

Improving Rheological Property of Polymer Melt Via Low Frequency Melt Vibration

Youbing Li,¹ Kaizhi Shen,² Jie Zhan¹

¹College of Material Science and Engineering, Chongqing Institute of Technology, Chongqing 400050, China

²The State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu, Sichuan 610065, China

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ABSTRACT: A pulse pressure was superimposed on the melt flow in extrusion, called vibration extrusion. A die ($L/D = 17.5$) was attached to this device to study the rheological properties of an amorphous polymer (ABS) and semicrystalline polymer (PP, HDPE), prepared in the vibration field, and the conventional extrusion were studied for comparison. Results show that the melt vibration technique is an effective processing tool for improving the polymer melt flow behavior for both crystalline and amorphous polymers. The enhanced melt rheological property is also explained in terms of shear

thinning criteria. Increasing with vibration frequency, extruded at constant vibration pressure amplitude, the viscosity decreases sharply, and so does when increasing vibration pressure amplitude at a constant vibrational frequency. The effect of vibrational field on melt rheological behavior depends greatly on the melt temperature, and the great decrease in viscosity is obtained at low temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5292–5296, 2006

Key words: rheology; extrusion; shear

INTRODUCTION

Recently it was established that melt vibration can be used to control morphology and enhance mechanical properties of injection-molded articles. The shear-controlled orientation injection molding (SCORIM) was generally thought to result in a high level of molecular orientation with highly improved mechanical properties in comparison to conventional injection moldings.^{1–3} Kalay and coworkers reported a 75% increase in stiffness of iPP following the SCORIM, and an increase of up to four times in the impact strength and a substantial increase in the Young's modulus achieved on the device.^{4,5} Guan and Shen used a similar technology, the oscillating packing injection molding (OPIM), to realize the self-reinforcement of PP and HDPE under low pressure.^{6,7} Chen and Shen prepared pronounced biaxially self-reinforced iPP specimens under a unidirectional shearing field of low pressure, displaying a 55–70% increase of the tensile strength and more than a 4-fold increase of the impact strength in the mechanical direction (MD), together with more than a 40% increase of the

tensile strength and a 30–40% increase of the impact strength in the transverse direction (TD).^{8,9} Therefore, melt vibration has been developed as an effective technology in controlling the morphology of injection moldings.

In a recent review Ibar summarized controlling polymer properties via melt vibration technology.¹⁰ The rheology of the polymer melt plays an important role in polymer processing; it can be changed greatly by applying a vibration field. The changes of rheology can influence the mechanical properties of the products. Some vibration techniques and apparatus^{11–13} have been developed to investigate such influences. Ibar¹⁰ explained that the effect of vibration frequency and amplitude on melt viscosity was in terms of shear-thinning criteria, and the effect of pressure and temperature on shear thinning was concluded at low frequency. In these investigations the effect of pulse pressure vibration field on the polymer melt flow property was not involved, our purpose was to study the effect of pulse pressure vibration on melt flow behavior in this article.

Correspondence to: Y. Li (li-youbing@163.com).

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EXPERIMENTAL

Material

The materials used in this work were PP (melt flow rate 1.5 g/10 min), HDPE (melt flow rate 1.1 g/10 min), and ABS (melt flow rate 1.5 g/10 min) provided by Yanshan Petrochemical, Qilu Petrochemical, and Lanzhou Petrochemical, China, respectively.

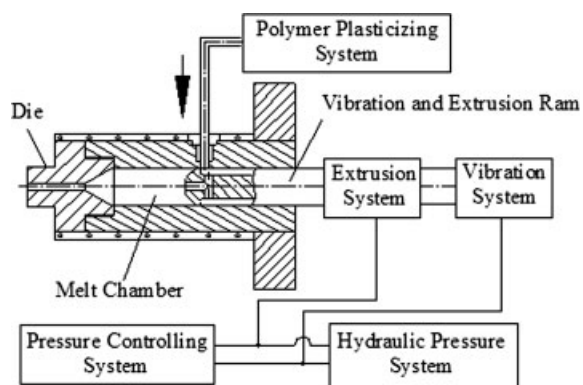


Figure 1 Schematic diagram of low frequency melt VE.

Sample preparation

As shown in Figure 1, an extruder was used to plasticate the materials. The vibration and extrusion ram can be driven by both extrusion and vibration systems, without action of the vibration system conventional extrusion (CE) was performed; otherwise vibration extrusion (VE) was realized. For VE, the pulsing pressure was superimposed on the melt in the melt chamber and the die, causing effective compression and decompression and shearing on the melt during extrusion. For this device, the main processing parameters of VE are vibration frequency (F_r) and vibration pressure amplitude (P_a). The melt temperature and pressure in the melt chamber can be monitored at any time.

Data processing method

For rheological research, a die with L/D 17.5 (length, 21 mm and diameter, 1.2 mm) was attached to the melt chamber. In the same duration the extruded melt was cooled to room temperature, and weighted. The device looked like a capillary rheometer, and the average apparent viscosity $\bar{\eta}_a$ can be calculated according to the following expression:

$$\bar{\tau}_\omega = \frac{\Delta\bar{P}R}{2L}$$

and

$$\bar{\gamma}_a = \frac{4\bar{Q}}{\pi R^3}$$

where

$$\bar{Q} = \frac{\bar{M}}{\rho t}$$

and $\bar{\eta}_a$ is defined as:

$$\bar{\eta}_a = \frac{\bar{\tau}_\omega}{\bar{\gamma}_a}$$

and

$$\bar{\eta}_a = \frac{\pi R^4 \rho}{8L} \times \frac{\Delta\bar{P}t}{M}$$

where $\bar{\tau}_\omega$, $\bar{\gamma}_a$ are called the average shear stress, and average shear rate, the R and L are the radius and the length of the die, respectively, \bar{M} and ρ are the mass and the density of the material at room temperature, respectively, $\Delta\bar{P}$ is the loss of average pressure extruded through the die and t is the extrusion time.

To investigate the effect of vibration frequency on melt flow, a constant pulse pressure (amplitude, 9.9 MPa) was superposed on the conventionally extruded melt (CE, 9.9 MPa), thus the average extrusion pressure was 14.85 MPa; for comparison the viscosity data was obtained at 14.85 MPa for CE pressure. The vibration frequency was selected at 0.7 Hz, to characterize the effect of different vibration pressure amplitude, and the base extrusion pressure was 9.9 MPa that was the extrusion pressure of CE for comparison. The processing conditions for CIM and VIM in detail are displayed in Table I.

RESULTS AND DISCUSSION

Viscosity affected by vibration frequency

The viscosity data was obtained at 14.85 MPa for CE pressure. In the vibration extrusion, a constant pulse

TABLE I
Processing Parameters for CE and VE

| Parameters | CE | VE | |
|---|-------|-----------------------|--------------------------------|
| | | Affected by frequency | Affected by pressure amplitude |
| Base extrusion pressure, P_b (MPa) | 14.85 | 9.9 | 9.9 |
| Vibration pressure amplitude, P_a (MPa) | - | 9.9 | 4.95, 9.9, 19.8, 29.7 |
| Vibration frequency, F_r (Hz) | - | 0.23, 0.47, ..., 2.33 | 0.70 |
| Extrusion pressure (MPa) | 14.85 | 9.9-19.8 | 9.9 ~ (9.9 + P_a) |
| Extrusion time (s) | 30 | 30 | 30 |

pressure (amplitude, 9.9 MPa) was superposed on the conventionally extruded melt (CE pressure, 9.9 MPa), thus the average extrusion pressure for VE was at 14.85 MPa.

For PP, the melt temperature was selected at 190 and 210°C, and at each temperature the average apparent viscosity influenced by vibration frequency was studied. The average apparent viscosity decreases first with increasing vibration frequency, and then tends to a plateau, as shown in Figure 2. At 190°C, the viscosity decreases from 2345 Pa s, obtained at 14.85 MPa of CE pressure, to ~ 401 Pa s of 0.7 Hz and 523 Pa s obtained at 2.1 Hz; the viscosity decreases from 1088 Pa s, at 210°C, to ~ 277 Pa s of 0.7 Hz and 330 Pa s obtained at 2.1 Hz. The corresponding maximum decrease percentages of viscosity are 82.9 and 74.5% at 190 and 210°C, respectively.

When HDPE was extruded the melt behavior affected by vibration frequency was investigated at 200 and 240°C, respectively. Compared with the average apparent viscosity of CE, the pressure vibration field makes the melt viscosity trend to increase after a minimum, as shown in Figure 3. The viscosity–vibration frequency relationship of a melt essentially depends on the relative melt temperature. For CE the viscosities are 10,108 and 5403 Pa s at 200 and 240°C, respectively. When the vibration was superimposed on the melt, the viscosities reach the minimum, 5763 Pa s of 0.23 Hz at 200°C and 2760 Pa s of 0.7 Hz at 240°C, respectively. When the vibration frequency is 2.1 Hz, the average apparent viscosity goes up to 7067 and 3564 Pa s for 200 and 240°C individually. At 200°C, the maximum decrease in percentage of viscosity is 43.0%, and a 48.9% decrease in viscosity at 240°C.

For ABS, applied melt pressure vibration, the average apparent viscosity also decreases first with increasing vibration frequency, and then tends to a

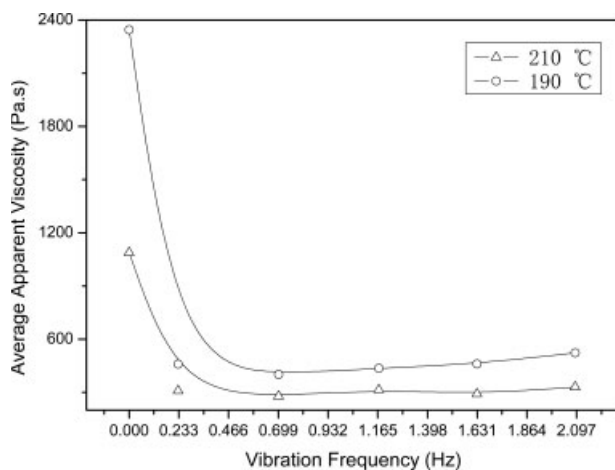


Figure 2 The average apparent viscosities of PP as a function of vibration frequency.

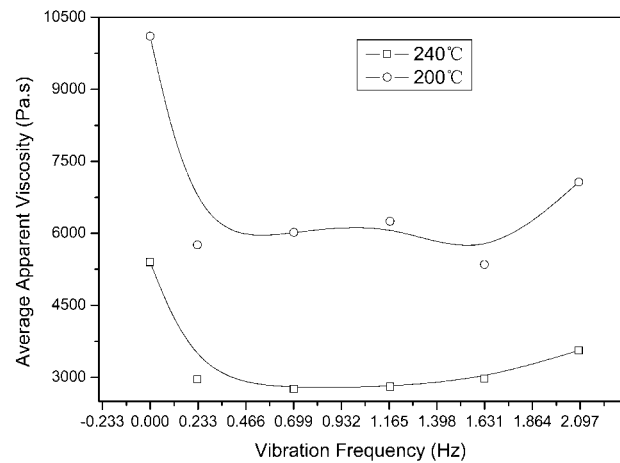


Figure 3 The average apparent viscosities of HDPE as a function of vibration frequency.

plateau, and the relationship of viscosities and vibration frequency strongly depends on the melt temperature, as shown in Figure 4. At 200°C, the viscosity trends to increase after a minimum, having decreased from a conventional viscosity (1314 Pa s) to 754 Pa s at 0.23 Hz, and back to 1021 Pa s at 1.63 Hz, and the maximum decrease percentage of viscosity is 42.6%; at 220°C, the vibration decreases the viscosity from 1055 Pa s for CE, to 351 Pa s at 0.7 Hz and then the viscosity increases little with increasing the vibration frequency, and the maximum decrease in viscosity is 66.7%.

In conclusion, the effect of vibration frequency on reducing the viscosities is mainly obtained at the lowest frequencies.

Viscosity affected by pressure vibration amplitude

Using the same melt vibration device, to characterize the effect of different vibration pressure amplitude

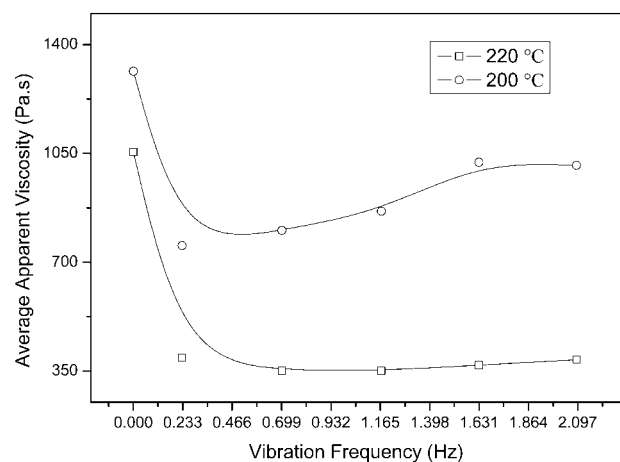


Figure 4 The average apparent viscosities of ABS as a function of vibration frequency.

on the melt flow behavior, the vibration frequency was optionally selected at 0.7 Hz, and the base extrusion pressure was 9.9 MPa of the extrusion pressure of CE for comparison, on which the increasing vibration pressure amplitude was superimposed.

Increasing with vibration pressure amplitude the average apparent viscosity of PP decreases sharply, as shown in Figure 5, when the pressure amplitude is beyond 9.9 MPa, the improvement of melt flow behavior is little with increasing vibration pressure amplitude. The viscosity decreases from a conventional viscosity (6738 Pa s at 190°C and 3496 Pa s at 210°C) to ~ 153 Pa s at 190°C and ~ 36 Pa s at 210°C when the amplitude is 29.7 MPa, and the corresponding decrease in percentage are 97.7 and 99.0%, respectively. The results show that the changes in melt flow behavior are little caused by high vibration pressure amplitude (beyond 9.9 MPa of vibration pressure amplitude), and the viscosities at different temperature tend to be at one value, which means that the high pressure amplitude make the molecular mobility to be uniform at different temperature.

Like PP, the melt flow property of HDPE improves by increasing the vibration pressure amplitude, as shown in Figure 6. The viscosities were 26,996 Pa s extruded at 200°C and 13,498 Pa s at 240°C, when the vibration pressure amplitude superposed on the extruded melt, the calculated average apparent viscosity at different temperature nearly reached one value at 39.6 MPa of vibration pressure amplitude, the viscosities are ~ 361 Pa s at 200°C and ~ 132 Pa s at 240°C, and the corresponding decrease percentage are 98.7 and 99.0%, respectively. It is obvious that the increased vibration pressure amplitude is favorable to improve the melt flow behavior of polymer melt.

As seen in Figure 7, increasing with vibration pressure amplitude, the viscosity decreases sharply

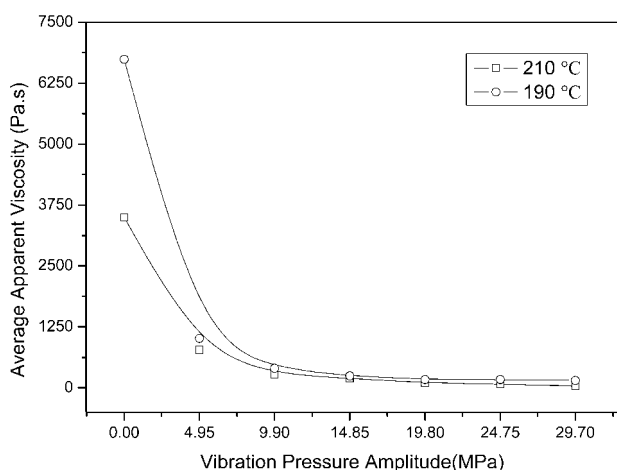


Figure 5 The average apparent viscosities of PP as a function of vibration pressure amplitude.

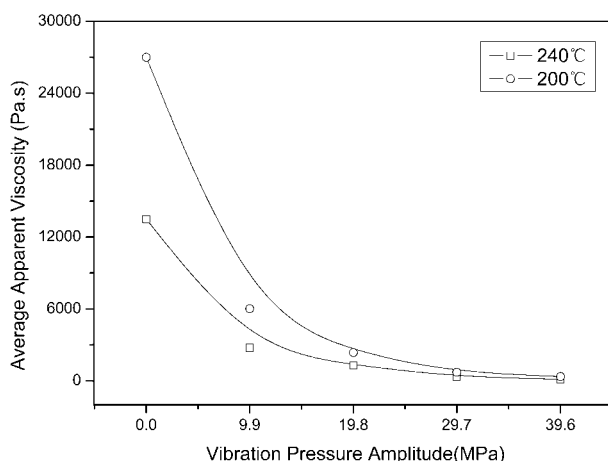


Figure 6 The average apparent viscosities of HDPE as a function of vibration pressure amplitude.

at 220°C with only a slight decrease at 220°C. The sharp change in viscosity at the lower temperature is related to the great shearing stress obtained at this temperature. At 200°C, the viscosity fell from 777 Pa s (777 Pa s at 220°C), the conventional value, to 190 Pa s (~ 91 Pa s at 220°C) when prepared at 29.7 MPa of vibration pressure amplitude, and the corresponding decreased percentage are 94.3% at 190°C and 88.3% at 220°C. Although the same pulse pressure was superimposed on the melt, at high temperature (e.g., 220°C) the molecular chain can move more freely than at low temperature e.g., 200°C, which may decrease part of effect of melt vibration at high temperature resulting in slight change in viscosity at 220°C.

In general, extruded at lower vibration frequency the melt flow property improves greatly by increasing vibration pressure amplitude, and the viscosities obtained at highest amplitude come to be at one at different temperature.

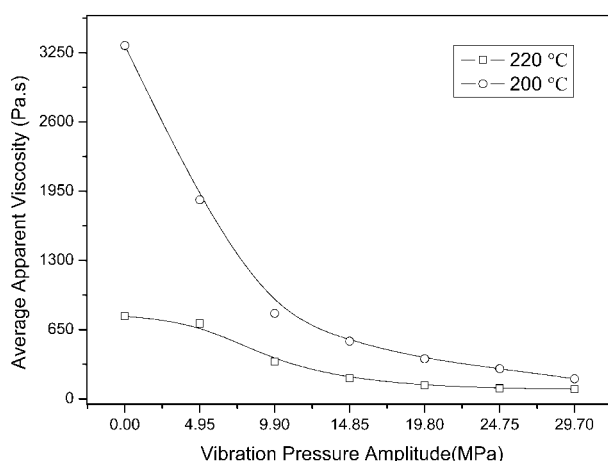


Figure 7 The average apparent viscosities of ABS as a function of vibration pressure amplitude.

Relationship between processing conditions and rheological results

From the above discussions of viscosity data affected by melt vibration, as long as the pulse vibration pressure is superposed to the melt, the average apparent viscosity decreases. Melt vibration in the melt chamber and the die can cause strong melt shear, which is beneficial to reduce the melt viscosity. The enhanced melt flow property is normally explained in terms of shear thinning criteria.

As shown in Figure 1, so long as the vibration and extrusion ram pushes the melt to flow through the die, the shearing force field exists in the die. When the same pulse vibration pressure amplitude was superposed to the melt in the die, resulting in the same shear stress, the shear rate increased with increasing vibration frequency, the increasing shear rate was beneficial to orientate and disentangle the molecular chains, with improved melt flow property. When the vibration frequency was set at a constant value, the shear stress and shear strain increased with increasing vibration pressure amplitude, the effects of enhanced shear stress and shear strain on rheological behavior are similar to that of increased shear rate, resulting in the sharp decrease in the average apparent viscosity.

The decreased viscosity, obtained at increased vibration frequency, is smaller than that resulting from increased vibration pressure amplitude; the reason may be that the melt shear produced by the former is weaker than that caused by the latter.

Another phenomenon should be paid attention. When the vibratory pressure was superposed to the melt in the die, the melt was compressed and expanded. It was known that the motion of polymer is realized through chain's motion and diffuseness. When the melt was sheared at static stress the melt pressure was constant, and the motion of polymer chains can be seen as a creeping motion. While the pulse pressure was superposed to the melt, the local melt pressure in the die was also vibratory, resulting in dynamic melt shearing. The effects of vibratory pressure can accelerate the chain's motion and diffuseness and decrease the polymer chain entanglement, with improved melt flow performance.

In brief, the superposed vibratory pressure to melt strengthens the melt shear thinning and accelerates the chain's motion and diffuseness, resulting in improved flow property of polymer melts, whether changed vibration frequency or vibration pressure amplitude.

CONCLUSIONS

From the above results and discussion, conclusions drawn are as follows:

The melt vibration technique is an effective processing tool for improving the polymer melt flow behavior for both crystalline and amorphous polymers. Increase in vibration frequency, extruded at constant vibration pressure amplitude, the viscosity decreases sharply, and so does when increase in vibration pressure amplitude at a constant vibration frequency. The effect of vibration field on melt flow behavior is also related to the melt temperature, and the great decrease in viscosity is obtained at low temperature.

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