Self-Reinforcement of Polypropylene by Oscillating Packing Injection Molding Under Low Pressure

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SYNOPSIS

The influences of processing variables on the mechanical properties of general grade polypropylene prepared by oscillating packing injection molding under low pressure were reported. The density as a function of oscillating holding pressure was measured using density gradient columns. The existence of spherulites and shear-induced shish-kebab crystals was confirmed from DSC measurements. The texture of self-reinforced polypropylene was investigated using an X-ray diffractometer and an X-ray flat film camera. Investigations indicate that the mechanical properties of polypropylene can be greatly enhanced using oscillating packing injection molding. The Young's modulus and tensile strength have been enhanced from original 1.4 GPa, 31.0 MPa to 3.0 GPa, 57.8 MPa, respectively. The improvement in mechanical properties is mainly ascribed to perfect spherulites, the existence of shear-induced shish-kebab crystals, and the orientation of molecular chains. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The self-reinforcement of high-density polyethylene (HDPE) was studied by various kinds of methods, which include drawing from flowing solutions, solid-state extrusion, high-pressure injection molding, etc.[1-4]

Only few studies of the self-reinforcement of polypropylene (PP) are known. M. Prox et al. increased the strength of polypropylene by high pressure injection molding.[5] However, the self-reinforcement is obvious only for high molecular weight polypropylene using high-pressure injection molding.

In our previous studies, it has been shown that the mechanical performance of HDPE can be greatly improved by oscillating packing injection molding under low pressure.[6-8] In this article, the self-reinforcement of general grade polypropylene using oscillating packing injection molding is dealt with.

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EXPERIMENTAL

Material

The material used in this work was injection grade polypropylene 1400 produced by Yanshan Petrochemical Corp. Its melt flow index was about 3 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 pressure transducers located at the two sides of specimen shown in Figure 1.

Sample Preparation

The injection molding machine SZ-100 g shot thermoplastic injection-molding machine equipped with an oscillating packing device, which has been described in ref. 6, was used to prepare samples. A typical process preparing a specimen using oscillat-

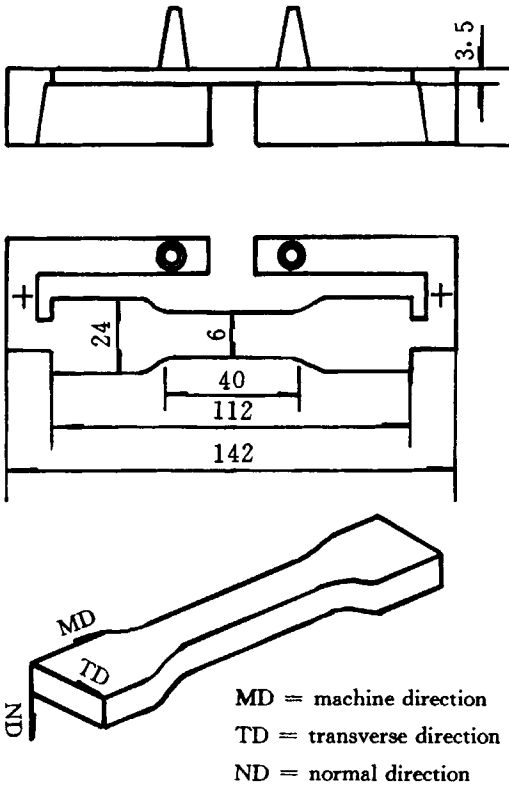

Figure 1 Outlines of the dumbbell specimen and reference axes. The dimensions are in millimeters. The locations of the two pressure transducers are indicated by the crosses.

ing packing injection molding is that when the mold is full, two pistons are activated and apply various modes of packing on the mold cavity for preset time under the control of a microprocessor. Two packing modes were used in the experiments. One is static packing, i.e., the two pistons are driven forth and exert static pressure on the cavity of the mold. The other is oscillating packing, i.e., the two pistons are driven back and forth at the same frequency but with a phase difference of 180°. The constant processing parameters used are listed in Table I.

Table I Values of Constant Processing Parameters

Processing Parameters	Value
Injection pressure (MPa)	83
Maximum holding pressure (MPa)	32
Mould temperature (°C)	42

Design of Experiment

In order to study the effects of oscillating frequency, holding mode, melt temperature, and holding time on the mechanical properties, a two level fractional factorial design was used to design the experiments in this article.[9] Table II is a 2_{IV}^{4-1} design matrix. For the quantitative variables, the low level is denoted by a minus sign, the high level by a plus sign. For a qualitative variable, the two versions are represented by minus and plus signs. The actual values of the four processing parameters studied here are presented in Table III.

Tensile Tests

The tensile tests were performed on an Instron Testing Machine (Model 4302) equipped with long travel extensometer at 20°C. The crosshead speed was 50 mm/min.

Density Measurement

The measurements of the densities of the specimens were performed using density gradient columns ac-

Table II A 2_{IV}^{4-1} Fractional Factorial Design

	Oscillating Frequency (Hz)	Holding Mode	Melt Temperature (°C)	Holding Time (min)
Experiment	1	2	3	4
1	−	−	−	−
2	+	−	−	+
3	−	+	−	+
4	+	+	−	−
5	−	−	+	+
6	+	−	+	−
7	−	+	+	−
8	+	+	+	+

Table III Values of Processing Variables Used in 2_{IV}^{4-1} Fractional Factorial Design

Processing Variables	High Level (+)	Low Level (−)
Oscillating frequency (Hz)	1	0.3
Holding mode	Oscillating packing	Static packing
Melt temperature (°C)	240	210
Holding time (min)	4	3

cording to ASTMD1505-85, The temperature of the water bath was kept at 23 ± 0.5°C.

SEM Investigation

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

X-Ray Measurement

The orientations of crystallographic planes of self-reinforced specimen were determined by wide-angle X-ray diffraction (WAXD) using a Y-4Q x-ray diffractometer. X-ray diffraction patterns were recorded on flat films by a VEM X-ray diffraction camera. The distance of specimen to the film was 35 mm.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed with slices (about 0.2 mm thick) taken parallel to the flow direction from the specimen 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.

RESULTS AND DISCUSSION

Table IV presents the average values for all 2_{IV}^{4-1} fractional factorial experiments. According to Table IV, by properly choosing the values of processing variables, the tensile strength of about 53 MPa could be obtained by oscillating packing injection molding under low pressure.

The main effect for each of the four processing variables and the interaction effects on tensile strength are shown in Figure 2. Comparison with standard error suggests that oscillating frequency and holding mode have influences on tensile strength. Interaction of oscillating frequency with holding time and interaction of oscillating frequency with holding mode exist. However, compared to holding mode, the influences of oscillating frequency and its interaction with other variables are not obvious.

The effect of holding mode is to greatly increase the tensile strength with the change of the holding mode from static packing to oscillating packing.

With the above results in mind, in the following study, the effect of oscillating pressure on the mechanical performance of polypropylene has been investigated. The relationship between oscillating pressure and the mechanical properties of the specimens prepared by oscillating packing injection molding are shown in Figure 3. As can be seen, oscillating pressure has little influence on stiffness and tensile strength. In present case, the stiffness of 3.0 GPa and the tensile strength of 57.8 MPa were obtained by oscillating packing injection molding. Compared with its original tensile strength of 31.0 MPa, the tensile strength of the oscillating packing injection molded specimens has been increased by about 86%. The stiffness increases from its original 1.4 GPa to about 3.0 GPa.

Figure 4 is the typical stress–strain curves for the specimens prepared by static packing injection molding and oscillating packing injection molding. As can be seen, the elongation of the specimen prepared by oscillating packing injection molding dramatically decreases. They exhibit a brittle break, whereas the specimens prepared by static packing injection molding are ductile.

Table IV Average Tensile Strength

Experiment	Tensile Strength ± Standard Error (MPa)
1	35.2 ± 0.6
2	35.3 ± 0.4
3	50.7 ± 1.3
4	47.3 ± 2.3
5	34.7 ± 0.5
6	34.0 ± 0.7
7	52.9 ± 0.3
8	49.5 ± 0.7

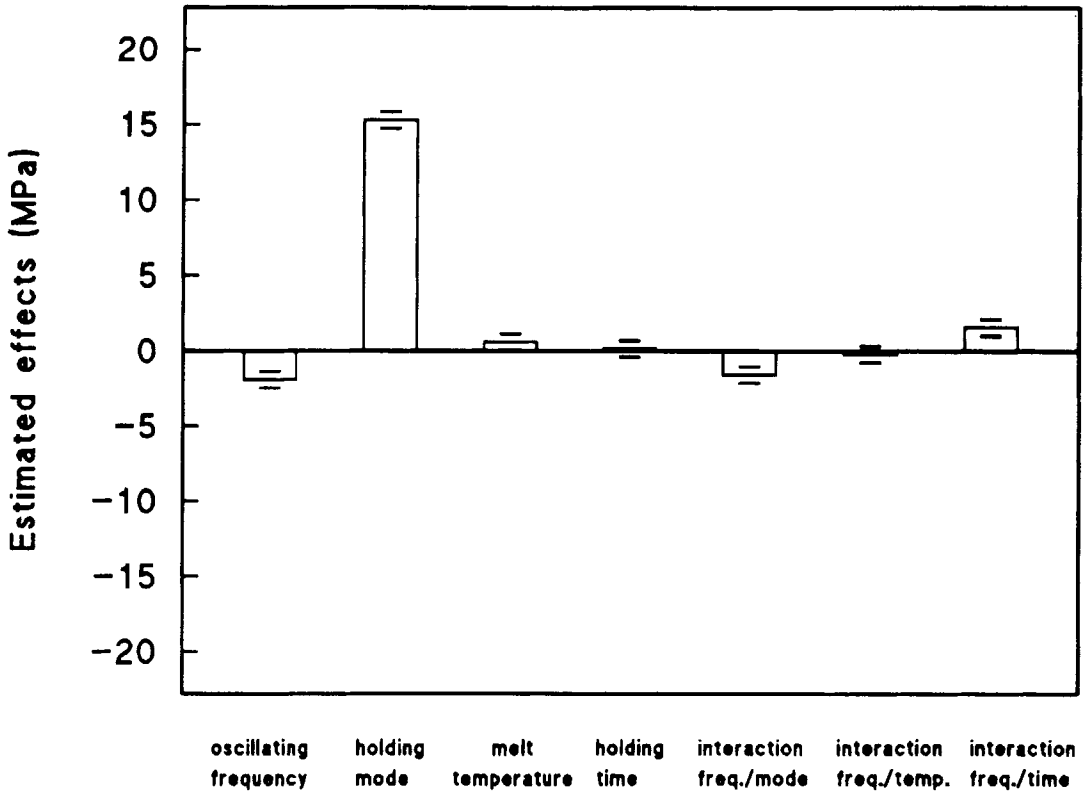

Figure 2 Estimated effects of main effects and interactions on the tensile strength.

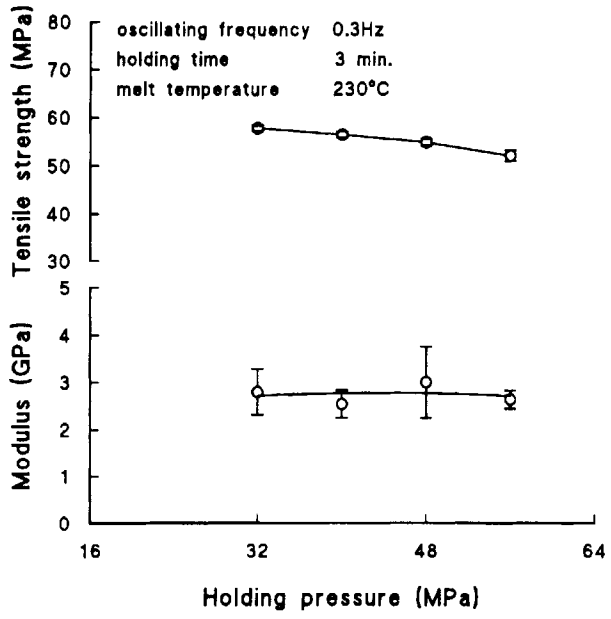

Figure 3 Modulus and tensile strength plotted against holding pressure for the specimens prepared by oscillating packing injection molding.

Scanning electron micrographs of fracture surface of the specimen prepared by oscillating packing injection molding also reveal a typical fracture surface of brittle failure, as shown in Figure 5. At lower magnification [Fig. 5(a)], it is clear that the fracture surface exhibits a multilayer structure that has been observed in molding HDPE by oscillating packing.[6] Three basic layers can be distinguished. Close to the surface is a skin layer, which is oriented due to elongational flow.[10] After the skin layer comes the shear layer, which itself is a multilayer structure and oriented by the shear stress during oscillating packing. This kind of multilayer structure is characteristic of oscillating packing injection moldings. Next comes the core layer, which is expected to have lower order. But under the case of oscillating packing, the center core is mainly composed of shish-kebab crystals, which is shown in DSC measurements.

The improvement in mechanical properties of the specimens prepared by oscillating packing injection molding indicates that the morphology underlying must be different from that by static packing.

Table V lists the densities and corresponding

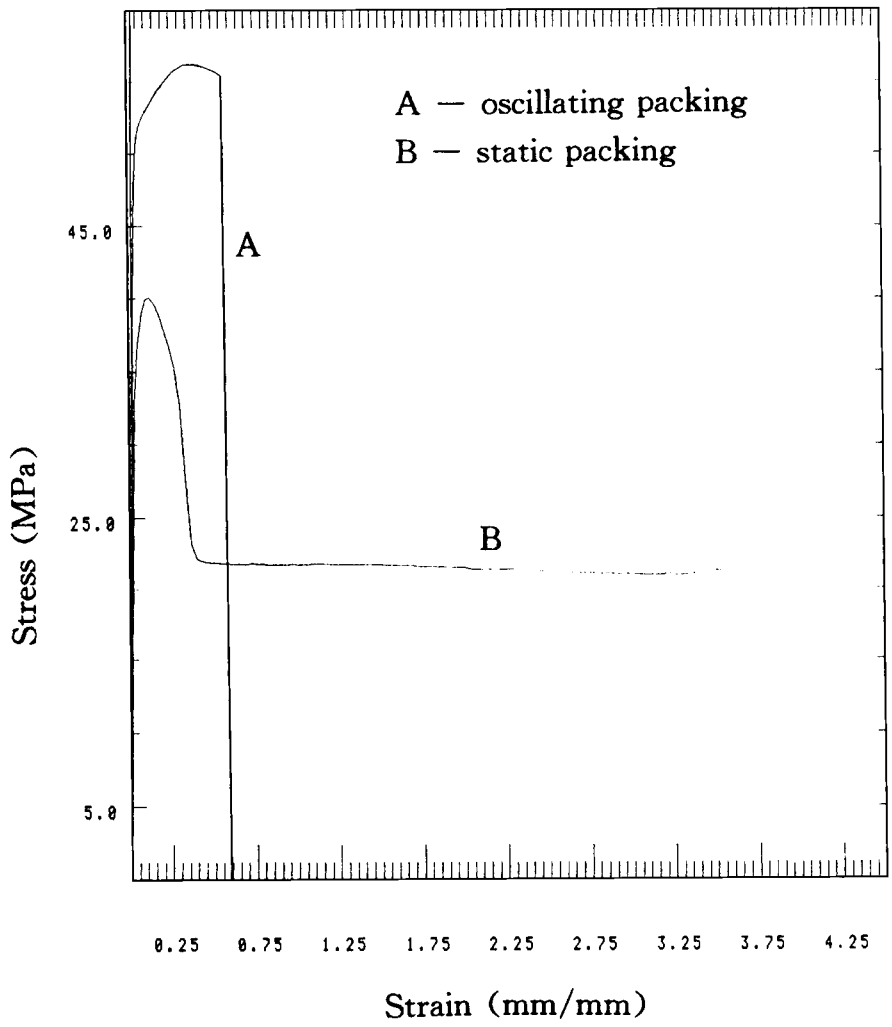

Figure 4 The variations of the stress/strain curves of the specimens prepared by oscillating packing injection molding and static packing injection molding.

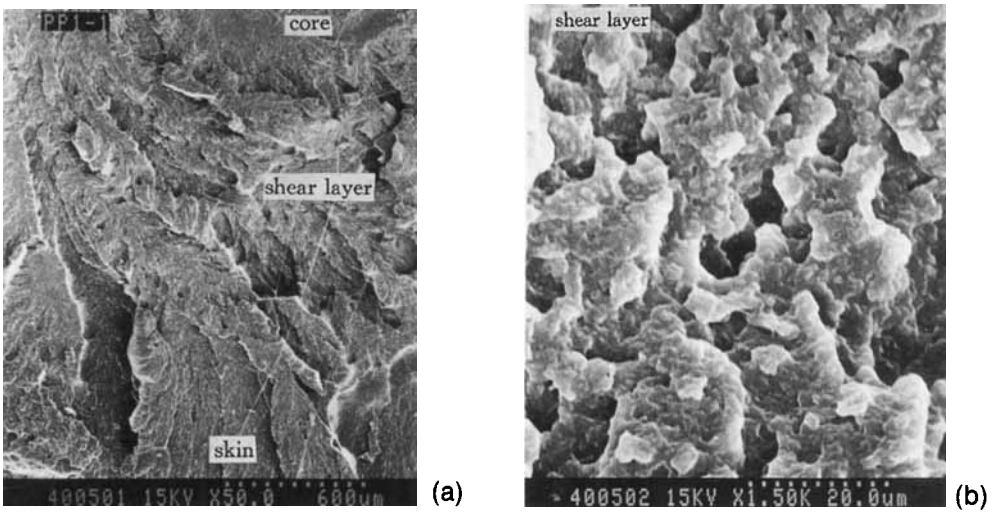

Figure 5 SEM micrographs of fracture surface of the sample prepared by oscillating packing injection molding.

Table V Density and Crystallinity of the Oscillating Packing Injection Molded Polypropylene at Various Oscillating Pressures

Oscillating Pressure (MPa)	Density (g/cm^3)	Crystallinity (%)
32	0.9067	67
40	0.9077	68
48	0.9079	68
56	0.9045	64
64	0.9106	71

Original density: 0.9014 g/cm^3, crystallinity: 61%.

crystallinities of the samples prepared by oscillating packing injection molding at various oscillating pressures. The tabulated crystallinities are based on ρ_a = 0.85 g/cm^3 for the amorphous phase and ρ_c = 0.938 g/cm^3 for the crystalline phase.[11] It shows that the crystallinity has some increase compared with its original crystallinity. This indicates that the tight degree of stacking of molecular chains has been increased. The increase of the tight degree of stacking is partly responsible for the improvement of the mechanical performance, but the influence is not prominent.

Figure 6 shows the DSC endotherms of the specimen prepared by oscillating packing injection molding. Similar to the result observed for self-reinforced high-density polyethylene, double peaks, one at ~ 163°C, the other at ~ 170°C, were observed. The peak at low temperature is due to spherulites, which are classic crystalline structure crystallizing

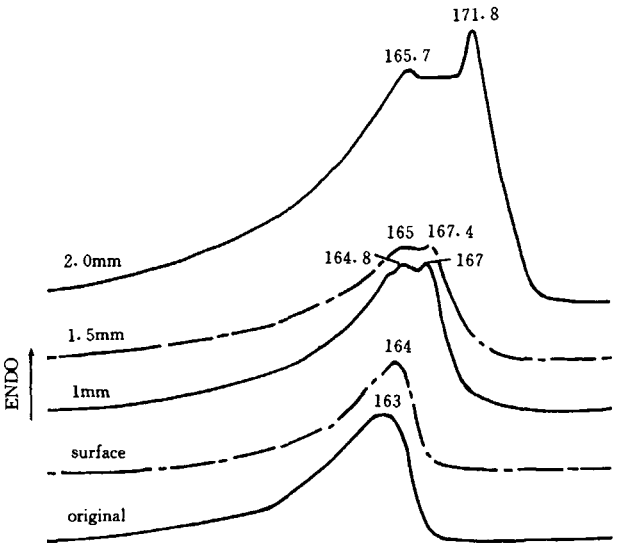

Figure 6 Melting endotherms of the sample prepared by oscillating packing injection molding. The distance of slices from the surface is marked above the curves.

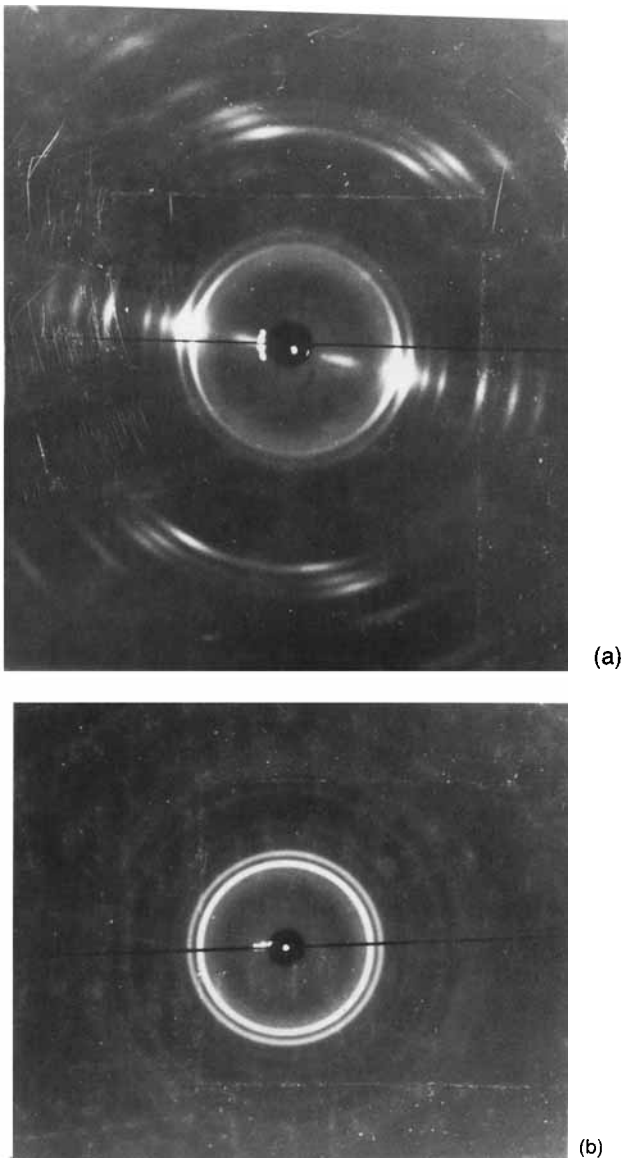

Figure 7 X-ray diffraction patterns of the specimens prepared by oscillating packing (a) and static packing (b). Exposure 4 h. With nickel-filtered CuKα radiation, 35 kV, 15 mA. The distance of specimen to the film is 35 mm.

from melt, whereas the peak at high temperature is due to shear flow induced shish-kebab crystals. First, comparison of low temperature peak with its original melting peak 160°C suggests that the low temperature peak shifts towards higher temperature from the surface to the core of the specimen. This indicates that the spherulites in the specimen prepared by oscillating packing are more perfect than its original spherulites. Next, the high temperature peak was not observed in original endotherm. For a sample prepared by oscillating packing, the high temperature peak is more and more pronounced from the surface to the core. Its intensity become stronger and stronger. At the core region, the quantity of high temperature structure—shish-kebab crystals—is quite large. It is more perfect spherulites and the production of shish-kebab crystals that contribute greatly to the improvement of the mechanical properties of self-reinforced polypropylene.

Figure 7 shows diffraction patterns of the specimens prepared by oscillating packing and static packing. Referring to Figure 7, 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 arc-like in shape. This diffraction effect arises from the orientation of the crystallites.

Any given mode of preferred orientation can be described by specifying the orientation of a crystallographic operator element (axis/plane) with respect to a set of orthogonal axes of reference in the polymer specimen, as shown in Figure 1. The reference axes in the sample, MD, TD, and ND, designate, respectively, the machine (flow), transverse, and normal directions in the customary manner. The diffraction spots can be indexed on a monoclinic unit cell of the α-form, with parameters given in Table VI.[12] The strong reflections on the equatorial layer line have indices (110), (040), (130), (060), and (220) in order of increasing distance from the center. Figure 7 shows that (040) and (060) reflections are present close to the equator only and other reflections are diffuse. Thus, crystallite b axes orient approximately perpendicular to MD, i.e., flow direction, while the c axes orient parallel to MD.

Table VI Unit-Cell Parameters for Isotactic Polypropylene

a = 6.65 Å
b = 20.96 Å
c = 6.50 Å
β = 99.3°

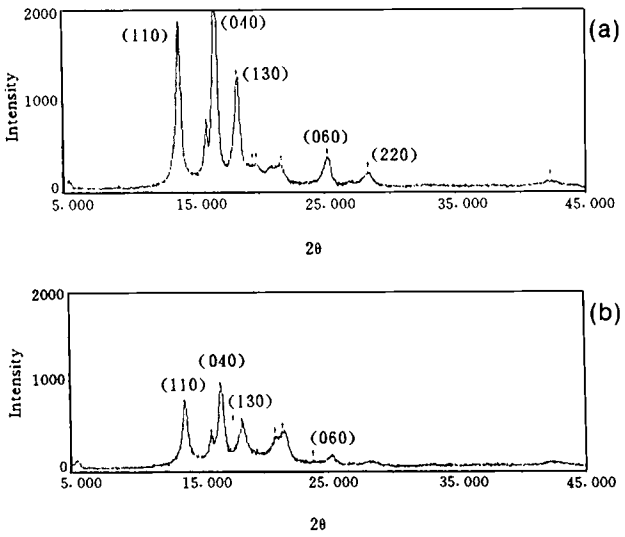

Figure 8 X-ray wide-angle scattering curves for the specimens prepared by oscillating packing (a) and static pacing (b).

Comparison of Figure 8(a,b) suggests that the intensity of the planes (040) increases a lot. Thus, the b axes orient not only perpendicular to MD, but also perpendicular to the plane of MD-TD. The a axes lie in the plane of MD-TD. Just like the case of oscillating packing injection molded self-reinforced HDPE, the highly orientation of the molecular chains along the flow direction is one of factors that should be responsible for the enhancement in mechanical performance of polypropylene.

CONCLUSIONS

By using oscillating packing injection molding, the self-reinforcement of general grade polypropylene can be achieved under low pressure. The holding mode has strong influence on the mechanical performance of self-reinforced polypropylene. The Young's modulus and tensile strength of the specimen prepared by oscillating packing injection molding have been significantly enhanced. The other processing variables such as oscillating frequency, melt temperature, holding time, and their interactions have little influence on the mechanical properties. The self-reinforcement of polypropylene under the action of oscillating shear stress is ascribed to the production of shear-induced shish-kebab crystals, the high orientation of c axes along the flow direction, and the perfect spherulites.

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