# Ultrasonic Oscillations Effect on Rheological and Processing Properties of Metallocene-Catalyzed Linear Low Density Polyethylene

**Hong Wu,[1] Shaoyun Guo,[1] Guangshun Chen,[1] Jia Lin,[1] Wei Chen,[2] Hongtao Wang[2]**

[1]*The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China*
[2]*Beijing Research Institute of Chemical Industry of SINOPEC, Beijing 100013, China*

Received 22 November 2002; accepted 3 March 2003

**ABSTRACT:** The effects of ultrasonic oscillations and die materials on die pressure, productivity of extrusion, melt viscosity of metallocene-catalyzed linear low density polyethylene (mLLDPE), as well as their mechanism were studied in a special ultrasonic oscillations extrusion system developed in our lab. Die materials used in our experiment included steel, brass, and polytetrafluoroethylene (PTFE). The experimental results showed that ultrasonic oscillations as well as die materials have great influence on the rheological and processing behavior of mLLDPE. Ultrasonic oscillations can greatly increase the productivity of mLLDPE melt extruded through different dies, and can decrease the die pressure and the melt viscosity of mLLDPE. Compared with steel or brass die, mLLDPE melt extruded through PTFE die is more sensitive to ultrasonic oscillations. A possible mechanism for the improved processability of mLLDPE is proposed in this article. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1873–1878, 2003

**Key words:** ultrasonic oscillations, die material, melt viscosity of metallocene-catalyzed linear low density polyethylene; rheology; processing behavior

## INTRODUCTION

Metallocene-catalyzed polyethylene (mPE), whose rheological behavior is much different from traditional PE, has many excellent properties due to its unique molecular characteristics.[1–6] From the rheological point of view, the molecular weight and the molecular weight distribution are controlling factors in determining the viscosity of polymer. Then relatively higher molecular weight and narrower molecular weight distribution of mPE lead to higher die pressure, higher apparent viscosity, and lower critical shear rate in the processing operations, which are main limits to its wide applications.[7–9] It has been generally accepted that a better understanding of the rheological behavior is an essential step to the successful processing of polymeric materials. In our previous work,[10] we studied die materials' effect on rheological and processing behaviors of metallocene-catalyzed linear low density polyethylene (mLLDPE). The results showed that mLLDPE melt extruded through polytetrafluorethylene (PTFE) die has clearly lower die pressure, lower apparent viscosity, and higher critical shear rate than those through steel or brass die.

In recent years, some new vibration technologies have been applied during polymer processing operations to control the flow pattern and/or the internal structure and morphology of the plastics.[11–20] The applications of ultrasonic oscillations in polymer processing mainly focused on the welding of thermoplastics, rubber vulcanization, etc., and many study results show that using ultrasonic oscillations has led to a significant decrease in the melt viscosity and increase in flow rate.[21,22]

In our previous studies,[23–25] the ultrasonic oscillations were induced to an extruder. The experimental results showed that ultrasonic oscillations can remarkably reduce the die pressure and apparent viscosity of polymer melt, and inhibit the unstable flow of polystyrene (PS) and traditional LLDPE during extrusion. In this work, the effect of ultrasonic oscillations on rheological and processing behaviors of mLLDPE are studied. The objective of this work is to provide a theoretical base for a new route to improve the processing properties of mLLDPE.

---

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

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

Contract grant sponsors: National Natural Science Foundation of China; State Education Ministry of China and Science Research, Foundation for youth of Sichuan University.

Journal of Applied Polymer Science, Vol. 90, 1873–1878 (2003)

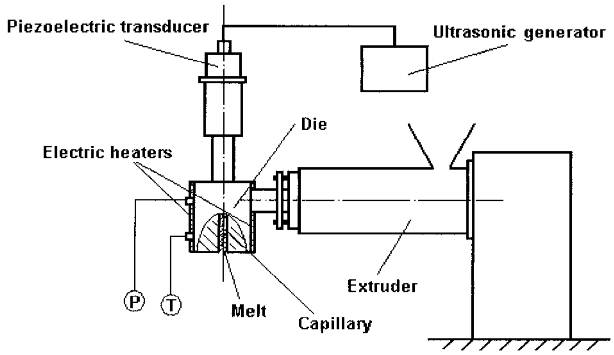

**Figure 1** Schematic diagram of ultrasonic oscillation extrusion system.

## EXPERIMENTAL

### Materials and equipment

The material used was mLLDPE with melt index (MI) =1.0 g/10 min and density = 0.919 g/cm$^3$, which was from Research Institute of Petroleum Processing, SINOPEC, Beijing, China. A special ultrasonic oscillations extrusion system developed in our lab was used for the experiment, whose schematic diagram is shown in Figure 1. The die, which is constructed by steel, brass, or PTFE, is a special horn capillary (length/diameter (L/D) = 10) attached to a single screw extruder. A probe of ultrasonic oscillations 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 oscillations are in the direction parallel to the flow of polymer melt. A pressure transducer and a thermal couple at the die entry are installed in order to record continuously the variation of die pressure and temperature during extrusion.

### Measurement and calculation of rheological parameters

A special ultrasonic oscillations extrusion system developed in our lab was used to measure rheological properties of mLLDPE in the presence of ultrasonic oscillations. Measurements for die pressure in the presence of ultrasonic oscillations were performed at melt temperatures in die between 180 and 200°C by steps of 10°C and superimposed ultrasonic intensities between 0 and 250 W by steps of 50 W.

The shear rate at wall $\gamma_w$ was calculated as follows:

$$\gamma_w = \frac{4Q}{\pi R^3}$$

The shear stress $\tau_{sw}$ and apparent viscosity $\eta_a$ were calculated as follows:

$$\tau_{sw} = \frac{PR}{2L} \qquad \eta_a = \frac{\tau_{sw}}{\gamma_w}$$

where $P$ is the die pressure, $L$ is the length of capillary, $R$ is the radius of capillary, and $Q$ is the volume flow rate.

## RESULTS AND DISCUSSION

### Steel die

Die pressure drop

The relative die pressure drop $\Delta P$ as a result of the presence of ultrasonic oscillations can be written as

$$\Delta P = \frac{P_0 - P_u}{P_0} \times 100\%$$

where $P_0$ and $P_u$ are the die pressure in the absence and the presence of ultrasonic oscillations, respectively. Die pressure changes with ultrasound intensity were measured at the die temperatures of 180, 190, and 200°C, respectively. As shown in Figure 2, $\Delta P$ almost shows a linear increase with increase of ultrasonic intensity, especially when $T_{\text{die}}$ = 180°C. The linear regression results are shown in Figure 3. $\Delta P$ amounts to 43% at a screw rotation speed of 5 rpm, melt temperature in die of 180°C, and ultrasonic intensity of 250 W, indicating that die pressure of mLLDPE could get markedly decreased in the presence of ultrasonic oscillations in extrusion. The presence of ultrasonic oscillations greatly improves the processing behavior of mLLDPE. Figure 3 shows that the slope of $\Delta P$ vs ultrasonic intensity decreases with screw rotation speed, indicating that the degree of dependence of $\Delta P$ on the ultrasonic intensity decreases with the increase of screw rotation speed at all experimental die temperature. On the other hand, at the same ultrasonic intensity, $\Delta P$ decreases with an increase of screw rotation speed at all experimental die temperatures. This indicates that the die pressure drop in the presence of ultrasonic oscillations depends on the residence time of polymer melt in the die. The lower the screw rotation speed, the longer the residence time of polymer melt in the die, so the longer the ultrasonic oscillations are applied on the mLLDPE, the larger the $\Delta P$. Figure 3 also shows that the slopes of $\Delta P$ vs ultrasonic intensity are nearly the same at different die temperatures, indicating that ultrasonic oscillations effect on die pressure of mLLDPE melt is less sensitive to the die temperature compared to other PEs.[24,25]

The effect of ultrasonic oscillations on the extrusion

Figure 4 shows the mass flow rate of mLLDPE vs die pressure at different ultrasonic intensities. As shown

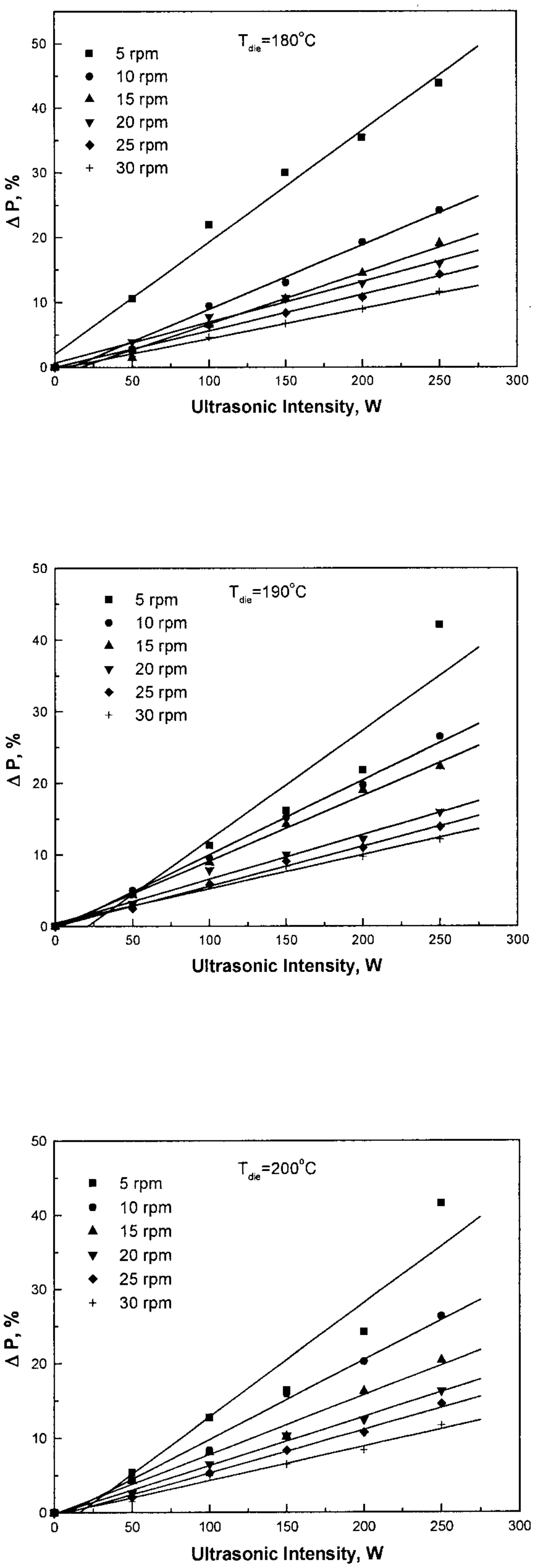

**Figure 2** Dependence of $\Delta P$ on ultrasonic intensity at various screw rotation speeds extruded through steel die at different die temperatures.

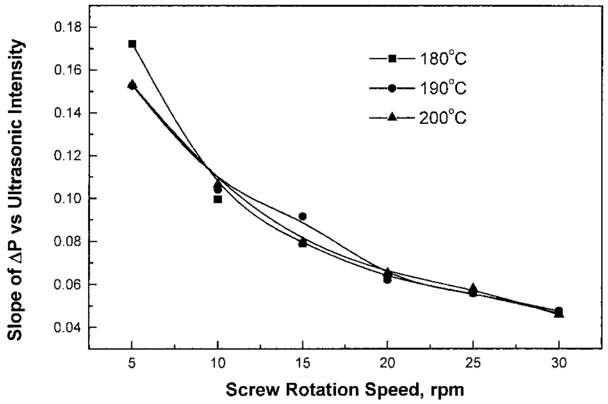

**Figure 3** Effect of screw rotation speed on the slope of $\Delta P$ vs ultrasonic intensity at different die temperatures.

in Figure 4, the mass flow rate of mLLDPE increases with the increase of die pressure, and the curves of flow rate vs die pressure move to left with the increase of ultrasonic intensity, indicating that mass flow rate of mLLDPE is increased with the increase of ultrasonic intensity at the same die pressure. As shown in Figure 5, flow rate of mLLDPE increases with the rise of ultrasonic intensity at 180°C. With 250 W ultrasonic oscillations, the flow rate of mLLDPE is increased nearly 30% compared to that obtained in the absence of ultrasonic oscillations. Thus ultrasonic oscillations can increase the productivity of mLLDPE extrusion through steel die due to die pressure drop in the presence of ultrasonic oscillations.

## Rheological behavior

Figure 6 shows viscosity curves during extrusion in the presence and absence of ultrasonic oscillations. It shows that $\log\eta_a$ vs $\log\gamma_w$ has a nonlinear relation in experimental shear rate range of 10–80 $s^{-1}$, indicating that with or without ultrasonic oscillations the relationship between apparent viscosity $\eta_a$ of mLLDPE

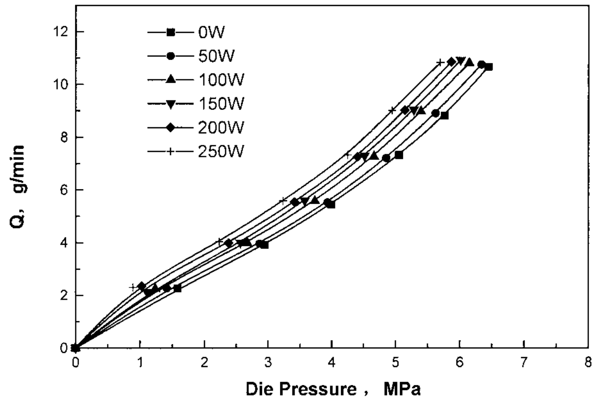

**Figure 4** Flow rate $Q$ vs die pressure in the presence of ultrasonic oscillations extruded through steel die at 180°C.

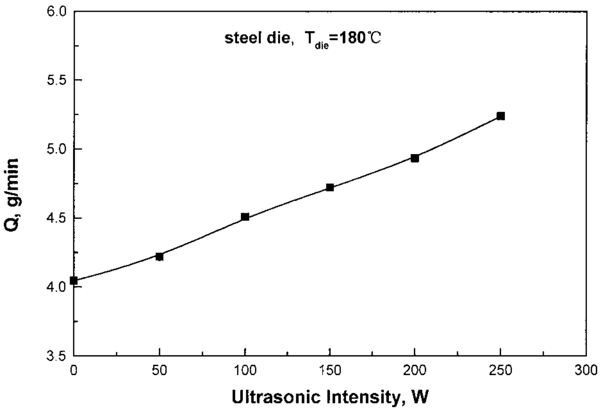

**Figure 5** $Q$ vs ultrasonic intensity at die pressure: 3 MPa.

and shear rate $\gamma_w$ does not obey the simple power law equation. It is also observed from this figure that the melt viscosity slightly increases from $\log\gamma_w = 1.2$ to $\log\gamma_w = 1.4$ in the absence of ultrasonic oscillations, which is ascribed to the transition from laminar flow to elastic turbulent flow in this region. The viscosity at $\log\gamma_w = 1.2$ gets much lower than that at $\log\gamma_w = 1.4$ as the increase of ultrasonic intensity due to the great decrease of $\Delta P$ at high ultrasonic intensity. In our study, we use apparent viscosity difference $\Delta\eta_a$ to describe ultrasonic oscillations effect on decreasing the apparent viscosity of the mLLDPE melt. Apparent viscosity difference $\Delta\eta_a$ in the presence of ultrasonic oscillations can be calculated as

$$\Delta\eta_a = \eta_0 - \eta_n$$

where $\eta_0$ and $\eta_n$ are apparent viscosity in the absence and the presence of ultrasonic oscillations respectively at a given shear rate value. As shown in Figure 7, $\Delta\eta_a$ of mLLDPE increases with the increase of average ultrasonic oscillation time, while the slope of the curves increases markedly with increasing the ultrasonic oscillation intensity. This indicates that, in the presence of ultrasonic oscillations, the apparent viscosity difference of mLLDPE melt is strongly dependent on ultrasonic oscillation intensity and average ultrasonic oscillation time.

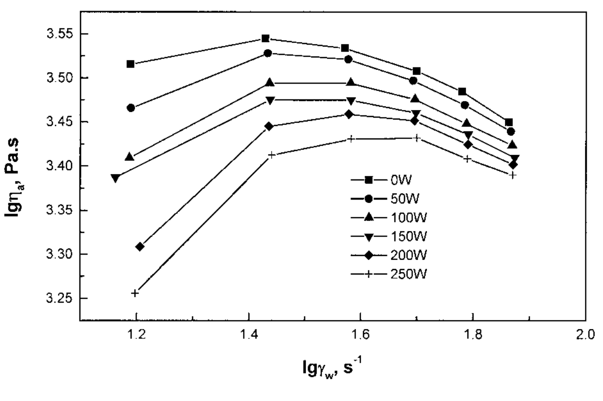

**Figure 6** Apparent flow curves of mLLDPE in presence of ultrasonic oscillations extruded through steel die at 180°C.

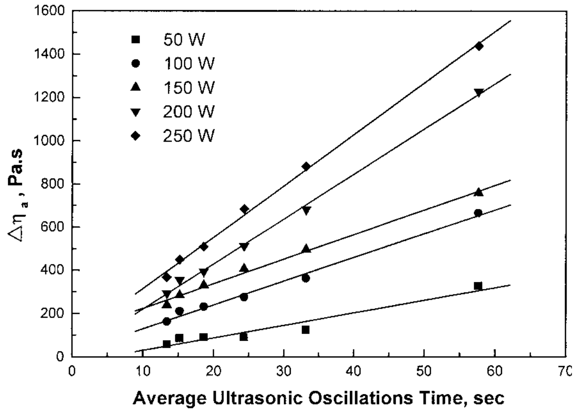

**Figure 7** $\Delta\eta_a$ vs average ultrasonic oscillation time at various ultrasonic intensities extruded through steel die at 180°C.

In this work, the effects of brass die on die pressure drop, extrusion, and rheological behavior of mLLDPE in the presence of ultrasonic oscillations were also studied. The trend of the curves of $\Delta P$ vs ultrasonic intensity of mLLDPE melt extruded through brass die nearly resembles that of steel die, $\Delta P$ amounts to 41% at a screw rotation speed of 5 rpm and ultrasonic intensity of 200 W. The mass flow rate of mLLDPE extruded through brass die increases with the increase of die pressure, and shows a similar trend to that of mLLDPE extruded through steel die. The mass flow rate of mLLDPE increases with the increase of ultrasonic intensity at 180°C, and flow rate of mLLDPE in the presence of 250 W ultrasonic oscillations increased almost 20% compared with that in the absence of ultrasonic oscillations.

## PTFE die

### Die pressure drop

As shown in Figure 8, $\Delta P$ amounts to 70% at a screw rotation speed of 5 rpm and ultrasonic intensity of 200 W, indicating that die pressure of mLLDPE could get decreased much more markedly in the presence of ultrasonic oscillations in extrusion through PTFE die than other dies. The presence of ultrasonic oscillations greatly improves the processing behavior of mLLDPE melt extruded through PTFE die. However, the curves of $\Delta P$ vs ultrasonic intensity do not show linear relationship. On the other hand, at the same ultrasonic intensity, $\Delta P$ decreases with the increase of the screw rotation speed.

### The effect of ultrasonic oscillations on the extrusion

As shown in Figure 9, the mass flow rate of mLLDPE increases with increase of die pressure through FTFE

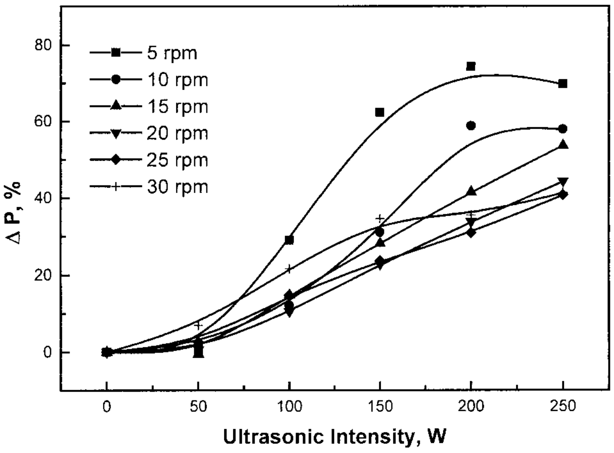

**Figure 8** Dependence of $\Delta P$ on ultrasonic intensity at various screw rotation speeds through PTFE die at 180°C.

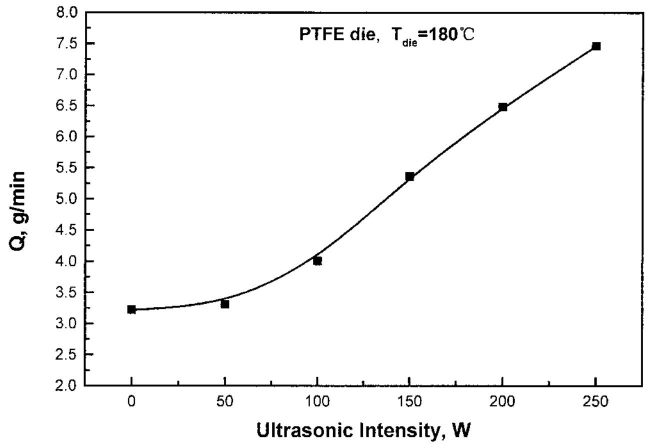

**Figure 10** $Q$ vs ultrasonic intensity at die pressure: 1 MPa.

die, and have almost the same trend to that of mLLDPE extruded through other dies. As shown in Figure 10, flow rate of mLLDPE increases with the increase of ultrasonic intensity at 180°C, and flow rate of mLLDPE in the presence of 250 W ultrasonic oscillations increased by 2 times compared with that in the absence of ultrasonic oscillations. It is clear that mLLDPE melt extruded through PTFE die is the most sensitive to ultrasonic oscillations among three types of dies. Ultrasonic oscillations can increase much more markedly the extrudability of mLLDPE extrusion through PTFE die due to die pressure drop in the presence of ultrasonic oscillations.

## Mechanism for ultrasonic oscillations and die materials effect on rheological behavior of mLLDPE melt

In our previous work,[23–25] we studied the effect of ultrasonic oscillations on the rheological behavior of LLDPE, HDPE, PS, and HDPE/PS blends. The general trend is that the die pressure and apparent viscosity of polymer melt is greatly decreased, while the extrudability increased markedly in the presence of ultrasonic oscillations. The reptation model is suitable for describing the motion of a polymer chain. Ultrasonic application could possibly activate the wriggling motion of minor chain segments in the polymer chain. High frequency and low amplitude ultrasonic oscillations can activate the wriggling motion of minor chain segments due to their short relaxation time, and break the entanglements of polymer chains. As a result, it causes a reduction in melt viscosity and elasticity. In this work, we have changed the material of construction of die in the experiments. From the results of this article, it is clear that the mLLDPE melt extruded through PTFE die is much more sensitive to ultrasonic oscillations than through steel or brass die. In fact, the changes in the flow properties of mLLDPE are more pronounced in the PTFE die. This is due to interfacial adhesion between mLLDPE melt and die wall. PTFE is a self-lubricating material, and has low surface energy. It almost has no adhesion with mLLDPE. So the mLLDPE slips on the PTFE die and this gives rise to the lower pressure during extrusion as compared with steel or brass die.

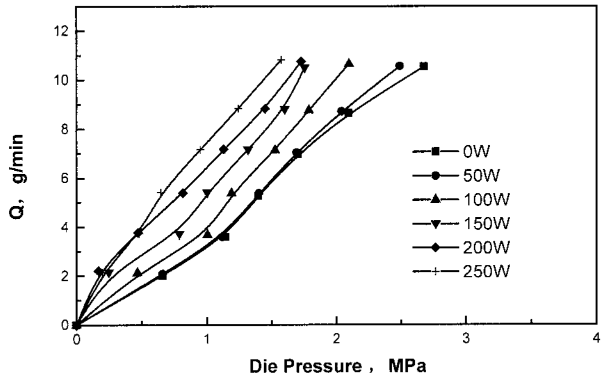

**Figure 9** Flow rate $Q$ vs die pressure in the presence of ultrasonic oscillations through PTFE die at 180°C.

## CONCLUSION

The die pressure and apparent viscosity of mLLDPE in extrusion through different dies is decreased in the presence of ultrasonic oscillations, more and more with an increase of the ultrasonic intensity. Three kinds of dies—steel die, brass die and PTFE die—were chosen for the investigation of effect of the material of construction of the die on processing behavior of mLLDPE in the presence of ultrasonic oscillations. The processability of mLLDPE extrusion increases with the increase of ultrasonic intensity. Die materials have great influence on processing behavior, too. Compared with steel or brass die, mLLDPE melt extruded through PTFE die is more sensitive to ultrasonic oscillations.

## References

1. Vega, J. F.; Munoz-Escalona, A.; Santamaria, A.; Munoz, M. E.; Lafuente, P. Macromolecules 1996, 29, 960.
2. Munoz-Escalona, A.; Lafuente, P.; Vega, J. F.; Munoz, M. E.; Santamaria, A. Polymer 1997, 38, 589.
3. Savvas, G.; Hatzikiriakos; I.; Kazatchkov, B. J Rheol 1997, 41, 1299.
4. Munoz-Escalona, A.; Lafuente, P.; Vega, J. F.; Santamaria, A. Polym Eng Sci 1999, 39, 2292.
5. Rana, D.; Kim, H. L.; Kwag, H.; Ghee, J.; Cho, K.; Woo, T.; Lee, B. H.; Choe, S. J Appl Polym Sci 2000, 76, 1950.
6. Sujan, E.; Bin, W.; Donald, G.; Baird J. Rheol, 2000, 44, 1151.
7. Knights, M. Plastics Technol 1995, February, 44.
8. Butler, T. Plastics Technol 1995, February, 50.
9. Knights, M. Plastics Technology 1995, June, 49.
10. Wu, H.; Guo, S.; Chen, G.; Chen, W.; Wang, H. Polymer-Plastics Technology & Engineering, accepted.
11. Manero, O.; Mena, B. Rheol Acta 1977, 16, 573.
12. Manero, O.; Mena, B.; Valenzuela, R. Rheol Acta 1978, 17, 693.
13. Mena, B.; Manero, O.; Binding, D. M. J. Non-Newt. Fluid Mech. 1979, 5, 427.
14. Kazakia, J. Y.; Rivlin R. S. Rheol Acta 1978, 17, 210.
15. Kazakia, J. Y.; Rivlin, R. S. J Non-Newt Fluid Mech 1979, 6, 145.
16. Casulli, J.; Clermont, J. R.; Von, Ziegler, A.; Mena, B. Polym Eng Sci 1990, 30, 1551.
17. Isayev, A. I.; Wong, C. M.; Zeng, X. Adv Polym Tech 1990, 10, 31.
18. Isayev, A. I.; Wong, C. M. J Polym Sci—Phys 1988, 26, 2303.
19. Qu, J. P. U.S. Pat. 5217302, 1993.
20. Qu, J. P. Proceeding of 16th Annual Meeting of the Polymer Processing Society International, June 18–23, 2000, Shanghai, China, pp 195–196.
21. Isayev, A. I.; Chen, J. U.S. Pat. 5284625, 1994.
22. Isayev, A. I.; Chen, J.; Tukachmsky, A. Rubber Chem Technol 1995, 68, 267.
23. Chen, G.; Guo, S.; Li, H. J Appl Polym Sci 2002, 84, 2451.
24. Chen, G.; Guo, S.; Li, H. J Appl Polym Sci 2002, 86, 23.
25. Guo, S.; Li, Y.; Chen, G.; Li, H. Polymer Int 2003, 52, 68.