Influence of HMW tail chains on the structure evolution of HDPE induced by second melt penetration

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Supplementary data for rheological classification

As shown in Fig. S1, the values of the complexity viscosity are improved with the content of HMW tail increase. On the other hand, the fitting curves coincides with the data points, suggesting Carreau-A model adapts well with the studied system. Fig. S2 shows the rheological behavior for obtaining the constant C_1 and C_2 in W-L-F equation, seeing 190 °C as the referred temperature. Then the conversion factor (a_T) in the time-temperature equivalence principle.



Fig. S1 The shear thinning behavior of various samples tested at 180 °C. The solid lines are the fitting curves from Carreau-A relation.



Fig. S2 The representative plots of relationship between elastic modulus and angular frequency: (a) HPE0, (b) HPE20.

Samples preparation for evaluating shear rate of M³IM

Although the coalescence and relaxation of the dispersed phase was the primary obstruction for shear field description via deformation of dispersed phase, it also can be appropriate for actual MFIM process ¹⁻³ using some classical models as follows ^{4, 5}.

$$Ca = \frac{\eta_m \kappa \gamma}{\sigma}$$
(a)

$$\frac{B}{2R_o} = (1+\gamma^2)^{-\frac{1}{4}}$$
(b)

$$\gamma = \dot{\gamma}t$$
 (c)

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The meaning of parameters therein are listed below:

Ca, the capillary number; η_m , the viscosity of matrix; *R*, the radius of dispersed phase; $\dot{\gamma}$, the shear rate; *B*, the diameter of ellipsoidal droplets; γ , the shear strain;

 R_0 , the radius of original droplets; t, the shear duration. There existed a critical capillary number (Ca_{crit}) for a given blend, exceeding which the droplet would irreversibly deformed into ellipsoidal or even fibrillar shape, in this case formulas (b) and (c) should be used to calculate the shear rate. Otherwise, formula (a) should be adopted in weak flow field, like core layers in M³IM parts.

Polystyrene (PS, Mn is 2.87%10⁵g/mol) was chose as dispersed phase blending with HPE0~HPE30 and MPE separately by twin-screw extruding, and the blends were named as B0~B30 and B6, respectively. The similar shear thinning performance of HDPE and HDPE/PS blends, tested on Rosand

Initial phase morphology of HDPE/PS blends

When the blends were prepared, they were observed by SEM at an accelerating voltage of 20kV after having brittle failure in liquid nitrogen. As shown in Fig. S4, the sea-island morphology was obvious in HDPE/PS blends and the dispersed phases were almost spherulites but a few ellipsoids, suggesting PS phase deformed slightly after extruding. Besides, the phase interface were clear indicating no interfacial adhesion between these two phases. The statistical results of PS particles were listed in Table RH7D capillary rheometer, suggests the deformation of dispersed



Fig. S3 The contrast of shear thinning behavior between HDPE and HDPE/PS tested at 220°C, in the shear rate range of 50~5000 s⁻¹.

phase and matrix in flow field would be closely to synchronization, especially at high shear rate (Fig. S3). Hence, it can be roughly thought HDPE/PS blends show similar rheological behaviors with neat HDPE under intense shear flow. The blends were subsequently injected following the same steps earlier with the same processing parameters (Table 1), namely the injection unit1 was B0~B30 and unit2 was B6. The M³IM samples were marked as 0M~30M corresponding to HPE0~HPE30, respectively.

S1, namely the initial diameters $2R_0$ in formula (b).

Table S1 The statistical initial diameters of PS phase in HDPE/PS blends.

Samples	B 0	B10	B20	B30	B6	
$2R_{\theta}$	3.28	3.27	2 97	2 92	3.26	
(µm)			2.91	2.92		



Fig. S4 The phase morphologies of HDPE/PS blends prepared by extrusion.

Morphological observation of M³IM parts and shear rate calculation



Fig. S5 Representative of scanning electron micrographs at different locations of the sample 20M. The

flow direction is vertical.

The samples for morphological observation were prepared in a similar way as represented in Fig. 2, but the PS phase was etched by xylene solution for 4 hours. After the samples were dried, they were observed by SEM in the same condition as depicted above. Fig. S5 is a representative SEM patterns in various positions at the content of 2.11% HMW tail (20M). It can be seen the aspect ratio of dispersed phase experienced two loops that increased first and then decreased with the distance (*d*) from the mold wall

extended. That's to say, the fibrillar dispersed phase appeared in the position where $d=100\mu\text{m}$, $200\mu\text{m}$, $300\mu\text{m}$ and $900\mu\text{m}$ meanwhile, implying the shear strength reached maximum both near the mold and center. Afterwards, the size of dispersed phase (*B*) can be statistically calculated out in order to get the values of shear rate according to the formulas (a) ~ (c). The specific evaluation of the parameters can be referred to our previous work 1,2, but it should be pointed out that the value of the shear duration (*t*) is different in this work. It was previously valued the injection time of secondary melt (t_p =1s), whereas actually the strong shear was only produced around the melt front while the shear action was very weak near the posterior part, similar to the GAIM ⁶. This is also the main reason why the shear rates were all low in our former work (the maximum was 140 s⁻¹)^{1, 2}. In this paper, we assume the shear duration of each sample are the same, and it can be roughly calculated as follows: $t = (l/L) \cdot tp \approx 0.11s$, where *l* is the length of melt front, representing the actual shear width ³, and *L* represents the whole injection distance, as presented in Fig. S6. Therefore, the shear rates were further calculated out and listed in Table S2. The maximum was 1343 s⁻¹ appeared in the position *d*=900 µm of HPE20, and the magnitude agreed with the case of

real injecting process.



L=65mm

Fig. S6 The sketch map of the melt front in the cavity during the melt penetration stage.

Samples	Position	100	200	300	600	900	1500	2000	2500			
		μm	μm	μm	μm	μm	μm	μm	μm			
0 M	<i>B</i> (µm)	0.536	0.418	0.447	0.414	0.343	0.566	0.832	1.921			
	$\dot{\gamma}$ (s ⁻¹)	345.30	568.93	496.06	576.94	839.18	308.51	142.74	0.08			
10 M	<i>B</i> (µm)	0.524	0.406	0.437	0.408	0.321	0.569	0.860	1.958			
	$\dot{\gamma}$ (s ⁻¹)	359.33	599.71	517.64	593.74	963.06	305.58	133.66	0.05			
20 M	<i>B</i> (µm)	0.364	0.278	0.311	0.387	0.272	0.466	0.894	1.143			
	$\dot{\gamma}$ (s ⁻¹)	615.15	1059.31	842.95	660.50	1343.03	455.04	123.64	0.03			
30 M	<i>B</i> (µm)	0.446	0.332	0.368	0.407	0.297	0.364	0.603	1.238			
		394.99	715.35	580.00	597.63	1123.35	747.83	272.12	0.03			

Table S2 The calculated values of shear rate at various positions for different samples.

Notes and references

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