

Ultrasonic Improvement of Rheological Behavior of Polystyrene

GUANGSHUN CHEN, SHAOYUN GUO, HUILIN LI

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

Received 26 January 2001; accepted 16 July 2001

ABSTRACT: The effects of ultrasonic oscillation on die pressure, productivity of extrusion, melt viscosity, and melt oscillating flow of polystyrene (PS) as well as their mechanism were studied in a special ultrasonic oscillations extrusion system developed in our lab. The experimental results show that in the presence of ultrasonic oscillations, the PS melt oscillating flow or surface distortion of PS extrudate is inhibited or disappears. The surface appearance of PS extrudate gets greatly improved. The die pressure, melt viscosity, flow activation energy, and consistency efficiency of PS decreased and the productivity of PS extrudate increased in the presence of ultrasonic oscillation. The shear sensitivity of PS melt viscosity is decreased because of the increase of its power law index in the presence of ultrasonic oscillation. Introduction of ultrasonic oscillation into PS melt can greatly improve the processibility of PS. Their possible mechanism is also proposed in this article. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2451–2460, 2002

Key words: polystyrene; ultrasound; rheological behavior

INTRODUCTION

The rheological behavior of polymer is an important parameter for polymer processing. The high hydrodynamic resistance caused by the high viscosity of polymer melt, elastic turbulence, or melt fracture are major obstacles to increasing the productivity of extrusion.¹ The traditional methods for controlling the surface and mechanical properties of polymers are the addition of processing aids or plasticizers and the adjustment of opera-

tion parameters (such as temperature, pressure, and rotation speed of extruder). However, these methods are found in many cases to be insufficient and even inapplicable and to be limited by polymer's thermal stability. These methods mainly rely on operators' experience and improvement of equipment, which means an increase in production cost. Therefore, development of new methods involving direct influence on the rheological characteristics of polymer melts, which would make it possible to expedite extrusion, is an urgent scientific and technological problem.

One new, attractive processing technique is the utilization of melt vibration technology. In general, there are three purposes for the application:

1. To homogenize and increase the density of materials molded;
2. To improve the processibility of polymer and control the morphological structure of polymer;

Correspondence to: S. Guo (nic7702@pridns.scu.edu.cn).

Contract grant sponsor: Special Funds for Major State Basic Research Projects of China; contract grant number: G1999064800.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 29774017.

Contract grant sponsor: State Education Ministry of China.

Journal of Applied Polymer Science, Vol. 84, 2451–2460 (2002)
© 2002 Wiley Periodicals, Inc.

- To generate heat locally by internal friction or decrease surface stress at the wall interface between melt and die to increase throughputs.

Mena et al.²⁻⁴ studied in detail the influence of vibrations on Poiseuille flow of a non-Newtonian fluid for the case of longitudinal vibrations, and Kazakia and Rivlin⁵⁻⁶ studied that in detail for transverse vibrations. Superimposing oscillations upon a constant pressure gradient flow of a viscoelastic liquid produces very large increases in flow rate as compared with the stationary flow. More recently, Casulli et al.⁷ studied the effect of superimposing longitudinal and transverse oscillations on the die section at the exit of an extruder. They found that the effect of the oscillations can increase the mechanical properties of the extrudate as well as reduce die pressure, and by the aid of vibrations, the flow rate through the die is enhanced and the die swell is diminished. Isayev et al.⁸⁻⁹ studied the effect of oscillations on rheological and mechanical properties of some polymers and found that the output could be increased without increasing the power consumption during extrusion for high extrusion rates. Qu¹⁰⁻¹¹ invented a novel electromagnetic dynamic plasticizing extruder for polymers. In the extruder, because of the harmonic vibration or forced vibration of the rotator, the vibration field caused by electromagnetic field is successfully applied to the entire process of the polymer extrusion. It was found that the mechanic properties of HDPE and LDPE films get improved under vibration force field. The vibration force field can enhance the compatibility of polymer blends and filled polymers.

High-intensity ultrasounds are high-frequency and low-amplitude oscillations as compared with sound oscillations and mechanical vibrations. They are widely employed in biology, welding of thermoplastics, machining, cleaning, chemical reactions, and so on. The major chemical effects of ultrasound are due to cavitation.¹² Cavitation in the ultrasonic field implies nucleation, growth, and subsequent claps of bubbles or cavities, resulting in violent shock waves with a high temperature of ~ 5000 K and a high pressure of ~ 1000 bar. The degradation of polymer in cavitation fields occurs by the action of hydrodynamic forces of cavitation. The macroradicals formed by scission of polymer chains under ultrasonic irradiation can initiate the polymerization of monomers and

the different kinds of macroradicals can recombine to form graft/block copolymers. A great deal of literature on degradation and copolymerization of polymers under ultrasonic irradiation has been generated.¹³⁻²⁰ A series of novel copolymers were produced under ultrasonic irradiation, some of which could not be synthesized from their monomers. However, most research focused on the degradation and copolymerization of polymers in solutions. In other applications, Isayev et al.²¹⁻²² reported a novel ultrasonic technology for devulcanization of vulcanized elastomer. The high-intensity ultrasonic waves in the presence of pressure and heat can rapidly break up the three-dimensional network in crosslinked rubber through the scission of C—S, S—S, and C—C bonds. The devulcanized rubber can be reprocessed, reshaped, and revulcanized in the same way as virgin rubber. Although the viscosity of polymeric fluids was found to decrease and the flow rate increased because of the superposition of ultrasonic wave in extrusion, the application of ultrasonic wave to polymer processing and its mechanism have received little attention. In our previous work,²³⁻²⁴ we introduced ultrasonic wave to polymer extrusion. It was found that the appearance of high-density polyethylene (HDPE) and LLDPE (linear low-density polyethylene) extrudates gets greatly improved in the presence of ultrasonic wave. The ultrasonic irradiation can greatly improve the processibility and mechanical properties of HDPE and LLDPE. In this article, the effects of ultrasonic intensity on the die pressure, apparent viscosity, melt fracture, and die swell of PS extrudate and its mechanism were studied. The variation of molecular weight and its distribution of polystyrene (PS) under ultrasonic wave were also discussed.

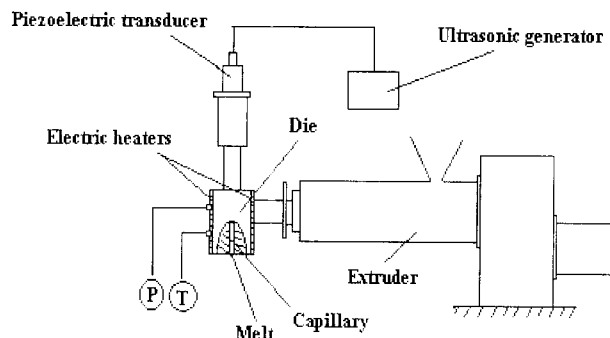


Figure 1 Schematic diagram of ultrasonic irradiation extrusion system.

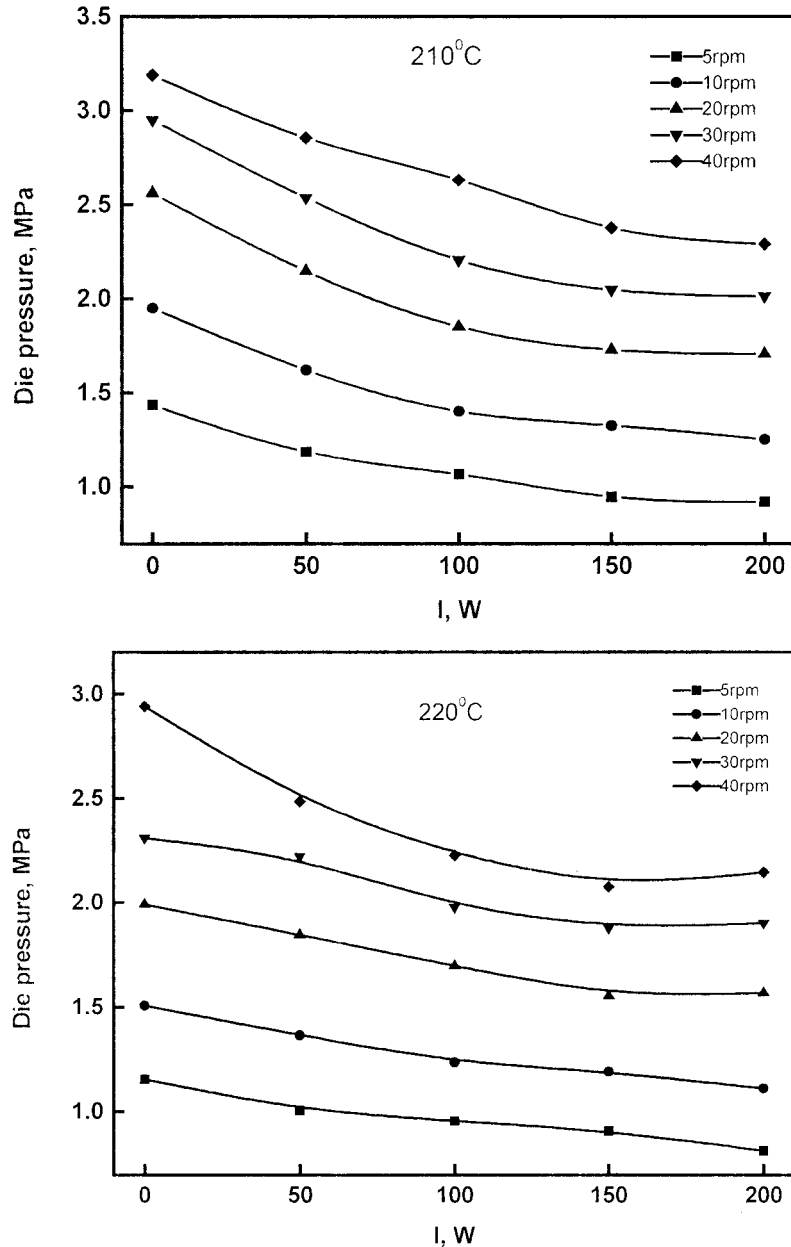


Figure 2 Die pressure of PS versus ultrasound intensity I .

EXPERIMENTAL

Materials and Equipment

Materials used were common-grade PS with a number-average molecular weight of 7.34×10^4 and polydispersity of 4.9, supplied by Nanjing Plastic Factory, Nanjing, China. The experiments were carried out in a special ultrasonic oscillations extrusion system developed in our lab, the schematic diagram of which is shown in Figure 1. It includes a die special horn capillary attached to

a single-screw extruder. A probe of ultrasonic oscillation with a maximum power output of 300 W and a frequency of 20 kHz is inserted into the polymer melt of the die and the oscillation is in the direction parallel to the flow of polymer melt. A pressure transducer and a thermal couple at the die entry are installed to record continuously the variation of die pressure and temperature during extrusion. Flow rate through the die was monitored by means of detecting the weight of the extrudate emerging from the die.

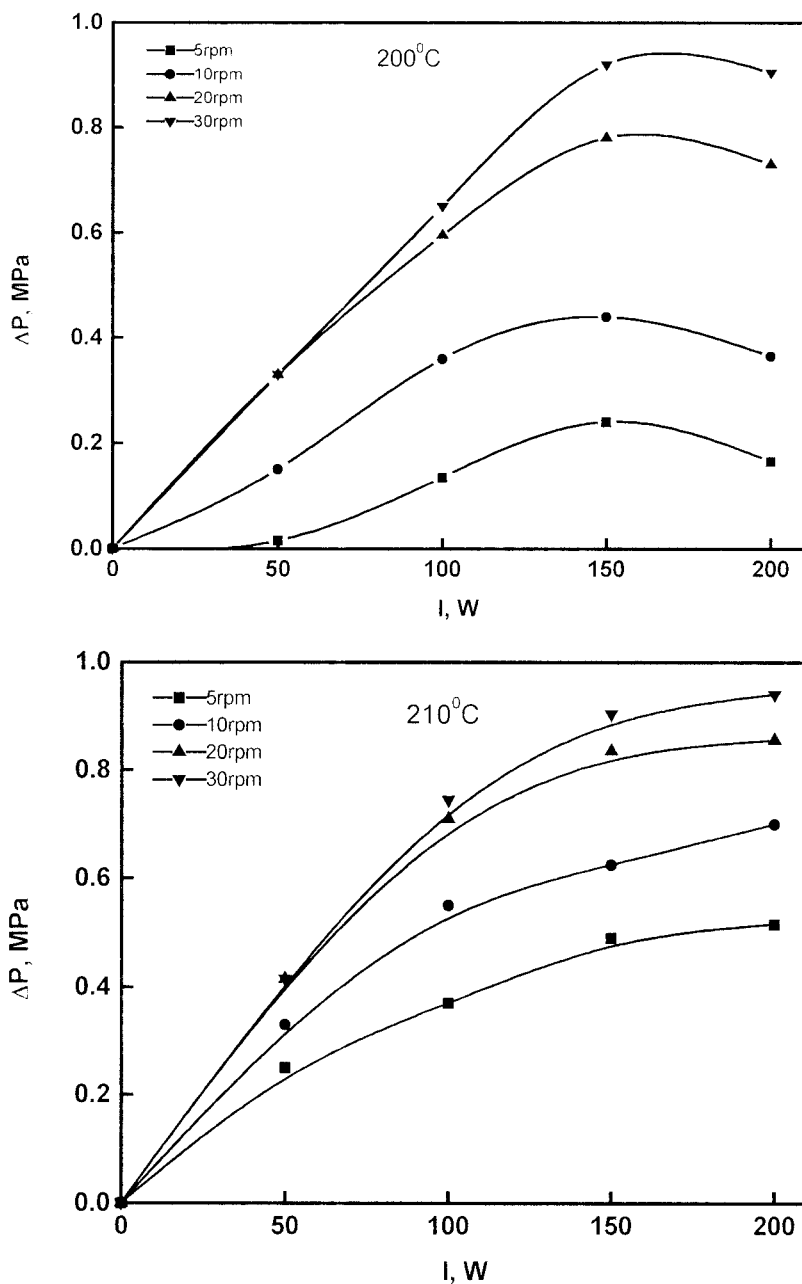


Figure 3 Absolute die pressure drop ΔP of PS versus ultrasound intensity I .

Measurement and Calculation of Rheological Parameters

A special ultrasonic oscillation extrusion system developed in our lab was used to measure rheological properties of PS in the presence of ultrasonic oscillations. Measurements for die pressure in the presence of ultrasonic oscillation were performed at melt temperatures in die between 200 and 240°C by steps of 10°C and superimposed ultrasonic intensities between 0 and 250 W by steps of 50 W.

The apparent viscosity η_a , shear rate $\dot{\gamma}_w$, and shear stress, σ_{sw} , are expressed as

$$\eta_a = \frac{\pi PR^4}{8QL}, \quad \dot{\gamma}_w = \frac{4Q}{\pi R^3}, \quad \sigma_{sw} = \frac{PR}{2L}$$

where P is the die pressure, L is the length of the capillary, R is the radius of the capillary, and Q is the volume flow rate. Viscous flow activation energy (ΔE_{η_a}) of melt obeys the Arrhenius equation:

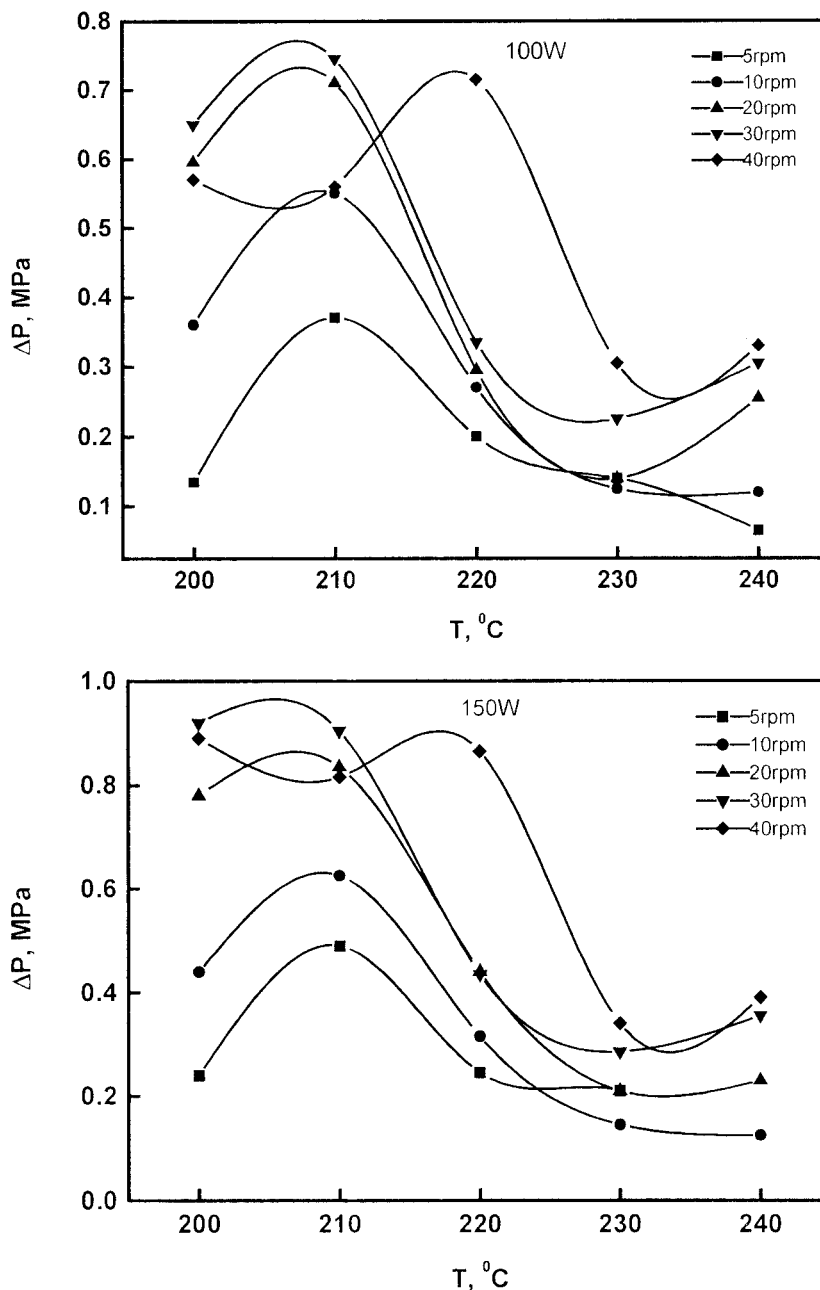


Figure 4 Absolute die pressure drop ΔP of PS versus melt temperature T .

$$\lg \eta_a = A + \frac{\Delta E_{\eta_a}}{2.303RT}$$

Molecular weight and its distribution of PS were measured by GPC-150C produced by Waters Associates Co. The solvent used was tetrahydrofuran (THF). Flow rate was 1.0 mL/min. The standard sample used was PS. The mechanochemical degradation of PS in the presence of ultrasonic wave was investigated throughout the measurement.

RESULTS AND DISCUSSION

Effects of Ultrasonic Oscillations on Die Pressure of PS

Die pressure changes with ultrasound intensity were measured at melt temperatures in die: 200, 210, 220, 230, and 240°C, respectively. Figure 2 shows the dependence of die pressure at different rotation speeds of extrusion on ultrasound intensity. The die pressure decreases with the increase

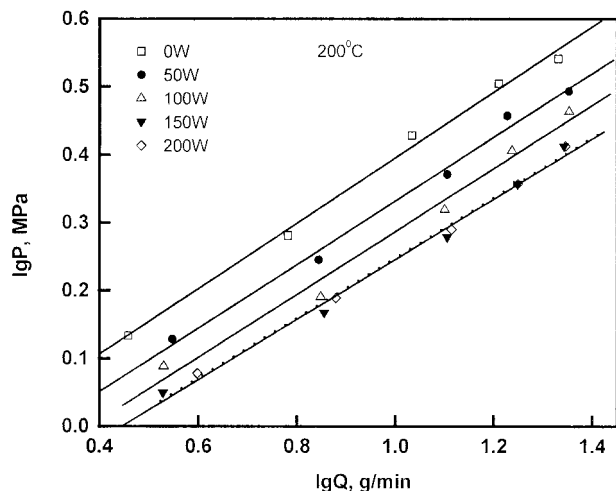


Figure 5 Die pressure P of PS versus volume flow rate Q .

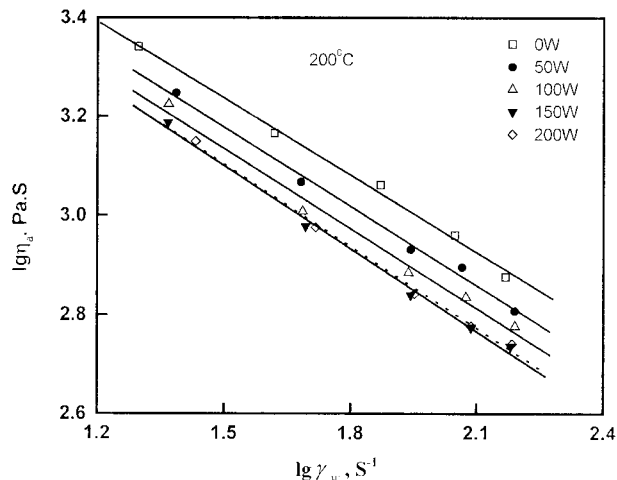


Figure 6 Apparent viscosity η_a of PS versus shear rate γ_w .

of ultrasound intensity and the decrease of rotation speed of extrusion. The decrease of die pressure in the presence of ultrasonic oscillations indicates that by the aid of ultrasonic oscillations the extrusion temperature could drop and the processibility of PS improved. As shown in Figure 3, absolute die pressure drops, ΔP ($\Delta P = P_1 - P_2$, where P_1 and P_2 are the die pressures in the absence of ultrasonic oscillation and in the presence of ultrasonic oscillations, respectively) goes up, as the ultrasound intensity rises and the ro-

tation speed of extrusion increases. Figure 4 indicates that ΔP strongly depends on melt temperature and rotation speed of extrusion. When the rotation speed of extrusion is ≤ 30 rpm, ΔP passes through a maximum at melt temperature of 210°C . Then, ΔP drops with the rise of melt temperature. If the rotation speed of extrusion is 40 rpm, ΔP passes through a maximum at a melt temperature of 220°C . This is quite different from that of our previous work on HDPE and LDPE extrusion in the presence of ultrasonic oscillations.

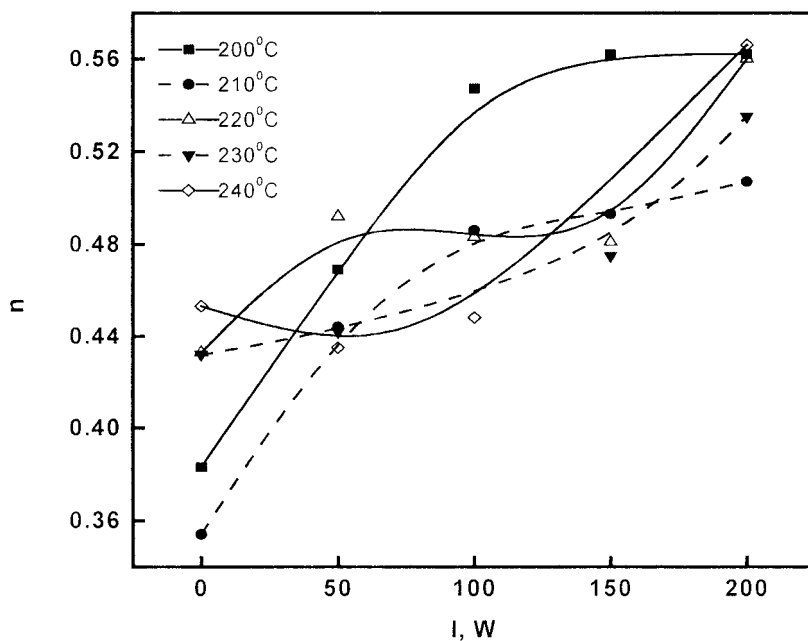


Figure 7 Power law index n of PS versus ultrasound intensity I .

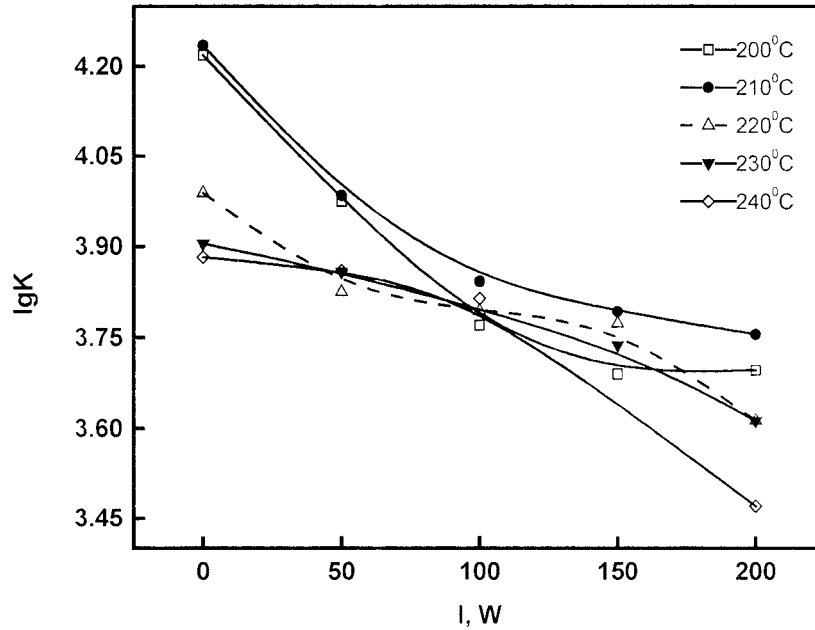


Figure 8 Consistency coefficient k of PS versus ultrasound intensity I .

tions.²⁴ This complicated phenomenon is ascribed to oscillating flow of PS melt in the extrusion through capillary die.

In our experiments, we observed that when PS extrudates showed visible oscillating flow, larger pressure oscillations appeared as compared with stable flow. At this moment, introduction of ultra-

sonic oscillations into PS melt could cause a remarkable decrease of die pressure and the oscillating flow can be inhibited or changed to stable flow. The maximum of ΔP in the presence of ultrasonic oscillations corresponds to the transition of oscillating flow to stable flow. The details will be discussed later.

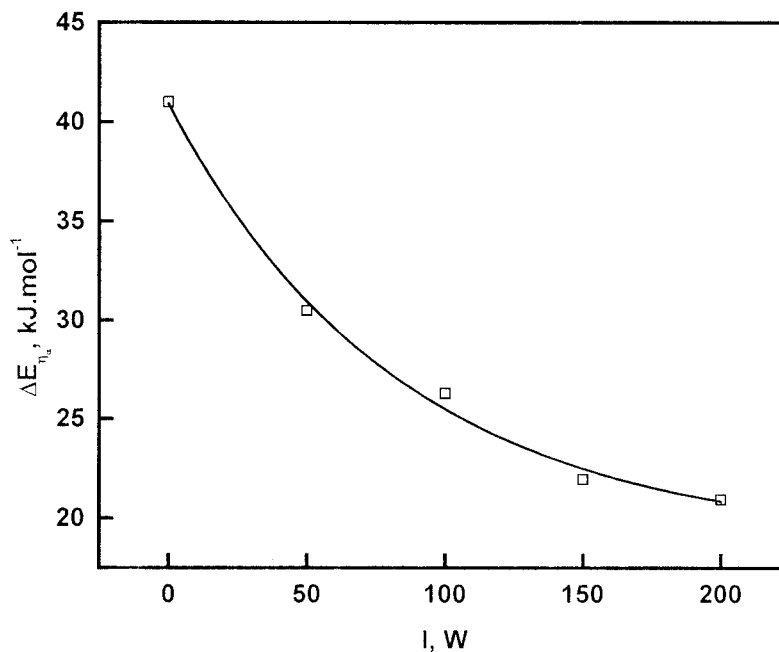


Figure 9 Viscous flow activation energy ΔE_{η_a} of PS versus ultrasound intensity I .

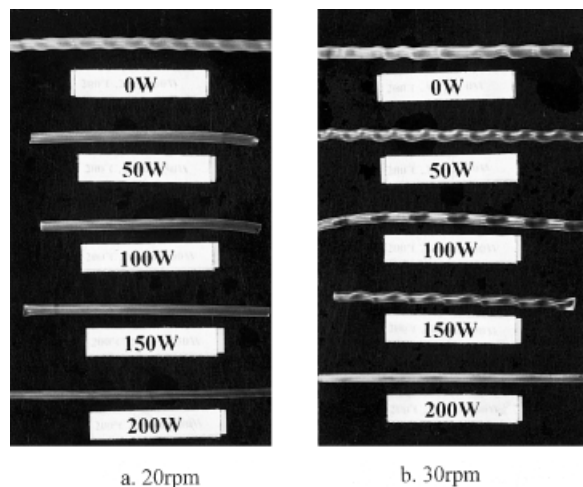


Figure 10 Photos of PS extrudates at 200°C.

Effect of Ultrasonic Oscillations on Productivity of Extrusion

Die pressure P versus volume flow rate Q at different temperatures were found highly affected by ultrasound intensity (Fig. 5). The curves of $\lg P$ versus $\lg Q$ move to the right with the increase of ultrasound intensity, indicating that volume flow rate Q gets increased in the presence of ultrasonic oscillations at the same P . It indicates that ultrasonic oscillations can increase the productivity of extrusion. This is similar to the result predicted by Kazakia and Rivlin and Leonov et al.^{6,25,26} The reason may be a decrease of surface stress at the wall interface between melt and die in the presence of ultrasonic oscillations.

Effect of Ultrasonic Oscillations on Melt Viscosity of PS

Figure 6 shows viscosity curves during extrusion in the presence and absence of ultrasonic oscillations. It shows that $\lg \eta_a$ versus $\lg \gamma_w$ has a linear relation, indicating that at different temperatures in the presence and absence of ultrasonic oscillations the relationship between apparent viscosity η_a of PS and shear rate γ_w obeys the following power law equation:

$$\eta_a = k \gamma_w^{n-1}$$

where k is the consistency coefficient and n is the power law index. As shown in Figure 7, n of PS increases with the rise of ultrasound intensity when ultrasonic oscillations are induced into PS

melt, indicating that the shear sensitivity of PS is decreased in the presence of ultrasonic oscillations. The consistency coefficient of PS gets decreased with the rise of ultrasound intensity (Fig. 8), showing that melt viscosity of PS gets decreased in the presence of ultrasonic oscillations. The viscous flow activation energy of PS versus ultrasound intensity is shown in Figure 9. It is observed from this figure that the viscous flow activation energy of PS reduces with the rise of ultrasound intensity.

Effect of Ultrasonic Oscillations on Unstable Flow of PS Melt and Die Swell of PS Extrudate

In general, a shark-skinned surface of polymer extrudates appears at a critical shear stress and shear rate, and at an even higher shear stress, polymer extrudates present an alternating section of smooth and shark-skinned surfaces, known as oscillating flow. Oscillating flow also causes large pressure oscillation. This is the major obstacle to increase the rate of production in polymer processing operations such as extrusion and film blowing. Therefore, increasing the critical shear rate and shear stress for elastic turbulence flow of melt is the focused task to increase productivity. As shown in Figure 10, the surface of PS extrudate shows apparent distortion when PS is extruded at 200°C and 20 rpm, and PS melt oscillating flow becomes more serious with the increase of rotation speed of screw. However, the melt oscillating flow phenomena disappear when PS is extruded at 200°C, 20 and 30 rpm with superimposing 50 and 200 W ultrasonic oscillations.

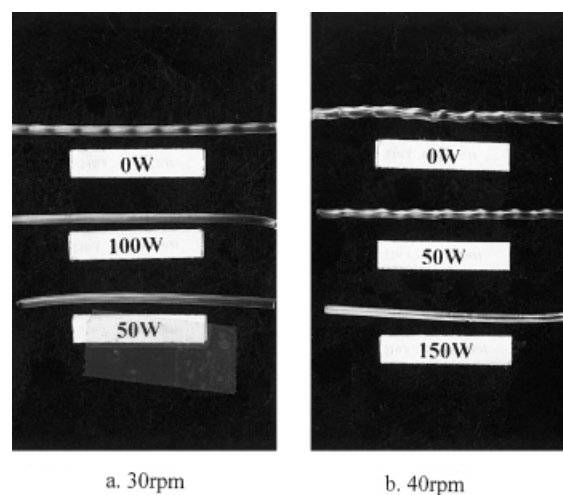


Figure 11 Photos of PS extrudates at 210°C.

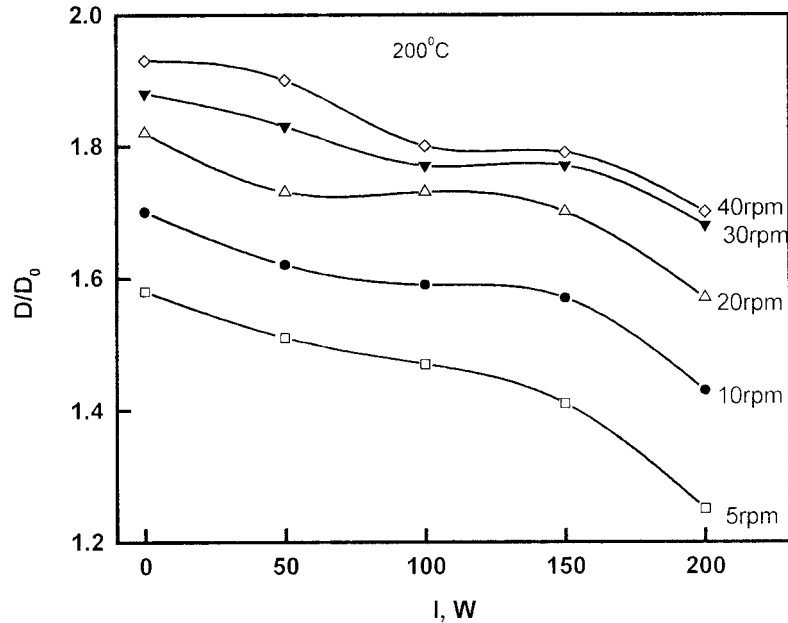


Figure 12 Die swell of PS extrudates versus ultrasound intensity I .

tions, respectively. This indicates that ultrasonic oscillations could increase critical shear rate for PS melt oscillating flow. The productivity of PS gets improved in the presence of ultrasonic oscillations. Figure 11 shows a similar result with that in Figure 10. Figure 12 shows that the die swell of PS extrudates reduces with the increase of ultrasound intensity due to the decrease of viscosity.

Mechanism for Improvement of Rheological Behavior of PS Melt

The reptation model is suitable for describing the motion of a polymer chain. According to the model, the motion of a polymer chain is carried out through the wriggling motion of minor chain segments in the polymer chain. High-frequency and low-amplitude ultrasonic oscillation can activate the wriggling motion of minor chain seg-

ments because of their short relaxation time and break through the entanglements of polymer chains.²⁷ It causes melt elasticity, and the interaction between polymer chains decreased. Therefore, the apparent viscosity flow activation energy of PS and elastic turbulence of PS during extrusion get decreased in the presence of ultrasonic oscillation. Specific details will be studied further in our future work.

The data listed in Table I show that ultrasonic oscillations cause the number-average molecular weight (\bar{M}_n) of PS extrudate to decrease and its molecular weight distribution to increase. \bar{M}_n of PS extrudate decreases and its distribution increases with the increase of ultrasound intensity. The low molecular weight PS formed by mechanochemical degradation under ultrasonic oscillations acts as a plasticizer for the high molecular

Table I Effect of Ultrasonic Oscillation on PS Molecular Weight and Its Distribution

Extrusion Conditions	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	\bar{M}_w / \bar{M}_n
5 rpm, 220°C, 0 W	7.09	33.04	4.7
5 rpm, 220°C, 200 W	5.52	34.69	6.3
5 rpm, 220°C, 250 W	4.45	27.49	6.2
10 rpm, 220°C, 0 W	6.62	33.82	5.1
10 rpm, 220°C, 200 W	4.54	35.52	7.8

weight of PS. The die pressure and melt viscosity of PS get decreased.

CONCLUSION

The die pressure, apparent viscosity, flow activation energy, and die swell of PS during extrusion get greatly decreased in the presence of ultrasonic oscillations and decrease as the ultrasound intensity increases. The productivity of PS extrusion increases with the increase of ultrasound intensity. The processibility of PS gets greatly improved. Ultrasonic oscillations hold up PS melt oscillating flow phenomenon. The appearance of PS extrudate gets improved in the presence of ultrasonic oscillations.

The authors are grateful to the Special Funds for Major State Basic Research Projects of China (G1999064800), National Natural Science Foundation of China (29774017), and the State Education Ministry of China for financial support of this work.

REFERENCES

- Ibar, J. P. *Polym Eng Sci* 1998, 38, 1–20.
- Manero, O.; Mena, B. *Rheol Acta* 1977, 16, 573–576.
- Manero, O.; Mena, B.; Valenzuela, R. *Rheol Acta* 1978, 17, 693–697.
- Mena, B.; Manero, O.; Binding, D. M. *J Non-Newtonian Fluid Mech* 1979, 5, 427–448.
- Kazakia, J. Y.; Rivlin, R. S. *Rheol Acta* 1978, 17, 210–226.
- Kazakia, J. Y.; Rivlin, R. S. *J. Non-Newtonian Fluid Mech.* 1979, 6, 145–154.
- Casulli, J.; Clermont, J. R.; Von Ziegler, A.; Mena, B. *Polym Eng Sci* 1990, 30, 1551–1556.
- Isayev, A. I.; Wong, C. M.; Zeng, X. *Adv Polym Tech* 1990, 10, 31–45.
- Isayev, A. I.; Wong, C. M. *J Polym Sci, Polym Phys Ed* 1988, 26, 2303–2327.
- Qu, J. P. U.S. Pat. 5,217,302, 1993.
- Qu, J. P. Proceeding of 16th Annual Meeting of the Polymer Processing Society International; Shanghai, China, June 18–23, 2000; pp 195–196.
- Mason, T. J. in *Chemistry with Ultrasound*; Mason, T. J., Ed.; Elsevier Applied Science: London/New York, 1991; pp 4–11.
- Price, G. J.; White, A. J.; Clifton, A. A. *Polymer* 1995, 36, 4919–4925.
- Price, G. J.; West, P. J. *Polymer* 1996, 37 (17), 3975–3978.
- Gonzalez De Los Santos, E. A. Joswefina Lozano Gonzalez, M.; Concepcion Gonzalez, M. *J Appl Polym Sci* 1998, 68, 45–52.
- Shen, Y.; Chen, K.; Wang, Q.; Li, H.; Xu, H.; Xu, X. *J Macromol Sci, Chem* 1986, 23, 1415–1431.
- Chen, K.; Chen, S.; Xu, X. *J Macromol Sci, Chem* 1986, 29, 55–64.
- Fujiwara, H.; Kimura, T. *Polym Bull* 1992, 28, 189–196.
- Fujiwara, H.; Goto, K. *Polym Bull* 1990, 23, 27–33.
- Fujiwara, H.; Kimura, K.; Mori, H.; Goto, K.; et al. *Polym J* 1981, 13, 927–933.
- Isayev, A. I.; Chen, J. U.S. Pat. 5,284,625, 1994.
- Isayev, A. I.; Chen, J.; Tukachmsky, A. *Rubber Chem Technol* 1995, 68, 267–280.
- Li, Y.; Guo, S.; Chen, G.; Li, H. *J Polym Mater Sci Eng (Chinese)* 1999, 15, 142–144.
- Li, Y.; Guo, S.; Li, H. Proceeding of 16th Annual Meeting of the Polymer Processing Society International; Shanghai, China, June 18–23, 2000; pp 187–188.
- Kazakia, J. Y.; Rivlin, R. S. *Rheol Acta* 1979, 18, 244–255.
- Leonov, A. I.; Lipkina, E. H.; Paskhin, E. D.; Prokunin, A. N. *Rheol Acta* 1976, 15, 411–426.
- Wool, R. P., Ed. *Polymer Interfaces—Structure and Strength*; Hanser Publishers: Munich/Vienna/New York, 1995; pp 41–60.