

## Morphology and properties of self-reinforced high density polyethylene in oscillating stress field

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This article reports the effect of mould temperature on the mechanical performance and microstructure of self-reinforced high density polyethylene (HDPE) prepared by melt deformation in oscillating stress field. The mechanical properties of HDPE have been improved greatly in oscillating stress field. The Young's modulus and yield strength of HDPE have been enhanced from its original 1 GPa, 23 MPa into 3.5 GPa, 87 MPa, respectively. Differential scanning calorimetry (d.s.c.) curves of slices taken from self-reinforced HDPE exhibit double-peak melting endotherm depending on their distances from the surface of the sample. The low-temperature peak is attributed to the presence of spherulites, and the high temperature peak to the melting of shish-kebab crystals. The amount of shish-kebab crystals amounts to 20% in the crystalline phase. Wide angle X-ray diffraction (WAXD) measurements show there exists preferred orientation of molecular chains. It is the production of shish-kebab crystals and the orientation of molecular chains that are origins of the great improvement of mechanical behaviour of HDPE prepared in oscillating stress field.  
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### Introduction

Since Wunderlich *et al.*<sup>1</sup> discovered the extended chain crystals of polyethylene under high pressure in 1962, much effort has been focused on the self-reinforcement of polyethylene. The film, rod, sheet, and fibre with high stiffness and high strength have been prepared by various solid and melt deformation methods<sup>2–4</sup>. High stiffness and high strength HDPE parts have also been moulded using high pressure in injection moulding<sup>5,6</sup>. However high pressure injection moulding has two definite shortcomings. The first one is high working pressure which has this route unacceptable in practical application. The second is that the self-reinforcement by high pressure injection moulding is significant only for high molecular weight high density polyethylene which is never used alone in injection moulding owing to low melt flow rate.

Our previous works<sup>7–9</sup> have discovered that the self-reinforcement is obvious for low molecular weight high density polyethylene and polypropylene in oscillating stress field under low pressure. As the working pressure in oscillating stress field is low and the self-reinforced materials have good processability, so this

method exhibits a good future. This article is to report the effect of mould temperature on the mechanical performance of self-reinforced high density polyethylene and investigate the relevant morphology in detail.

### Experimental

**Material.** The polyethylene used in this study was HDPE grade 7006A from Qilu Petrochemical Corp. with a melt flow index of 6.8 g/10 min.

**Sample preparation.** Dumbbell specimens shown in *Figure 1* were prepared by an injection-moulding machine equipped with an oscillating packing device which has been described in ref. 10. The processing variables used are listed in *Table 1*.

**Tensile tests.** The yield strength and Young's modulus were measured using an Instron universal testing instrument Model 4302 equipped with a long travel extensometer at room temperature. The crosshead speed was 5 mm min<sup>-1</sup>.

**X-ray measurement.** The morphological changes of self-reinforced HDPE were determined by wide-angle X-ray scattering (WAXS) using a Y-4Q X-ray diffractometer.

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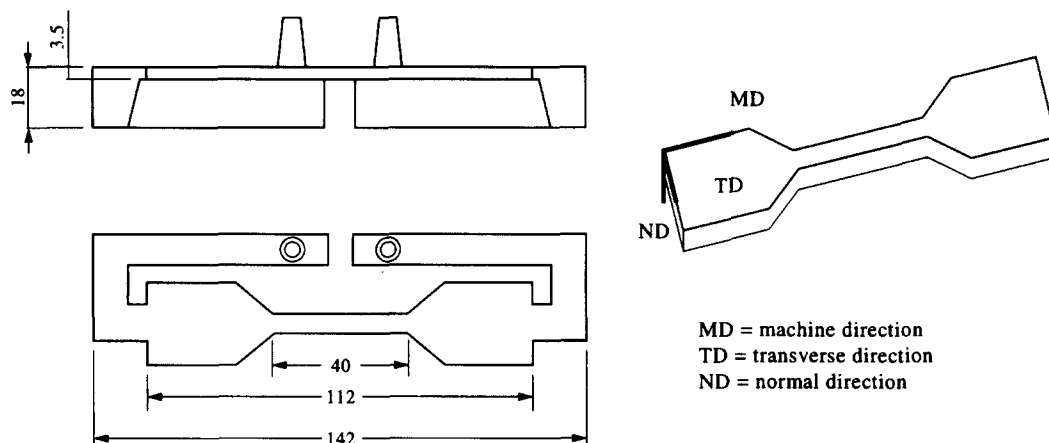


Figure 1 Outlines of the dumbbell specimen and reference axes. The dimensions are in millimetres

Table 1 Values of processing variables

Injection pressure (MPa)	35
Maximum oscillating pressure (MPa)	16
Oscillating frequency (Hz)	0.3
Oscillating time (min)	5
Temperature at feed zone (°C)	150
Temperature at melting zone (°C)	220
Temperature at metering zone (°C)	230
Mould temperature (°C)	47, 60, 65, 70, 75

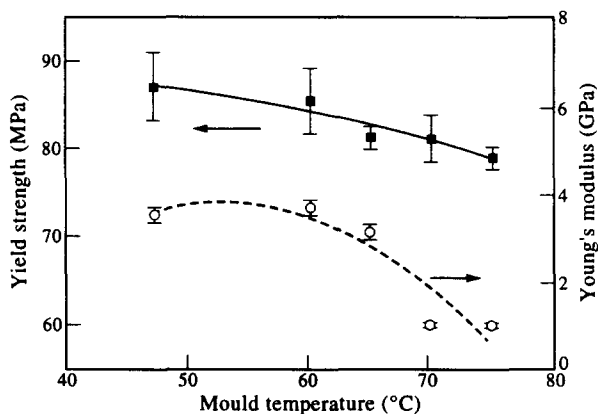


Figure 2 Mechanical properties vs. mould temperature for self-reinforced HDPE prepared in oscillating stress field

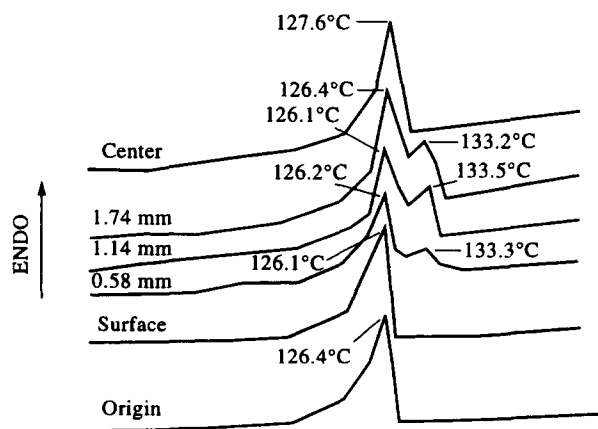


Figure 3 D.s.c. curves of slices taken from self-reinforced HDPE. The distances of slices from the surface of sample are indicated above the curves

*Differential scanning calorimetry (d.s.c.).* D.s.c. measurements were performed with slices (about 0.5 mm thick) taken parallel to the flow direction from the self-reinforced samples on a Perkin-Elmer DSC-2. The slices were cut at varying distances from the surface. The heating rate was  $5^{\circ}\text{C min}^{-1}$ . Sample weight was about 2.0–2.5 mg.

#### Results and discussion

Figure 2 presents the Young's modulus and yield strength of self-reinforced samples prepared in oscillating stress field at different mould temperature. The Young's modulus and yield strength decrease with increasing the mould temperature. The maximum Young's modulus of 3.5 GPa and yield strength of 87 MPa are achieved at the mould temperature of 47°C. The extent of improvement of mechanical properties of self-reinforced HDPE prepared in oscillating stress field is determined partly by the relaxation of molecular chains which orient in oscillating stress field. When the melt of HDPE is subjected to oscillating stress, the molecular chains tend to orient along the direction of stress. Meanwhile the oriented molecular chains would relax owing to molecular motion. At higher mould temperature, the relaxation time is shorter owing to higher melt temperature. And thus the extent of relaxation of molecular chains is larger. The competition of orientation and relaxation of molecular chains results in the decrease in mechanical performance with increasing the mould temperature. However, different from static stress field in conventional injection moulding which cannot significantly influence the structural formation of PE<sup>11</sup>. Oscillating stress can change the crystallization behaviour of PE and produce a pronounced effect on its mechanical performance.

D.s.c. measurements of self-reinforced HDPE show that there exist different crystal structures as shown in Figure 3. Lower temperature melting peak is due to spherulites and overgrown lamellae in shish-kebab crystals which exhibit lower thermal stability. Higher temperature melting peak is produced by the melting of shish cores of shish-kebab crystals which are more stable. The lower temperature peaks for slices taken from the self-reinforced HDPE hold in the same position as that for virgin. This indicates that the spherulites in self-reinforced HDPE has little change compared to spherulites in virgin.

**Table 2** Fusion heat and content of shish-kebab crystal in self-reinforced HDPE prepared in oscillating stress field

Distance (mm)	Fusion heat (cal g <sup>-1</sup> )	Ratio (%)
Surface	38.95	0.0
0.58	44.38	20
1.14	45.97	49
1.74	47.3	43
Centre	43.94	0.0
Average	44.11	22.0

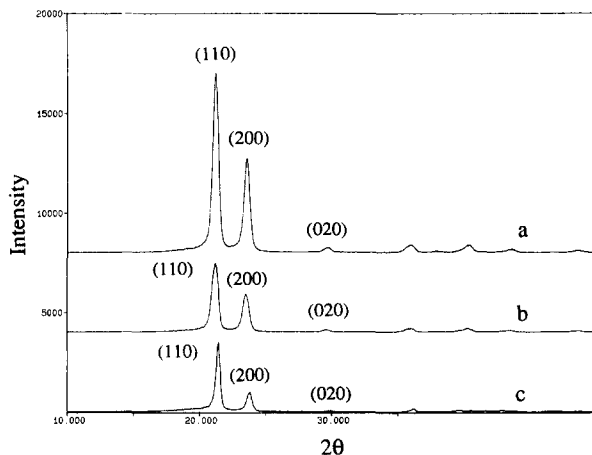
**Figure 4** X-ray curves of conventional injection moulded HDPE sample (c) and oscillating packing injection moulded HDPE sample (a, b). (a) In the plane MT, (b) in the plane MN

Table 2 gives the fusion heat per unit weight of the crystals and content of shish-kebab crystals in slices of self-reinforced HDPE. It shows that shish-kebab crystals are absent at surface and core area, which exist mainly between surface and core. The average content of shish-kebab crystals in self-reinforced HDPE is about 20% which is much higher than that of static stress prepared HDPE. It is the formation of shish-kebab crystals in oscillating stress field that markedly improves the stiffness and yield strength of HDPE.

Figure 4 shows diffraction curves of the samples prepared by oscillating and static stress. It shows that the diffraction intensities of crystallographic planes (110) and (200) increase significantly compared with that of HDPE prepared in static stress field. There exists

preferable orientation in self-reinforced HDPE sample. Previous investigation shows the crystallographic planes (110), (200), and (020) are cylindrically distributed about  $M^1$ . So the C-axes orient parallel to MD. Referring to Figure 4a, b, it is suggested the diffraction of (200) is much stronger in the plane of MT than that in the plane of MN. So crystallographic planes (200) mainly lie in the plane of MT. The A-axes orient along the ND direction. The B-axes orient along the TD direction. The orientation of molecular chains along the MD direction is one of the reasons which contribute to the enhancement of mechanical behaviours of self-reinforced HDPE prepared in oscillating stress field.

#### Conclusion

The mechanical performances of HDPE are significantly improved in oscillating stress field. The improvement of mechanical properties is strongly dependent on the mould temperature. The formation of shish-kebab crystals and the orientation of molecular chains both contribute to the enhancement of mechanical behaviours of self-reinforced HDPE prepared in oscillating stress field. The oscillating stress has profound effect on the properties of HDPE.

#### Acknowledgement

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