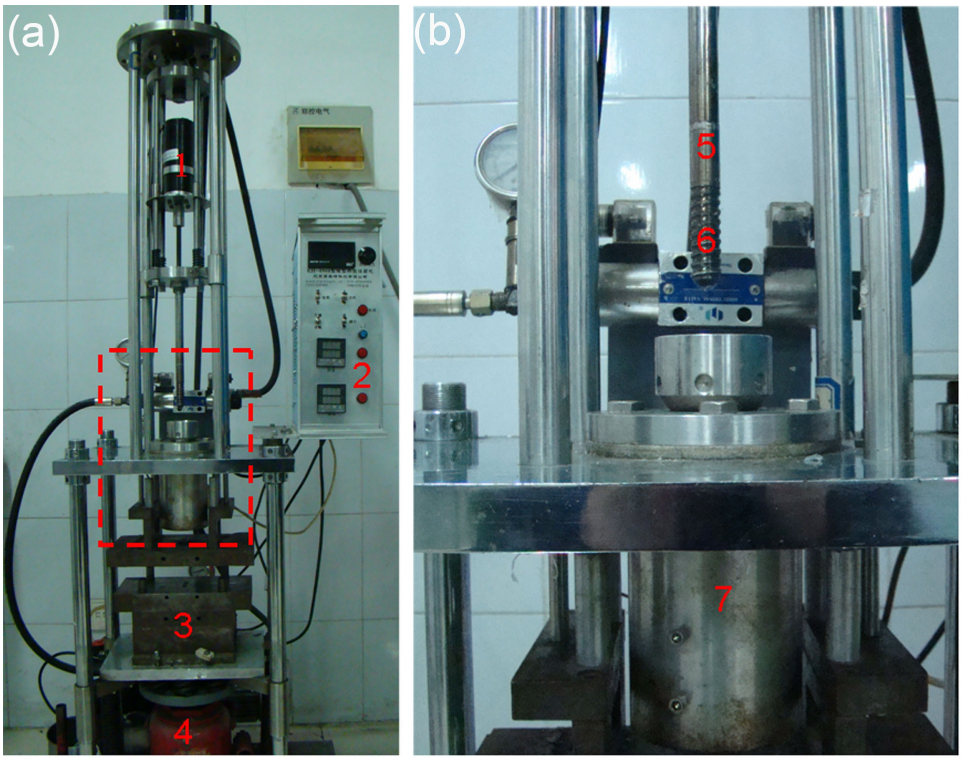

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Fig. S1. The photographs of mixing-Injection molding machine. The numbers represent: 1-electromotor; 2-control box; 3-mold; 4-pump; 5-plunger piston; 6-screw; 7-barrel.

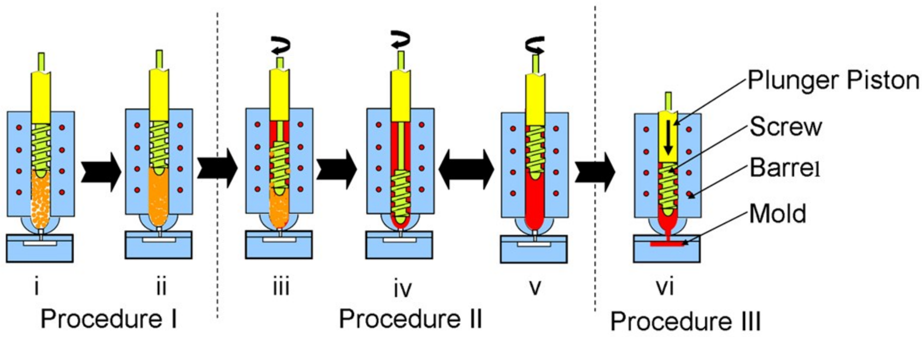

Fig. S2. The schematic representation of mixing-injection molding process.

The feature of this machine is that the screw can not only rotate circumferentially but also simultaneously move down and up repeatedly. During this process, pre-shear can be introduced to the HDPE melt by the rotating screw. More importantly, the pre-sheared melt can be immediately injected into the mold once the plasticizing process was finished. There was hardly any delay time between the mixing process and injection process. That is to say, the oriented precursors induced by pre-shear do not have enough time to relax in the duration between the plasticizing process and the melt injection process. In this case, the pr-shear-induced precursors could be in-situ injected into the mold cavity and considerably influence the subsequent crystallization which has been confirmed in our previous studies[1-3].

The overlap concentration of UHMWPE was estimated based on the equation

$$c^* = 3M_w / (4\pi\left[\left\langle R_g^2 \right\rangle^{1/2}\right]^3 N_a) \qquad (1)$$

where $\langle R_g^2 \rangle^{1/2}$ is the root-mean-square radius of gyration and N_a is Avogadro's number[4, 5]. The characteristic ratio of $\langle R_g^2 \rangle^{1/2} / M_w$ for PE was 0.46, based on SANS measurements[6]. In our case, M_w=3.0×10[6] g/mol, so the calculated $c*$ is 0.3 wt%.

Pre-shear is imposed to the melt during the mixing-plasticization process. The shear rate $\dot{\gamma}$ applied to the melt in the barrel brought by the rotating screw can be roughly calculated according to the following simplified equation[7]:

$$\dot{\gamma} = \pi \mathrm{Dn} / \mathrm{H}$$

where D and H are the diameter and groove depth of the screw, respectively. n is the screw speed. In our case, $n = 20$ rpm, $D = 16$ mm and $H = 1$ mm, so the calculated shear rate $\dot{\gamma}$ is 16.75 s^{-1}.

The preparation of samples for SEM observation and 2D-WAXD/SAXS measurements is shown in Fig. S3. It should be noted that, for both SEM observation and 2D-WAXD/SAXS measurements, shear region and core region are about 200 μm and 1200 μm down from skin surface, respectively.

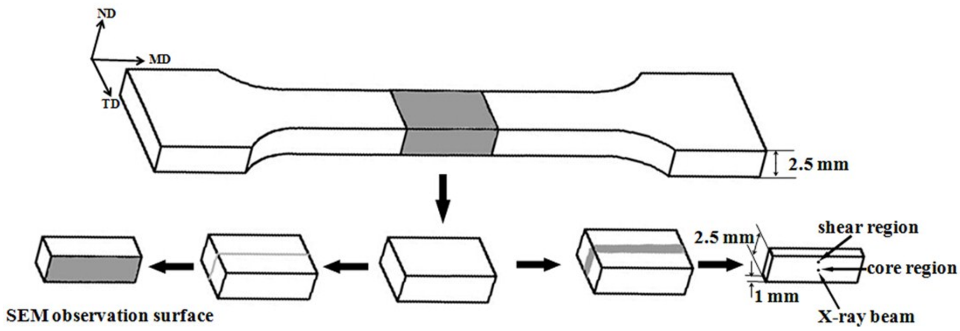

Fig. S3. The schematic representation for SEM observation and 2D-WAXD/SAXS measurements of injection-molded parts. MD is short for "Melt flow direction", TD for "Transverse direction" and ND is the normal direction of the "MD-TD" plane.

In this study, before define the different regions, the conventional injection-molded sample of PE-S0 was characterized layer by layer by 2D-WAXD measurement. 2D-WAXD patterns of shear region and core region for PE-S0 are presented in Figure S4. As can be seen, sharp diffraction focused arcs can be found in the regions from 100 μm to 300 μm, (see Fig. S4), which is the signal of molecular orientation; while isotropic circles are observed in regions from 600 μm to 1200 μm, indicating a random orientation of molecular chain. To quantitatively evaluate the orientation level of injection-molded blend sample, the (110) intensity distribution along the azimuthal angle from 0 to 360^{o} is presented in Fig. S5, and accordingly the orientation parameters are calculated. As can be seen, very high orientation level exists in regions from 100 μm to 300 μm, which can be considered as the shear region. Therefore, the region at the depth of 200 μm, which has the highest molecular orientation level, is defined as shear region in this study. Generally, core region is usually defined as the center of parts. In this study, the thickness of the sample is about 2500 μm, thus core region is at the depth of about 1200 μm to the skin surface.

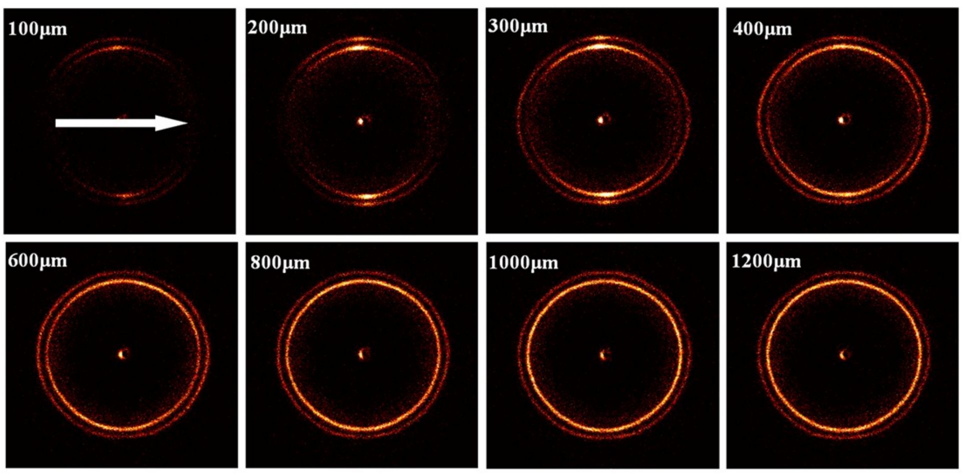

Fig. S4 Selected 2D-WAXD patterns of PE-S0 at different depth. The numbers located at upper left represent for the depth to the skin surface. The arrow represents the melt filling direction.

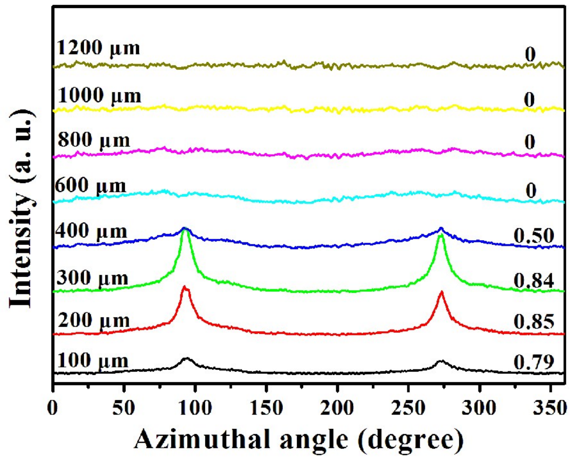

Fig. S5 Intensity distribution of (110) lattice plane of 2D-WAXD. The numbers located at left side represent for the depth away from the surface. The numbers located at right side represent the orientation parameter.

In order to better demonstrate the synergetic effect of UHMWPE and pre-shear on the suppression of skin-core structure of PE-D5. Blend sample containing 5 wt% UHMWPE (PE-S5) was also prepared without pre-shear. Two-dimensional wide-angle X-ray diffraction (2D-WAXD), a typical characterization method to investigate the orientation parameters of different regions and further evaluate the skin-core structure, was performed on PE-S5. 2D-WAXD patterns of shear region and core region for PE-S5 are presented in Figure S6. As can be seen, sharp diffraction focused arcs can be found in shear region (see Fig. S6a), while clear diffraction focused arcs cannot be observed in core region (see Fig. S6b). This result indicates a distinct difference in orientation parameters between shear region and core region. To quantitatively evaluate the orientation parameter of injection-molded blended sample, the (110) intensity distribution along the azimuthal angle from 0 to 360^{o} is presented in Fig. S7, and accordingly the orientation parameters were also calculated. The orientation parameters of shear region and core region are 0.96 (f_{shear}) and 0.14 (f_{core}), respectively. Hence, there is a large Δf (the difference of orientation parameters between shear region and core region, which can be calculated by the equation: $\Delta f = f_{shear} - f_{core}$), i.e., 0.82.

Moreover, with respect to PE-S0, the orientation parameters of shear region and core region are 0.85 (f_{shear}) and 0 (f_{core}), respectively, leading to a large Δf, i.e., 0.85 (see Table 1). Clearly, in the absence of pre-shear, UHMWPE has a weak effect on enhancing the orientation level of core region. That is, UHMWPE has no effect on the suppression of skin-core structure in the absence of pre-shear. In light of this, a conclusion can be safely concluded: it is the synergetic contribution of pre-shear and UHMWPE that substantially suppresses the skin-core structure of injection-molded part rather than the sole contribution of UHMWPE.

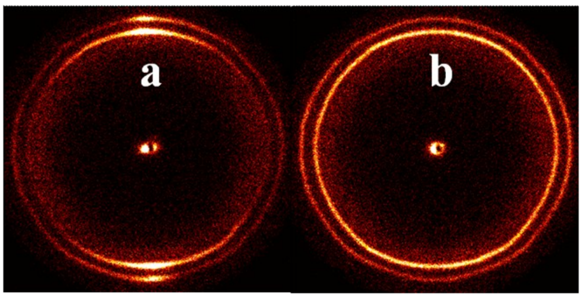

Fig. S6 2D-WAXD patterns of shear region (a) and core region (b) for PE-S5. The arrow represents the melt filling direction.

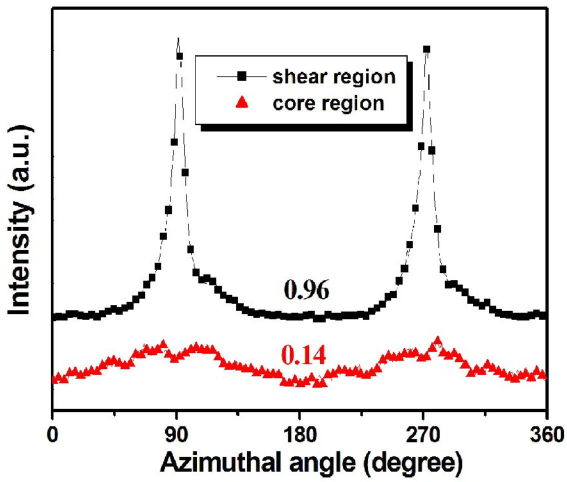

Fig. S7 Intensity distribution of (110) crystal plane of 2D-WAXD along the azimuthal angle from 0 to 360° for PE-S5.

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