Effects of Ultrasonic Oscillations on Processing Behavior and Mechanical Properties of Metallocene-Catalyzed Linear Low-Density Polyethylene/Low-Density Polyethylene Blends

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ABSTRACT: The influences of ultrasonic oscillations on rheological behavior and mechanical properties of metallocene-catalyzed linear low-density polyethylene (mLLDPE)/low-density polyethylene (LDPE) blends were investigated. The experimental results showed that the presence of ultrasonic oscillations can increase the extrusion productivity of mLLDPE/LDPE blends and decrease their die pressure and melt viscosity during extrusion. Incorporation of LDPE increases the critical shear rate for sharkskin formation of extrudate, crystallinity, and mechanical properties of mLLDPE. The processing behavior and mechanical properties of mLLDPE/LDPE blends were further improved in the presence of ultrasonic oscillations during extrusion. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2522–2527, 2004

Key words: low-density polyethylene (LDPE); blends; rheology; ultrasonic oscillations; metallocene catalysts

INTRODUCTION

Metallocene catalysts confer substantial physical and mechanical properties to polyethylene blends compared with those synthesized by conventional Ziegler–Natta catalysts. On the other hand, metallocene-catalyzed linear low-density polyethylene mLLDPE), other than Ziegler–Natta (ZN)-catalyzed LLDPE, has a higher melt viscosity and is much more difficult to process because of its narrow molecular weight distribution and absence of long-chain branching.[1] It is well known that low-density polyethylene (LDPE) has good processability because of its long-chain branching, which has a substantial effect on the rheological properties of the polymer. In the commercial field, blending LLDPE with LDPE is considered to combine the superior mechanical properties of LLDPE with the good processability of LDPE. To a certain extent, LDPE can improve the processing property of mLLDPE. In recent years many studies, focused on structure and properties of blends of mLLDPE/LDPE or ZN–LLDPE/LDPE, have been reported.[2–14]

Recently ultrasonic oscillations technology has been introduced into polymer processing, mainly in thermoplastics welding, extrusion of plastics, rubber vulcanization, and *in situ* compatibilization of immiscible polymer blends, for example.[15–21] In our laboratory a special ultrasonic oscillations extrusion system was developed to improve the rheological and processing properties of polystyrene (PS), LLDPE, polypropylene (PP), and so forth, and the compatibility of immiscible polymer blends.[22–25] The presence of ultrasonic oscillations provides an effective route for the improvement of processability of polymers during extrusion.

In our previous studies[26,27] we investigated the effects of ultrasonic oscillations and die materials on rheological and processing behaviors of mLLDPE. It was found that the die pressure and apparent viscosity of mLLDPE, in extrusion through different dies, decrease in the presence of ultrasonic oscillations, and to even higher degrees with increasing intensity of ultrasonic oscillations. We also found that die materials also have a great influence on the processing behavior.[27]

The merger of ultrasonic oscillations and the addition of LDPE, used to improve the processability and mechanical properties of mLLDPE, are reported in this article. The effects of ultrasonic oscillations and LDPE on processing behavior and mechanical properties of mLLDPE were also investigated.

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EXPERIMENTAL

Materials and equipment

mLLDPE was supplied by the Research Institute of Petroleum Processing [SINOPEC, Beijing, China; melt index (MI) = 1.0 g/10 min; density = 0.919 g/cm^3]. LDPE was supplied by Shanghai Petrochemical Co. (SINOPEC, Shanghai, China; MI = 2.8 g/10 min; density = 0.925 g/cm^3).

Our main experimental equipment was a specially designed ultrasonic oscillations extrusion system[26] developed in our laboratory, which includes a single-screw extruder and a cylinder die connected to a generator of ultrasonic oscillations. The die includes a special horn serving as a capillary. The maximum power output and fixed frequency of the generator are 300 W and 20 kHz, respectively. The ultrasonic oscillations are in the direction parallel to the flow of the polymer melt. A pressure transducer and a thermocouple at the die entry were 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.

Preparation of samples

mLLDPE and LDPE blends, with different mass ratios (100/0, 90/10, 70/30), were prepared in a single-screw extruder with the diameter of 25 mm and L/D ratio of 30. The extrusion temperature, at different zones from hopper to die, were set at 150, 180, 200, and 180°C.

The samples were prepared through extrusion at 10 rpm, in the absence of ultrasonic oscillations or in the presence of 200 W ultrasonic oscillations. The test specimens for differential scanning calorimetry (DSC) analysis were cut from the extrudates. Some extrudates were pelletized and compression molded at 180–190°C, then samples were cut from the molded sheets for mechanical properties testing.

Measurements

Measurements for die pressure and flow rate, in the presence of ultrasonic oscillations, were performed at superimposed ultrasonic oscillations intensities between 0 and 250 W by increments of 50 W.

The shear rate on the capillary wall $\dot{\gamma}$ was calculated as follows:

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

The shear stress τ and apparent viscosity η_a were calculated as follows:

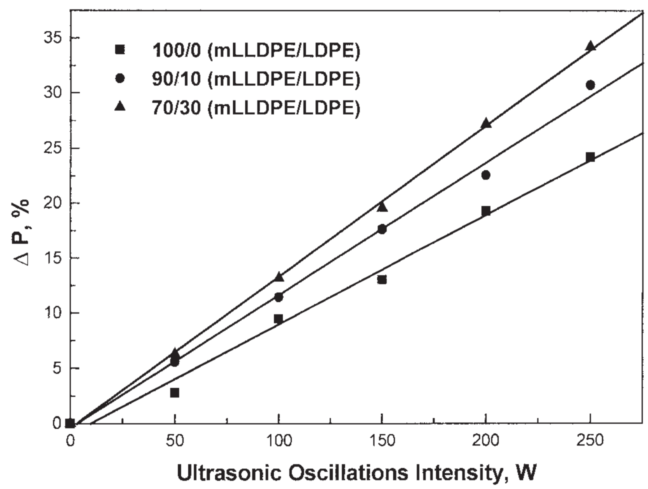

Figure 1 Effect of ultrasonic intensity on the relative die pressure decrease of mLLDPE/LDPE blends.

$$\tau = \frac{PR}{2L} \qquad \eta_a = \frac{\tau}{\dot{\gamma}}$$

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

DSC measurements were performed using a Perkin–Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT). The samples, of about 5 mg weight sealed in aluminum pans, were heated from room temperature to 463 K at a ratio of 10 K min^{-1}, maintained at 463 K for 5 min, and then cooled to room temperature at the same ratio under nitrogen atmosphere.

Stress–strain behavior was measured on an Instron 4302 tension machine (Canton, MA), with specimen dimensions of 25 × 6.5 × 1 mm and a crosshead speed of 100 mm/min.

RESULTS AND DISCUSSION

Rheological and processing properties

Die pressure drop

The relative die pressure drop ΔP, induced by ultrasonic oscillations in extrusion, is quantified by

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

where P_0 and P_u are the die pressure in the absence and the presence of ultrasonic oscillations, respectively. Die pressure changes with ultrasonic oscillations intensity were measured at a die temperature of 180°C. As shown in Figure 1, ΔP almost shows a linear decrease with increasing ultrasonic oscillations intensity. The presence of ultrasonic oscillations decreases the die pressure of mLLDPE and mLLDPE/LDPE blends during extrusion. Calculated from Figure 1, ΔP for mLLDPE/LDPE blends (70/30, 90/10), whose values are 34.2 and 30.7%, are respectively 40 and 25% higher than that for virgin mLLDPE, whose value is 24.2%, at a screw rotation speed of 10 rpm and ultrasonic oscillations intensity of 250 W, indicating that die pressure of mLLDPE/LDPE blends could be substantially reduced with the incremental addition of LDPE in the presence of ultrasonic oscillations during extrusion. It is clear from the above results that the combination of ultrasonic oscillations with the addition of LDPE shows a synergistic effect on the improvement of the processing behavior of mLLDPE.

Productivity in extrusion

Figure 2 shows the mass flow rate of mLLDPE/LDPE blends versus die pressure at different ultrasonic oscillations intensities. As shown in Figure 2, the mass flow rate of mLLDPE/LDPE blends (100/0, 90/10, 70/30) increases with increasing die pressure. On the other hand, the mass flow rate increases with the rise of ultrasonic oscillations intensity at the same die pressure level. The curves in Figure 3 are the results of fitting the flow rate data of mLLDPE/LDPE blends to a linear relation, suggesting that the flow rates of mLLDPE/LDPE blends vary almost linearly with the rise of ultrasonic intensity when the die pressure is 4 MPa. The slopes of the flow rate versus ultrasonic oscillations intensity curves of mLLDPE/LDPE blends (90/10, 70/30) are obviously higher than that of virgin mLLDPE, indicating that mLLDPE/LDPE blends have much greater dependency on ultrasonic oscillations in extrusion because ultrasonic oscillations cause a larger decrease of die pressure of mLLDPE/LDPE blends compared to that of virgin mLLDPE.

Apparent viscosity

Figure 4 shows apparent viscosity curves, during extrusion without ultrasonic oscillations, verifying that log η_a versus log $\dot{\gamma}$ of mLLDPE/LDPE blends (90/10, 70/30) has a much steeper linear relation, at experimental shear rate range, than that of virgin mLLDPE. This outcome suggests that the addition of LDPE can improve the shear sensitivity of mLLDPE in extrusion, and cause the relationship between apparent viscosity η_a of mLLDPE/LDPE blends and shear rate $\dot{\gamma}$ to obey, approximately, the power law equation at the level of low shear rate. Bubeck[28] concluded that shear thinning alone is a strong indicator of the presence of long-chain branches. Clearly, the addition of LDPE provides some long-chain branches for the blends, which is favorable to the processing of mLLDPE. Figure 4 also shows that incorporation of 10 wt % LDPE into mLLDPE causes an increase of melt viscosity of mLLDPE at the experimental shear rate, indicating that the addition of a small amount of LDPE may enhance the molecular entanglement between LDPE and mLLDPE. In our study, we used apparent viscosity drop $\Delta\eta_a$ to describe the ultrasonic oscillations

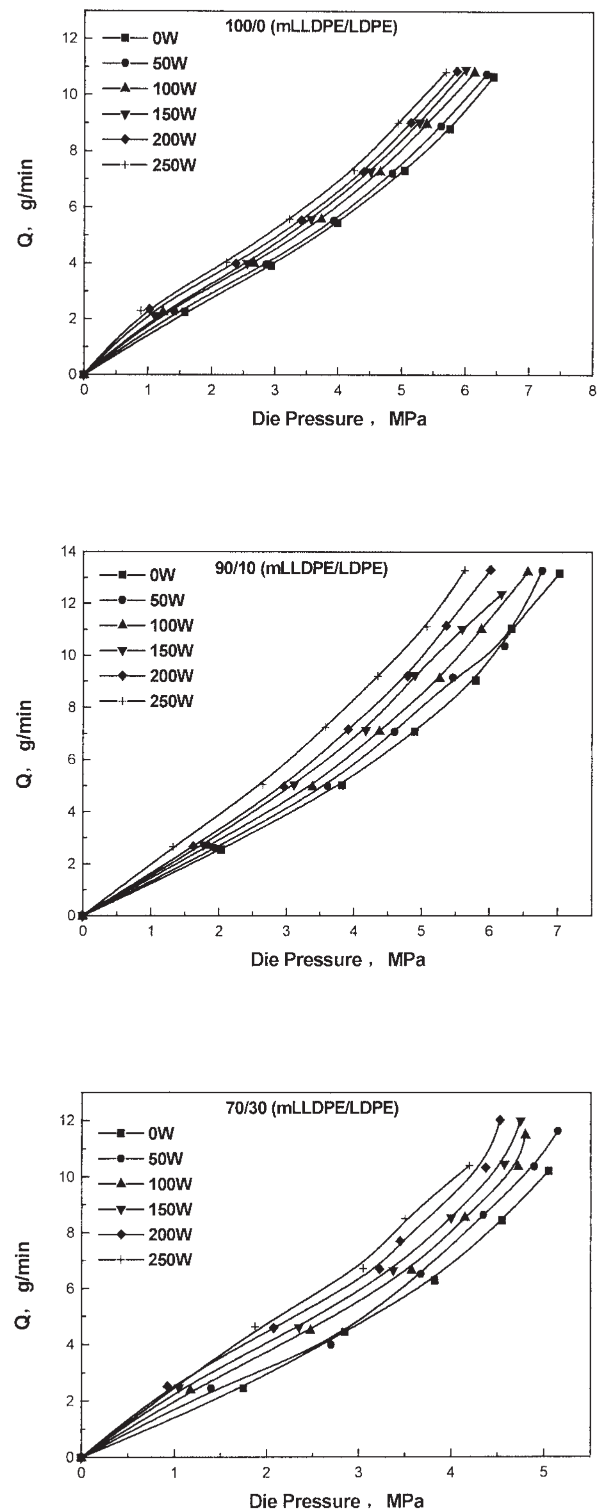

Figure 2 Effect of ultrasonic intensity on the mass flow rate Q of mLLDPE/LDPE blends.

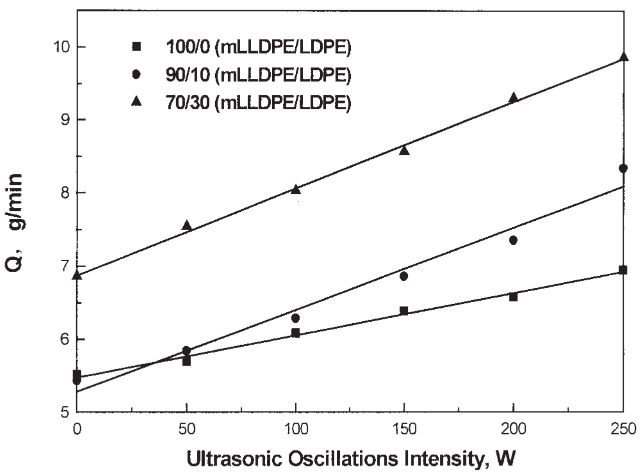

Figure 3 Plots of Q versus ultrasonic oscillations intensity at a die pressure of 4 MPa.

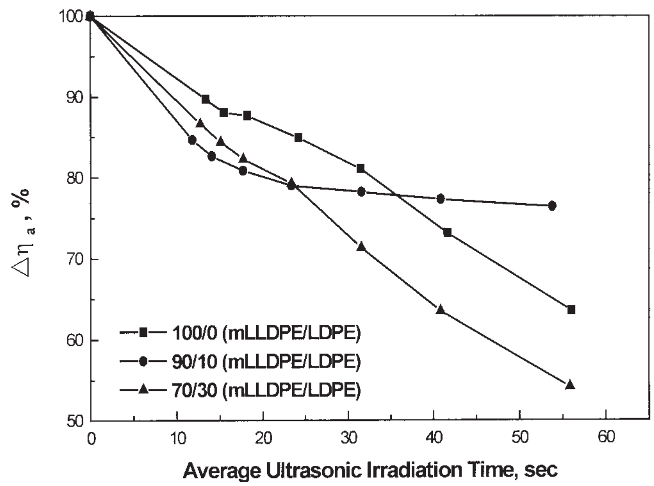

Figure 5 Effect of average ultrasonic oscillations time on $\Delta\eta_a$ of mLLDPE/LDPE blends in the presence of 200-W ultrasonic oscillations.

effect on reducing the apparent viscosity of mLLDPE/LDPE blends. Apparent viscosity drop $\Delta\eta_a$, in the presence of ultrasonic oscillations, can be quantified as

$$\Delta\eta_a = \frac{\eta_n}{\eta_0} \times 100\%$$

where η_0 and η_n are apparent viscosity in the absence and the presence of ultrasonic oscillations, respectively, at a given shear rate level. It can be seen in Figure 5 that $\Delta\eta_a$ of mLLDPE/LDPE blends decreases with increasing average time of ultrasonic oscillations, suggesting that the apparent viscosity drop of mLLDPE/LDPE blends is strongly dependent on average time of ultrasonic oscillations in the presence of ultrasonic oscillations. It is also found in Figure 5 that the trend of the apparent viscosity drop of mLLDPE/LDPE blend (90/10) becomes flatter after about 25 s of average ultrasonic oscillations time, whereas that of mLLDPE/LDPE blends (100/0, 70/30) decreases monotonously over the range of experimental average ultrasonic oscillations times, indicating that there are some interactions between mLLDPE and LDPE, especially in the 90/10 composition ratio in the presence of 200-W ultrasonic oscillations. In our work, we prolonged the ultrasonic oscillations time by decreasing the shear rate. The lower the shear rate, the longer the ultrasonic oscillations time: an average ultrasonic oscillations time of 25 s corresponds to a shear rate of 40 s^{-1}. The melt viscosity of mLLDPE/LDPE (90/10) blend remains unchanged when the shear rate is less than 40 s^{-1} because of the molecular entanglement between mLLDPE and LDPE; thus the apparent viscosity drop remains unchanged.

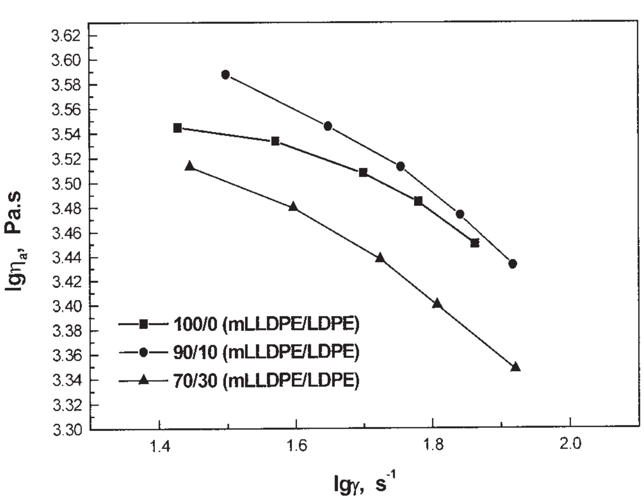

Figure 4 Plots of log η_a versus log $\dot{\gamma}$ of various mLLDPE/LDPE blends.

Critical shear rate

The observed critical shear rates (the onset of sharkskin or flow instability) of mLLDPE/LDPE blends,

TABLE I
Critical Shear Rate of mLLDPE/LDPE Blends in the Presence of Ultrasonic Oscillations

Blends mass ratio	Ultrasonic oscillations intensity, W	Critical shear rate (s^{-1})
100/0	0	26 ± 1
	100	28 ± 1
	200	31 ± 1
90/10	0	41 ± 1
	100	44 ± 1
	200	49 ± 1
70/30	0	62 ± 1
	100	66 ± 1
	200	72 ± 1

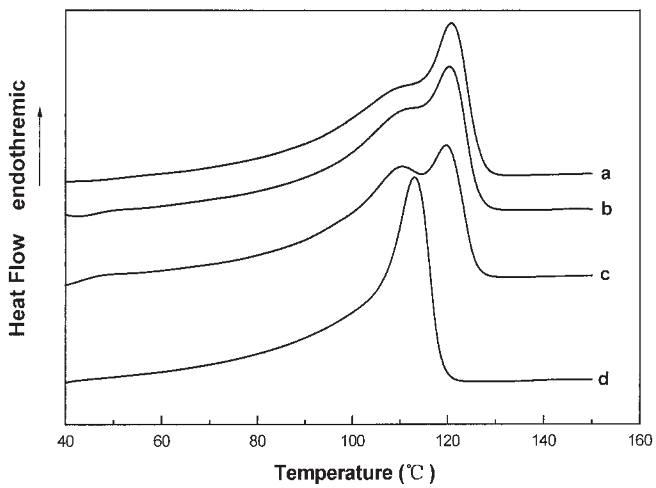

Figure 6 DSC melting curves of various mLLDPE/LDPE blends: (a) 100/0; (b) 90/10; (c) 70/30.

with different mass ratios, in the presence of different intensities of ultrasonic oscillations are listed in Table I. The data show that ultrasonic oscillations have scarcely any influence on the critical shear rate; nevertheless, the addition of LDPE has a distinct influence on the critical shear rate. Furthermore, it was found that the critical shear rate of mLLDPE/LDPE blends increases with increasing LDPE content and intensity of ultrasonic oscillations. Thus, based on the processing improvement of mLLDPE through the addition of a small amount of LDPE, the presence of ultrasonic oscillations could further increase the productivity of extrusion or film blowing of mLLDPE/LDPE blends by increasing the extruder's run speed.

Crystalline behavior

DSC melting curves for mLLDPE/LDPE blends are shown in Figure 6. The melting curves of mLLDPE/LDPE blends show two overlapping peaks, corresponding to 110 and 120°C. The pronounced peak at 120°C is attributed to the crystalline phase of long linear segments in mLLDPE. The unconspicuous peak at 110°C is attributed to the crystalline fraction of branched chains in mLLDPE and that of LDPE. The DSC results of mLLDPE/LDPE blends are listed in

TABLE II
DSC Results of mLLDPE/LDPE Blends

Sample	ΔH_m (W)	Crystallinity (%)	T_m		$I_{110°C}/I_{120°C}$
			T_{m1}	T_{m2}	
100/0	90.7	31.7	110.0	120.8	0.54
90/10	95.5	33.4	111.5	120.7	0.66
70/30	101.4	35.5	110.1	119.7	0.79
0/100	89.0	31.1	113.6	—	—

Table II. The data listed in Table II show that incorporation of LDPE increases the crystallinity of mLLDPE/LDPE blends and has a slight effect on their crystalline melting points, confirming the existence of cocrystallization phenomena between mLLDPE and LDPE. The

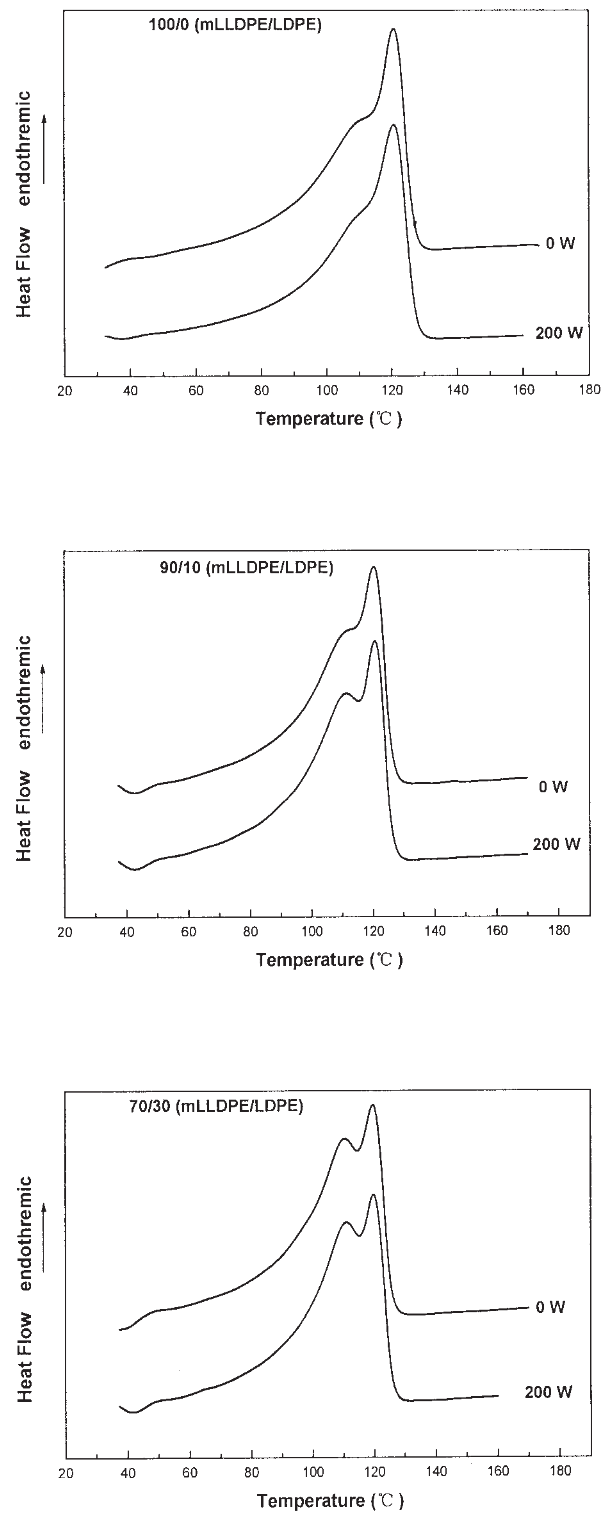

Figure 7 Effect of ultrasonic oscillations on DSC melting curves of mLLDPE/LDPE blends.

TABLE III
Effect of Ultrasonic Oscillations and LDPE on Mechanical Properties of mLLDPE/LDPE Blends

Blends mass ratio	Ultrasonic oscillations intensity (W)	Yield strength (MPa)	Stress at break (MPa)	Elongation at break (%)
100/0	0	10.8 ± 0.5	14.1 ± 0.8	435.7 ± 24.5
	200	10.4 ± 0.8	17.2 ± 0.4	586.4 ± 18.7
90/10	0	10.5 ± 0.4	16.5 ± 0.6	513.3 ± 30.3
	200	10.4 ± 0.6	19.5 ± 0.5	619.1 ± 25.6
70/30	0	10.5 ± 0.5	18.9 ± 0.7	595.4 ± 28.2
	200	10.6 ± 0.6	19.6 ± 0.2	663.8 ± 19.6

peak intensity ratio of the peak at 110°C, over that of the peak at 120°C, increases with the increasing amount of LDPE, attributed to the contribution of LDPE to the peak at 110°C. As shown in Figure 7, the presence of ultrasonic oscillations hardly changes the crystalline structure of mLLDPE/LDPE blends.

Mechanical properties

A uniaxial tensile test of mLLDPE/LDPE blends was performed at 293 K, the data from which are listed in Table III. It was found that with increasing LDPE content in the blends of mLLDPE/LDPE, the stress and elongation at break of the blends increase. It was also found that the stress and elongation at break of the blends were further increased in the presence of ultrasonic oscillations. Ultrasonic oscillations and the addition of LDPE have only a slight influence on the yield strength of mLLDPE/LDPE blends, which indicates that ultrasonic oscillations can enhance molecular diffusion in the amorphous region between mLLDPE and LDPE, resulting in increases of stress and elongation at break of the blends.

CONCLUSIONS

Under the experimental conditions of shear rates, varying from 20 to 80 s^{-1}, and test temperature at 180°C, ultrasonic oscillations, as well as the addition of LDPE, have distinct influences on both the processing behavior and mechanical properties of mLLDPE/LDPE blends. The die pressure and apparent viscosity of mLLDPE/LDPE blends during extrusion is decreased and productivity is increased in the presence of ultrasonic oscillations. The addition of LDPE can clearly increase the critical shear rate for melt fracture during extrusion, shear, and ultrasonic-oscillation sensitivity of mLLDPE/LDPE blends, attributed to long-chain branching in LDPE molecules.

The merger of ultrasonic oscillations and the addition of LDPE show a synergistic improvement of processing behavior and mechanical properties of mLLDPE/LDPE blends.

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