Improving the Mechanical Properties of Polypropylene via Melt Vibration

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ABSTRACT: The effect of melt vibration on the mechanical properties of polypropylene prepared by low-frequency vibration-assisted injection molding (VAIM) has been investigated. With the application of melt vibration technology, the mechanical properties of polypropylene are improved. The yield strength increases with the increment of the vibration frequency, and a peak stands at a special frequency for VAIM; the elongation at break decreases first and then increases with increasing vibration frequency, and a valley stands at a special frequency. The tensile properties increase sharply at an enlarged vibration pressure amplitude with sharply decreased elongation at break. The Young's modulus and impact strength also increase with the vibration frequency and pressure vibration amplitude. When it is prepared at 59.4 MPa and 0.7 Hz, the maximal yield strength is approximately 40 MPa versus 33.7 MPa for a conventional sample; an 18.7% increase in the tensile strength is produced. Self-reinforcing and self-toughening polypropylene molded parts have been found to be prepared at a high vibration frequency or at a large pressure vibration amplitude. Scanning electron micrographs have shown that, in the vibration field, the enhancement of the mechanical properties is attributable to more pronounced spherulite orientation and increased crystallinity in comparison with conventional injection moldings. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 90–96, 2008

Key words: injection molding; mechanical properties; orientation; poly(propylene) (PP)

INTRODUCTION

As is well known, polypropylene (PP) has a good combination of properties but low impact ductility at low temperatures. It is important to prepare PP that is both self-reinforced and self-toughened. Recently, the vibration energy introduced into polymer processing has been found to affect the molecular movement and rheological behavior of the polymer melt, and this affects the mechanical properties of the final products. To date, several types of melt vibration techniques[1–11] have been investigated. Ibar[1,2] introduced vibration into injection molding when PP was molded. The results showed that the elongation rose 80%, and the yield strength and modulus were increased greatly. Allen and Bevis[3–5] used their invention of the multi-live feed molding apparatus to introduce shearing oscillation into the melt flow within the cavity and found that it increased the strength of molded parts and eliminated the effect of weld lines. Isayev and coworkers[6,7] reported that during extrusion high-intensity ultrasonic waves affected the die characteristics by reducing the pressure and extrusion swelling and postpone melt fracture. Keishiro[8] applied 20–100-kHz ultrasound waves in a direction vertical to the rubber discharging direction through an extrusion and obtained rubber sheets with low extrusion swelling occurrence and good dimensional accuracy. It was also found that the ultrasonic vibrations had a good effect on the structure and performance of polymer composites. Khamad[9] reported that the application of ultrasound to high-density polyethylene melts containing a small amount of butyl rubber resulted in an increase in the crystallinity, a reduction in structural defects, and an enhancement of the mechanical properties. Peshkovskii[10] discovered that the average size of fillers was smaller and the size distribution was more homogeneous with ultrasonic treatment than without ultrasonic treatment in kaolin-clay-filled high-density polyethylene. Using the vibration-assisted injection molding (VAIM) process, Coulter et al.[11] indicated that the degree of strength improvement depended on at least four parameters, namely, the vibration frequency, vibration ampli-
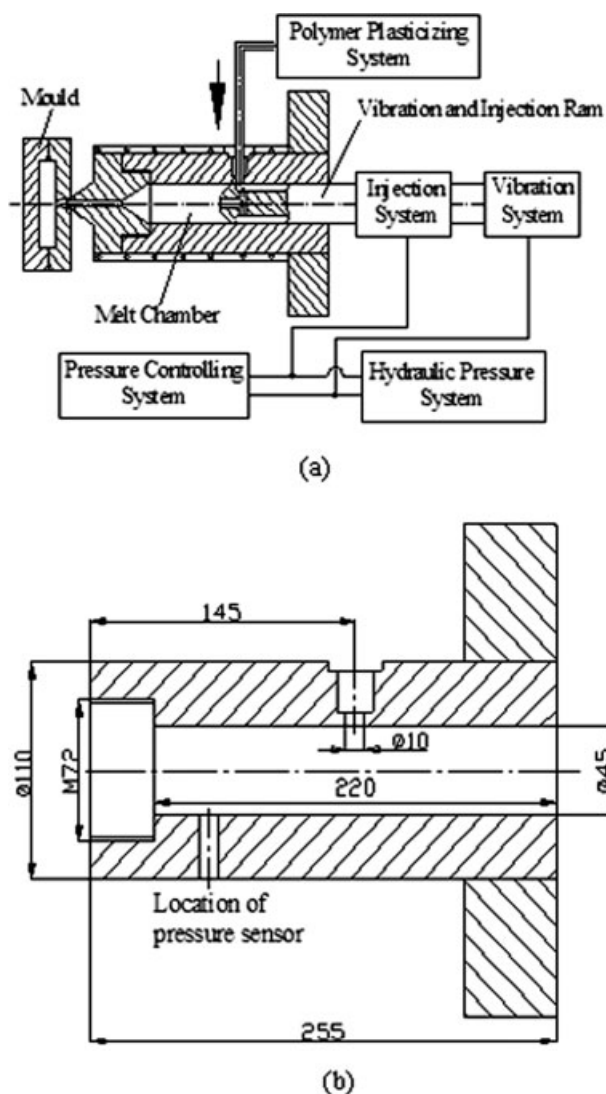
Figure 1 (a) Schematic diagram of VAIM and (b) dimensions of the melt chamber (mm).

tude, vibration duration, and delay time between the injection start and the vibration start. Furthermore, when these parameters were optimized, for polystyrene a 28% strength improvement was observed, accompanied by an increase in toughness.

In this study, the VAIM device was used to explore the effect of vibration fields on the mechanical properties of PP injection moldings. Here we mainly discuss the effects of vibration parameters on the mechanical properties and aim to determine the vibration processing conditions for the injection molding of self-toughened and self-reinforced PP.

EXPERIMENTAL

Apparatus

Schematic diagrams of the vibration injection molding device are shown in Figure 1. As shown in Figure 1(a), the vibration and injection ram were driven by both injection and vibration systems: without action of the vibration system, conventional injection molding (CIM) was performed; otherwise, vibration injection molding was realized. For VAIM, the main processing parameters are the vibration frequency and vibration pressure amplitude. During the injection and holding pressure stages for VAIM, the pulsing pressure vibration amplitude was superimposed on the melt in the runner system and mold; this caused compression and decompression on the melt and shearing at the melt–solid interface as it progressed from the surface to the core of the dumbbell specimen during the solidification stage. The melt temperature and pressure in the melt chamber could be monitored at any time.

Material

The material was grade F401 PP (Gansu Langang Petrochemical Corp., Ltd., Lanzhou, China) with a melt flow rate of 2.5 g/10 min measured at 250°C under 2.16 kg according to ASTM D 1238.

Mold geometry

The dimensions (mm) of the dumbbell specimen are shown in Figure 2, and the thickness was 5 mm.

Sample preparation

PP was plasticized and pumped into the melt chamber by a single-screw extruder. During the injection and holding pressure stages for VAIM, the melt was vibrated for about 25 s in the dumbbell specimen mold and then cooled for about 20 s. For VAIM, the samples were prepared at different vibration frequencies and pressure vibration amplitudes. Compared with VAIM, CIM was also applied to prepare a conventional sample. The melt injection temperature and mold temperature were set at 250 and 40°C, respectively.

In the experiment, injected PP moldings influenced by the vibration frequency and vibration pressure amplitude were prepared. The conventional specimen was prepared for comparison. For VAIM affected by different vibration frequencies, the vibration pressure amplitude was set at 19.8 MPa, and for
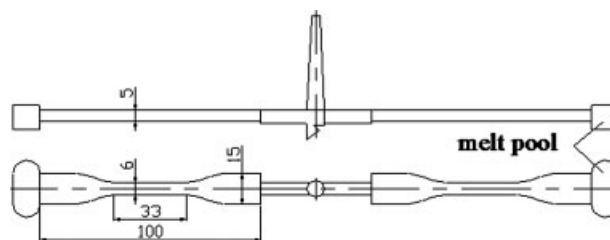
Figure 2 Layout of dumbbell specimens in the mold (mm).

VAIM affected by different vibration pressure amplitudes, the vibration frequency was set at 0.7 Hz. The injection pressure for CIM and the base pressure for VAIM were 39.5 MPa.

Tensile testing

An Instron model 4302 tensile machine (Instron Corp., Ltd., MA, USA) was employed for tensile testing at room temperature, and the crosshead moving speed was 50 mm/min.

Impact testing

An Izod impact-testing machine (Model U-40, Chengde Materials Testing Company, Chengde, China) was used to test the impact value of the notched conventional sample and vibration sample at room temperature.

Scanning electron microscopy (SEM) investigation

A small sample was cut from the tensile bar, ground, and polished down to the planes from one side, which were 0.7 and 2.5 mm below the original surface, respectively. The polished specimens were etched by the permanganic etching technique developed by Olley and colleagues,[12–14] and the structure was examined on a Hitachi S-450 scanning electron microscope (Tokyo, Japan). A thin layer of gold was sputtered on the specimens before the SEM observations. The shear region and core were studied for both CIM and VAIM specimens.

X-ray measurement

To characterize the crystal forms of PP, wide-angle X-ray diffraction experiments on a Philip X'pert Pro MPD (Amsterdam, Netherland) were carried out. The planes for measurement, 0.7 mm below surface, were ground and polished. A conventional Cu Kα X-ray tube at 45 kV and 40 mA was used to obtain wide-angle X-ray diffraction spectra, and the diffraction data were acquired at a scanning rate of $0.6°/s$ and over a Bragg angle range of $15° < 2θ < 50°$.

Differential scanning calorimetry (DSC) analysis

Samples used for thermal analysis were removed from the CIM- and VAIM-processed moldings. The thickness of the slices was about 0.3 mm, and they weighed about 8 mg for each test. A Netzsch DSC 204 (Bayem, Germany) differential scanning calorimeter was employed for scanning at $10°C/min$ in an atmosphere of N_2. The crystallinity was calculated from the measured heat of fusion, which was based on a perfect crystal heat of fusion of 138 J/g.[15]

RESULTS

Mechanical properties affected by the vibration frequency

As shown in Figure 3, the tensile strength of the conventional sample is 33.7 MPa, which is the minimal strength compared with the corresponding values of vibration injection moldings. For the samples prepared by VAIM, the maximal strength is approximately 35.2 MPa at 0.93 Hz, and the corresponding percentage increase is approximately 5%. The tensile results show that the application of melt vibration technology favors an improvement of the mechanical strength of injection-molded PP.

An interesting phenomenon is that the elongation at break changes with the vibration frequency. In the low-frequency range of 0–1 Hz, the elongation decreases first and then increases with the vibration frequency. There is a valley for the elongation at break, and the value is approximately 250% at 0.47 Hz, below the value of 440% for the conventional sample. In the same frequency range, the tensile strength increases, and a peak stands at 0.47 Hz. In the high-frequency range of 1–2.5 Hz, the elongation at break increases and reaches approximately 540% at 2.33 Hz, which is above the value of 441% for the conventional sample, and the corresponding percentage increase is about 23%. This phenomenon shows self-reinforced and self-toughened PP injection moldings can be produced at a high vibration frequency with VAIM.

Young's modulus is shown in Figure 4. The changes in Young's modulus with the vibration frequency are similar to the changes in the tensile strength. Young's modulus of the conventional sample, about 1 GPa, is minimal compared with the modulus of the vibration sample. The maximal value is approximately 1.3 GPa, and the percentage increase is 30%.
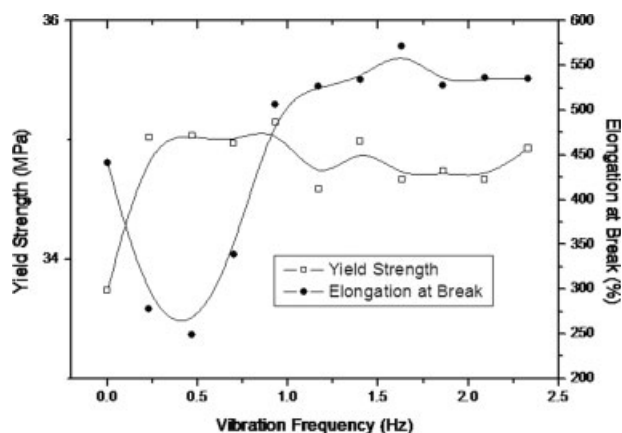
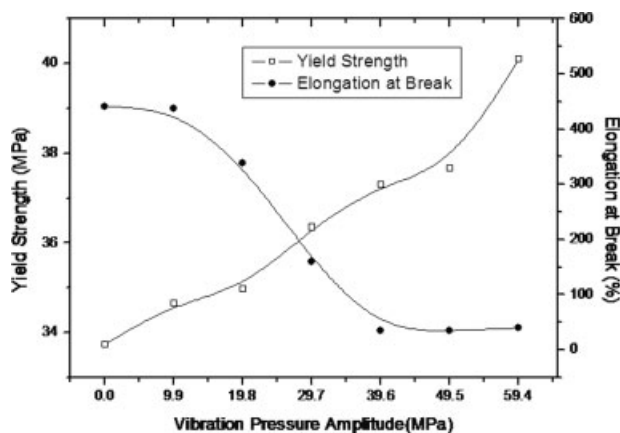**Figure 3** Yield strength and elongation at break as a function of the vibration frequency.
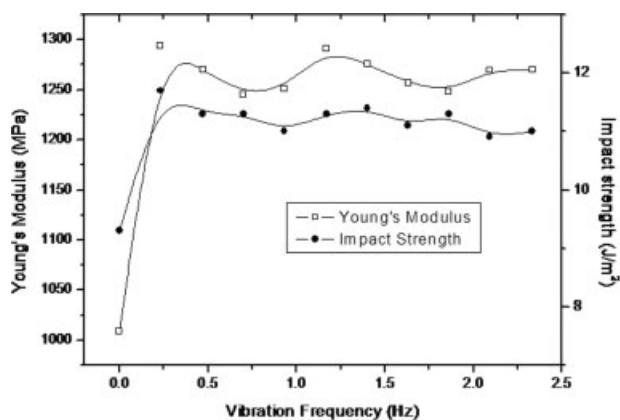
Figure 4 Young's modulus and impact strength as a function of the vibration frequency.

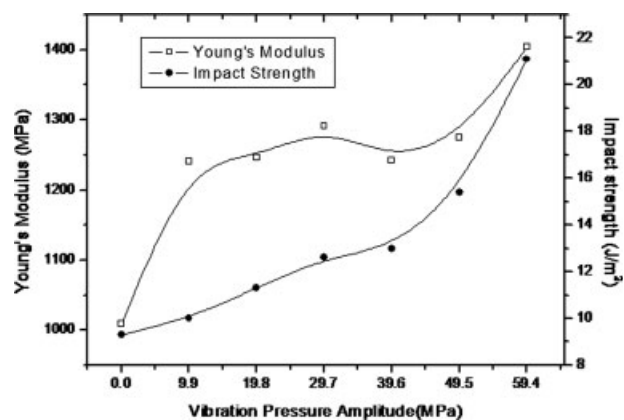**Figure 6** Young's modulus and impact strength as a function of the vibration pressure amplitude.

The injection-molded dumbbell specimens were also used to test the impact strength. The impact test results are also shown in Figure 4. The impact strength is 9.3 J/m^2 for the conventional sample. The impact strength first increases sharply with the application of melt vibration, and the impact strength reaches a plateau at a high frequency. The maximal impact strength is approximately 12 J/m^2 at 0.23 Hz, and the percentage increase is 29%.

Mechanical properties affected by the vibration pressure amplitude

The curves in Figure 5 show that the changes in the tensile properties for PP are sharp with increasing vibration pressure amplitude. Compared with that from CIM, the yield strength of the vibration sample increases with the vibration pressure amplitude; when the vibration amplitude is 59.4 MPa, the yield strength is approximately 40 MPa versus 33.7 MPa for the conventional sample. An 18.7% increase in the tensile strength is produced; however, the break-
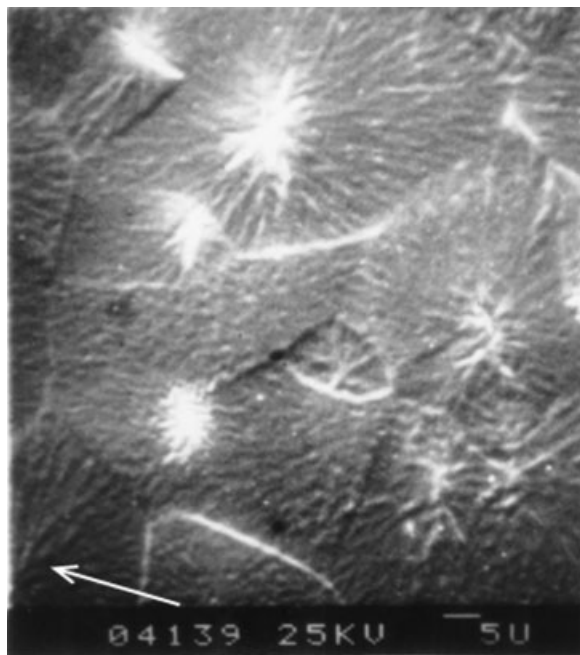
ing elongation sharply decreases from 441% for the conventional sample to approximately 40% at a pressure vibration amplitude of 39.6 MPa. When the vibration amplitude is above 39.6 MPa, the elongation at break tends to plateau.

Young's modulus is also raised greatly by an increase in the vibration pressure amplitude, as shown in Figure 6. For vibration injection molding, the maximal modulus is approximately 1.4 GPa versus 1.0 GPa for the conventional sample (an increase of 40%).
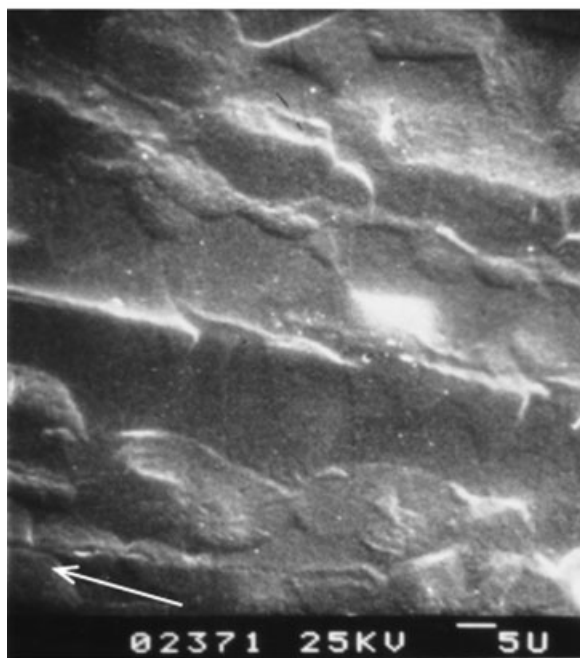
The impact strength, influenced by different vibration pressure amplitudes, is summarized in Figure 6. By the application of VAIM processing, the impact strength is greatly enhanced by increased vibration pressure amplitude. The impact strength increases from approximately 9.3 J/m^2 for the conventional sample to 21.1 J/m^2 at 59.4 MPa; this is a 126.9% increase in the impact strength.

DISCUSSION

As is well known, an injection molding is composed of layers called the skin, shear layer, and core region. The melt is cooled when it comes into contact with the cold mold wall, so the vibration force is nearly unavailable for the skin structure of injection moldings. Here we mainly observe the microstructures of the shear layer and core region of injection samples. To compare the microstructures of CIM moldings and VAIM moldings, SEM has been used to observe the microstructure of the shear layer and core region, and photographs of the shear layers are displayed in Figure 7. In conventional moldings, as shown in Figure 7(a), a spherulitic morphology predominates in the shear layer for the conventional sample; for vibration injection molding, along the melt flow direction, structures called ellipsoids are elongated in shape, as shown in Figure 7(b). The microstructures

Figure 5 Yield strength and elongation at break as a function of the vibration pressure amplitude.

direction and are called ellipsoids, as displayed in Figure 8(b). The melt in the mold chamber is subjected to static injection and holding pressures; in particular, the crystal grows nearly freely in the core region. When the injection and holding pressures are
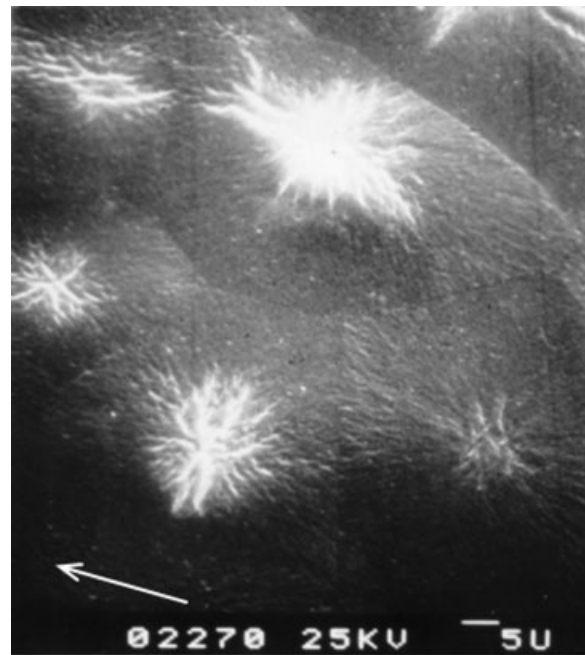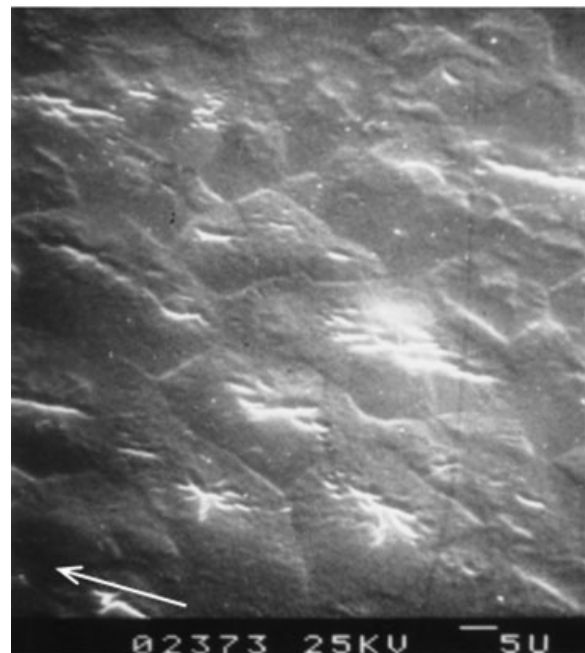

Figure 7 SEM photographs of shear layers of PP injection moldings prepared by (a) CIM and (b) VAIM (vibration frequency = 0.7 Hz, vibration pressure amplitude = 19.8 MPa). The arrow shows the melt direction.

of the core regions of injection samples are shown in Figure 8. For CIM, as shown in Figure 8(a), the microstructures of the core regions for conventional samples are spherulitic structures; for the VAIM samples, the spherulites deform obviously along the flow
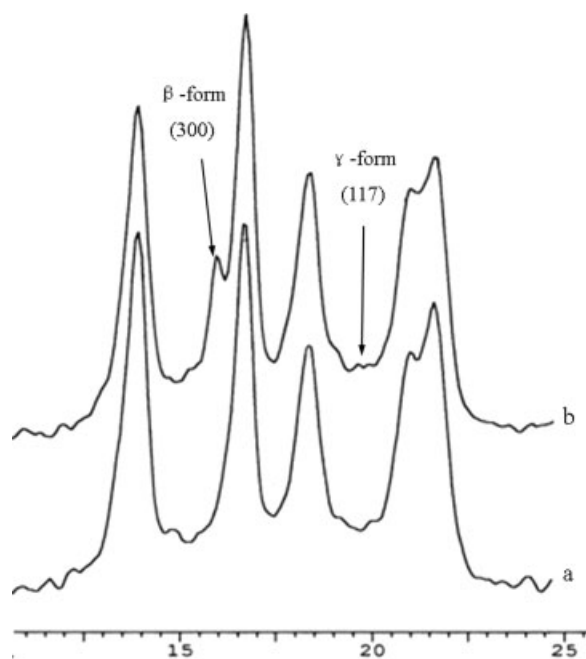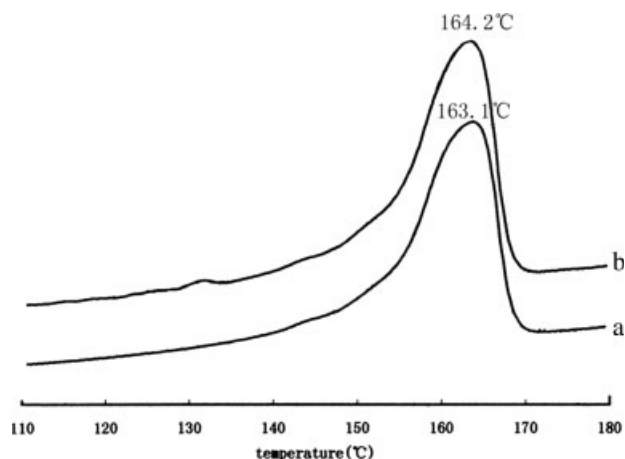

Figure 8 SEM photographs of core regions of PP injection moldings prepared by (a) CIM and (b) VAIM (vibration frequency = 0.7 Hz, vibration pressure amplitude = 19.8 MPa). The arrow shows the melt direction.

Figure 9 Wide-angle X-ray diffraction curves of core regions of PP injection moldings prepared by (a) CIM and (b) VAIM (vibration frequency = 0.7 Hz, vibration pressure amplitude = 19.8 MPa).

Figure 10 DSC curves of PP injection moldings prepared by (a) CIM and (b) VAIM (vibration frequency = 0.7 Hz, vibration pressure amplitude = 19.8 MPa).

vibrating, the shearing and elongation force fields are obtained along the melt flow direction, and this results in an elongated spherulite in the shear layer and core region of VAIM samples. The more pronounced spherulite elongation is favorable for increasing the mechanical properties of VAIM samples.

Isotactic PP can be obtained in three crystalline structures, the α, β, and γ phases, and the three crystal forms are dependent on the processing parameters. The α phase is often obtained in injection molding; the β phase is normally obtained in a shearing force field,[16,17] in a gradient temperature field,[18,19] and with the addition of a nucleated agent;[20,21] and the γ phase is usually obtained under a high pressure.[22,23] As shown in Figure 9(b), produced by vibration fields, the intensity of the (300) β-phase reflection from the VAIM sample is obvious in comparison to that of the conventional molding; in addition, a small peak corresponding to the (117) γ-crystal plane exists in the VAIM moldings. In the CIM

moldings, only the α-phase crystals exist, as shown in Figure 9(a). Because a stronger shear rate is obtained in the shear layer, the intensity of the (300) β-phase reflection from the shear layer is stronger than that in the core region. For CIM-processed PP, whether in the shear layer or in the core region, the (300) β-phase crystal form does not occur. Therefore, the β-phase crystal form of PP can be induced in the vibration force field. The β-phase crystal is beneficial for toughening the VAIM-processed samples.

DSC was used to investigate the thermal behavior, as shown in Figure 10. The crystallinity can be calculated according to the followed equation:

$$\alpha_c = \frac{\Delta h_f}{\Delta h_f^0} \times 100\% \tag{1}$$

where α_c is the amount of crystallinity, Δh_f is the measured heat of fusion from the DSC thermogram, and Δh_f^0 is the perfect crystal heat of fusion. The DSC curves are shown in Figure 10, and the temperature of the melting peak for PP specimens prepared by different processing conditions and calculated crystallinity values are shown in Table I.

A comparison of the thermal behaviors of CIM and VAIM shows that the melting point of VAIM, produced at 0.7 Hz and a vibration pressure amplitude of 19.8 MPa, shifts toward a high temperature.

TABLE I
DSC Results Obtained by Different Processing Variables

Sample	Vibration frequency (Hz)	Vibration pressure amplitude (MPa)	Melting point (°C)	Measured heat of fusion (J/g)	Crystallinity (%)
CIM	—	—	163.1	50.35	36.5
VAIM	0.7	19.8	164.2	58.60	42.5

This means that under this processing condition more perfect lamellae can be achieved. Table I also shows that VAIM is responsible for the increase in the crystallinity of the samples: a 6% improvement in the crystallinity compared with the value for the CIM moldings. The superimposed vibration pressure is more beneficial for enhancing the crystallinity of VAIM moldings, which is in line with the enhanced yield strength. Thus, the application of VAIM favors not only the molecular arrangement but also increased crystallinity.

CONCLUSIONS

With the application of melt vibration injection molding, the mechanical properties of isotactic PP are improved. The yield strength increases with the increment of the vibration frequency, and a peak stands at a special frequency for VAIM; the elongation at break decreases first and then increases with increasing vibration frequency, and a valley stands at a special frequency. The tensile properties increase sharply with an increased vibration pressure amplitude, with a sharply decreased elongation at break. The impact strength and Young's modulus also increase with the pressure vibration amplitude and vibration frequency. Self-reinforcing and self-toughening PP molded parts have been found to be prepared at a high vibration frequency or at a large pressure vibration amplitude. SEM micrographs have shown that, in the vibration field, the enhancement of mechanical properties is attributable to increased crystallinity and more pronounced spherulite orientation in comparison with CIM.

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