

Mechanical Properties and Structure of High-Density Polyethylene Samples Prepared by Injection Molding with Low-Frequency Vibration

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ABSTRACT: To better understand the formation of different crystal structures and improve the mechanical properties of high-density polyethylene samples, melt vibration technology, which generally includes shear vibration and hydrostatic pressure vibration, was used to prepare injection samples. Through melt vibration, the crystal structure changed from typical spherulites of the traditional injection sample to obviously orientated lamellae of vibration samples. Sizes and orientation degrees of lamellae were different according to different vibration conditions. Crystallinity degrees of

vibration samples increased notably. Therefore, the tensile strength of vibration samples increased with increasing vibration frequency and vibration pressure, whereas elongation of vibration samples decreased during the first stage and then continued to increase as the vibration frequency increased. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 818–823, 2005

Key words: high-density polyethylene (HDPE); melt vibration; mechanical properties; crystal structures; spherulites

INTRODUCTION

The performance of semicrystalline polymers is closely related to its final crystal structure and morphology. The mechanical properties of polymer injection products can be improved by controlling their structure. For example, Bevis,^{1,2} Shen et al.,³ and other authors used an oscillation technique to control the molecular orientation and crystal morphology to enhance the mechanical performance. Ibar^{4,5} adopted rheomolding technology to investigate the change in mechanical properties and crystallinity of polypropylene. To better understand the structure and mechanical properties of high-density polyethylene (HDPE) under vibration, we designed an injection machine with vibration equipment to carry out pressure vibration experiments. Results indicate that the crystal structure of the vibration samples is very different from that of the static sample, and the mechanical properties are significantly enhanced under low-frequency vibration.

EXPERIMENTAL

Materials

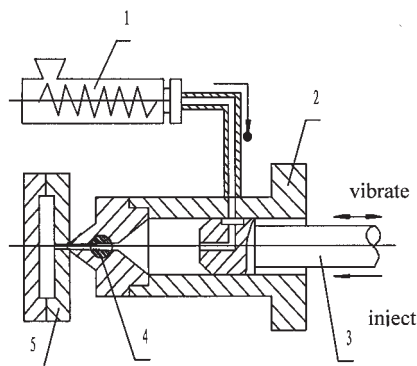
HDPE DGDA6098 (MW = 21×10^4 , melt flow index = 0.4 g/min), used in the experiment, was a commercial product from Qi Lu Petrochemical Corp. (Hong Kong, China).

Preparation and characterization of samples

A schematic representation of the melt vibration injection apparatus is shown in Figure 1, and schematic drawings of injection samples are shown in Figure 2. First, HDPE was uniformly molten at designated temperatures. Then the melt was injected into the mold. A pulsation pressure was introduced during both stages of injection and packing, which caused the melt vibration to oscillate at certain frequencies and pressures. The processing parameters are listed in Table I. We can vary three parameters: melt temperature (T); frequency (f); and vibration pressure (Pv), which represents the maximum value of the pulsation pressure. We also carried out injection molding under static packing (no vibration) by using the same processing parameters, except for pulsation pressure for the purpose of comparison. The specimen obtained by vibration injection molding was designated the vibration sample, and the specimen obtained by static injection molding was designated the static sample.

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1-plasticizing equipment, 2-barrel,
3-vibrating and injecting piston, 4-valve, 5-injection mold

Figure 1 Schematic representation of vibration injection molding.

Tensile testing

A Shimadzu universal testing machine (Model AG-10TA, Shimadzu, Kyoto, Japan) was used for tensile testing at room temperature (23°C), at a crosshead speed of 50 mm/min.

SEM measurement

A Hitachi scanning microscope (Model S-450, Hitachi, Osaka, Japan) was used for SEM measurements. The specimens were gold-sputtered after being etched in a solution of $\text{KMnO}_2\text{-H}_3\text{PO}_4\text{-H}_2\text{SO}_4$. The temperature of specimens at every test step was strictly controlled at <45°C.

DSC measurement

A computerized Perkin-Elmer differential scanning calorimeter (Model Pyris 1, Perkin Elmer Cetus Instruments, Norwalk, CT) was used for DSC measurements. The specimens were weighed in the range 3–5 mg. During the measurement, dried N_2 gas was purged at a constant flow rate. The heating rate was 10

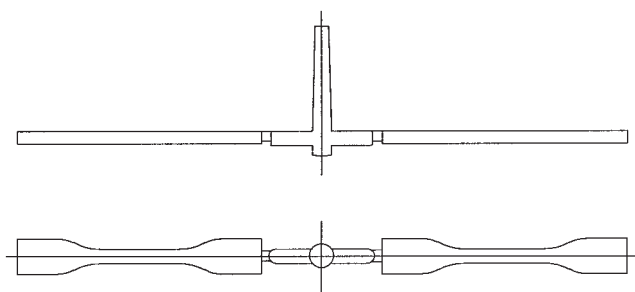


Figure 2 Schematic drawings of injection samples.

TABLE I
Processing Parameters in Vibration Injection Molding

Processing parameter	Parameter value
Injection pressure, MPa	40
Packing pressure, MPa	40
Melt temperature, °C	200/220/240
Mold temperature, °C	40
Vibration pressure, MPa	0–75
Vibration frequency, Hz	0–2
Vibration time, s	20

K/min. The temperature reading and calorific measurement were calibrated by using standard indium.

RESULTS AND DISCUSSION

Mechanical properties

Figure 3 shows the effect of vibration frequency on tensile strength and elongation, at a vibration pressure of 35 MPa. One observes that the tensile strength of vibration samples increases with increasing vibration frequency. The maximum increment of tensile strength is 28.0%, from 41.0 MPa of the static sample to 51.5 MPa of the sample obtained at highest vibration frequency at 200°C. The elongation of vibration samples decreases, although elongation of samples obtained at high vibration frequency increases, which may indicate that samples will become tough when the vibration frequency reaches a certain range.

Figure 4 shows the effect of vibration pressure on tensile strength and elongation, at a vibration frequency of 0.5 Hz. The tensile strength of vibration samples increases with increasing vibration pressure. When the vibration pressure reaches its largest value, the tensile strength has a maximum increment. For example, the tensile strength of the vibration sample obtained at $T = 200^\circ\text{C}$ and $Pv = 75$ MPa, which is 57.8 MPa, increases by 41% compared with that of the static sample obtained at the same temperature, which is 41.0 MPa. At the same time, elongation of the vibration samples decreases with increasing vibration pressure.

To determine the correct vibration time, we also carried out experiments of vibration time versus tensile strength. Figure 5 shows the experimental results, carried out at a vibration frequency of 1 Hz and vibration pressure of 35 MPa. The tensile strength increases as vibration time increases when the vibration time is <20 s, whereas the tensile strength remains consistent when the vibration time is >20 s.

SEM analysis

The micrograph of the static sample obtained by SEM measurements, which is shown in Figure 6, indicates

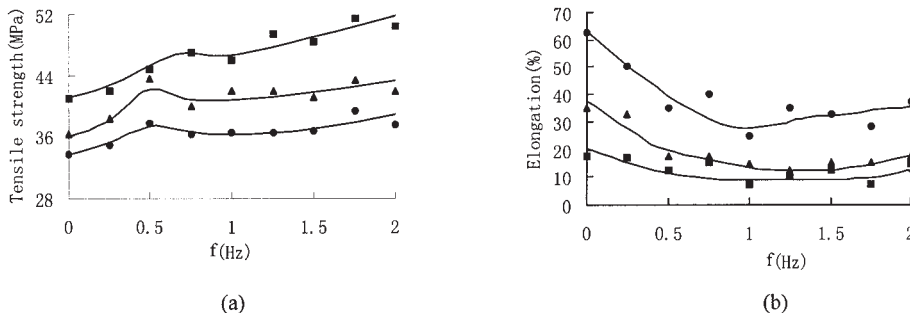


Figure 3 Effect of vibration frequency on tensile strength and elongation (■, $T = 200^\circ\text{C}$; ▲, $T = 220^\circ\text{C}$; ●, $T = 240^\circ\text{C}$).

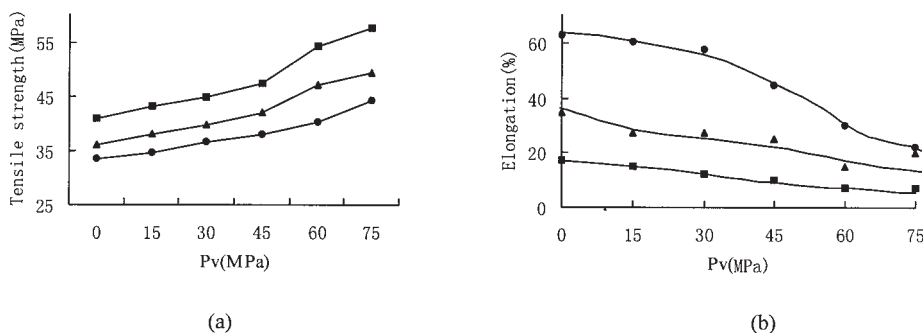


Figure 4 Effect of vibration pressure on tensile strength and elongation (■, $T = 200^\circ\text{C}$; ▲, $T = 220^\circ\text{C}$; ●, $T = 240^\circ\text{C}$).

that the crystal structure of the HDPE sample, molded using the traditional method, typically constitutes spherulites that are about 1–1.5 μm in size and consist of many platelets, reflecting a disorderly distribution in all directions.

Figure 7 and Figure 8 show SEM micrographs of samples obtained at $T = 200^\circ\text{C}$, $f = 2$ Hz, and $Pv = 35$ MPa and $T = 200^\circ\text{C}$, $f = 0.5$ Hz, and $Pv = 75$ MPa. Instead of spherulites, the crystal structures of both samples constitute lamellae that are obviously orientated along the melt flow direction. By comparing these two figures, one observes that the orientation degree of lamellae of the sample obtained at higher vibration frequency (2 Hz) is lower, whereas the size of lamellae is smaller. At the same time, the orienta-

tion degree of lamellae of the sample obtained at higher vibration pressure (75 MPa) is higher, whereas the size of lamellae is larger. The lamellae are interlocked with each other to a certain extent, which indicates that high vibration pressure will foster the arrangement of polymer chains to form large lamellae, and high vibration frequency will foster an increase in the amount of lamellae.

DSC analysis

The DSC heating curves of samples are shown in Figure 9 and Figure 10. Compared with the widths of

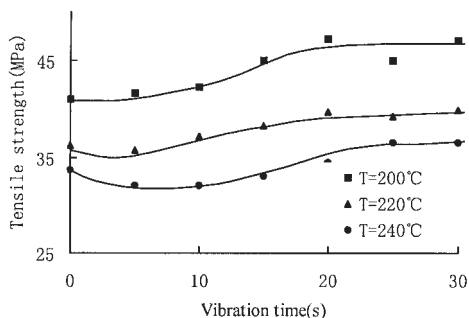


Figure 5 Effect of vibration time on tensile strength (■, $T = 200^\circ\text{C}$; ▲, $T = 220^\circ\text{C}$; ●, $T = 240^\circ\text{C}$).

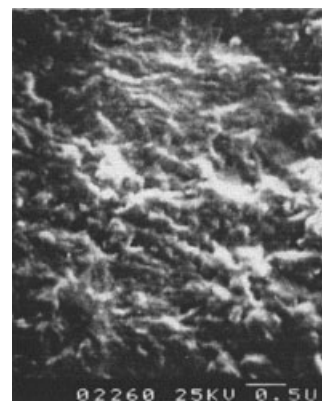


Figure 6 SEM micrograph of static sample (\rightarrow melt flow direction).

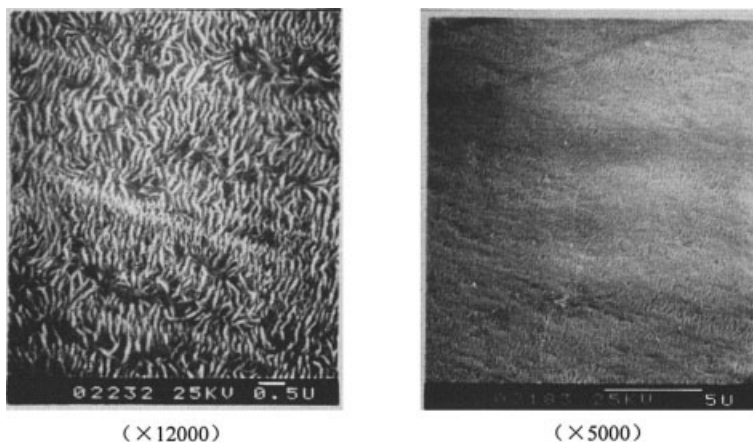


Figure 7 SEM micrographs of vibration sample obtained at $T = 200^{\circ}\text{C}$, $f = 2$ Hz, and $Pv = 35$ MPa (\rightarrow melt flow direction).

melting peaks of the static samples [Figs. 9(a) and 10(a)], those of the vibration samples with high vibration frequency [Figs. 9(b) and 10(b)] or vibration pressure [Figs. 9(c) and 10(c)] are broader. Melting points of samples with high vibration frequency are higher than others, which indicates that the crystal structures of those samples are more perfect.

It may also be observed in Figure 9 and Figure 10 that fusion heats of samples, prepared at different vibration conditions, are very different. The relationship of fusion heat and crystallinity degree is as follows:

$$\alpha_c = \frac{\Delta H_f}{\Delta H_{f\alpha}} \times 100\%$$

where α_c is the crystallinity degree; ΔH_f is the fusion heat of samples; and $\Delta H_{f\alpha}$ is the fusion heat of sample with 100% crystallinity degree, which is about 273 J/g for HDPE.⁶

DSC results were calculated and are listed in Table II. Crystallinity degrees of vibration samples, especially samples with high vibration pressure, are higher than those of static samples. The result shows that vibration will increase the crystallinity degree, which has a larger increment when the vibration pressure is higher.

CONCLUSION

Vibration develops a pulsation pressure on the polymer melt in the mold cavity. The pressure produces a "press-and-release" effect on the melt because of its viscoelasticity. Thus, unlike traditional injection molding, there are continuous shear stresses even between the inner layers of a sample during both stages of injection and packing, which induce crystal structure and mechanical properties of vibration samples that are very different from those of static samples. The crystal structure of static samples typically constitutes

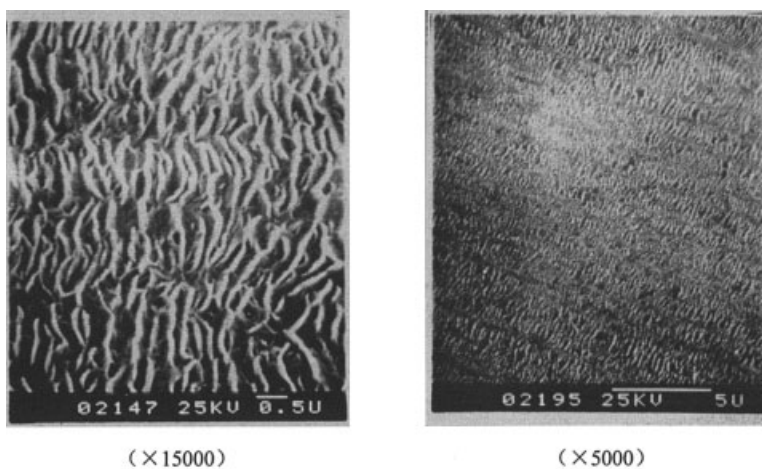


Figure 8 SEM micrographs of vibration samples obtained at $T = 200^{\circ}\text{C}$, $f = 0.5$ Hz, and $Pv = 75$ MPa (\rightarrow melt flow direction).

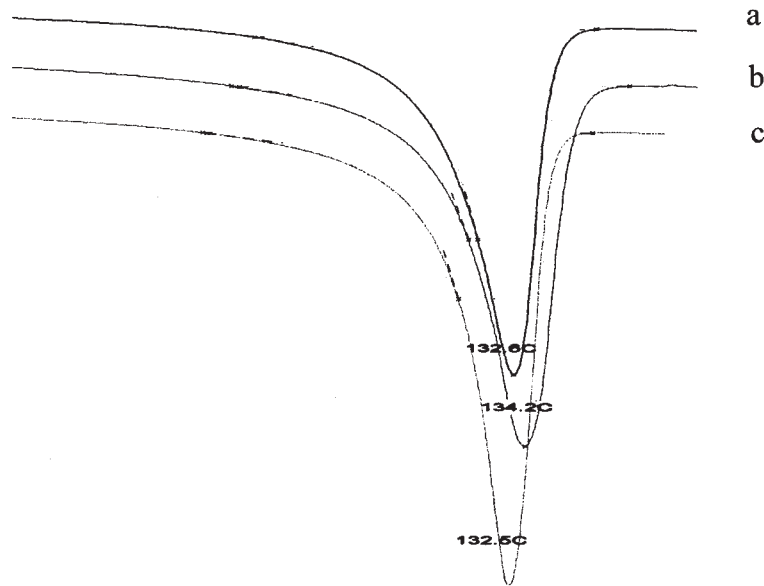


Figure 9 DSC heating curves of samples obtained by vibration injection molding at 200°C: (a) static sample; (b) $f = 2$ Hz, $Pv = 75$ MPa; (c) $f = 0.5$ Hz, $Pv = 75$ MPa.

spherulites, whereas the crystal structure of vibration samples constitutes lamellae that are orientated along the melt flow direction. According to vibration conditions, the sizes and orientation degrees of lamellae of vibration samples are different. When the vibration frequency is high, the lamella size is small and the orientation degree is low; when the vibration pressure is high, the lamella size is large and the orientation degree is high. Furthermore, vibration molding will

change the crystallinity degrees of HDPE samples. Crystallinity degrees of vibration samples substantially increase compared with those of static samples. Vibration intensity will increase when both the vibration frequency and the vibration pressure increase. As a result, the tensile strength of vibration samples increased with increasing vibration frequency and vibration pressure. It is clear that higher vibration pressure will promote a stronger “press-and-release” ef-

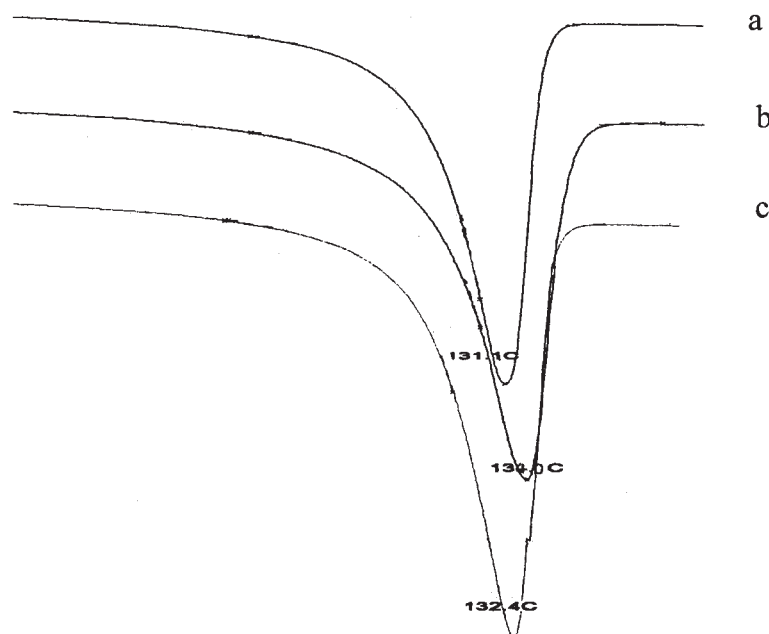


Figure 10 DSC heating curves of samples obtained by vibration injection molding at 240°C: (a) static sample; (b) $f = 2$ Hz, $Pv = 75$ MPa; (c) $f = 0.5$ Hz, $Pv = 75$ MPa.

TABLE II
DSC Results

Sample	Temperature (°C)	f (Hz)	Pv (MPa)	Melting point	ΔH_f (J/g)	α_c (%)
1	200			132.6	145.34	53.2
2	200	2	35	134.2	164.84	60.4
3	200	0.5	75	132.5	172.77	63.3
4	240			131.1	149.06	54.4
5	240	2	35	134.0	155.99	57.1
6	240	0.5	75	132.4	169.84	62.2

fect, so the mechanical properties of the sample obtained at the highest vibration pressure are the best. The elongation of vibration samples is decreased because orientation will decrease the toughness of the samples. As the vibration frequency reaches a certain

range, however, elongation will increase because crystallites of vibration samples will become smaller under high vibration frequency.

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