Effects of Ultrasonic Oscillation on Processing Behaviors of PS, EPDM, and PS/EPDM Blend

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ABSTRACT: In this study, the extrusion processing behaviors of polystyrene (PS), ethylene–propylene–diene terpolymer (EPDM), and their blend (PS/EPDM, 80/20) were studied by using a special ultrasonic oscillation extrusion system developed in our laboratory. The die pressure and volume flow rate were measured at different ultrasonic intensities and screw rotation speeds. The dependences on ultrasonic intensity of die pressure, volume flow rate, and apparent viscosity of polymers, as well as die swell at the same screw rotation speed were investigated. The effects of screw rotation speed on the processing behaviors of polymers and their blend at the same ultrasonic intensity were also studied. The experimental results showed that in the presence of ultrasonic irradiation, the processibilities of polymers and their blend were improved. Their possible mechanism is discussed in this article. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1856–1863, 2006

Key words: ultrasound; extrusion; polystyrene; ethylene–propylene–diene terpolymer; blend

INTRODUCTION

The high hydrodynamic resistance caused by the high viscosity of polymer melt, elastic turbulence, or melt fracture is a major obstacle to increasing the productivity of extrusion.[1] To overcome these disadvantageous conditions, the traditional methods are the addition of processing aids or plasticizers and the adjustment of extrusion parameters (such as temperature, pressure, and rotation speed of extruder). However, in many cases these methods are found to be insufficient and even inapplicable or to be limited due to polymer's thermal stability. At the same time, these methods rely on the operators' experience and improvement of extruder, which means an increase in production cost. Therefore, the development of new methods for the improvement of polymer processibility is a profound work in science and technology.

Recently, many researchers paid great attention to the introduction of mechanical vibration into polymer melts. Mena and coworkers.[2–4] found that longitudinal vibrations increase the flow rate of polymer melts. Kazakia and Rivlin[5,6] also found the same phenomenon in their studies for transverse vibrations. More recently, Casulli et al.[7] studied the effect of superimposing oscillation on the die section at the exit of extruder. They found that the oscillation increases the mechanical properties of the extrudates and the flow rate through the die, as well as reduces the die pressure and the die swell. Qu[8,9] invented a novel electromagnetic dynamic plasticizing extruder for polymers. In the extruder, the vibration field caused by electromagnetic field is successfully applied to the entire process of the polymer extrusion. It was found that the mechanical properties of HDPE and LDPE films improve under vibration force field. The vibration force field also enhances the compatibility of polymer blends and filled polymers.

As compared with mechanical vibration, power ultrasonic irradiation has high-frequency and low-amplitude vibration. Ultrasonic irradiation has been widely applied to synthesis, degradation, and modification of polymers in solution due to ultrasonic cavitation.[10–12] In polymer processing, Isayev et al. found that high-intensity ultrasonic irradiation rapidly breaks 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.[13,14] Despite the potential uses of ultrasonic effect on extrusion process and modification of polymers, little attention has been focused on this field. To the best of our knowledge, many reports are from Isayev's group (USA), Hyungsu Kim's group

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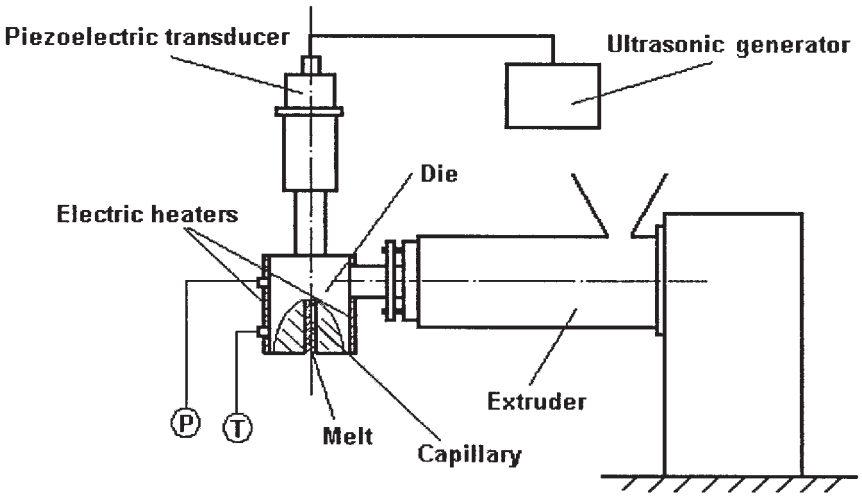

Figure 1 Schematic diagram of ultrasonic oscillation extrusion system.

(Korea), and Guo's group (China). The researches mainly focus on the following:

1. effects of ultrasonic irradiation on characteristics of extrusion process including die temperature, die pressure, flow rate of polymer melt, and rheological behavior of polymer melt.[15–17]
2. ultrasonic improvement of compatibility and enhancement of mechanical properties of polymer blends.[18–22]

In our laboratory, a special power ultrasonic oscillation extrusion system was developed to study the appearance and processibility of polymers and their blends under ultrasonic irradiation. In our previous work, it was found that ultrasonic irradiation improves obviously the processibility and mechanical properties of HDPE, LLDPE, mLLDPE, HDPE/PS, and HDPE/Illite.[15–18]

As an excellent rubber for outdoor application, ethylene–propylene–diene terpolymer (EPDM) rubber was used to enhance the impact strength of polystyrene (PS). To improve the compatibility of PS/EPDM blend, the usual method is to add a compatibilizer or an organic peroxide during reactive extrusion.[23] Unlike this method, we utilized ultrasonic oscillation extrusion system to improve their compatibility and processibility. In this article, the effects of ultrasonic irradiation on the rheological behavior, productivity, and die swell during extrusion processing of PS, EPDM, and PS/EPDM blend were studied.

EXPERIMENTAL

Materials and equipment

The materials used in our work were common-grade PS (PG383M), supplied by Zhenjiang Chi Mei Chemical Co., Ltd., (Zhenjiang, China) and EPDM (3745P), obtained from DuPont Dow Elastomers L.L.C. (Wilmington, DE) The ratio of PS and EPDM is 80 : 20 in PS/EPDM blend. The experiments were carried out in a special ultrasonic oscillation extrusion system developed in our laboratory, the schematic diagram of which is shown in Figure 1. The die is the special horn capillary, with diameter and length of 3 and 24 mm, respectively, 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 the 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 process and to indicate the rheological properties of the polymer melt. The set temperature of extruder was 210°C.

Measurements and characterization

The rheological properties of PS, EPDM, and PS/EPDM blend were in situ measured during extrusion processing. The die of extruder shown in Figure 1 is treated as a capillary rheometer, and the apparent shear rate $\dot{\gamma}_w$, apparent shear stress τ_w, and apparent viscosity η_a at wall can be calculated as follows.

$$\tau_w = \frac{PD_c}{4L_c} \tag{1}$$

$$\dot{\gamma}_w = \frac{32Q}{\pi\rho D_c^3} \tag{2}$$

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

where P is the die pressure; L_c, the length of capillary; D_c, the diameter of capillary; Q, the volume flow rate of melt; and ρ, the density of melt.

To confirm the permanent change of rheological behaviors of PS, EPDM, and their blend induced by ultrasonic oscillation, the intrinsic viscosities and melt viscosities of ultrasonic extrudates were involved. The intrinsic viscosities of PS, EPDM, and PS/EPDM blend were measured at 25°C by capillary viscometer, according to ISO 1628/1–1984 (E). The diameter, length, and apparatus constant of capillary are 0.54, 120, and 0.01190 mm^2/s^2, respectively. The solvent used is toluene, and the concentration of solution for all samples is about 2.000 mg/mL. The intrinsic viscosity ($[\eta]$) is calculated by the following equation.

$$[\eta] = \frac{\sqrt{2 \times [(\eta_r - 1) - \ln \eta_r}}{C} \tag{4}$$

where η_r is the relative viscosity and C is the concentration of solution.

The rheological properties of ultrasonic extrudates were measured by high-pressure capillary rheometer (Rheograph 2002 made by Gottfert Co., Germany). L/D ratio is 30 and the experimental temperature is 210°C.

RESULTS AND DISCUSSION

Rheological behavior

The die pressure was measured by the pressure transducer installed at the die entry at different screw rotation speeds, meanwhile the temperature of the die was 210°C to exclude the effect of temperature on the die pressure. The relative die pressure drop ΔP in the presence of ultrasonic irradiation is expressed as:

$$\Delta P = \frac{P_0 - P_u}{P_0} \tag{5}$$

where P_0 is the die pressure in the absence of ultrasonic irradiation and P_u is the die pressure in the presence of ultrasonic irradiation.

Figure 2 shows the dependence of relative die pressure drop ΔP at different rotation speeds of screw on ultrasonic intensity. As shown in Figure 2, ΔP increases with the increase in ultrasonic intensity. ΔP amounts to 32, 42, and 23% for PS, EPDM, and PS-EPDM, respectively, at a screw rotation speed of 9 or 16 rpm and an ultrasonic intensity of 250 W, indicating that the die pressure greatly decreased during ultrasonic extrusion process. In Figure 2, it is also found that ΔP increases with decrease in screw rotation speed at the same ultrasonic intensity. This indicates that the relative die pressure drop, in the presence of ultrasonic irradiation, depends on the stay time of polymer melt in die. The lower the screw rotation speed, the longer the stay time of polymer in die; and the longer the ultrasonic action time of melt, the higher the value of ΔP. In detail, ΔP of EPDM is highest among samples compared at constant screw rotation speed and ultrasonic intensity. This may attribute to the highest melt viscosity of EPDM, meaning that ultrasonic irradiation can greatly affect polymer with higher melt viscosity.

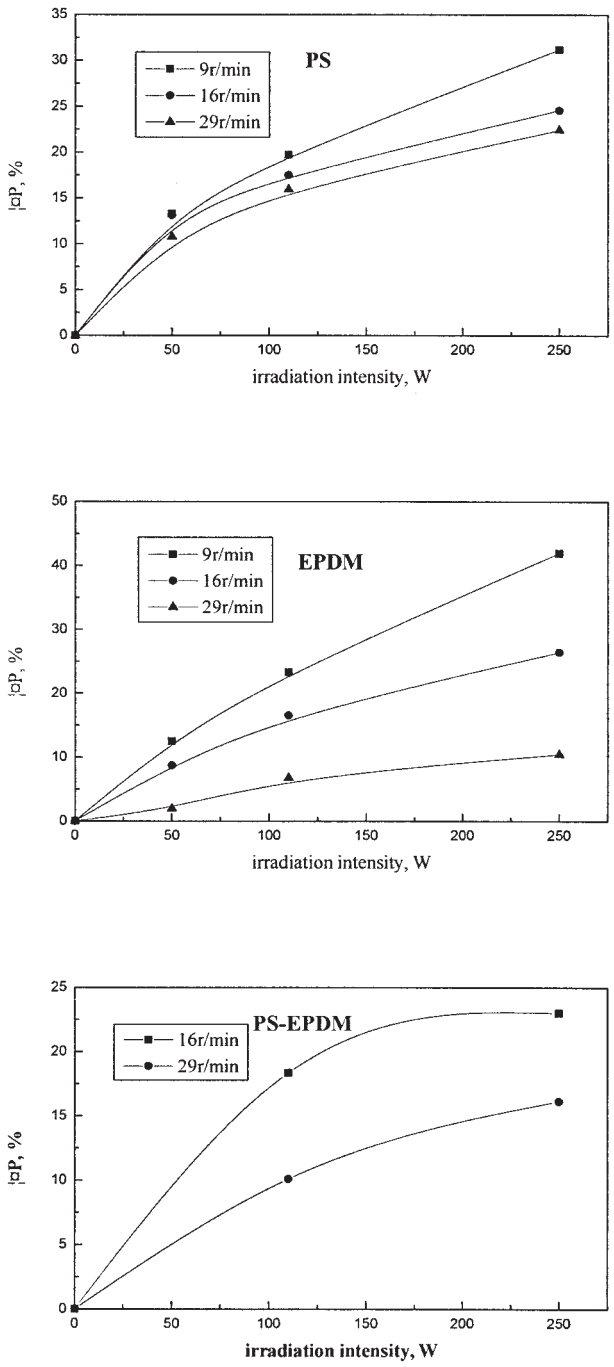

Figure 2 Effect of ultrasonic irradiation on die pressure during extrusion process.

TABLE I
Effect of Ultrasonic Intensity on the Apparent Viscosities of PS, EPDM and PS/EPDM (80/20) Blend During Extrusion

Samples	log $\dot{\gamma}_w$, (s^{-1})	logη_a, (Pa*s)			
		0W	50W	110W	250W
PS	1.34	3.53	3.47	3.44	3.39
	1.57	3.26	3.20	3.17	3.09
	1.88	3.09	3.02	3.00	2.97
EPDM	1.26	3.91	3.85	3.80	3.68
	1.50	3.82	3.77	3.74	3.67
	1.75	3.70	3.69	3.70	3.66
PS/EPDM (80/20)	1.59	3.39	3.29	3.27	1.59
	1.87	3.18	3.12	3.09	1.87

The decrease in die pressure is useful to the improvement of processing behavior of polymer materials. In our opinion, the reason causing the decrease in die pressure in the presence of ultrasonic irradiation could be the decrease in apparent viscosity of polymer melts during ultrasonic extrusion processing.

The value of apparent viscosity is calculated according to eqs. (1)–(3) in the range of 18–76 s^{-1} of shear rate. The data listed in Table I show that during extrusion processing, the apparent viscosities of PS, EPDM, and their blend depend not only on the shear rate but also on the ultrasonic intensity. The increase in ultrasonic intensity obviously led to the decrease in apparent viscosities. Especially, the apparent viscosity of EPDM remains almost unchanged with the increase in shear rate when the ultrasonic intensity is 250 W. Figure 3 shows clearly that at different screw rotation speeds, the apparent viscosities of polymer melts decrease with the rise in ultrasonic intensity. The relative apparent viscosity drop $\Delta\eta_a$ in the presence of ultrasonic irradiation can be expressed as $\eta_{a0} - \eta_{au}$, where η_{a0} and η_{au} are the apparent viscosities in the absence and the presence of ultrasonic irradiation, respectively. Figure 4 indicates that $\Delta\eta_a$ strongly depends on ultrasonic intensity and screw rotation speed. The higher ultrasonic intensity and longer irradiation time lead to the rise in $\Delta\eta_a$. Similar to ΔP, $\Delta\eta_a$ of EPDM is higher than those of PS and PS/EPDM blend due to the highest melt viscosity of EPDM.

Mechanism for improvement of rheological behavior

Some researchers attributed the decrease in apparent viscosity during ultrasonic extrusion processing to the ultrasonic degradation of polymer melts during extrusion process.[15–17] In other words, they thought that the apparent viscosity of polymer changed perpetually after ultrasonic extrusion. To confirm this, the extents of degradation of ultrasonic extrudates were measured. Here, the relative intrinsic viscosity drop $\Delta[\eta]$ in the presence of ultrasonic irradiation is used to express the extent of degradation of ultrasonic extrudate. $\Delta[\eta]$ is as follows.

$$\Delta[\eta] = \frac{[\eta]_0 - [\eta]_u}{[\eta]_0} \tag{6}$$

where $[\eta]_0$ and $[\eta]_u$ are the intrinsic viscosities of extrudates in the absence and the presence of ultrasonic irradiation, respectively.

Table II shows that the extents of degradation of PS and EPDM extrudates at ultrasonic intensity of 250 W are less than 3.69% and 5.26%. In our opinion, the degradation extents of polymer melts are too low to change greatly the apparent viscosities of melts in the experimental shear rate of 18–76 s^{-1} during ultrasonic extrusion. The change in apparent viscosity should be reversible physical course, therefore the apparent viscosities of melts will increase to initial value when ultrasonic irradiation is removed. To approve this, the rheological behaviors of ultrasonic extrudates were measured by high-pressure capillary rheometer. The experimental temperature is the same as that of the die of extruder. The experimental results are shown in Figure 5. Compared with the data listed in Table I, Figure 5 shows that the curves of log η_a versus log $\dot{\gamma}_w$ of extrudates with different ultrasonic intensities and screw rotation speeds are almost kept at the same curve, implying that the ultrasonic irradiation did not cause a permanent decrease in the polymer melt viscosity. In other words, this experiment proves that the decrease in apparent viscosities of melts during ultrasonic extrusion could not be interrelated with the ultrasonic degradation.

High frequency and low amplitude are the features of ultrasonic irradiation, which make it easy to act with microstructure of polymer. The true reason causing the ultrasonic decrease in apparent viscosities of polymer melts during extrusion from a viewpoint of macromolecular motion is discussed here.

1. According to the definition of apparent viscosity, the lower the value of apparent viscosity, the

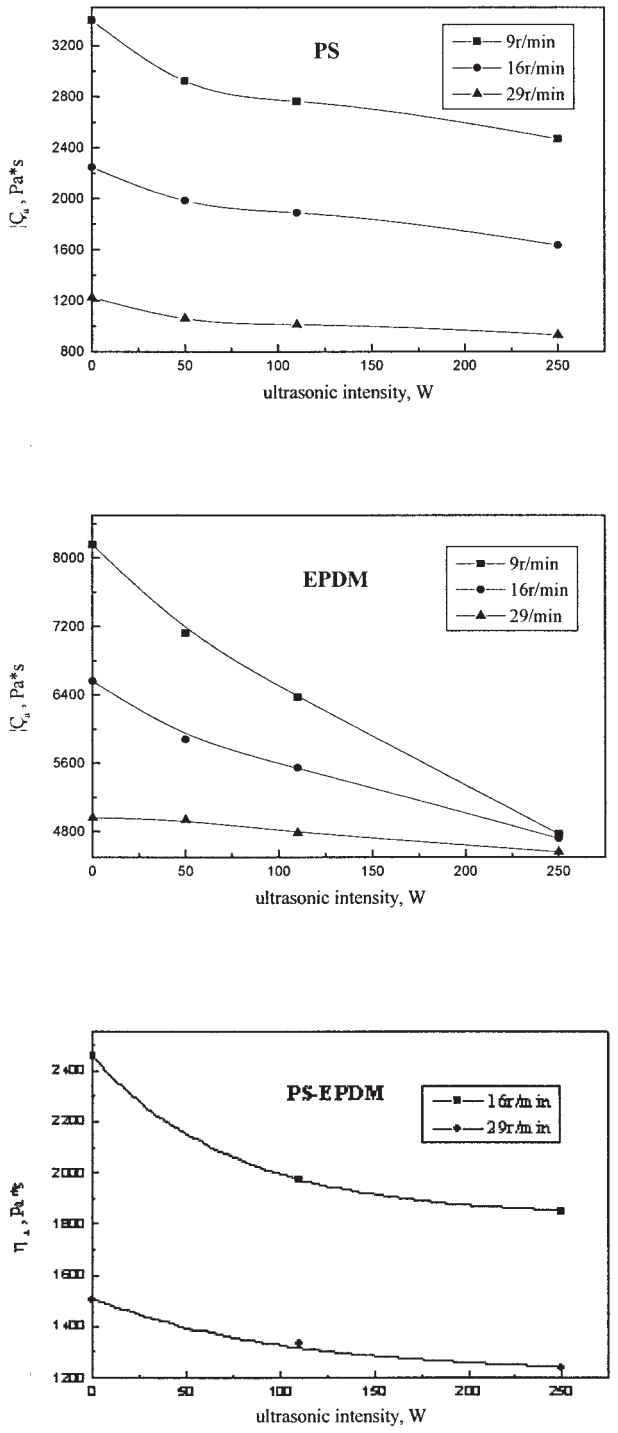

Figure 3 Dependence of η_a on ultrasonic intensity at different screw rotation speeds.

better the flowability of polymer melt. Whereas, the flow of polymer melt is carried out by the motion of chain segments. Ultrasonic shake wave activates the molecules of polymer melts, hence it enhances macromolecular motion ability, and shortens relaxation time of macromolecules and accelerates the disentanglement of polymer melt molecules, leading to an increase of flowability of polymer melts.

2. Apparent viscosity can be calculated by equation as follows.

$$\eta_a = Ae^{\Delta E_\eta / RT} \tag{7}$$

where A is the constant; R and T are the gas constant and absolute temperature, respectively;

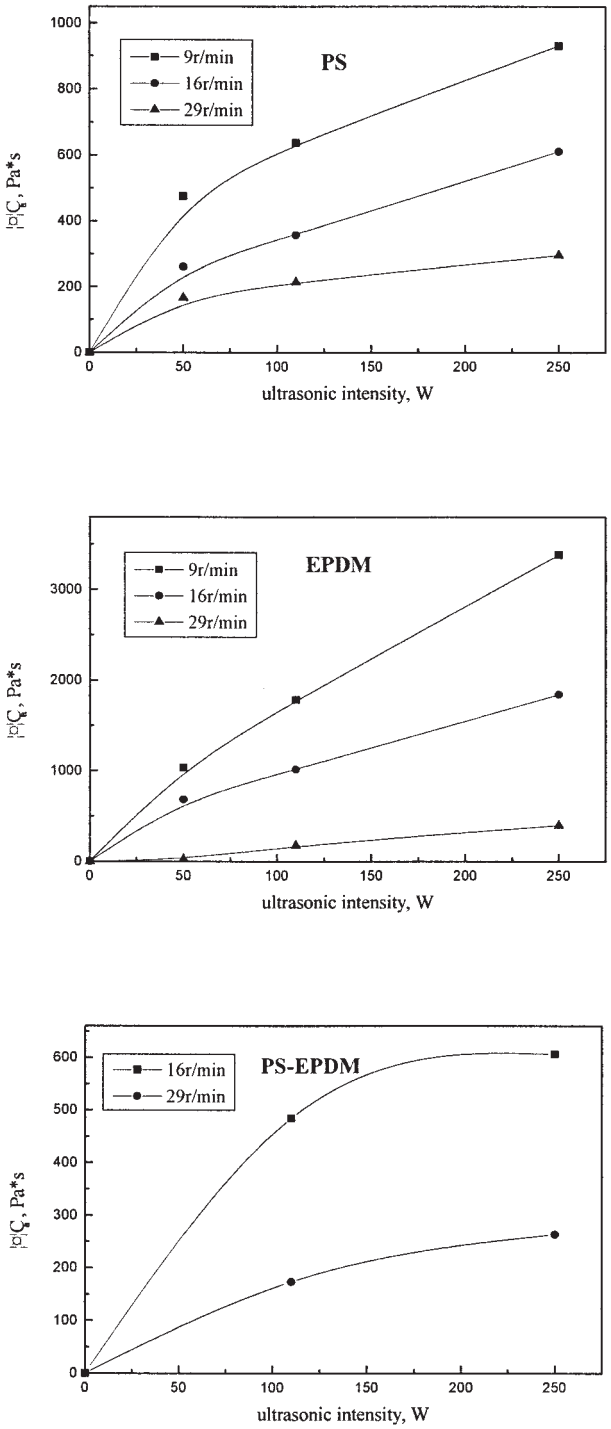

Figure 4 $\Delta\eta_a$ versus ultrasonic intensity at different screw rotation speeds.

TABLE II
Degradation Extent of Extruded Polymers in the Presence of Ultrasonic Irradiation

Samples	Rotate speed (r/min)	Irradiation intensity (W)	Degradation extent $\Delta[\eta]$ (%)
PS	9	250	2.41
	16	250	3.58
	29	250	3.69
EPDM	9	250	4.68
	16	250	5.26
	29	250	2.94

and ΔE_η is the activation energy of flow. Ultrasonic oscillation weakens the mutual action of macromolecules, causing a decrease in ΔE_η. Our previous studies have proved this reduction.[15,16] According to eq. (7), the decrease in ΔE_η would lead to the decrease in apparent viscosity.

3. In our experiments, it was found that the die of extruder is also vibrated by the drive of ultrasonic oscillation. This could conduce to the decrease in friction force between polymer melt and die wall and the decrease in die pressure, implying that ultrasonic irradiation decreases apparent viscosity of polymer melt during extrusion.

Productivity of extrusion and die swell

In general, the volume flow rate of polymer can be increased during extrusion by the enhancement of screw rotation speed. Therefore, to increase the extrusion productivity of polymer with high melt viscosity, it is necessary to enhance screw rotation speed. But this would lead to the increase in die pressure and the melt fracture of polymer melts. The introduction of ultrasonic irradiation into extrusion can solve this contradiction.

Figure 6 shows the relationship between die pressure and volume flow rate at different ultrasonic intensities. As shown in Figure 6, the volume flow rate increases with the rise in die pressure at the same ultrasonic intensity. When die pressure remains invariable, ultrasonic irradiation enhances the volume flow rate, and the volume flow rate increases with the rise in ultrasonic intensity. The cause may be a decrease in surface stress at the wall interface between melt and die in the presence of ultrasonic oscillation. The introduction of ultrasonic oscillation into the die of extruder can make the volume flow rate of the polymer remain higher at the lower die pressure. This has a very important practical significance for the improvement of quantity and quality of extrusion product.

Die swell of extrudate is a universal phenomenon during extrusion process, which is caused by the deformation of polymer in die and the relaxation of melt molecules at the exit of die. Therefore, the shorter relaxation time of macromolecules or less deformation decreases the die swell of extrudate. On the contrary, the decrease of die swell, when processing parameters are unchanged, means the enhancement of motion ability of polymer molecules or the reduction of deformation. Here, the ratio of the diameter of extrudate

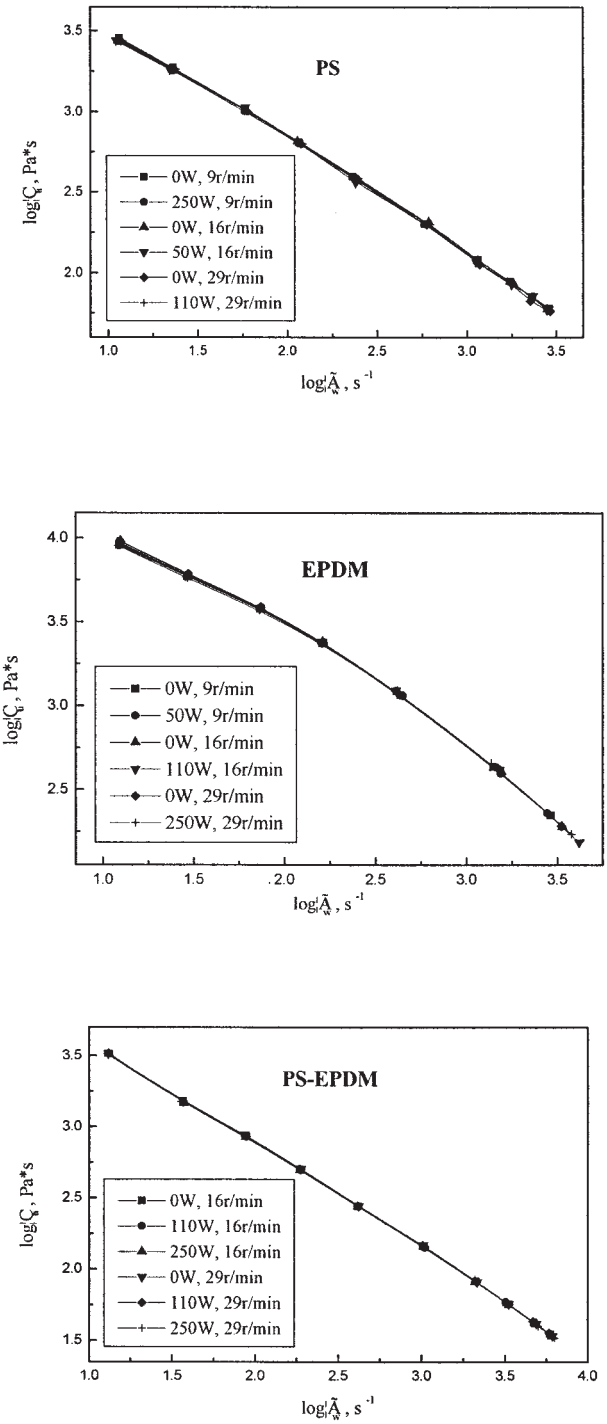

Figure 5 Apparent viscosity η_a versus apparent shear rate $\dot{\gamma}_w$ in high-pressure capillary rheometer.

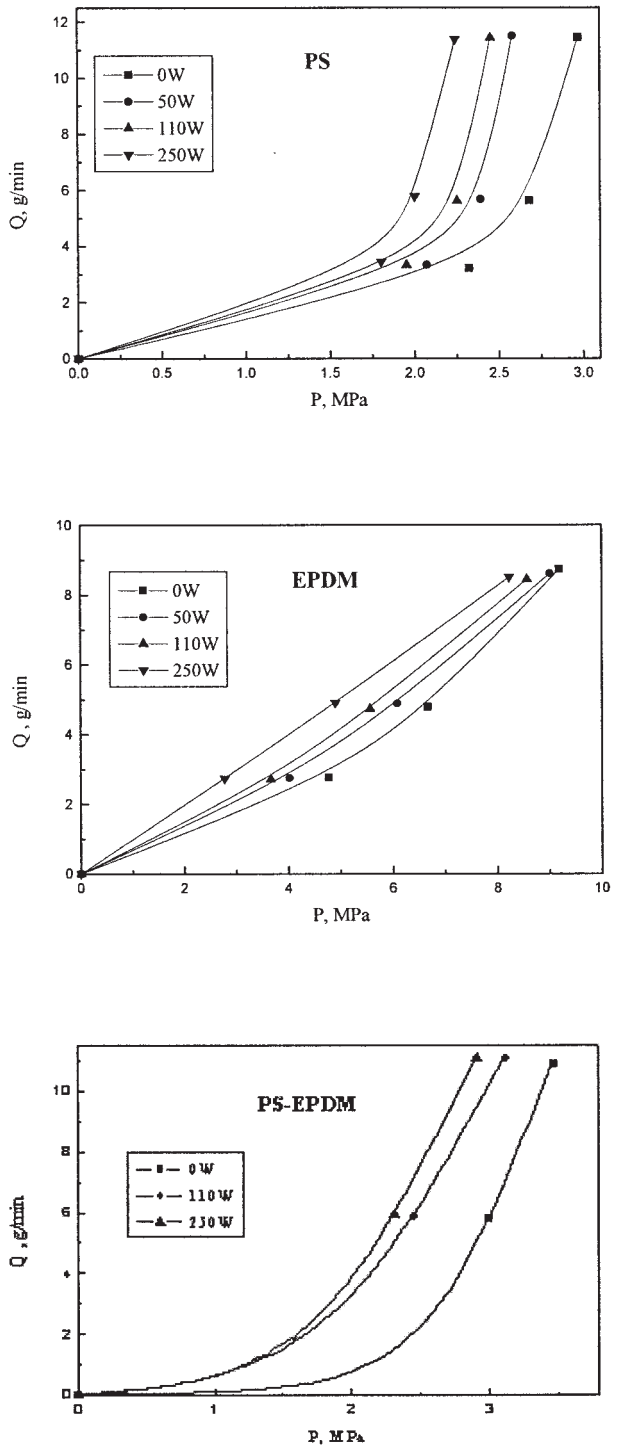

Figure 6 Relationship between volume low rate and die pressure at different ultrasonic intensities.

(D) and the diameter of die (D_c) is defined to express die swell rate. Figure 7 shows the effect of ultrasonic irradiation on die swell rate of extrudates. It indicates that the die swell rates strongly depend on the ultrasonic intensity and screw rotation speed. With the rise of ultrasonic intensity or the decrease in screw rotation speed, the die swell rate decreases greatly. As stated earlier, experimental results show that ultrasonic irradiation quickens motion of macromolecules and causes the decrease in deformation of polymer due to slip, and decreases the die swell rate.

CONCLUSIONS

Ultrasonic treatment can obviously improve the extrusion processing behaviors of PS, EPDM, and PS/EPDM (80/20). The die pressures, apparent viscosi-

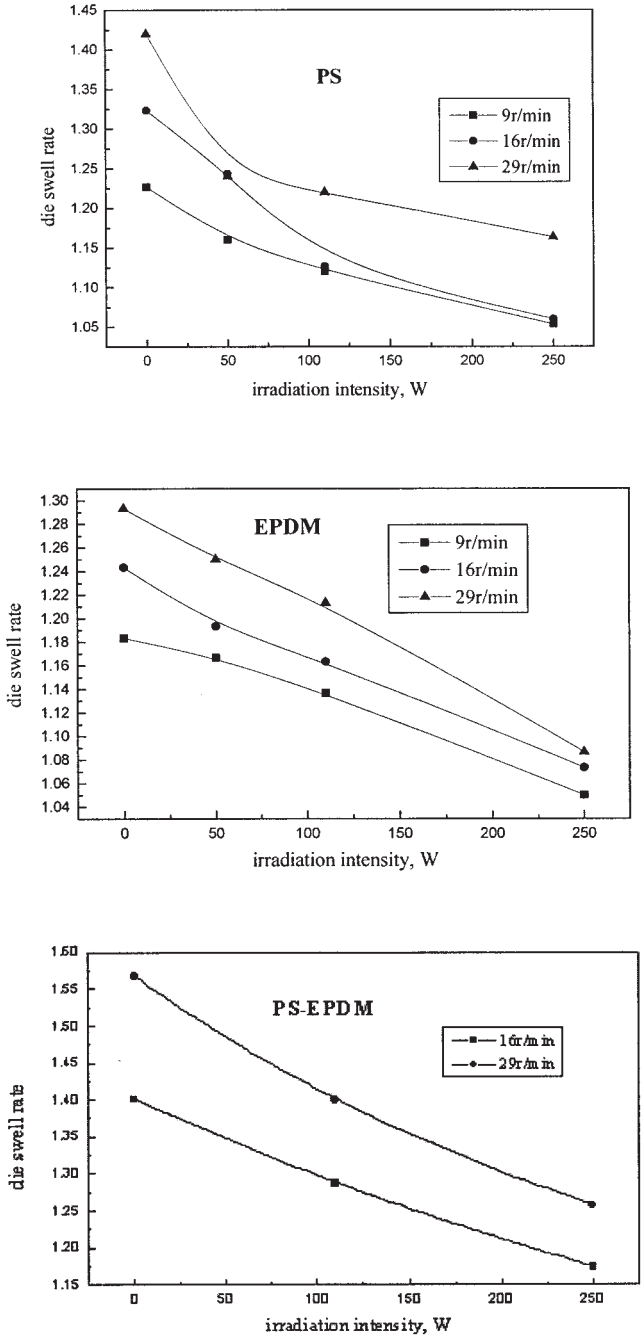

Figure 7 Dependence of die swell of melt on ultrasonic intensity.

ties, and die swells of polymer melts during extrusion get decreased in the presence of ultrasonic irradiation and decrease as the ultrasonic intensity increases. Ultrasonic application makes the volume flow rates of PS, EPDM, and PS/EPDM blend remain high at low die pressure, and the volume flow rates increase with the rise in ultrasonic intensity when the die pressure keeps invariable. Ultrasonic effects on extrusion process of polymer melts are more significant at lower screw rotation speed owing to the longer irradiation time.

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