Structure and Properties of Self-Reinforced Polyethylene Prepared by Oscillating Packing Injection Molding Under Low Pressure

QING GUAN,[1,*] KAIZHI SHEN,[1] JILIANG JI,[2] and JUMU ZHU[3]

[1]Plastics Engineering Department, Sichuan Union University, Chengdu, Sichuan 610065, People's Republic of China; [2]Taiyuan Mechanical Institute, Taiyuan Shanxi 030051, People's Republic of China; [3]Department of Material Science, Sichuan Union University, Chengdu, Sichuan 610064, People's Republic of China

SYNOPSIS

This article reports the influence of oscillating pressure on the mechanical performance of general-grade high-density polyethylene (HDPE). The tensile strength of 93 MPa and the Young's modulus of 5 GPa were obtained by an oscillating packing technique. The great improvement of the mechanical properties of HDPE specimens is due to the existence of the shish-kebab crystalline structure, the orientation of the molecular chains along the flow direction, and the more perfect crystallites. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In our previous articles,[1,2] the influence of processing parameters on mechanical properties was investigated and the tensile strength of 76.5 MPa and the Young's modulus of 3 GPa of general-grade high-density polyethylene (HDPE) prepared by oscillating packing injection molding under low pressure have been obtained. Initial SEM studies showed that the orientation of molecular chains and microfibril structures exist in the flow direction. In this article, the influence of oscillating pressure on mechanical properties will be discussed. In addition, the structure and morphology of the samples prepared by oscillating packing injection molding will be studied in detail by WAXD, SEM, TEM, DSC, etc., in conjunction with properties.

EXPERIMENTAL

Material

The material used in this work was HDPE grade 7006A produced by Qilu Petrochemical Corp. Its melt flow index was 6.8 g/10 min.

Mold Geometry

A dumbbell specimen mold according to ASTM-638M was used for injection molding. Changes of cavity pressure were monitored by two pressure transducers located at the two sides of the specimens shown in Figure 1.

Injection Molding

The injection-molding machine was an SZ-100g shot thermoplastic injection-molding machine produced by Nanning No. 2 Light Industry Machinery Factory equipped with an oscillating packing device which has been described in Ref. 3. The processing parameters used are listed in Table I.

Tensile Tests

The tensile strength and Young's modulus were measured on an Instron Universal Testing Machine (Model 4302) equipped with a long travel extensometer at 20°C. The crosshead speed was 5 mm/min.

Density Measurement

The measurements of the densities of the specimens were performed using density-gradient columns according to ASTM D1505-85. The temperature of the water bath was $23 \pm 0.5°C$.
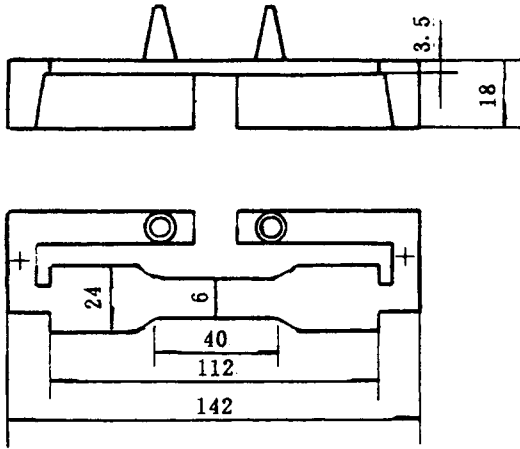
Figure 1 Outlines of the dumbbell molding cavity used in the experiments. The dimensions are in millimeters. The locations of the two pressure transducers are indicated by the crosses.

SEM Investigation

The fracture surfaces of the tensile test were observed on an X-650 Hitachi scanning electron microscope.

X-ray Measurement

The orientations of crystallographic planes of specimens were determined by wide-angle X-ray scattering (WAXS) using a Y-4Q X-ray diffractometer. X-ray diffraction photographs were recorded on flat films by a VEM X-ray diffraction camera. The distance between the specimen and film was 35 mm.[4]

Differential Scanning Calorimetry (DSC)

DSC measurements were performed with slices (about 0.5 mm thick) taken parallel to the flow di-
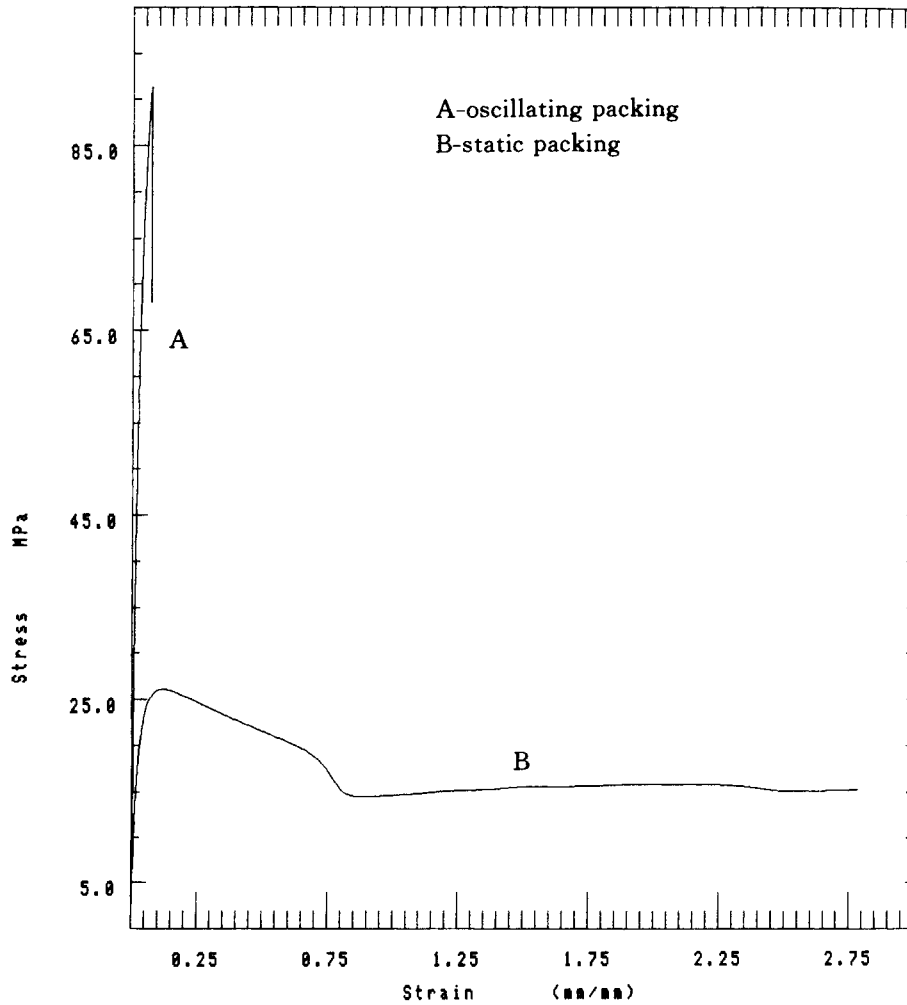

Figure 2 The variations of the stress/strain behavior of the specimens prepared by oscillating packing (curve A) and static packing (curve B). Oscillating pressure: 40 MPa.

Table I Processing Parameters in Oscillating Packing Injection Molding of HDPE

Parameters	Values
Injection pressure (MPa)	41
Packing mode	Mode A[3]
Oscillating packing pressure (MPa)	32, 35, 40, 48
Oscillating frequency (Hz)	0.3
Holding time (min)	4
Melt temperature (°C)	220
Mold temperature (°C)	42

rection from the specimens prepared by oscillating packing injection molding on a Perkin-Elmer DSC-7. The slices were cut at varying distances from the surface. The heating rate was 20°C per min.

Transmission Electron Microscopy (TEM)

Transmission electron micrographs were obtained on a JEM-100CX electron microscope operated at 80 kV. The specimens were stained with chlorosulfonic acid and then using uranyl actate to enhance the contrast.[5,6] The samples were then microtomed using an LKB-V ultromicrotome at superlow temperature.

RESULTS AND DISCUSSION

Figure 2 shows the typical stress/strain curves of specimens prepared by oscillating packing and static packing. Comparison of these two curves suggests that the specimens prepared by oscillating packing break in a brittle manner, whereas the specimens by static packing are ductile. The tensile strength and Young's modulus of the oscillating packing molded samples are much higher than are the ones of static packing molded samples.

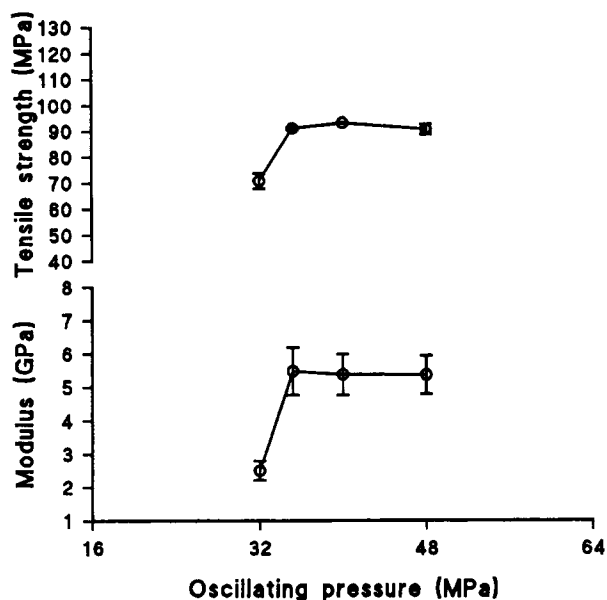The tensile strength and Young's modulus of the

Figure 3 Modulus and tensile strength plotted against oscillating pressure for the specimens prepared by oscillating packing injection molding.

specimens prepared at various oscillating pressures by oscillating packing are shown in Figure 3. As can be seen, the mechanical properties have a pronounced dependence on the oscillating pressure. Increasing oscillating pressure from 32 to 35 MPa produces an apparent increase in the tensile strength and Young's modulus. After that, the influence of oscillating pressure on the mechanical performance is little, which may be that the influence of the oscillating pressure on the orientation is little after the value exceeds a critical value (incidentally, the pressures are far below those required for the formation of the familiar extended-chain crystals).

Table II lists the densities and corresponding crystallinities of the specimens prepared at various oscillating pressures. The tabulated crystallinities are based on $\rho_a = 0.852$ g/cm^3 for the amorphous

**Table II Density and Crystallinity of the Specimens Prepared at Various Oscillating Pressures**

Oscillating Pressure (MPa)	Density for Static Packing (g/cm^3)	Crystallinity for Static Packing (%)	Density for Oscillating Packing (g/cm^3)	Crystallinity for Oscillating Packing (%)
35	—	—	0.9569	71
40	0.9492	66	0.9532	69
48	0.9508	67	0.9560	70

Original density: 0.9504 g/cm^3, crystallinity: 67%.
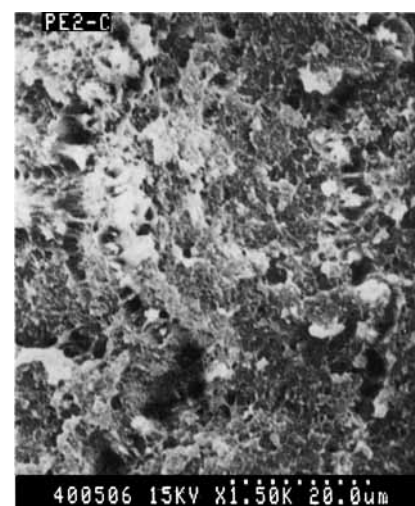
(a)
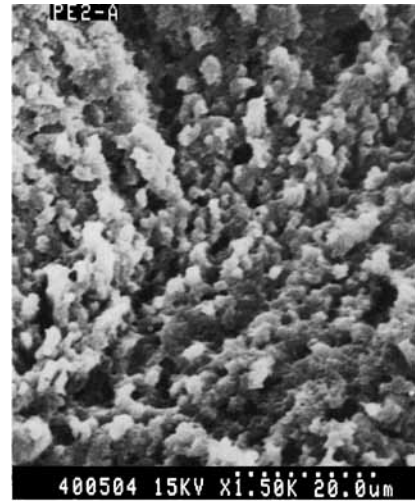
(b)

(c)

(d)

Figure 4   SEM micrographs of the fracture surface of the sample prepared by oscillating packing at oscillating pressure of 40 MPa.
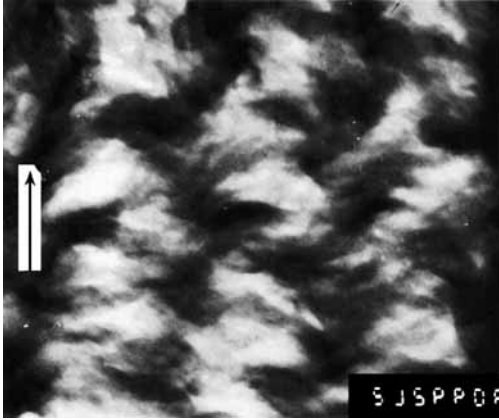
Figure 5 Transmission electron micrographs of thin sections parallel to the flow direction (arrowed). The structure is stained by the kanig technique.

phase and $\rho_c = 1.008$ g/cm^3 for the crystalline phase.[7] Comparison of the densities and crystallinities of the oscillating packing injection-molded specimens with corresponding densities and crystallinities of

the specimens by static packing suggests that the density and crystallinity vary slightly with packing modes. Therefore, in the present case, the tight degree of stacking of molecular chains varies little. The structural features that determine the improvement of the mechanical properties are essentially unaffected by the tight degree of stacking of molecular chains. This feature is an inherent part of the system. The micrographs of the fracture surface observed by SEM are shown in Figure 4. At low magnification, a multilayer structure was observed, which was discussed in Ref. 2. At high magnification, the central zone exhibits a brittle fracture [Fig. 4(d)]. For the shear layers A and B, there exists a microfibril structure. In Figure 4(b) and (c), it is very clear that the microfibrils arrange perpendicularly to the fracture surface, i.e., they orient along the flow direction. The nature of these microfibrils is of shish-kebab crystals, which was revealed by TEM (Fig. 5), with lamellar overgrowths forming the greater part of the material. Here, it should be pointed out the occurrence of shear flow-induced shish-kebab crystals is required for the achievement of high
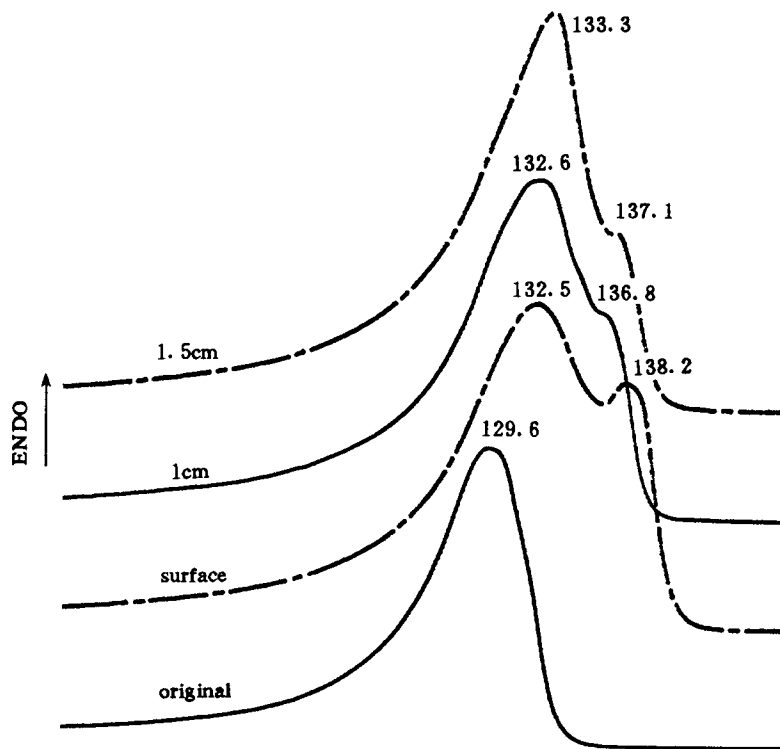

Figure 6 Melting endotherms of polyethylene prepared by oscillating packing injection molding at oscillating pressure of 40 MPa. The distance of slices from the surface is indicated above the curves.

modulus and high strength. But the existence of shish-kebab crystals is, in itself, insufficient.

The formation of different crystalline structures in high-modulus and high-strength injection molding can be demonstrated with the aid of DSC analysis. Figure 6 shows the DSC thermographs of the slices taken parallel to the flow direction from the oscillating packing injection-molded specimen. Referring to Figure 6, two definite melting peaks can be distinguished: a crystalline form exhibiting lower thermal stability at 132°C and a crystalline form
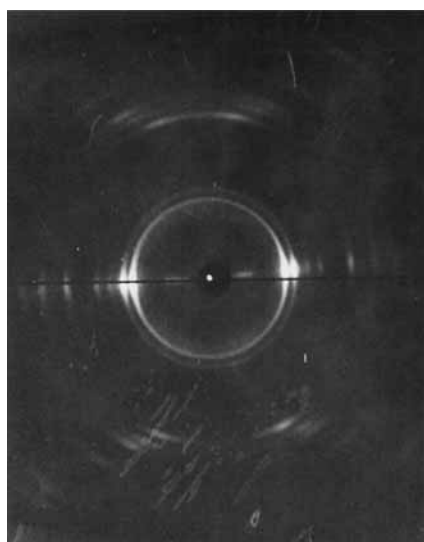
(a)
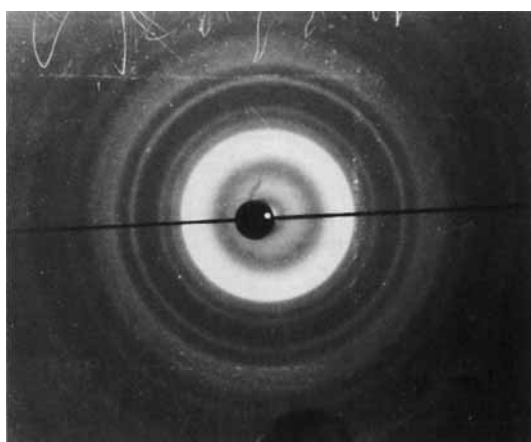
(b)

Figure 7 X-ray diffraction patterns of the specimens prepared by (a) oscillating packing and (b) static packing. Exposure 4 h with nickel-filtered CuKα radiation, 35 kV, 15 mA. The distance of specimen to the flat film is 35 mm.
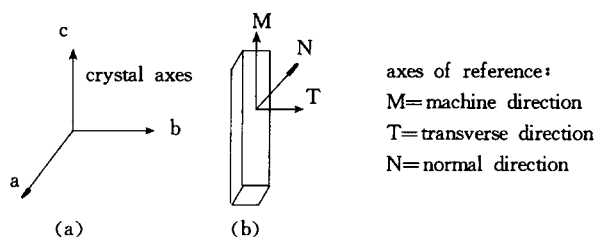

Figure 8 Diagrams of crystal axes and reference axes.

exhibiting higher thermal stability at ~ 137°C. It can be clearly seen that the surface region of the specimen has a higher proportion of the crystalline form exhibiting higher thermal stability. This decreases with increasing distance from the surface, while the crystalline form exhibiting lower thermal stability increases. Comparison of the low-temperature peak with its original melting peak of 129.6°C suggests that the low-temperature peak shifts to a higher temperature of 133°C from the surface to the core and, thus, the corresponding crystalline structure is more perfect than that of original crystals. In addition, the high-temperature peak is absent in the original endotherm. This indicates that the higher-temperature structure was formed during the oscillating packing injection molding.

The results of the DSC analyses show the melting behavior of a high-strength specimen with different crystalline forms. The peak at about 132°C is due to spherulites and individual lamellae in shish-kebab crystals, which are the first to dissolve in the melt, while the peak of about 137°C is due to shear-induced crystals, i.e., the stretched-chain crystals in shish-kebab crystals which melt only at higher temperature.[8]

In general, the amount of shish-kebab crystals in the specimen is not high and this may be partially responsible for the low modulus obtained in comparison with the theoretical value.[9-11] To obtain high modulus and high strength, there must be enough shish-kebab crystals in the specimens. However, it should be noted that here the quantity of shish-kebab crystals is insufficient.[12,13,17]

Figure 7 shows diffraction patterns of the samples prepared by oscillating packing and static packing. From the diffraction patterns, we see that the diffraction effects of the specimen prepared by static packing consist of a number of sharp concentric circles. It indicates that the crystallites are statistically random. The reflections of the specimen prepared by oscillating packing are diffuse and arclike in shape. These diffraction effects arise from the orientation of the crystallites.
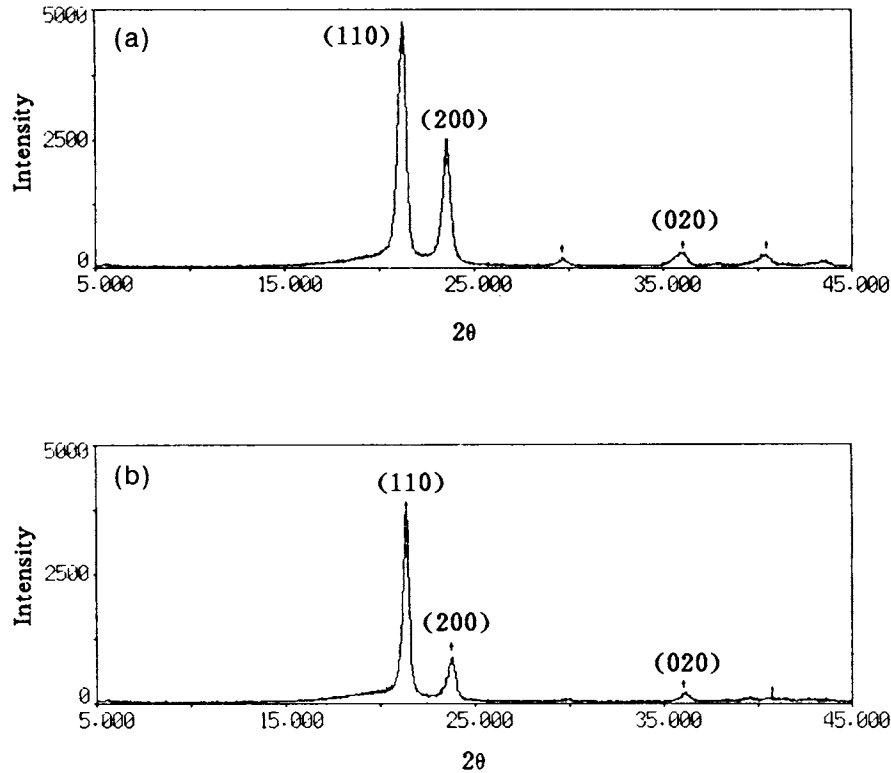
Figure 9   X-ray scattering curves for HDPE prepared by (a) oscillating packing and (b) static packing. The oscillating pressure is 40 MPa.

Any given mode of preferred orientation can be described by specifying the orientation of a crystallographic operator element (axis or plane) with respect to a set of orthogonal axes of reference in the polymer specimen, as shown in Figure 8(a) and (b). The reference axes in the sample, M, T, and N, designate, respectively, the machine (flow), transverse, and normal directions in the customary manner.[14,15,16] From Figure 7(a), the probabilities that the crystallographic planes (110), (200), and (020) are cylindrically distributed about M have increased. The increase in probability is the most apparent for planes (110) and (200). So, the probability that c-axes orient parallel to M has increased. Referring to Figure 9(a) and (b), it is suggested that the intensity of the planes (200) greatly increases. Therefore, the a-axes tend to orient parallel to the N direction. The b-axes tend to orient parallel to T and lie in plane of MT. The c-axes tend to orient parallel to M, i.e., the macromolecular chains of the samples prepared by oscillating packing tend to orient along the flow direction. The orientation of molecular chains in polyethylene is prerequisite for the achievement of high-modulus and high-strength of HDPE.

CONCLUSION

By properly selecting the processing parameters, the mechanical performance of HDPE can be greatly enhanced by oscillating packing injection molding. There exist a multilayer structure and microfibrils in the oscillating packing injection moldings. The nature of the microfibrils is of shish-kebab crystals. The quantity of the shish-kebab crystals varies across the cross section. The c-axis tends to orient along the flow direction. The degree of the improvement of the mechanical properties of HDPE is dependent on the amount of the shish-kebab crystals and the degree of the orientation of the c-axis.

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