Effect of Ultrasound on the Viscoelasticity and Rheology of Polystyrene Extruded Through a Slit Die

Yingzi Chen, Huilin Li

The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, People's Republic of China

Received 13 November 2003; accepted 13 April 2004
DOI 10.1002/app.20831
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The rheological and processing behavior (melt fracture performance) of polystyrene extruded through a slit die is studied as a function of the ultrasound vibration intensity. The apparent viscosity reduces 29% and die pressure reduces 22% compared with that without ultrasound vibration. The viscosity of the melt decreases exponentially as ultrasound intensity increases and an Arrhenius equation fits the data well. Ultrasound vibration also leads to a decrease of the die swell ratio and a postponement of melts fracture. Characteristic relaxation times at the onset of melt fracture are calculated according to the hypothesis that the melt fracture behavior of a polymer is affected by a balance between its viscous (viscosity) and elastic properties (recoverable shear). Ultrasound vibration shortens the relaxation time of polystyrene molecular chains. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2907–2911, 2006

Key words: polystyrene; viscoelastic properties; irradiation

INTRODUCTION

The technology of melt vibration to reduce viscosity during the processing of plastics and to enhance the mechanical performance of the solidified parts has been studied extensively.[1] Ultrasound is one sort of elastic mechanical wave of frequency $10^4 \sim 10^9$Hz. Compared with low frequency mechanical oscillation, ultrasound can influence the viscoelasticity and rheology of polymer melt in a micron dimension. Isayev and coworkers[2–4] reported that, during extrusion, high-intensity ultrasonic waves affect the die characteristics by reducing the pressure and die swell ratio and postpone melt fracture. Keishiro[5] applied a 20 ~ 100 kHz ultrasound wave in a direction vertical to the rubber discharging direction through an extrusion and obtained rubber sheets with low die swell occurrence and good dimension accuracy. Peshkovskii et al.[6] described a method for eliminating the unstable flow of polybutene melt by application of ultrasonic irradiation.

This paper presents the results of work regarding the influence of ultrasound vibration on polystyrene extruded through slit die. The effect of varying the ultrasonic intensity during extrusion on die characteristics, die swell, and viscosity is described. The relaxation characteristic of the polystyrene melt is analyzed as well.

Correspondence to: H. Li (nic7703@scu.edu.cn).

Journal of Applied Polymer Science, Vol. 100, 2907–2911 (2006)

EXPERIMENTAL

Materials

Polystyrene (PS) PG-383M (Zhenjiang Chimei Co., LTD, Jiangsu, China) properties are as follows: density, 1.05 g/cm^3; melt flow index, 3.0 g/10 min (200°C, 5 Kg, D-1238).

Equipment

The ultrasound–extrusion experimental setup consists of a single-screw extruder (d = 20 mm, L/D = 25) with a slit die, and an ultrasonic generator (Fig. 1). The ultrasonic frequency is 20 kHz and power ranges from 0 to 300 W. The direction of ultrasonic vibration coincides with that of the melt flow during extrusion. With a size of width (W) = 9.2 mm, height (H) = 0.5 mm, length (L) = 6.5 mm, the slit die has a temperature sensor and high-temperature pressure transducer on it.

Rheology

Treating the extruding die as an extrusion slot die rheometer, we obtained a rheological curve of PS at various ultrasonic intensities with a die temperature of 200°C.

$$\tau_w = \frac{\Delta P H}{2L} \tag{1}$$

$$\dot{\gamma}_w = \frac{6Q}{WH^2} \tag{2}$$

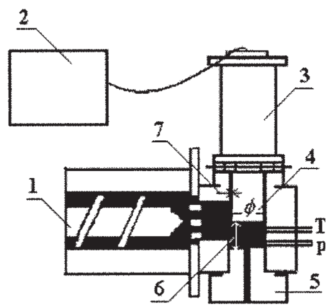

Figure 1 Scheme of ultrasonic wave—extrusion system: 1, extruder; 2, ultrasonic generator; 3, piezoelectric transducer; 4, cylindrical horn with diameter ϕ = 10 mm; 5, slit die; 6, gap between horn tip and entry to the slit die is 10 mm; 7, gap between the lateral surface of horn and the die wall is 1 mm; P, pressure transducer; t, thermocouple.

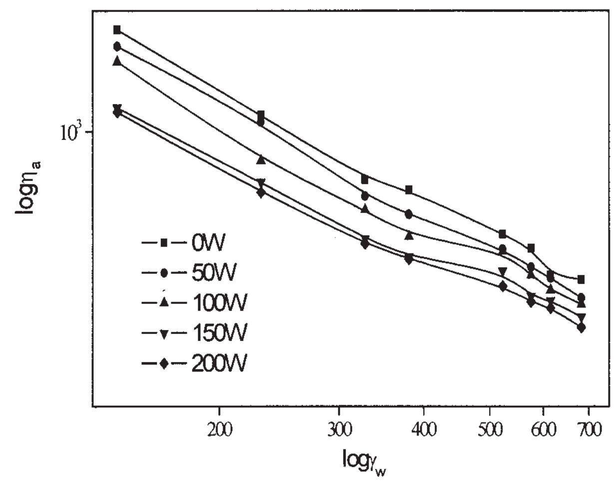

Figure 2 Apparent flow curves of PS in presence of ultrasonic irradiation.

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} \tag{3}$$

Where τ_w is shear stress on the slit wall; $\dot{\gamma}_w$ is the apparent shear rate; η_a is the apparent viscosity; W, H, and L are the width, height, and length of the slit, respectively; ΔP is the pressure drop along the slit, obtained from the pressure transducer at the entrance of the die; and Q is the flow rate, obtained by measuring the extrudate weight per second.

Die swell ratio

Using the same die and extrudion conditions as were used in the rheology experiment, the die swell measurements were also conducted for each sample at different shear rates. The measurements were performed on samples, which were unaffectedly cooled to the ambient temperature after emerging from the die in melt state. The die swell ratio (B) of the PS was calculated using the following equation:

$$B = \frac{h}{H} \tag{4}$$

where H is the height of the die, and h is the height of the extrudates, which was based on the size of the extrudate in the fully swollen sample, i.e., ~ 2 in. away from the die exit.[7]

The onset of melt fracture was identified by means of visual inspection of the cooled extrudates.

RESULTS AND DISCUSSION

Rheology characteristics

Figure 2 depicts the apparent viscosities of PS as a function of ultrasound intensity. When ultrasonic vibration is applied, the apparent viscosity of PS decreases markedly compared with that without ultrasonic vibration. Since low shear rate means a long duration ultrasonic treatment of the melt, the apparent viscosity of PS is reduced more at lower shear rate with ultrasonic irradiation. At the reference shear rate 230.3 s^{-1}, the apparent viscosity changes from 1,076.8 Pa · s when there's no ultrasound to 765.8 Pa · s when the ultrasound intensity is 200 W, i.e., a reduction of 29%. The fluctuation of the apparent viscosities emerges when the shear rate is over 400 s^{-1}. The influence of ultrasound intensity on the apparent shear rate for the onset of melt fracture (critical shear rate) is shown in Figure 3. The critical shear rate increases dramatically between an ultrasound intensity of 0 and 100 W and then slowly increases as the ultrasound intensity increases from 100 to 200 W. Figure 4 shows the extrudates' appearance of PS at different ultrasound intensities. At the shear rate of 522.6

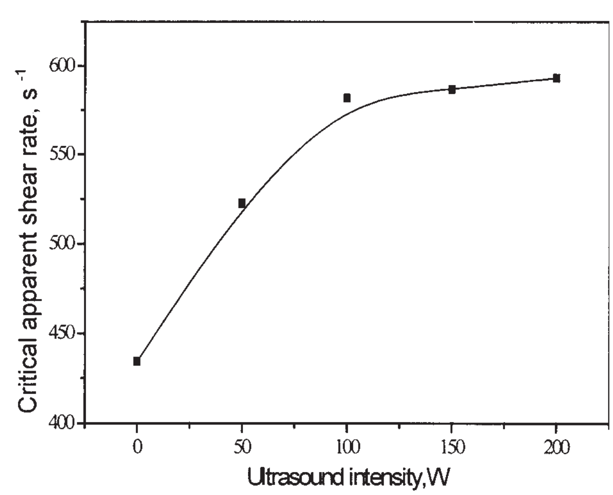

Figure 3 Critical apparent shear rate of PS for the onset of melt fracture with different ultrasound intensity.

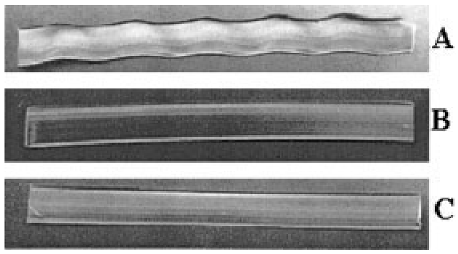

Figure 4 The appearance of the PS extrudates at shear rate 522.6 s^{-1}: (a) 0 W, (b) 100 W, (c) 200 W.

s^{-1}, the extrudate without ultrasound irradiation shows a distorted appearance, which indicates serious melt fracture. No melt fractures occur in the extrudates with ultrasound irradiation at the same shear rate, and the extrudate with 200 W ultrasound irradiation appears to have better dimension accuracy than that with 100 W ultrasound irradiation. It can be concluded that ultrasound vibrations improve the flow of PS melt and postpone melt fracture.

Figure 5 plots the logarithm of apparent viscosities against the reciprocal of ultrasound intensities in a fitted line. An Arrhenius equation is found to fit the data well. That is,

$$\ln \eta_a = \frac{E_a}{KU} + \ln A \quad (5)$$

where U is the ultrasound intensity in W; E_a is the flow activation energy in J/mol; A is a relative constant; and K, with the dimension of s/mol, is a constant related to the ultrasound absorption coefficient of the materials.

This implies that the viscosity of the melt decreases exponentially as ultrasound intensity increases. When ultrasound vibration is applied, the free volumes of the PS melt and the activity of the molecular chains increases, and the interaction of molecules becomes poor. Accordingly, the flow of PS melt is improved.

TABLE I
Flow Activation Energy at Various Shear Rates

Shear rate, (s^{-1})	230.3	327.7	380.2
E (J/mol)	*20.30 K*	*13.83 K*	*13.44 K*

The values of the calculated relative flow activation energy, E_a, are listed in Table I. Since K is a constant at a decided ultrasound frequency, the flow activation energy deceases as the shear rate increases. This means the sensitivity of the viscosity of PS melt to ultrasound vibration decreases as the shear rate increases. It suggests that ultrasound vibration cooperates with the shear in disentangling the molecular network to increase the flow of PS melt. This may be very useful in improving the flow of the polymer melt, which is not sensitive to shear.

Elastic effect

The die pressures at various ultrasonic intensities were plotted in Figure 6 as a function of the flow rate. It is shown that higher ultrasonic intensity contributes to a larger reduction of die pressure. In the case of 0.1 g/s of flow rate and 200 W of ultrasonic intensity, the die pressure decreases 22% of that without ultrasound vibration.

The die pressure ΔP is the sum of three parts, i.e.:

$$\Delta P = \Delta P_{\text{ent}} + \Delta P_{\text{die}} + P_{\text{exit}} \quad (6)$$

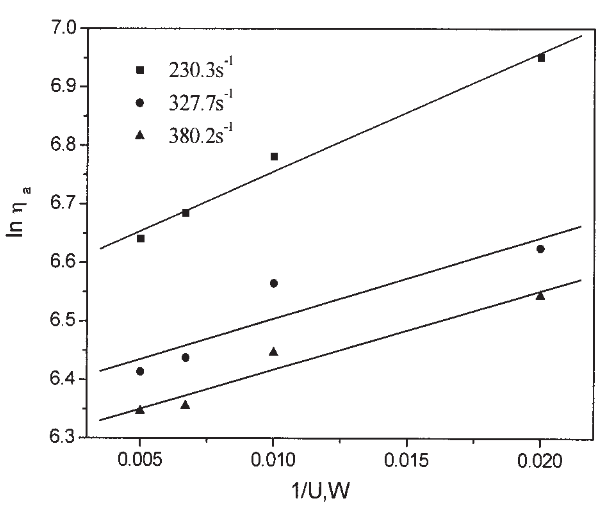

Figure 5 Correlation between apparent viscosity and ultrasound intensity at various shear rates.

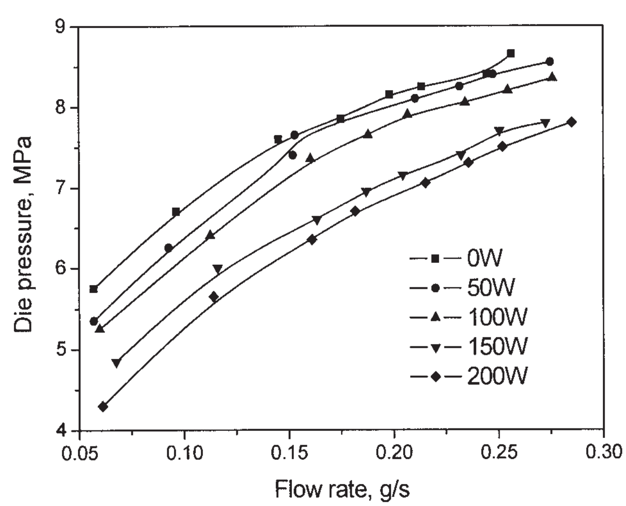

Figure 6 Die pressure of PS as a function of flow rate with various ultrasound intensities.

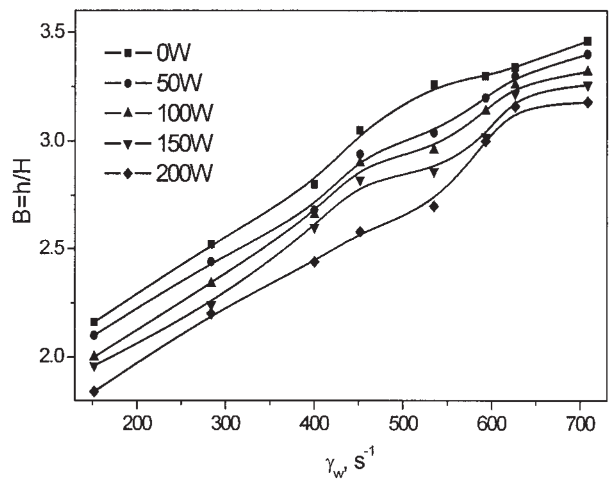

Figure 7 The die swell ratios of PS with various ultrasound intensities.

where ΔP_{ent} is the entrance pressure loss induced by elastic deformation and viscous dissipation; ΔP_{die} is induced by the viscous dissipation when the melt flows along the die; and ΔP_{exit} is the residual exit pressure, which is usually very small and therefore has been considered as negligible in our data treatment. Since the flow passage of the slit die used in this study is very short (length of the die is 6.5 mm), the value of ΔP_{die} is not very notable and ΔP_{ent} contributes to ΔP in a great measure.

As shown in Figure 1, the ultrasonic horn is right above the die. There is a 10-mm gap between the horn tip and entry to the slit die to form the ultrasound-affecting zone. When there is no ultrasound vibration, convergent flow of the melt happens in the entry zone. Elastic tensile strains of the molecules result in a great decrease in the die pressure. When ultrasound vibration is applied, it is speculated to influence the PS melt flow in two ways such as:

1. Ultrasound wave activates the molecular chains, so that elastic tensile strains can be recovered very quickly.
2. Intensive ultrasound vibrations disturb the convergent flow of the melt in the entry zone so much that it changes the stream pattern to a way in which there is less elastic tensile strain.

Ultrasound vibration reduces the elastic effect of the PS melt and thus reduces the die pressure.

The changing of the die swell ratio also supports ultrasound vibration reducing the elastic deformations of the PS melt. As shown in Figure 7, ultrasound vibration reduces the die swell ratio visibly. The higher the ultrasound intensity, the smaller the die swell ratios.

Apparent characteristic relaxation time

It was discussed that a characteristic relaxation time may be a relevant quantity to formulate a criterion/correlation for the onset of melt fracture.[8–10] Based on these studies, a hypothesis may be formulated that the melt fracture behavior of a polymer is affected by a balance between its viscous (viscosity) and elastic properties (recoverable shear). This hypothesis was tested by calculating characteristic relaxation times for all polymers at the onset of melt fracture. Such an apparent characteristic relaxation time, λ, can be defined[11] as the ratio of polymer viscosity, η, and shear modulus, G, that is:

$$\lambda = \eta / G \tag{7}$$

The shear modulus can be estimated through the measurement of the die swell ratio at the onset of melt fracture, such that $G = \tau/\gamma_\infty$; τ is the recoverable shear strain at the die wall. The values of γ_∞ for different polymer samples were calculated[12] from the following equation:

$$B_L^2 = \frac{2}{3}\gamma_\infty\left[\left(1+\frac{1}{\gamma_\infty^2}\right)^{\frac{2}{3}} - \frac{1}{\gamma_\infty^3}\right] \tag{8}$$

where B_L is the die swell ratio.

Figure 8 plots the characteristic relaxation time as a function of the ultrasound intensity. The apparent relaxation time decreases sharply as ultrasound intensity is increased from 0 to 50 W and then decreases slowly between ultrasound intensity of 50 and 200 W.

The elasticity and non-Newtonianism of polymer melt are attributed to the orientation of the molecular chains in the flow. The entanglements of molecular

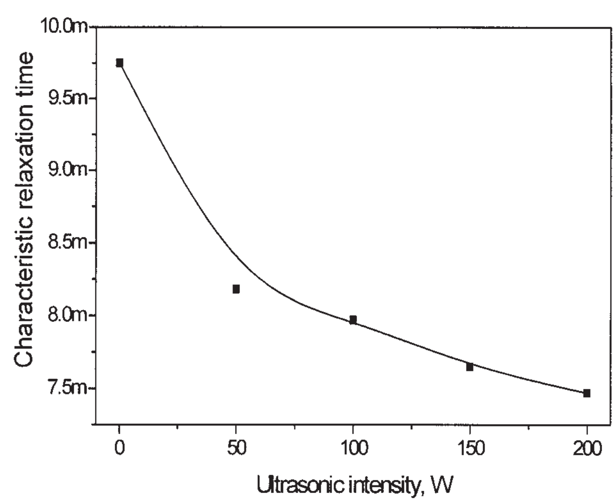

Figure 8 The characteristic relaxation time versus ultrasound intensities.

chains increase the possibilities of molecular chains orientation and slow down the relaxation. When ultrasound is applied, its powerful vibration, shatter, and cavitations help to arouse and activate molecular chains, which leads to disentanglement of molecular chains. Therefore, the orientation of the molecular chains can recover very quickly.

CONCLUSION

The ultrasonic vibration has a significant effect on the flow of PS melt in the slit die. With an increase in ultrasound intensity, the apparent viscosity, die pressure, and die swell ratio decrease, and the melt fracture is postponed. The viscosity of the melt decreases exponentially as ultrasound intensity is increased and an Arrhenius equation fits the data well. Ultrasonic vibration disturbs the convergent flow of the melt in the entry zone, activates molecular chains, and makes them disentangled, which reduces the molecular chains orientation and elastic deformation. Therefore, the relaxation time decreases as ultrasound intensity is increased.

This paper is based on the results from the subject supported by the Special Funds for Major State Basic Research Projects of China (G1999064809) and National Nature Science Foundation of China (50233010).

References

1. Ibar, J. P. Polym Eng Sci 1998, 38, 1.
2. Isayev, A. I.; Wong, C. M.; Zeng, X. SPE ANTEC Tech Paper 1987, 33, 207.
3. Isayev, A. I. In Proceedings of the 23rd Israel Conference of Mechanical Engineering., Paper 5.2.3, 1990; p 1.
4. Isayev, A. I.; Wong, C. M.; Zeng, Z. Adv Polym Technol 1990, 10, 31.
5. Keishiro, O. Jpn Patent 91 253 323, 1991; from Chem Abstr 1992, 116, 108130v.
6. Peshkovskii, S. L.; Feidman, M. L.; Tukachinskii, A. I. Polym Compos 1983, 4, 126.
7. Sombatsompop, N.; Dangtungee, R. J Appl Polym Sci 2001, 82, 2525.
8. Sukhadia, A. M. SPE ANTEC Tech Paper 1997, 43.
9. Wang, S. Q.; Drda, P. A.; Inn, Y. W. J Rheol 1996, 40, 875.
10. Kazatchkov, I. B.; Bothnet, N.; Goyal, S. K.; Hatzikiriakos, S. G. J Appl Polym Sci 1996, 39, 804.
11. Cogswell, F. N. Polymer Melt Rheology: A Guide to Industrial Practice; John Wiley & Sons: New York, 1981.
12. Wang, J.; Porter, R. S. Rheol Acta 1995, 34, 496.