

Synergic Enhancement of High-density Polyethylene through Ultrahigh Molecular Weight Polyethylene and Multi-flow Vibration Injection Molding: A Facile Fabrication with Potential Industrial Prospects

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Abstract General-purpose plastics with high strength and toughness have been in great demand for structural engineering applications. To achieve the reinforcement and broaden the application scope of high-density polyethylene (HDPE), multi-flow vibration injection molding (MFVIM) and ultrahigh molecular weight polyethylene (UHMWPE) are synergistically employed in this work. Herein, the MFVIM has better shear layer control ability and higher fabrication advantage for complex parts than other analogous novel injection molding technologies reported. The reinforcing effect of various filling times and UHMWPE contents as well as the corresponding microstructure evolution are investigated. When 5 wt% UHMWPE is added, MFVIM process with six flow times thickens the shear layer to the whole thickness. The tensile strength and modulus increase to 2.14 and 1.39 times, respectively, compared to neat HDPE on the premise of remaining 70% impact strength. Structural characterizations indicate that the enhancement is attributed to the improvement of shish-kebab content and lamellae compactness, as well as related to the corresponding size distributions of undissolved UHMWPE particles. This novel injection molding technology with great industrial prospects provides a facile and effective strategy to broaden the engineering applications of HDPE materials. Besides, excessive UHMWPE may impair the synergistic enhancement effect, which is also reasonably explained.

Keywords Self-reinforced composites; Self-reinforced structure; Shear layer thickness; Mechanical property

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INTRODUCTION

As one of the most general-purpose plastics, high-density polyethylene (HDPE) has been a crucial component in packaging, transportation, building and electrical industries due to its outstanding properties such as low toxicity, excellent chemical durability, excellent electrical insulation and relatively low cost.^[1–4] However, despite its good toughness, conventional injection molded HDPE products cannot meet the requirements of some technical and engineering applications because of some other poor mechanical performances such as strength and modulus of HDPE.^[5] Therefore, effective reinforcement strategy is of great significance for broadening the industrial applications of HDPE products. Chemical modification and physical blending are the most common ways to improve polymer performance. For chemical modification of HDPE, the PE100 with bimodal molecular weight distributions is a typical case for pipe fabrication.^[6] In addition, cross-linked polyethylene

and ultrahigh molecular weight polyethylene (UHMWPE) with high wear resistance and good biocompatibility are also developed for the manufacture of bearings and artificial joints.^[7] Even so, it has been greatly challenged at present to further develop PE materials with higher mechanical properties through molecular design and polymerization technology optimization.^[6,8] In recent decades, the strengthening strategy through physical blending is still fascinating for people due to its simple, economical and efficient industrial value. Especially for HDPE, the UHMWPE/HDPE composites with excellent compatibility and self-reinforcement performance have been widely studied.^[9–12]

Since polymer crystallization is a kinetic event, controlling micro morphology is another effective way to strengthen the products.^[6,13] As accepted, highly oriented structure (such as shish-kebab), resulting from strong flow, is a self-reinforced structure.^[14–18] There have been a number of unusual injection molding techniques reported to improve the shish-kebab content by applying strong shear flows during the packing stage. Among them, shear-controlled orientation and oscillating shear forming technologies have proven their valid-

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ity for developing UHMWPE/HDPE self-reinforced composites with high performance.^[19–22] However, these reports only stay at a fundamental study level, because the action direction of the additional oscillating shear field determines that it can only be used on plate or dumbbell parts.

Our research group focuses on investigating novel injection molding technologies with more industrial application prospects. So far, a technique named multi-flow vibration injection molding (MFVIM) has been developed, of which the details have been reported.^[23,24] In the mold with a flash groove, the oscillatory pressure is applied during the packing stage to form the subsequent flows after the cavity is filled at the injection stage. As shown in Fig. 1, each additional flow will bring new high shear regions. Meanwhile, a part of the melt will be pushed out through the flash groove. It is worth noting that MFVIM has obvious technical advantages compared with the technologies mentioned above. First of all, the thickness and position of the shear layer can be controlled by adjusting the multi-flow times and interval time. Mi^[23] studied the relationship between shear layer thickness and mechanical properties of isotactic polypropylene (iPP) by changing the MFVIM parameters, reporting that both tensile strength and impact strength increase exponentially with shish-kebab content. Hou^[24] endowed iPP specimen with shear layer-spherulite layer alternated structure, which can significantly improve the impact strength, due to the larger plastic deformation caused by crack deflection during failure. Based on it, Liu^[25] and Gu^[26,27] studied the synergistic toughening effect of thermal annealing process and epitaxy crystalline structure on the multilayer alternated structure, respectively. These studies indicate that MFVIM can quantitatively control the content and distribution of self-reinforced structures in polymers including HDPE, which has not been reported in other studies. Besides, the molding cycle of MFVIM contains only tens of seconds, matching that of the conventional injection molding (CIM). Most importantly, among these analogous injection molding technologies for reinforcing fabrication, MFVIM is the only technique that has proven its applicability for complex parts by enhancing the self-reinforcing cup samples.^[28] Therefore, the HDPE enhancement strategy

through the combined employment of MFVIM and UHMWPE has high expectations and great potential value for industrial applications.

In the current work, we used the combination strategy of MFVIM and UHMWPE to reinforce the HDPE samples. Filling times and UHMWPE content were regarded as variable quantities, and the reinforcing effect of various combinations and the corresponding microstructure evolution in the samples were investigated. Mechanical tests indicated that specimens with 100% shear layer content prepared with specific UHMWPE levels and MFVIM parameters achieve excellent tensile properties while maintaining good impact toughness. By characterizing the structure using rheological characterization, differential scanning calorimetry (DSC), polarized light microscopy (PLM), wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS) and scanning electron microscopy (SEM), the reinforcing mechanism is discussed accordingly.

EXPERIMENTAL

Materials

The HDPE used in this study (PE100, trade name 4902T, density = 0.95 g/cm³, melt flow rate = 0.225 g/10min under the pressure of 2.15 kg at 190 °C) was commercially available from Yangzi Petrochemical Company Limited (China). UHMWPE powders (model M-II) were purchased from Beijing No. 2 Auxiliary Agent Factory and featured the following characteristics: 90% of them are smaller than 278.9 μm with a median powder size of 186.7 μm; The density is 0.964 g/cm³; $M_w=2.5 \times 10^6$ g/cm³.

Sample Preparation

HDPE and UHMWPE were melt-mixed together through CTE20 co-rotating twin-screw extruder with the barrel temperature of 160–200 °C. Composite granules containing 1 wt%, 5 wt%, 10 wt%, 20 wt% and 30 wt% UHMWPE were prepared. Then the dried pellets were molded through CIM and MFVIM, respectively. The mold temperature was fixed at 50 °C, and the barrel temperature was 160–200 °C from the hopper to the nozzle. The flow times were adjusted to control the thickness of shear layer and spherulite layer based on Mi's work.^[23] The CIM process provided only one melt flow. While the injection processes with two flows and six flows were performed for MFVIM.

For simplicity, the composite pellets are named as xU/H, where x represents the UHMWPE content (wt%). CIM specimens of neat HDPE and UHMWPE/HDPE composites are designated as N-CIM and xU/H-CIM, respectively. MFVIM specimens of neat HDPE are noted as N-VIM1 and N-VIM2, in which VIM1 or VIM2 represents the MFVIM process with two or six flow times. Similarly, composite specimens prepared by MFVIM are named as xU/H-VIM1 or xU/H-VIM2. The dimensions of rectangular injection molded part are 60 mm × 60 mm × 3 mm, as displayed in Fig. 2.

Characterization

Dynamic rheological characterization

Rheological tests were performed using a plate-plate rotational rheometer (Thermo Scientific MARS III, Haake) with a plate

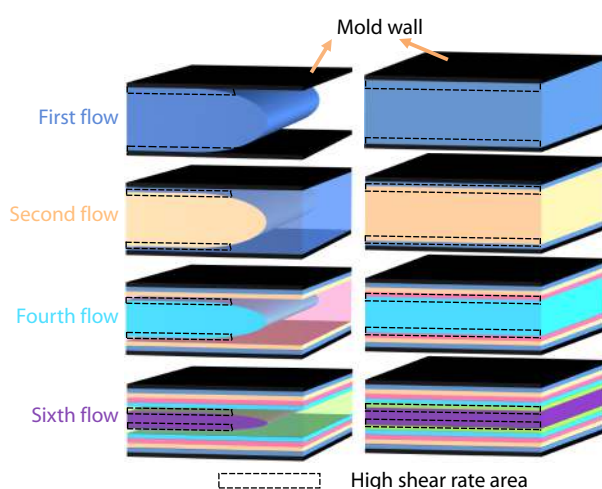


Fig. 1 Schematic of multi-flow vibration injection molding (MFVIM): from the first flow to the sixth flow.

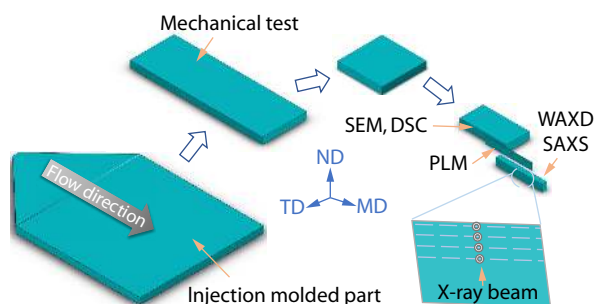


Fig. 2 Schematic diagram of sampling method for characterization. (MD, melt flow direction; TD, transverse direction; ND, the direction normal to MD-TD plane).

diameter of 20 mm and gap size of 0.8 mm. The disk-shaped samples of neat HDPE and composites granules (diameter of 20 mm and thickness of 1 mm) were compression molded with a pressure of 10 MPa at 200 °C. All the samples were heated at 200 °C for 2 min in the gap to get a homogeneous melt before dynamic frequency sweeps. The test temperature is selected according to the commonly processing temperature of HDPE and is employed in injection molding experiment. The dynamic frequency sweeps covering a frequency range from 100 Hz to 0.024 Hz (angular frequency from 628.32 rad/s to 0.15 rad/s) were carried out with 1% strain to ensure that the tests are in the linear viscoelastic region.

Differential scanning calorimeter (DSC)

A DSC (TA Q200) device was used for analyzing thermal behavior of the raw materials and injection specimens under a nitrogen atmosphere. For raw granules, each sample was firstly heated from 40 °C to 200 °C at a rate of 50 °C/min and maintained for 10 min to eliminate the thermal history, and then cooled to 40 °C with a cooling rate of 10 °C/min. Subsequently, the sample was heated to 200 °C for the second time at a rate of 10 °C/min. While for injection molding specimens, each sample was tested by heating from 40 °C to 200 °C at a rate of 10 °C/min. Crystallinity of the samples was determined by normalizing the integral of the enthalpy peak from 60 °C to 180 °C with the enthalpy of melting of 100% crystalline polyethylene, 291 J/g.

Mechanical property

The test specimens were cut off along the flow direction. No less than five specimens are tested in each category. The dumbbell shaped specimens for tensile test (20 mm × 4 mm × 3 mm for the narrow section) were prepared according to ASTM D638-14. The tensile properties were measured at a constant temperature of 25 °C using a universal testing machine (Instron 5567, US) with a cross-head speed of 20 mm/min. For impact test, the specimen's dimension was 60 mm × 10 mm × 3 mm. The notched Izod impact strength of the specimens was measured with a VJ-40 Izod machine at room temperature. Before the test, a 45° V-shaped notch (depth 2 mm) was made.

Polarization light microscopy (PLM)

The 30 μm-thickness films along the MD-ND plane were sliced by microtome at the middle location of injection specimens. The optical observation was performed using the optical microscope (DX-1, Phoenix Optical Co., China) equipped with a camera (Nikon 500D digital camera).

X-ray measurements

Two-dimensional wide-angle X-ray diffraction (2D-WAXD) and two-dimensional small-angle X-ray scattering (2D-SAXS) experiments were conducted on the BL16B1 beamline in the Shanghai Synchrotron Radiation Facility (SSRF), China. The sample-to-detector distance for WAXD and SAXS was 96 mm and 1850 mm, respectively. The light wavelength was 0.124 nm. The rectangular beam with the dimension of 0.8 mm × 0.5 mm irradiated at 4 positions moved from the surface to center region, viz. 200, 600, 1000 and 1400 μm away from the edge of MD-ND plan, respectively.

The orientation of crystals was evaluated using the Hermans orientation function, f , which is defined as:

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

The flow direction was taken as the reference direction. For a set of hkl planes, the average orientation, expressed as $\langle \cos^2 \varphi \rangle_{hkl}$, was calculated using the equation:

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

with φ being the azimuthal angle and $I(\varphi)$ being the scattered intensity at angle φ . When the c axes of all crystals are completely parallel or perpendicular to the flow direction, the value of orientation function f is 1.0 or −0.5, respectively. For completely random oriented crystals, $f = 0$.

Scanning electron microscopy analysis (SEM)

The cross section in MD-ND plane was acid etched for crystalline morphology detection. Each 100 mL of etch solution contained sulfuric acid, phosphoric acid, and distilled water at the volume ratio of 10:4:1 and 1.5 g of potassium permanganate. The samples' surface was immersed in the solution at 60 °C for 7 h to remove the amorphous phase. After gold sputtering treatment, the impact fractured surface and etched surface were characterized with a FEI (Nova Nano SEM450) SEM device.

RESULTS AND DISCUSSION

Rheological Property

The processability and rheological behavior of raw materials are initially evaluated through dynamic rheological tests, as displayed in Fig. 3. It can be clearly seen from Fig. 3(a) that the complex viscosity of melt increases with UHMWPE content. The zero-shear viscosity of 30U/H composite is about 18 times higher than that of neat HDPE, which is related to the average molecular mass of polymer melts.^[29] On the other hand, a transition from liquid-like behavior (loss modulus (G'') > storage modulus (G')) to pseudo-solid behavior ($G' > G''$) can be observed in the low frequency range as the UHMWPE content increases (see Fig. 3b).^[30] As is proved, in the UHMWPE/HDPE blend prepared by conventional melt mixing, the movement and diffusion of long molecular chains of UHMWPE are limited due to the extremely serious entanglement of long chains, so part of UHMWPE cannot be dissolved in HDPE.^[31–33] This assertion will be corroborated by the following PLM results. Thus, it can be reasonably believed that the excellent interface compatibility between matrix and undissolved UHMWPE particles as well as the strong topological entanglement

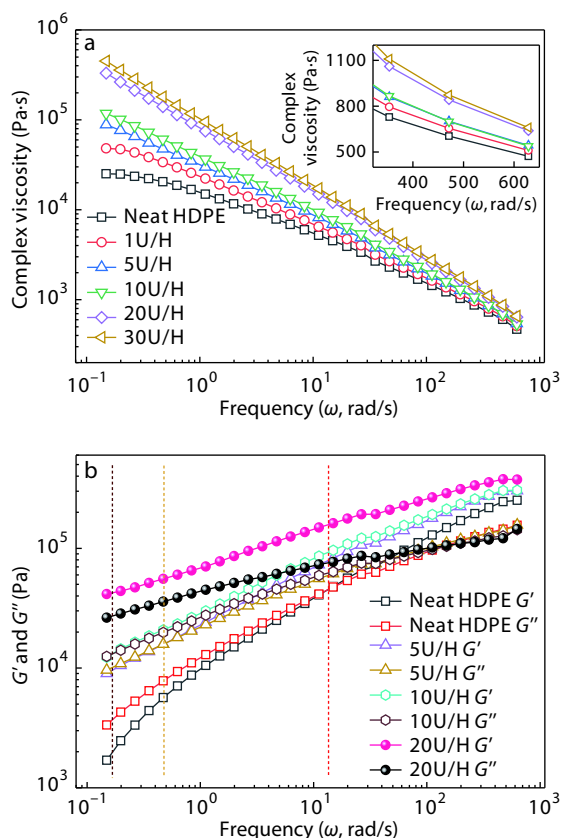


Fig. 3 Dynamic rheological properties of neat HDPE and UHMWPE/HDPE blends.

between the miscible UHMWPE and HDPE molecular chains facilitate the large transient elastic response^[34,35] as “gel” characteristics. Nevertheless, the thermoplastic matrix of dissolved UHMWPE and HDPE is still major in composite melt. In the high angular frequency range, the melts exhibit typical shear thinning behavior and the complex viscosity gap between neat HDPE and composites narrows gradually. When the angular frequency reaches 628 rad/s, the complex viscosities display in the same order of magnitude. Based on the empirical Cox-Merz rule,^[36] the angle frequency and complex viscosity in linear viscoelastic region can be approximately converted into shear rate and shear viscosity. That is, for injection molding with a shear rate higher than 10^2 s^{-1} , the composites exhibit good processability similar to that of neat HDPE.

Furthermore, the characteristic experimental relaxation time (t_x) is calculated by the reciprocal of frequency at the intersection between G' and G'' curves (Table 1).^[37,38] The increase in relaxation time means that in the cooling stage of injection molding, the non-equilibrium state of the molecular

Table 1 Characteristic experimental relaxation time (t_x) of neat HDPE and composite granules.

Sample	t_x (ms)
Neat HDPE	67.1
5U/H	2122.4
10U/H	6106.6
20U/H	>>6711.4

chain can be maintained for a longer period of time, which will have a potential impact on the structure and property of the samples.

Thermal Behavior

DSC test was performed to analyze the thermal behaviors of the raw granules and the injection specimens, as shown in Fig. 4. The melting temperature (T_m) and crystallinity (X_c) calculated by melting enthalpy are listed in Table 2. In order to avoid the effect of thermal history, the secondary heating curve is studied for raw granules (Fig. 4a). As shown Fig. 4(a), UHMWPE has a higher T_m than HDPE, signifying its higher lamellar thickness. Nevertheless, UHMWPE molecular chains possess weaker mobility than HDPE molecular chains due to the extremely high molecular weight, which makes it more difficult to arrange into the crystal lattice, thus, exhibiting lower crystallinity. Reasonably, the 30U/H composite granule exhibits an increased melting point but a decreased crystallinity compared to that of neat HDPE.

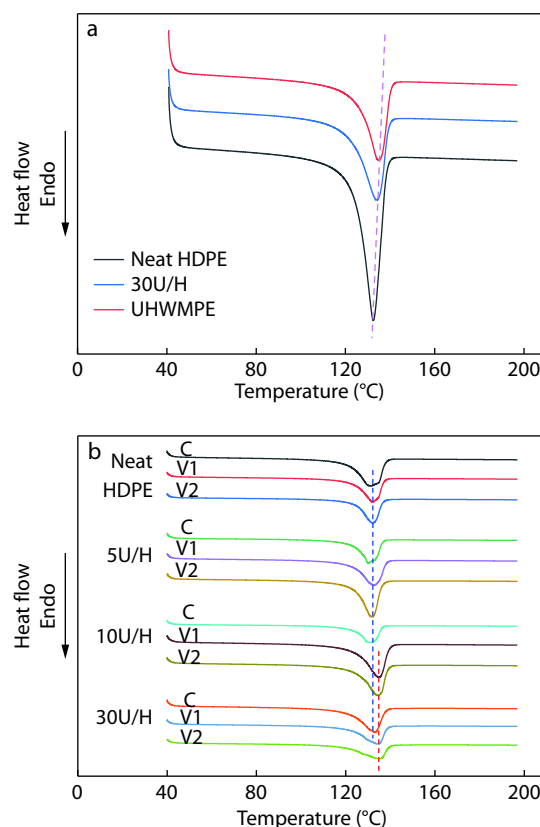


Fig. 4 DSC heating curves of (a) the raw granules of neat HDPE, UHMWPE and 30U/H composite (b) injection specimens of neat HDPE and composites.

Fig. 4(b) shows the melting curves of CIM and VIM specimens with various UHMWPE levels. Note that the entire injection molding cycle takes tens of seconds, while in the DSC test, the first cooling stage after eliminating the thermal history takes 16 min. That is, raw granules experience much longer residence time at crystallization temperature during the first cooling stage of DSC test than specimens during the cooling stage of injection molding. Therefore, neat HDPE and 30U/H injection specimens exhibit lower X_c values than raw

Table 2 T_m and X_c of raw granules and injection specimens.

Raw material	T_m (°C)	X_c (%)	Injection specimen	T_m (°C)			X_c (%)		
				C	V1	V2	C	V1	V2
Neat HDPE	132.5	75.0	Neat HDPE	131.0	132.0	132.0	69.2	69.9	71.3
			1U/H	130.8	131.9	132.3	68.9	68.7	71.1
			5U/H	130.0	132.5	131.9	68.0	69.2	70.2
UHMWPE	134.9	62.2	10U/H	131.6	135.0	134.4	67.6	68.8	70.2
			20U/H	132.2	135.9	135.0	65.6	69.0	71.2
			30U/H	133.1	134.4	135.3	64.5	66.7	68.1

granules. Furthermore, it can be easily seen that the T_m and X_c of VIM specimens are generally higher than those of CIM ones. It benefits from the multiflow-induced crystallization: the continuous shear flow provides more oriented molecular chains, which are more easily aligned into the crystal lattice, resulting in higher crystallinity. Furthermore, due to the low crystallinity characteristic of UHMWPE, the composite specimens with high content of UHMWPE exhibit low X_c , especially for CIM ones.

Mechanical Property

Fig. 5 shows the mechanical properties of CIM and VIM specimens, from which we can find that multi-flow filling plays a significant role. For neat HDPE specimens, tensile strength and Young's modulus increase dramatically from 29.5 and 1091.8 MPa for N-CIM to 37.5 and 1150.5 MPa for N-VIM1, and 52.8 and 1423.8 MPa for N-VIM2 (increase by 79.0% and 30.4%, respectively). With the increase of flow time, the

VIM specimens show lower values of elongation at break, but the notched impact strength decreases first and then increases to the value comparable to N-CIM. The UHMWPE also exhibits positive effects on tensile strength and Young's modulus, but it has a negative impact on the tensile ductility and impact toughness. On the experimental scale, the tensile strength of CIM specimens increases steadily with the increase of UHMWPE content, and the maximum tensile strength is 42.1 MPa for 30U/H-CIM. While for VIM specimens, it seems that there is an optimum content. The highest strength of VIM1 specimens is 48.7 MPa for 20U/H-V1. Different from it, the maximum values of VIM2 ones appear at both 5U/H-V2 and 10U/H-V2, which exhibit the tensile strengths of 63.1 and 63.7 MPa, respectively (113.9% and 115.9% more than that of N-CIM). The optimal UHMWPE content for Young's modulus decreases from 10 wt% for CIM and VIM1 specimens to 5 wt% for VIM2 specimens

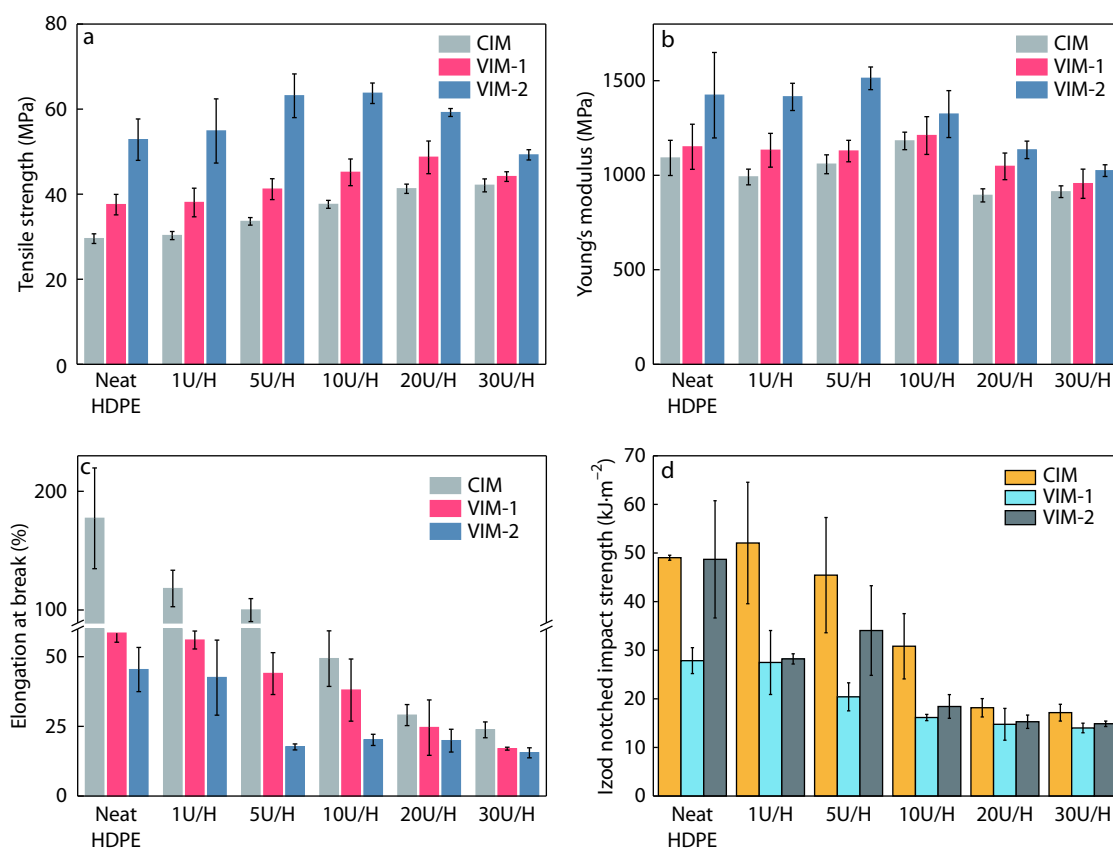


Fig. 5 Mechanical properties of injection specimens: (a) tensile strength, (b) Young's modulus, (c) elongation at break, (d) izod notched impact strength.

(1512.8 MPa, increasing by 38.6% than that of N-CIM). In summary, the 5U/H-VIM2 specimen possesses optimum mechanical properties, with the tensile strength and Young's modulus increased by 113.9% and 38.6%, respectively, compared with N-CIM specimens. Although the fracture mode changed from ductile fracture to brittle fracture, the impact strength still remains 70% of the N-CIM specimen.

Structure Evolution

The ultimate properties of polymer are highly dependent on the microstructure formed during molding process. In order to clarify the following questions: 1. how the UHMWPE and multi-flow synergistically act on the crystallinity and mechanical properties of the injection specimens; 2. why the mechanical properties decrease when UHMWPE content exceeds the optimum; 3. why the two kinds of VIM specimens show a significant difference in impact toughness; further characterization will be performed from the perspectives of specimen

structure, crystal orientation, lamella structure and crystal morphology.

PLM observation

Fig. 6 shows PLM photographs of the cross-sectional (MD-ND plane) morphology of specimens. As is well known, a typical CIM specimen consists of skin, shear and core layer from surface to central area. This layer structure essentially corresponds with the spatial discrepancy of chain conformation caused by the nonlinear shear rate distribution in the thickness direction.^[39,40] With the action of strong shear, the initially well-entangled chains find themselves in a new environment that allows them to obtain a sufficiently high level of chain orientation, meeting the requirements for the formation of highly oriented structures (highly oriented lamellae or shish-kebab).^[41] In N-CIM, the colored areas marked with double-headed arrows represent shear layers containing highly oriented structures caused by intensive shear flow,^[26] while core layers with light color consist

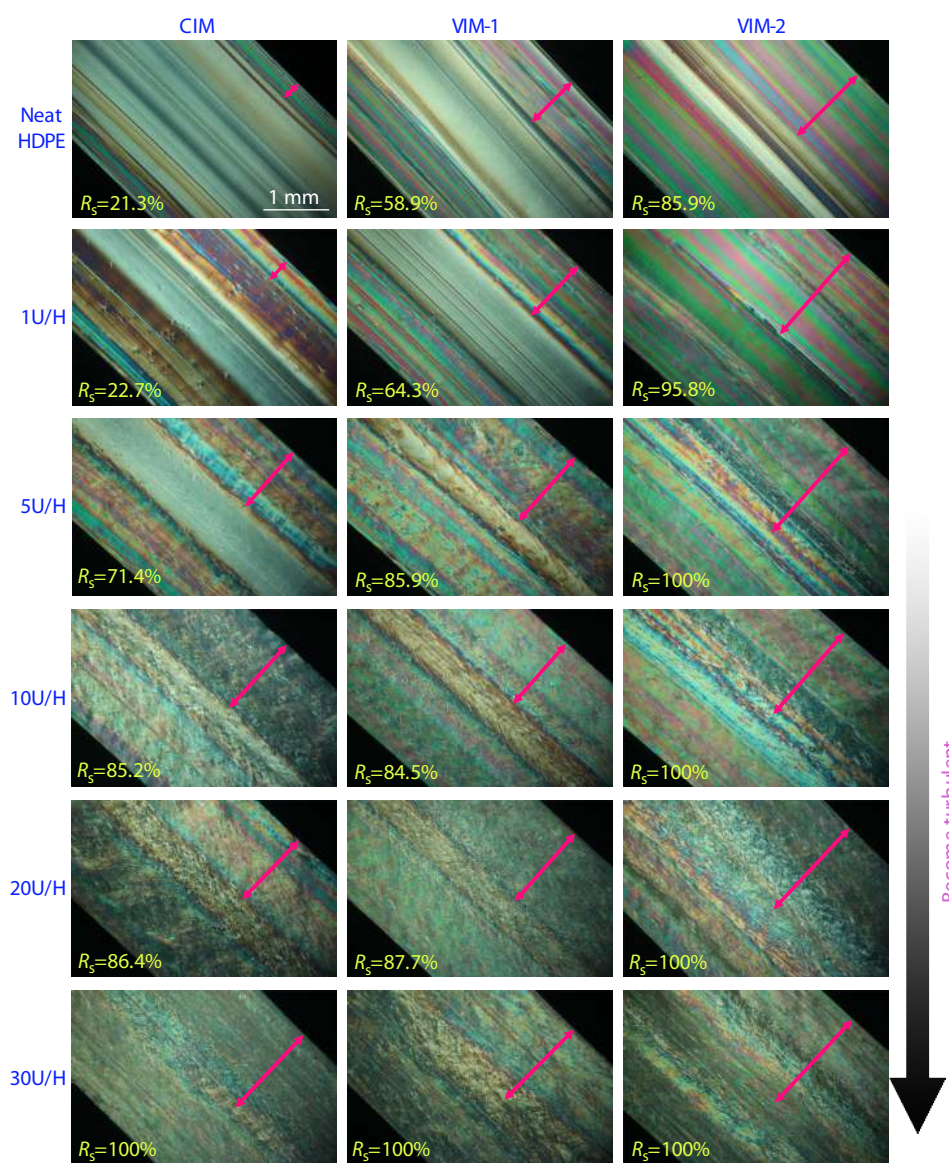


Fig. 6 PLM images of the specimens. " R_s " represents the ratio of apparent shear layer thickness to the whole sample thickness measured by Image-pro software with the ruler tool.

of spherulitic structures formed under relatively static conditions, on the other hand, the molecular chain has sufficient time to relax from oriented state due to the slower cooling process. The skin layer is very thin, and for convenience, it is regarded as part of the shear layer. Here, the relative thickness of apparent shear layer (R_s) is obtained through calculating the thickness ratio of the shear layer to the specimen (the whole thickness of specimen is 3000 μm). The R_s of N-CIM specimen is only 21.3%. As we know, the shear layer melt closer to the mold surface cools faster and solidifies first. With the introduction of additional melt flow, new areas of high shear rate will appear as shown in Fig. 1. Meanwhile, the melt inside will be pushed out as the solidified shear layer thickens. In this way, the R_s values of the N-VIM1 and N-VIM2 specimens significantly increase to 58.9% and 85.9%, respectively. The weakly oriented area in the core layer of N-VIM, similar to 1U/H-CIM, is not counted in R_s since it seems to be quite different from that in the shear layer.

The apparent shear layer is also thickened by UHMWPE because the relaxation time of oriented chains is improved. In CIM and VIM1 specimens, the R_s increased to 100% when adding 30 wt% UHMWPE, indicating that the apparent shear layer is full of entire specimen. In passing, it can be easily observed that undissolved UHMWPE particles exist in composite specimens. While for VIM2 specimens, the R_s is promoted up to 100% with just 5 wt% UHMWPE loading. The R_s vari-

ation shows that the flow time and UHMWPE content play synergistic roles in thickening the oriented shear layer. It is interesting that when UHMWPE loading is 10 wt% or more, the melt flow seems to be more turbulent. The boundaries between shear layer and core layer become indistinguishable even for CIM and VIM1 specimens. Wang^[42] reported that the melt behavior of polymer is related to the degree of chain entanglement, in other words, the constitutive instability is produced by the conformational oscillation of the interfacial chains between their coil and stretch states. UHMWPE with high loading improves the polydispersity of molecular chains greatly and makes them exhibit different disentanglement and orientation states under the same shear condition. After adding 30 wt% UHMWPE, even the CIM specimen shows a R_s of 100% visually. Obviously, there is a correlation between layer structure evolution and mechanical properties. The 5U/H-VIM2 with 100% R_s shows the highest tensile and Young's modulus while the enhancement effect weakens as the unstable flow becomes obvious in higher UHMWPE level samples. In order to clarify the layer structure, further characterization is needed.

2D-WAXD analysis

2D-WAXD is performed to further investigate quantitative information on crystal orientation of internal structure. The 2D-WAXD patterns of CIM and VIM specimens are shown in Fig. 7,

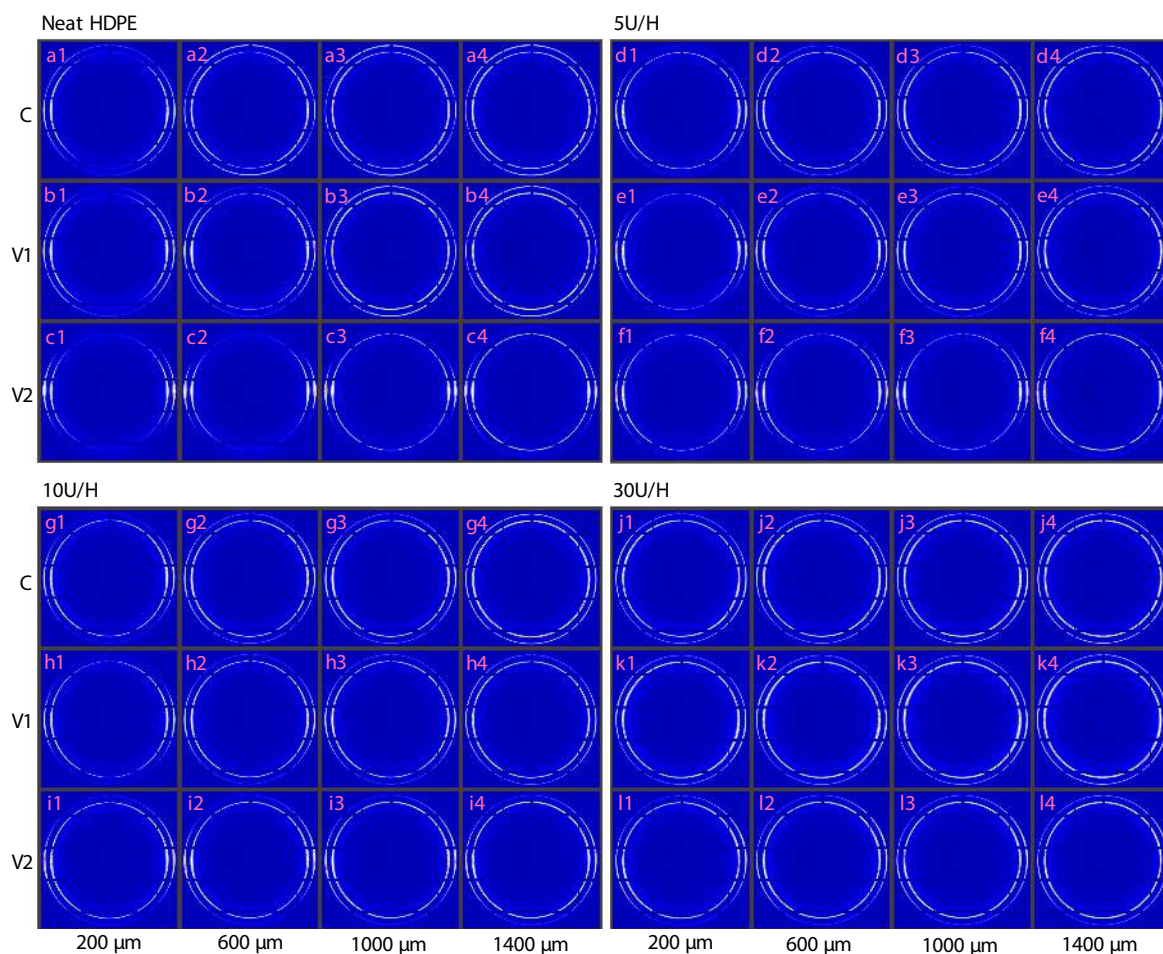


Fig. 7 2D-WAXD patterns for specimens at different positions from surface to core region; the melt flow direction is vertical.

with neat HDPE, 5U/H, 10U/H and 30U/H selected. Based on the variation of shear layer thickness displayed in the PLM characterization, four scan points are chosen for each specimen at positions 200, 600, 1000 and 1400 μm from the specimen surface. Two Debye-Scherrer diffraction rings are shown corresponding to the (110) and (200) planes of the PE orthorhombic unit cell ($a=7.40$ Å, $b=4.93$ Å, $c=2.54$ Å). In general, the homogeneous diffraction ring of 2D-WAXD pattern is the signal of isotropic structure, while the arc-like diffraction in the equatorial direction indicates the formation of oriented structure. For N-CIM, a weak arc-like diffraction of the shear layer can be observed at 200 μm (Fig. 7a1), while the isotropic diffraction rings are shown in the other three locations (Figs. 7a2–7a4). As the flow time increases, the orientation signal appears at positions closer to the center compared to that of N-CIM. For example, acute arc diffraction maximums can be observed from the surface to the center of N-VIM2 specimen (Figs. 7b1–7b4), indicating that the highly oriented structures are formed throughout it. Similarly, for CIM and VIM1 specimens with 5 wt% and 10 wt% UHMWPE loadings, the arc reflections appear at more central locations than those of the neat HDPE ones. However, although 5U/H-VIM2 and 10U/H-VIM2 always exhibit narrow arc diffraction from surface to center like N-VIM2, their intensity decreases. All the 30U/H specimens exhibit 2D-WAXD patterns with weak and broad arc-like diffraction.

The azimuthal angle scan is performed along the (110) diffraction plane from 0° to 180° , and the orientation degree calculated.^[43] The calculation process is exhibited as Eqs.(1) and (2) in the previous section. Figs. 8 and 9 show the 1D intensity-azimuthal angle curves and the orientation degree distribution respectively (in Fig. 8, bad data points caused by ras-

ter occlusion in 2D-WAXD test have been removed). It is clear that the flow times can remarkably influence the orientation results, yet the effect varies with different UHMWPE loadings. For N-VIM2 specimen, the 1D intensity-azimuthal angle curve peak at specimen center becomes sharper, in accordance with the thickened shear layer. Similarly, corresponding curve peaks of 5U/H and 10U/H specimens become sharper as the flow times increase. With six flow times, their orientation degrees increase to a very high level from surface to center. Although PLM indicates that UHMWPE helps to thicken the shear layer, high levels of additives seem to reduce the highly oriented structures. The orientation degrees in 10U/H-VIM start to decrease compared to that in 5U/H-VIM. While for 30U/H specimens, multi-flows can only enhance the orientation degree at the specimen center. However, all the 1D curves of 30U/H specimens show weak and broad peaks, with orientation degrees lower than low UHMWPE content samples. Herein, the excessive undissolved UHMWPE particles, acting as random fillers, will account for the reduction of orientation degree. In fact, the reduced orientation degree corresponds to the shear layer observed in the PLM characterization that is more easily formed but more turbulent, which can be responsible for the degradation of the mechanical properties of the high UHMWPE content specimens.

2D-SAXS and SEM analysis

2D-SAXS provides rich information on periodic crystal structures and lamella sizes, as shown in Fig. 10. In 2D-SAXS pattern, a pair of meridional maxima indicates the formation of periodically stacked lamellar crystals or kebab structure, and the equatorial streak parallel to the flow direction can be attributed to the

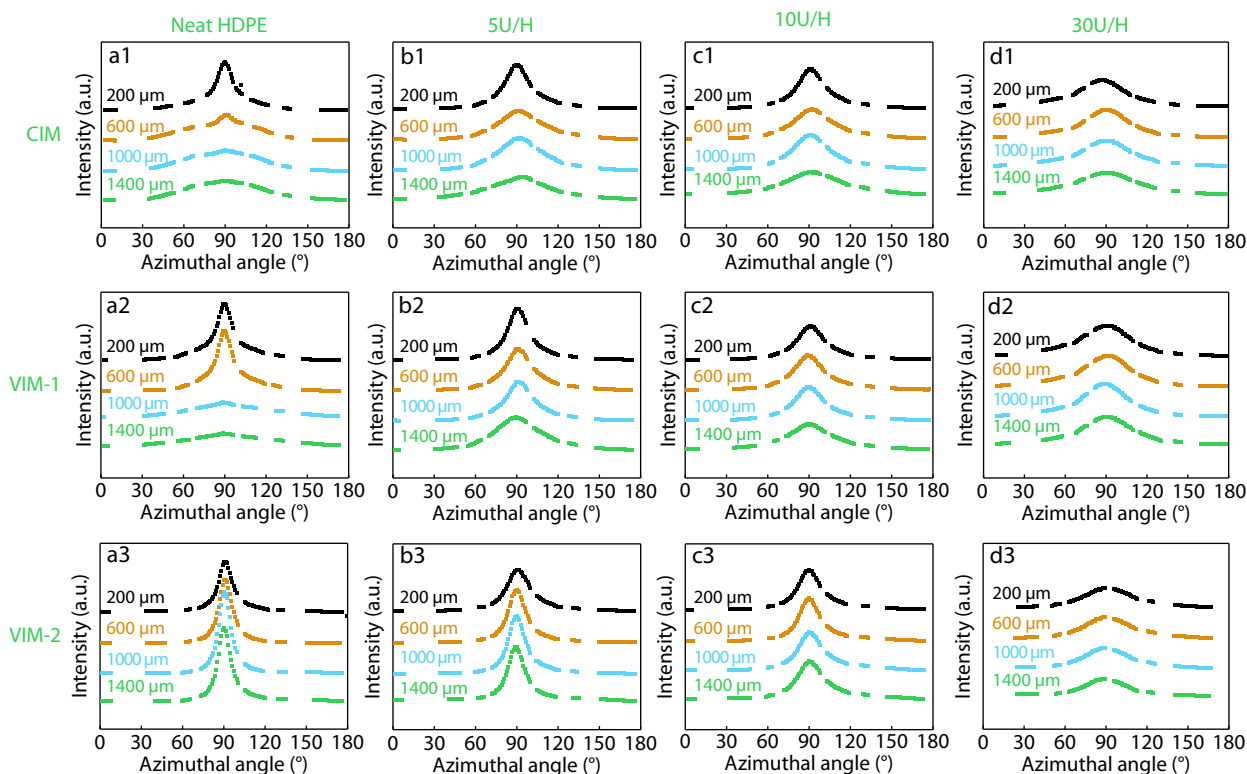


Fig. 8 1D-WAXD patterns of CIM and VIM specimens corresponding to 2D-WAXD patterns.

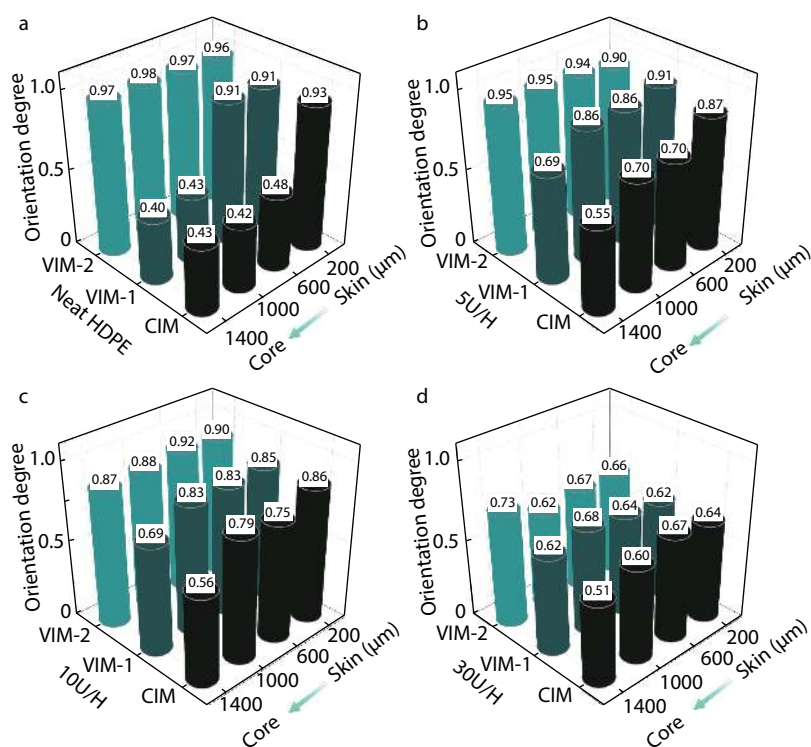


Fig. 9 Orientation degree distributions for the specimens at different positions from surface to core region.

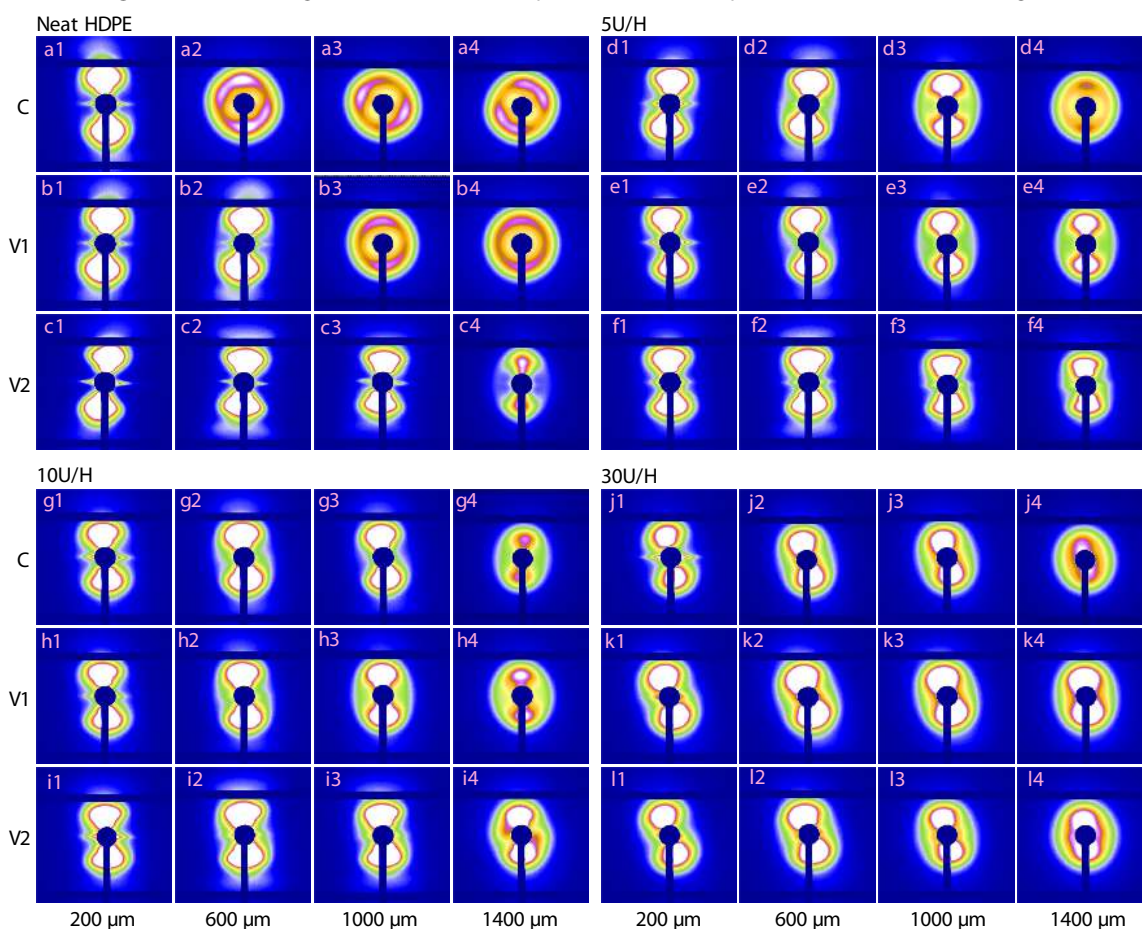


Fig. 10 2D-SAXS patterns of the specimens at different positions from surface to core region; the melt flow direction is vertical.

shish structure.^[44] There are three kinds of 2D-SAXS patterns, including shish-kebab signal, only periodically stacked lamella signal, and random lamella signal. For each sample, the 2D-SAXS signal is basically consistent with the variation of shear and core layers shown in PLM observation. The random lamella signals appear only in the apparent core layer of the N-CIM, N-VIM1 and 5U/H-CIM specimens. 2D-WAXD results confirm that their orientation degree is relatively low. In the apparent shear layers, 2D-SAXS patterns present different kinds of highly oriented structure signals. Distinct shish-kebab signals are easily observed in neat HDPE and 5U/H specimens, especially in their VIM2 ones. Nevertheless, it is worth noting that the shish streaks of 5U/H specimens become shorter compared to those of neat HDPE ones. When the UHMWPE content reaches 10 wt% or more, the shish streaks disappear except at the position of 200 μm . Meanwhile, the kebab patterns shrink gradually as the UHMWPE content increases.

In order to clarify whether the 2D-SAXS signals accurately show the structure evolution in specimen, the crystal morphologies of etched MD-ND plane is characterized. The SEM micro-morphologies of CIM and VIM2 specimens are shown in Figs. 11 and 12 respectively. Locations of 200, 800 and 1400 μm from the surface are chosen. Tightly arranged shish-kebab structures always exist at 200 μm for both the CIM and VIM2 specimens. In Fig. 11, the lamellae are randomly distributed at 800 and 1400 μm for the N-CIM specimen, while some periodically stacked lamellae appear at 800 μm for the other three CIM specimens, which matched the 2D-SAXS patterns.

Shish-kebab structures are visible at 800 μm for all the VIM2 specimens (Fig. 12). Among them, the shish-kebab

structures are continuously and regularly arranged for N-VIM2 (Fig. 12a2), yet there are obvious gaps between the lamellae (marked by red arrows for example). While for 5U/H-VIM2 (Fig. 12b2), the lamellae become very dense and the amount of shish observed reduces at 800 μm . When the UHMWPE content increases to 10 wt% or more, the lamellae become loose again, and the regularity and length of shish-kebab decrease compared to those of N-VIM2 (Figs. 12c2 and 12d2). These changes will not only lead to the decrease of orientation degree in 2D-WAXD results, but also result in the shortening of the shish signal and the shrinking of the kebab signal in 2D-SAXS. Even so, there are still a lot of shish-kebab structures at 800 μm of 30U/H-VIM2 specimen (Fig. 12d2). But in their 2D-SAXS patterns, the shish signal unreasonably disappears at either 600 or 1000 μm region (Fig. 10I2 and 10I3). Of course, UHMWPE should be responsible. It is worth noting that the visible UHMWPE particles are inserted into gaps between the lamellae of shish-kebabs in the micro-morphology of 10U/H-VIM2 and 30U/H-VIM2. These particles, which have undergone dissolution and shear fragmentation, are much smaller than their raw powders. Thus, we can rationally speculate that the undissolved UHMWPE could affect the SAXS and WAXS results, and that the crystal inside UHMWPE will alter the final scattering pattern. In addition, it seems that the sizes of undissolved UHMWPE particles in high orientation areas (shish-kebab) are generally smaller than those in the periodic or random lamellae areas for both 10U/H and 30U/H specimens (see Figs. 11 and 12), which may be due to the better dissolution^[45] or further fragmentation in the high shear regions. Therefore, the particle size distributions in their

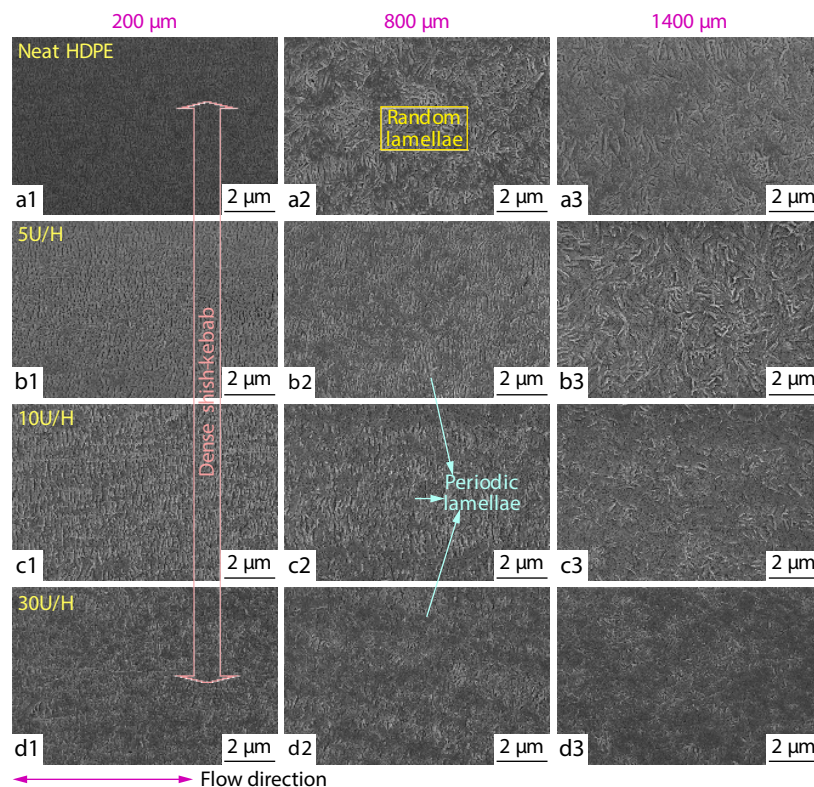


Fig. 11 SEM morphologies of the selected CIM specimens from surface to center locations.

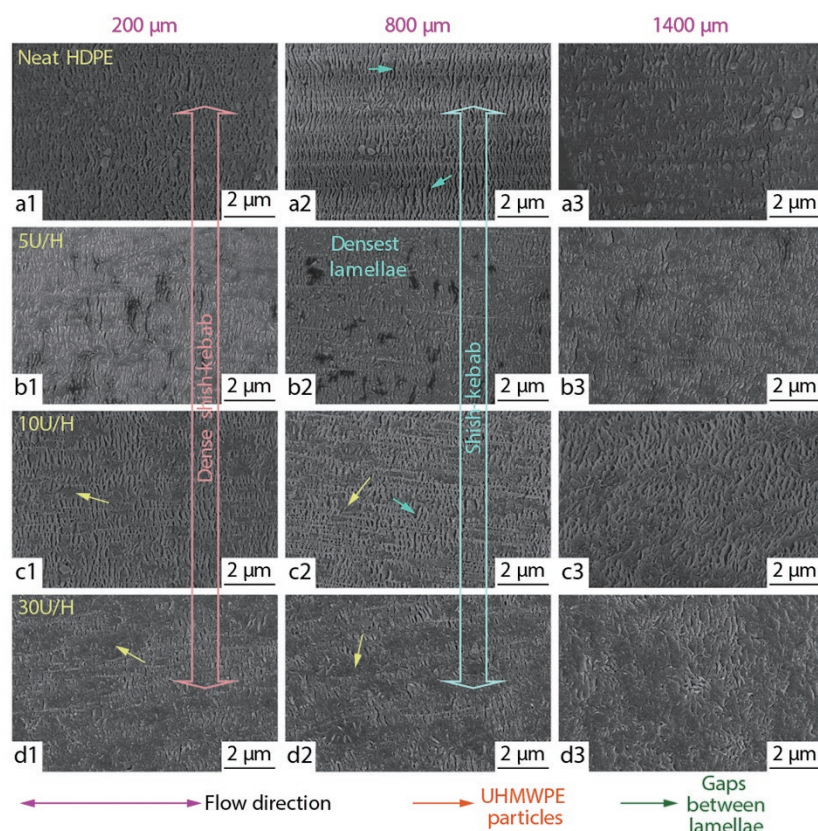


Fig. 12 SEM morphologies of VIM2 specimens from surface to center locations.

VIM2 specimens are more uniform than those in CIM specimens, corresponding to the additional high shear areas.

Fig. 13 shows the 1D SAXS intensity profiles of fan-shaped integrated 2D SAXS patterns. The variation of scattering intensity from surface to core is related to the crystal structure evolution of the specimens. Long period (L) of lamellae is calculated according to the Bragg equation ($L=2\pi/q$) from the peak position (q) of Lorentz-fitted 1D SAXS intensity profiles, which is given in Table 3. The long period consists of the crystal thickness and any amorphous material separating the domains ignoring the interface thickness.^[46] Overall, VIM2 specimens generally show higher L than the CIM ones. It has been reported that the thickening of amorphous layers induced by stretching or shear flow can lead to an increase in L .^[47,48] But in our case, the crystallinity improved by VIM process indicates that the increased L is also ascribed to the growth of lamellae benefiting from the multiflow-induced crystallization. Furthermore, a more significant increase in L is caused by UHMWPE. Compared with N-VIM2, the increased L and narrowed separating domains between lamellae in 5U/H-VIM2 indicate that the 5 wt% UHMWPE loading and six flow times synergistically promote the growth of lamellae and induce the shish-kebab to be denser. With the higher content of UHMWPE inserted into the gaps between lamellae, the spacing-expansion effect of UHMWPE nanofiller becomes apparent. Eventually, the combined effect of crystallization induction and spacing expansion resulted in a very high L for the 30U/H-VIM2 specimen, especially in the core area.

Herein, the structure evolution and self-reinforcing mech-

anism of the UHMWPE/HDPE composites prepared by MFVIM technology can be deduced in Fig. 14. The core layer consisting of isotropic spherulite structures constitutes a significant proportion of N-CIM specimen. The matrix can yield at a fast speed to absorb energy, thus exhibiting high tensile ductility and impact property despite of the low tensile strength. For N-VIM2, the shear layer occupies the majority of the specimen with aligned lamellae existing at center location. The shish-kebab structures are closely connected with each other in the super-thick shear layer. Although the ductility is very low, these shish-kebabs are more likely to transfer stress to deeper areas. Therefore, the tensile property is greatly improved while the impact property is preserved comparable to that of N-CIM. It can be considered that the declined impact strength for N-VIM1 is caused by the transfer velocity difference of impact stress from the surface to the center. Moreover, for 5U/H-VIM2, the synergistic self-reinforcing effect of UHMWPE and MFVIM not only increases the relative thickness of shear layer to 100%, but also improves the thickness and compactness of oriented lamellae. These structural variations will enhance the ability of the specimen to withstand tensile loads and ensure the rapid and uniform transfer of stress throughout the specimen. Compared with the N-CIM specimen, the tensile strength and modulus of 5U/H-VIM2 increase to 1.39 and 2.14 times respectively, while the impact strength remains at 70%. However, for 30U/H-VIM2, the spatial expansion of excess UHMWPE causes the lamellae to become loose again. The size distribution of the undissolved UHMWPE particles, corresponding with oriented structure

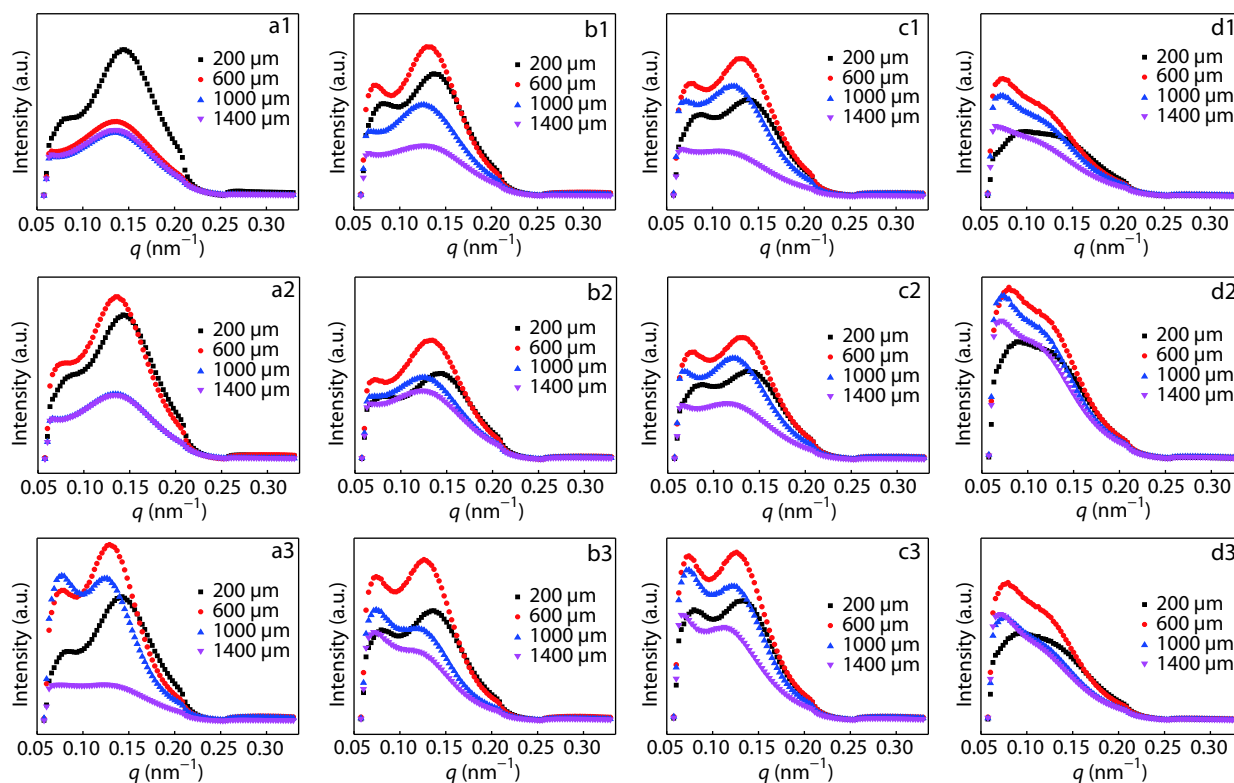


Fig. 13 1D SAXS intensity profiles of fan-shaped integrated 2D SAXS patterns.

Table 3 L for specimens at different position from surface to core region (nm).

Locations from surface	Neat HDPE			5U/H			10U/H			30U/H		
	CIM	VIM1	VIM2	CIM	VIM1	VIM2	CIM	VIM1	VIM2	CIM	VIM1	VIM2
200 μm	43.5	44.0	44.3	45.6	44.5	46.5	45.7	45.6	48.2	52.1	58.0	60.7
600 μm	46.9	46.4	48.7	47.8	47.8	49.9	48.3	48.4	50.4	59.3	59.7	64.0
1000 μm	47.1	47.2	50.9	50.3	51.0	52.7	52.0	52.1	52.0	63.4	60.2	71.5
1400 μm	47.1	47.2	51.6	50.3	51.4	55.9	56.8	55.0	56.1	69.9	63.5	72.9

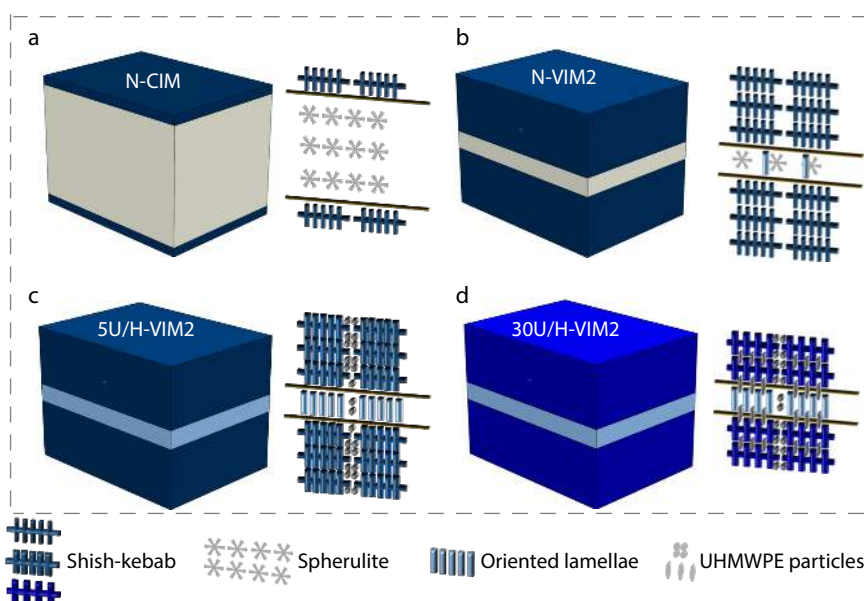


Fig. 14 Schematic diagram for structure evolution and the synergistic effect of multi-flow and UHMWPE: (a) N-CIM, (b) N-VIM2, (c) 5U/H-VIM2, (d) 30U/H-VIM2.

distribution in injection specimens, will be a potential on final properties. Moreover, high levels of UHMWPE also increase the failure risk as the stress concentration point. Eventually, both of them will lead to a weakening of the enhancement.

CONCLUSIONS

In this work, ultrahigh molecular weight polyethylene (UHMWPE)/high density polyethylene (HDPE) self-reinforced composites were prepared using multi-flow vibration injection molding (MFVIM). The mechanical property characterization shows that the synergistic effect of six flows and UPE with 5 wt% content enhances the tensile strength and tensile modulus of HDPE to 1.39 and 2.14 times, respectively, and retains 70% of the impact performance. By observing the variation of microstructure, the reinforcing mechanism is discussed detailedly. Ultra-thick shear layers (ultra-high shish-kebab content) and denser oriented lamellae not only enhance the capability of the specimen to withstand tensile loads, but also ensure the rapid and uniform transfer of stress throughout the specimen. However, excess UHMWPE actually weakens the synergistic effect. Compared with other novel injection molding technologies, MFVIM can not only control the thickness and distribution of the shear layer, but also be more suitable for the fabrication of complex parts. Therefore, the synergistically enhancement method through MFVIM with UHMWPE shows great industrial application value for HDPE material.

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