Dynamic Rheological Behavior of Polypropylene Melts with Pulsatile Pressure Flow in a Dynamic Capillary Rheometer

Guang Jian He, Jin Ping Qu, Xiao Chun Yin

National Engineering Research Center of Novel Equipment for Polymer Processing, The Key Laboratory of Polymer Processing Engineering, Ministry of Education, China South China University of Technology, Guangzhou 510640, China

ABSTRACT: A self-made dynamic capillary rheometer (DCR) was designed to investigate the dynamic viscoelastic characteristic of polypropylene (PP) melt during the pulsatile pressure extrusion. A vibration force field was parallel superposed upon steady shear flow in this DCR by means of a vibration driven piston. During the pulsatile pressure extruding process in DCR, the PP melt displayed apparent viscoelasticity. The experiment results proved the pressure pulsatile extrusion could reduce the viscosity of polymer melts effectively. The phase difference between the shear stress and the shear rate decreased with the superposed vibration. But, at large amplitude conditions, the viscosity has an increasing tendency. This maybe illuminated that large amplitude could be harmful for the vibration-assistant polymer processing. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1834–1838, 2006

Key words: pulsatile pressure extrusion; dynamic rheological behavior; polypropylene

INTRODUCTION

Polymer processing is one of the most significant approaches to increase the properties of the polymer materials. Recently, the vibration technique has been applied to polymer processing and gained a lot of investigations.[1–11] The vibration energy introduced into polymer processing affects the molecular movement and the rheological behavior of the polymer melt, which in turn affects the morphological development of the final products and then final performance.[4–6]

To date, several types of melt vibration techniques have been investigated.[7–11] Ibar studied the effect of vibration on the molding using rheomolding technique and found that the vibration had a great effect on the physical performance.[8] Shen and Yan developed an oscillating packing technology to study the strength of the molded products.[9] Professor Qu and coworkers[10,11] invented the electromagnetic dynamic plasticating extruder, introducing the vibration field into the plasticating and extruding stage of the poly-

mer processing. The novel extruder has significant advantages, compared with the traditional extruder, such as low energy consume, low melt apparent viscosity, and low melt die swell ratio.

According to Ibar, there are three categories of patented processes using vibration to modify the molding process and/or the properties of molded materials[3]: (a) One is the use of mechanical shaking/oscillation of ultrasonic vibration devices to homogenize and increase the density of the material molded, either in the liquid stage or in the solidifying stage, either at a macroscopic or microscopic level. (b) The second is based on the fact that material rheology is a function of vibration frequency and amplitude in addition to temperature and pressure. This can be put to practical use to influence diffusion and rate-sensitive processes, which depend on viscosity and relaxation kinetics, such as nucleation and growth of crystals, blending, and orientation. (c) In a third category, vibration is essentially used to generate heat locally by internal friction or to decrease surface stresses at the wall interface between the melt and the barrel or the die to increase throughputs.

However, because of the complex flow patterns and viscoelastic behaviors of polymer melt, it is difficult to exactly describe the behavior of polymer melts in vibration force field with proper rheological theory and constitutive equations.[12,13] So, the dynamic rheological measurement becomes very important, which can
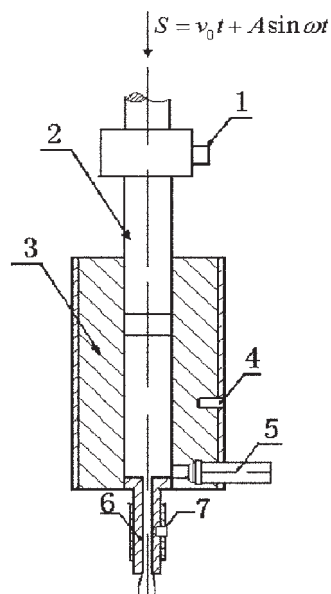
$$S = v_0 t + A \sin \omega t$$

Figure 1 Schematic diagram of dynamic capillary rheometer. 1 – displacement transducer; 2 – plunger; 3 – barrel; 4,7 – temperature transducer; 5 – pressure transducer; 6 – capillary.

provide basic rheological data for dynamic processing. Booij[14] presented that a phase shift between oscillatory deformation and shear stress greater than 90° could be obtained in parallel superposition. Isayev and coworkers[15,16] studied the parallel and orthogonal superposition of small- and large-amplitude oscillations upon steady shear flow of polymer fluids. On the basis of Leonov viscoelastic constitutive equation, they compared the dynamic rheological data with experimental data. For the parallel superposition of oscillations, the experimental results for shear stress components had good agreement with theoretical predictions, although there existed some deviations for storage modulus at high shear rates that seemed to be dependent on material. For the orthogonal superposition of oscillations, the theoretical data were found to be only in a qualitative agreement with the experimental dada for storage modulus and dynamic viscosity.

The majority of the available literature dealing with the superposition of oscillation upon steady shear flow was pursued on the Weissenberg rheogoniometer,[15–18] which is capable of measurement during parallel superposition. But this type flow is mainly about oscillatory shear flows, not involved the oscillatory pressure flow. Here we designed a dynamic capillary rheometer, which can provide parallel superposition of sinusoid vibration on pipe extrusion flow for the polymer melt, to evaluate the dynamic rheological behavior with applied pressure vibration.

Experimental

Material

Materials used in this study are polypropylene (iPP) in the form of pellets with a melt flow rate of 3.0 g/10 min (230°C, 2.16 kg), spinning grade, supplied by the Wuhan Phoenix, China.

Equipment

The schematic diagram of the DCR used in this experiment is shown in Figure 1, designed from the conventional capillary rheometer incorporated with vibration power generator. The vibration displacement of the plunger and the pressure drop of polymer melt can be instantaneously measured during extruding process using two precision transducers. Both data are transmitted synchronously to the computer through a data-collection card with 100 data per second. The pressure transducer is located at the capillary entrance, and the displacement transducer is located on the plunger. The die used in this experiment has L/D of 20/1 ($L = 60$ mm, $D = 3$ mm).

Two rectilineal lines in Figure 2 are the displacement of the plunger and the entrance pressure drop detected during steady extruding experiment. The two sinusoidal curves in Figure 2 are the vibration displacement of the plunger and the entrance pressure drop detected during pulsatile extruding experiment. With the superposition of the sinusoidal vibration, the movement of the plunger consists of a steady velocity and a sinusoidal vibration velocity. Also, the pressure drop of polymer melt fluctuates sinusoidally.

The entrance pressure drop of the polymer melt consist of two components, one component is the constant shear stress arising from the steady extrusion, and the other part is the vibration stress that is out of phase with respect to the sinusoidal vibration motion.
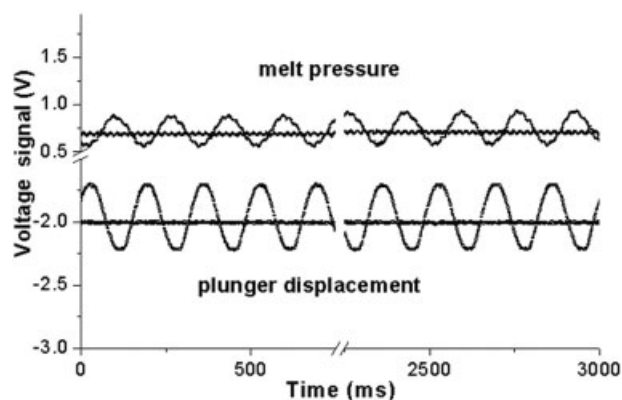
Figure 2 Plunger displacement and melt entrance pressure during steady and pulsatile extruding processing (voltage signal).

According to the superposition of a sinusoidal vibration displacement on a steady displacement, the displacement S of the plunger can be written as

$$S = v_0 t + A \sin \omega t \qquad (1)$$

Here t is the time, v_0 the steady speed of the plunger, A the vibration amplitude, and ω the circular frequency of the vibration ($\omega = 2\pi f$, f is the vibration frequency).

Rheology study

The measurement procedure of dynamic rheological behavior of polymer melt under vibration is as follows: when the temperature in the barrel reached 220°C, approximately 5 g pure iPP was placed into the barrel, packed with the plunger, and heated for 5 min. The vibration then was imposed on the plunger with the definite frequency and amplitude. Subsequently, the melt PP was extruded with the speed of 600 mm/min superposed with the vibration during the extrusion processing. So, the rheological parameters of polymer melt studied can be obtained according to the in situ measurement and subsequent calculations.

When the sinusoidal vibration superposed on the steady flow, the maximum strain amplitude of polymer melt in the capillary can be described as:

$$q = \frac{R_0^2}{R^3} A \qquad (2)$$

where R_0 and R are the radius of the barrel and the capillary, respectively.

So, the total shear rate $\dot{\gamma}$ at the wall during the pulsatile extruding processing can be described by the equation

$$\dot{\gamma} = \dot{\gamma}_0 + q\omega \cos \omega t \qquad (3)$$

where $\dot{\gamma}_0$ is the steady shear rate and $q\omega$ the vibration shear amplitude.

For the polymer melt flow in the capillary, some assumptions can be made as follows (Fig. 3)

1. The polymer melt is isothermal and incompressible along the capillary length.
2. The flow is sufficiently developmental, which means the velocity of melt is zero in the direction of r and θ.
3. There is no slipping on the inside wall of the capillary ($r = R$), which means the velocity is zero at the wall.
4. The gravitational force is ignored for the simplicity of rheological analysis of polymer melt.
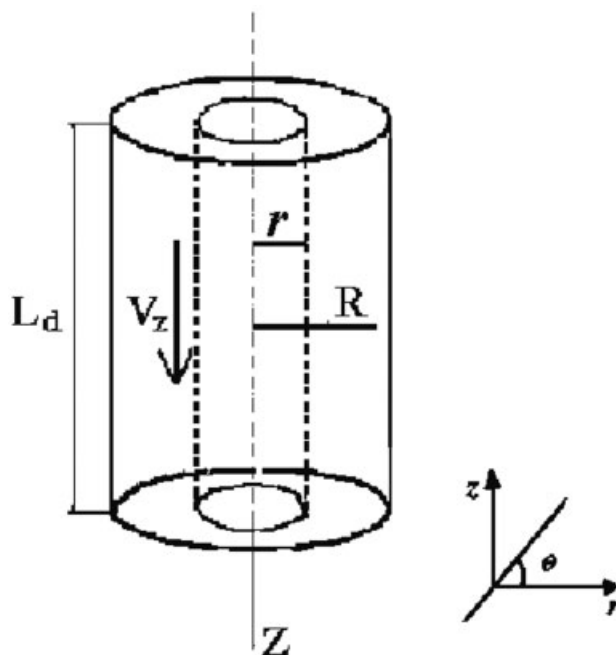

Figure 3 The coordinate used in the capillary for polymer melt flow.

According to the assumptions, the motion equation along the flow direction could be written as:

$$\rho \frac{\partial v_z}{\partial t} = -\frac{\partial P}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r}(r\tau) \qquad (4)$$

To resolve eq. (4), we can get the wall shear stress:

$$\tau = \frac{R}{2} \frac{\Delta P}{(L + N)} - \frac{\rho R_0^2}{2R} A\omega^2 \sin \omega t \qquad (5)$$

where ΔP is the entrance pressure drop of the polymer melt, L, the length of the capillary, N, the Bagley correction coefficient, ρ, the melt density.

With the shear stress and the shear rate, we can define the dynamic apparent viscosity η_d:

$$\eta_d = \frac{\bar{\tau}}{\bar{\dot{\gamma}}} \qquad (6)$$

where $\bar{\tau}$ is the time-average shear stress and $\bar{\dot{\gamma}}$ is the time-average shear rate.

RESULTS AND DISCUSSION

Phase difference between the shear stress and shear rate

In the DCR, two fine transducers are used to record the transient signals of the entrance pressure drop and the sinusoidal displacement of the plunger. With the
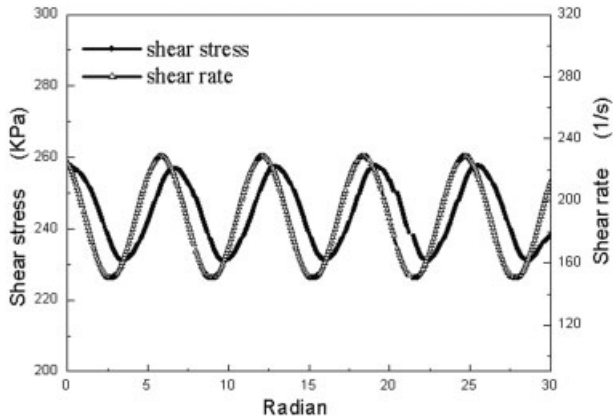
Figure 4 The phase difference between the shear stress and shear rate during pulsatile extruding in the DCR (extruding speed, 600 mm/min; vibration frequency, 6 Hz; vibration amplitude, 0.1 mm).

Figure 6 The effect of vibration frequency on dynamic apparent viscosity during pulsatile pressure extruding (extruding speed, 600 mm/min; vibration amplitude, 0.1 mm).

theory above, the shear stress and shear rate can be got conveniently. Because of the viscoelastic character of polypropylene melt, the shear stress and the shear rate is not synchronous in pulsatile extruding processing (Fig. 4), that is, the phase angle appears. Because of the compressibility of polypropylene melt, the figures of the two curves are not perfectly sinusoidal shape. By comparing the peak position of the shear stress and the shear rate, the phase angle can be easily determined.

At fixed vibration frequency and amplitude, the phase angle δ is almost constant. But, with the increase of the vibration frequency, the phase angle during the pulsatile extruding processing is reduced (Fig. 5). When the vibration frequency exceeds 12 Hz, the phase angle reduces slowly. Perhaps, the phase angle would have a further decrease with the increase of the vibration frequency. However, the higher frequency is
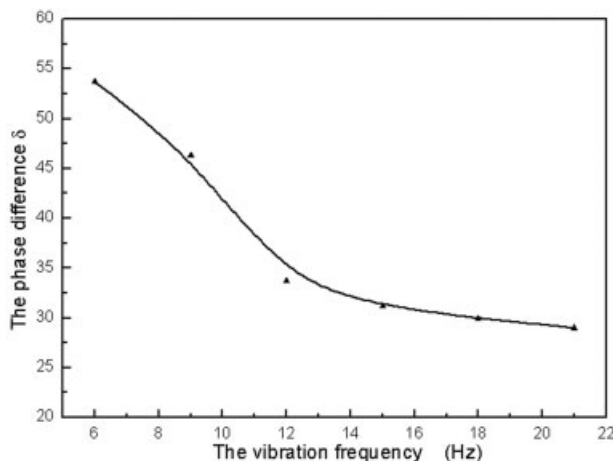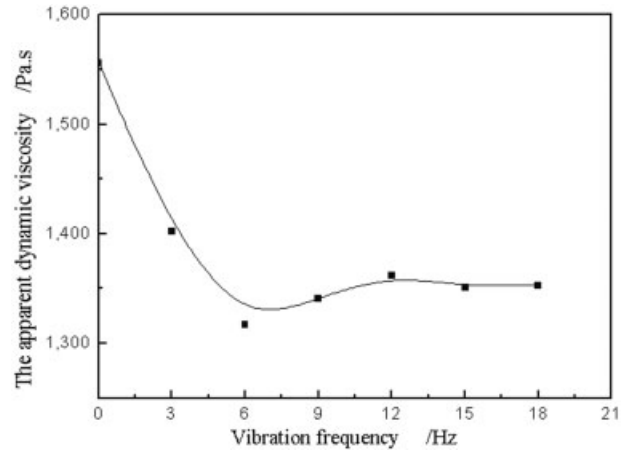
hard to get because of the melt resistance. This phenomenon proves that the iPP melt exhibits more elastic character during the pulsatile extruding processing with the increase of the vibration frequency. This result is quite the same with the literature,[14] in which the superposition of sinusoidal vibration on steady shear flow was done in a Weissenberg rheogoniometer.

The effect of vibration on the dynamic apparent viscosity

According to the eq. (6) the dynamic apparent viscosity could be got. Two vibration parameters can be adjusted during the pulsatile extruding processing, that is, vibration frequency and amplitude., As shown in Figure 6, the dynamic apparent viscosity is reduced with the applied vibration frequency, but further viscosity reduction is difficult to obtain by increasing frequency further. It seems that the dynamic apparent viscosity is stabilized at high vibration frequency. However, with increasing of the vibration amplitude, the dynamic apparent viscosity decreases at first and gets to increase at high vibration amplitude (Fig. 7).

The viscosity reduce with the frequency increase could be explained by the Cox-Merz' rule that plots of the complex viscosity versus the angular frequency were similar to plots of viscosity versus shear rate. It is clear that either increasing the shear rate or the vibration frequency can obtain the shear thinning. But, as for the vibration amplitude, the situation is different. The vibration amplitude contributes much to the melt compressibility and increases the melt viscosity. The changes of the melt viscosity reflect the changes of the molecular entanglement. It is obvious that the shear or the vibration frequency can reduce molecular entanglement in polymer melt. Another evidence of the disentanglement is the improvement of the perfect
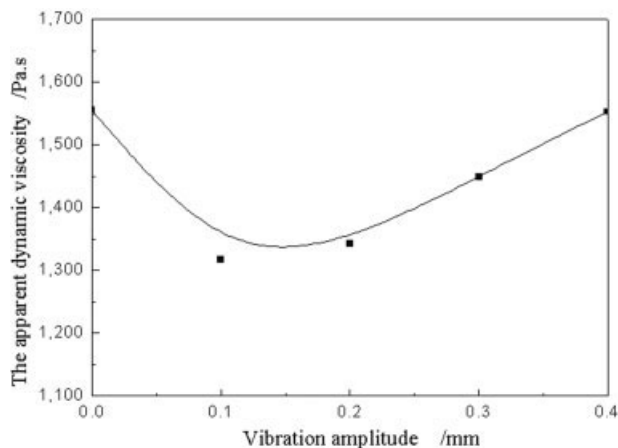

Figure 5 The phase angle decrease with the vibration frequency (extruding speed, 600 mm/min; vibration amplitude, 0.1 mm).

Figure 7 The effect of vibration amplitude on dynamic apparent viscosity during pulsatile pressure extruding (extruding speed, 600 mm/min; vibration frequency, 6 Hz).

crystals of the iPP extruded under vibration conditions.[6]

Previous papers[2] have indicated that the viscosity reduction in vibration flow can be (1) a nonlinear interaction of vibration and pressure flow leading to the reduction of storage moduli and loss moduli of polymer melt and (2) the dissipation of vibration energy leading to a temperature rise in polymer melt. The reduction of dynamic apparent viscosity showed here is obviously influenced by only the interaction of vibration and pressure flow because of the isothermal flow conditions.

SUMMARY

The DCR provides another way to study the viscoelastic character of polymer melt with the superposition of vibration pressure upon the steady flow. The PP melt exhibits obvious viscoelastic characteristic during the pulsatile pressure extrusion. The experiment results

showed that, with the frequency increase of the vibration pressure, the phase angle decreased. Under low amplitude conditions of vibration pressure, the dynamic apparent viscosity of polymer melt decreased with vibration pressure frequency increase. The frequency of the vibration pressure has the same result as the shear thinning. But at large pressure amplitude conditions, the dynamic apparent viscosity has an increasing tendency. This experiment results could be helpful for the vibration-assistant processing for polymer melt.

References

1. Isayev, A. I.; Wong, C. M.; Zeng X. Adv Polym Technol 1990, 10, 31.
2. Isayev, A. I.; Wong, C. M.; Zeng, X. J Non-Newt Fluid Mech 1990, 34, 375.
3. Ibar, J. P. Polym Eng Sci 1998, 38, 1.
4. Kalay, G.; Bevis, M. J. J Polym Sci Part B: Polym Phys 1997, 35, 241.
5. Kalay, G.; Bevis, M. J. J Polym Sci Part B: Polym Phys 1997, 35, 415.
6. Qu, J. P.; He, G. J.; He, H. Z.; Yu, G. H.; Liu, G. Q. Eur Polym J 2004, 40, 1849.
7. Zhang, A. Y.; Jisheng, E.; Allan, P. S. et al. J Mater Sci 2002, 37, 3189.
8. Ibar, J. P. ACS Polym Prep 1980, 21, 215.
9. Yan, Z.; Shen, K. Z.; Zhang, J.; et al. J Appl Polym Sci 2002, 85, 1587.
10. Qu, J. P.; Xu, B. P.; Jin, G.; et al. Plastics Rubber Compos 2002, 31, 432.
11. Qu, J. P. Polym-Plastics Technol Eng 2002, 41, 115.
12. Giacomia, A. J.; Jeyaseelan, R. S.; et al. J Rheol 1993, 37, 811.
13. Yosick, J. A.; Giacomin A. J. J Non-Newt Fluid Mech 1996, 66, 193.
14. Booij, H. C. Rheol Acta 1966, 5, 215.
15. Wong, C. M.; Isayev, A. I. Rheol Acta 1989, 28, 176.
16. Isayev, A. I.; Wong C. M. J Polym Sci Part B: Polymer Physics 1988, 26, 2303.
17. Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. Macromolecules 1997, 30, 1426.
18. Mewis, J.; Kaffashi, B.; Vermant, J. Macromolecules 2001, 34, 1376.