

# Analysis of Melt Spinning Master-Curves of Low Density Polyethylene

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**ABSTRACT:** The extensional rheological properties of a low density polyethylene (LDPE) melt were studied by using melt spinning technique. Based on the extension properties of the LDPE melt under experimental conditions, the melt spinning master-curves were plotted by introducing scaling factor  $b$  and the draw ratio  $\lambda$ . The scaling factor  $b$  shows the combination effects on the preorientation before extension, the unwrapping and orientation of molecular chains during extension. Several linear relationships between  $b$  and temperature,  $\log b$  and the logarithm

of extrusion flow rate  $v_0$  ( $\log v_0$ ) have been investigated. By using the values of  $b$  and the reference curve, the extension viscosity curves with different temperature and extrusion flow rate could be calculated, thus the measurement range of melt spinning technique would be extended effectively. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2202–2206, 2012

**Key words:** low density polyethylene; rheology; melt extension property; measurement

## INTRODUCTION

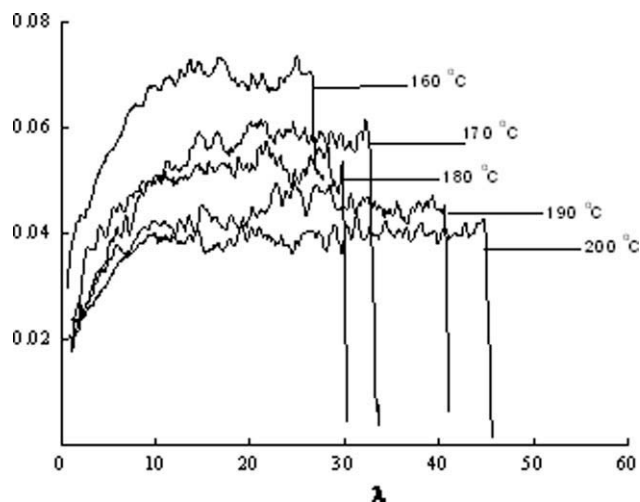
The extensional flow of polymer melts is a common flow pattern in processing, such as entrance converging flow in die extrusion or runner injection of polymer melts from an extruder barrel,<sup>1–8</sup> blow molding, blowing film, sheet casting and melt spinning. It is useful to know the extensional behavior during processing of polymer melts.<sup>7</sup> There has been a great deal of interest in recent years in determining the uniaxial extensional flow properties from a number of different techniques. For example, the melt strength and extensional viscosity are measured using extensional rheometers from purely extensional flows.<sup>9–13</sup> The measurement carried by the extensional rheometer extends the sample under an isothermal uniform flow condition, so the dependence of the extensional viscosity on the strain, under constant strain or constant stress, is measured directly. However, these instruments are typically very expensive and difficult to operate. Because the achievement of a pure isothermal extensional flow is quite difficult, there is still a great deal of disagreement between results obtained from different rheometers.

The difficulties in using extensional rheometers have pushed the researchers to develop alternative experimental techniques for the determination of extensional viscosities. Cogswell,<sup>14</sup> Binding,<sup>15,16</sup> and Liang<sup>2,4</sup> used converging flow to determine the extensional rheology indirectly. During the measurements, polymer melts flow from the barrel of capillary rheometer into a capillary die, based on the data like pressure drops and specific models, the extensional rheology can be determined indirectly.

Melt spinning used to be a typical method to evaluate the melt strength and drawability of polymer melts. Recently, more and more researchers regarded it as an alternative method for the measurements of the extensional viscosities.<sup>1,17–20</sup> Melt spinning is easy to use, shows excellent reproducibility, and it has a close modeling of many polymer processes like film blowing and fiber spinning. The relation of extensional viscosity obtained from melt spinning to the true extensional viscosity of the material is still not completely understood. Laun and Schuch<sup>17</sup> and Wagner et al.<sup>21–23</sup> compared the results from Rheotens measurements with steady-state viscosities from extensional experiments at constant strain rate or tensile stress and found a rough agreement; he proposed an idea of Rheotens-master-curves and analyzed the rules of scaling factor  $b$  to develop a method that could calculate the extensional viscosities under any setting temperatures and velocities. Though Baldi et al.<sup>20</sup> found that for high strain rate, the viscosity from melt spinning

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**Figure 1** Melt spinning curves at various temperatures (extrusion rate 11.25 mm/s).

was quite close to the transient extensional viscosity values obtained from the tensile tests.

In general, both temperature and extrusion flow rate have important effects on the rheological measurement results during polymer melt spinning test. It is difficult to obtain correct results if the temperature is too high or low or the velocity is too fast or slow, because the melt tends to stick or wind-up on the wheels. It is, therefore, quite meaningful to solve this problem either in rheological study or in polymer processing. The objective in this work is to investigate the effects of temperature and extrusion flow rate on the extension properties including extensional stress and viscosity of a low density polyethylene (LDPE) by analyzing the melt spinning master-curves.

## EXPERIMENTAL

### Raw material

The resin used in this study was the LDPE (951-000) with density of 0.92 g/cm<sup>3</sup> and melt flow index of 2.17 g/10 min, supplied by China Petroleum and Chemical Corporation, Maoming City in Guangdong Province.

### Instruments and method

The extensional rheological measurements were performed by using a capillary rheometer Rheologic 5000 equipped with a specific stretching unit manufactured by Ceast SpA in Italy.

Polymer melts measured by melt spinning were stretched in uniaxial extension. For each measurement, the material was heated at certain temperature and then extruded at a constant flow rate through a capillary die, subsequently. Then, the melt was drawn by a set of pinching rotating wheels positioning at some distance downstream. At the beginning,

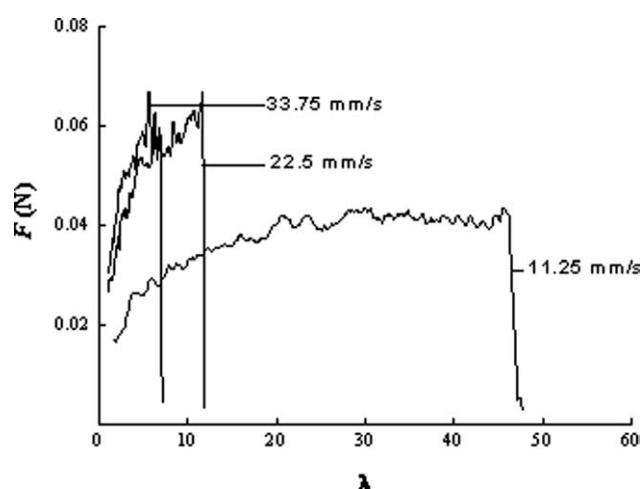
the take-up speed of the wheels was adjusted to the velocity of the extruded polymer strand. Then, the speed was increased with constant acceleration rate to stretch the melt until it broke. During the test, the draw-down force measured was plot as a function of velocity of the rotating wheels. For each temperature, the tests were repeated at least three times, the one with the highest draw ratio at break was used to calculate the extensional viscosity. For all the measurements, the length of the spin-line  $L$  was 200 mm, the diameter of extrusion die was 1 mm, the ratio of length to diameter  $l/d = 30 : 1$ , the entrance angle was 90°, the acceleration rate was 5 mm/s<sup>2</sup>. The test temperatures of LDPE were 160°C, 170°C, 180°C, 190°C, and 200°C, respectively, and the extrusion flow rate for 160°C and 200°C was 11.25 mm/s, the melt drawing velocities for 170°C were 11.25, 22.5, 33.75, and 45 mm/s, for 180°C and 190°C were 6.75, 11.25, and 15.75 mm/s.

## RESULTS AND DISCUSSION

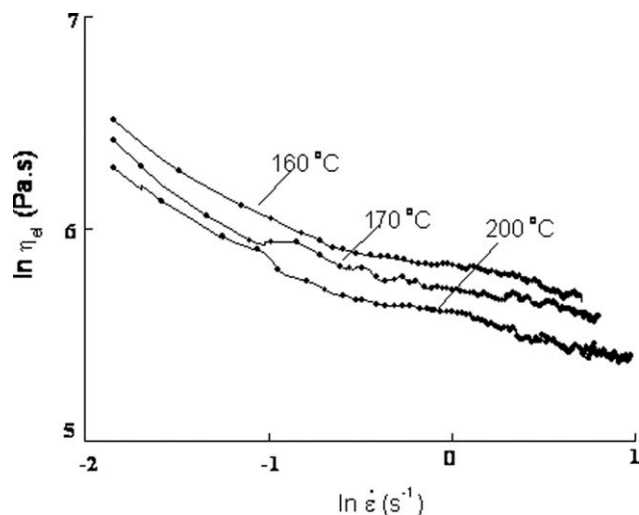
### Melt spinning curves

Figure 1 shows the melt spinning curves at various test temperatures obtained from the tests of the LDPE. It can be seen that the draw-down force ( $F$ ) increases with an increase of the draw ratio ( $\lambda$ ) as temperature is constant, especially when  $\lambda$  is smaller than 20. When  $\lambda$  is fixed, the  $F$  decreases with a rise of temperature. This is because that the movement ability of macromolecular chain will be enhanced with a rise of temperature, and the force needed for the macromolecular chain orientation reduces relevantly. Hence, the draw-down force of the LDPE melts decrease with a rise of temperature during elongation flow.

Figure 2 illustrates the melt spinning curves at various melt drawing velocities at temperature of



**Figure 2** Melt spinning curves at various melt drawing velocities (melt temperature 170°C).



**Figure 3** Melt apparent extension viscosity versus strain rate at various temperatures (extrusion rate 11.25 mm/s).

170°C. It seems that the draw-down force ( $F$ ) increases with increasing the draw ratio for a fixed temperature, and the higher the extrusion flow rate, the higher is the force needed for stretching the melt at a prescribed draw ratio. The main reason might be that the extensional strain rate increases with an increase of the extrusion flow rate when the draw ratio is constant, and the draw-down force increases with increasing the extensional strain rate at a fixed temperature, leading to the draw-down force increases with increasing extrusion flow rate.

### Extension viscosities

Based on the melt spinning curves, the extensional strain rate  $\dot{\epsilon}$  and the melt apparent extensional viscosity  $\eta_{el}$  may be determined by eqs. (1) and (2), which were as follows<sup>17,21–23</sup>:

$$\dot{\epsilon} = \frac{v_0}{L} \cdot \lambda \cdot \ln(\lambda) \quad (1)$$

$$\eta_{el} = \frac{F \cdot L}{Q \cdot \ln(\lambda)} \quad (2)$$

where  $v_0$  is the melt drawing velocity,  $L$  is the spinline length,  $\lambda$  is the draw ratio,  $F$  is the draw-down force at the prescribed draw ratio, and  $Q$  is the volume flow rate. Moreover, eqs. (1) and (2) should be based on the assumption of Newtonian viscosity.

The melt apparent extensional viscosities of the LDPE at 160°C, 170°C, and 200°C determined by eqs. (1) and (2) are shown in Figure 3. It can be seen that the melt extension viscosities decrease with the rise of extensional strain rate as temperature is constant. This is reasonable because the shape of extension viscosity curve is supposed to be similar to its shear thinning curve. In addition, it is obvious that

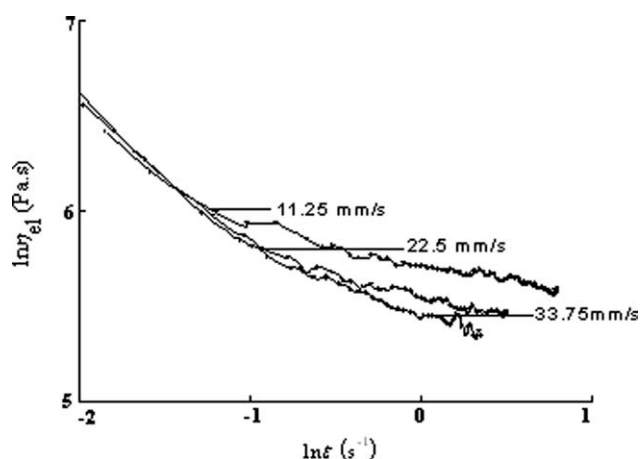
for a prescribed strain rate, the higher temperature when performing the test, the lower is the value of the apparent extension viscosity. This can be explained on the basis of the fact that the macromolecular chains become more active at higher temperature, their unwrapping motions will be speeded up and the associated viscosity becomes lower.

Figure 4 illustrates the melt apparent extensional viscosity curves obtained at 170°C and different melt drawing velocities. It shows that for a prescribed strain rate, the higher the melt drawing velocities, the lower is the value of melt apparent extensional viscosity. This is possible that when performing the test with lower melt drawing velocity, the cooling effect of the ambience to the strand is stronger, so the value of the viscosity is higher. More than 10 years ago, Wagner et al.<sup>21–23</sup> observed this phenomenon and believed that it could be due to the “preorientation” of molecules in the die at higher shear rates.

### Master-curves

It can be seen from Figures 1 and 2 that all the curves have a similar shape. Wagner obtained similar results by performing his tests by means of the Rheotens apparatus. He then proposed the idea named Rheotens grand master-curves, which means that for the same material, curves obtained by different process conditions can finally superimposed to a curve considered as the reference by rescaling with a specific scaling factor. The procedures of plotting master-curves are as below: first, choose a reference curve; second, calculate the scaling factor of the curve considered to be rescaled; finally, plot the rescaling curve according to eq. (3).

$$b_i F_i(\lambda_i) = F_r(\lambda_i/b_i) \quad (3)$$



**Figure 4** Melt apparent extension viscosity versus strain rate at various melt drawing velocities (melt temperature 170°C).

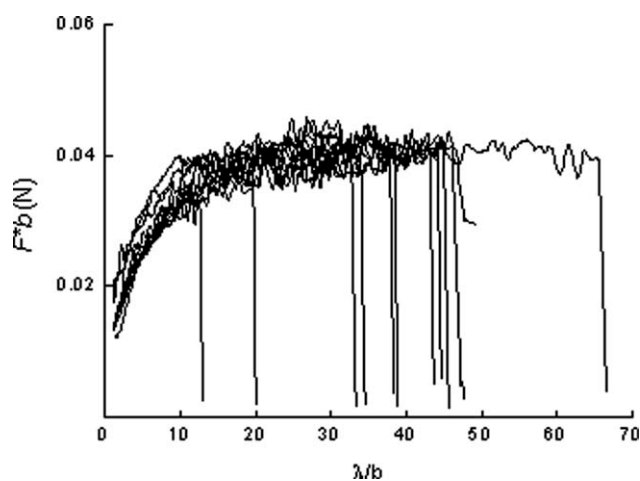


Figure 5 Melt spinning master-curves.

where  $b$  is the scaling factor, the term with subscript  $i$  refers to the curves to be rescaled, and the term with subscript  $r$  refers to the reference curve. In this work, the reference curve were measured at temperature of  $200^{\circ}\text{C}$  and  $v_0 = 11.25 \text{ mm/s}$ .

Figure 5 shows the results of the curves rescaled according to eq. (3). It clearly shows that the curves obtained by different temperatures and melt drawing velocities are overlapped and display on the corresponding reference curve after rescaling. This master-curve clearly simplifies the description of material behavior in the spinline.

### Scaling factor $b$

The dependence of the scaling factor  $b$  and temperature is plotted in Figure 6, the temperatures range is from  $160^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ . From Figure 6, one can see that the  $b$  increases with a rise of temperature at the same extrusion flow rate. A linear relationship between the  $b$  and temperature has been observed.

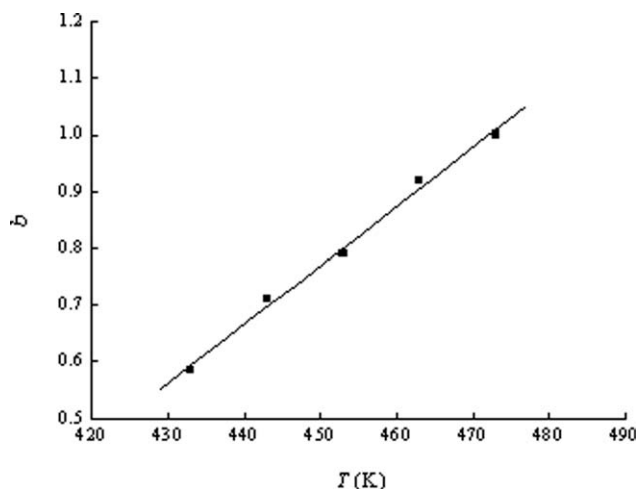


Figure 6 Dependence of  $b$  on temperature (extrusion rate  $11.25 \text{ mm/s}$ ).

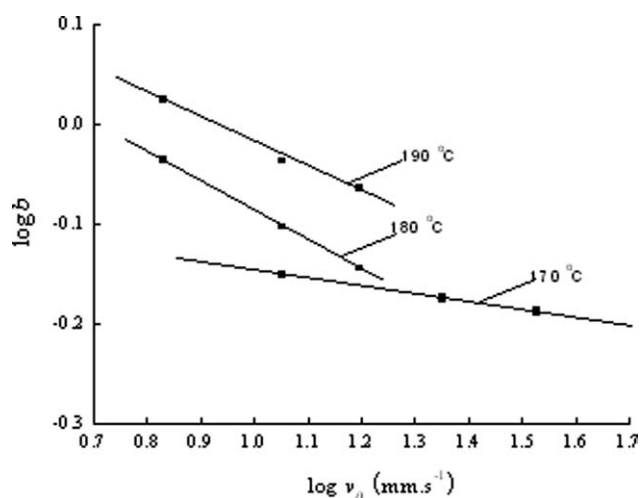


Figure 7 Relationship between  $\log b$  and  $\log v_0$ .

The temperature will speed up the unwrapping and modify the orientation of molecular chains, so the  $b$  can be regarded as a useful index of these combination effects during extension. Figure 7 displays the relationship between the  $b$  and extrusion flow rate  $v_0$  under various temperatures. For a prescribed temperature, the  $b$  declines with the rise of the extrusion flow rate. Furthermore, the linear correlation between  $\log b$  and  $\log v_0$  can be explored for each temperature, despite the slope for each line is different. With the increase of  $\log v_0$ ,  $\log b$  decreases. It is known that the extrusion flow rate affects the preorientation before the extension. Therefore, the  $b$  can also be seen as an index to indicate the degree of preorientation of the melt.

### Estimation of melt apparent extension viscosity and comparison

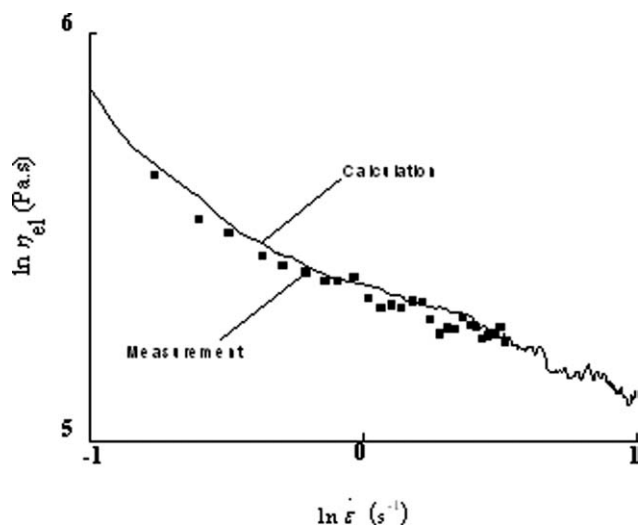
From the master-curves refer to temperature of  $200^{\circ}\text{C}$  and  $v_0 = 11.25 \text{ mm/s}$ , one may find that the value of  $b$  for any condition is unique. In other words, each curve has only one corresponding  $b$ . Therefore, by using the value of  $b$  and the reference curve, the curve of any setting temperature and melt drawing velocities can be constructed. In this case, according to the relation shown in Figures 6 and 7, specific  $b$  can be determined easily, with the data of strain rate and viscosities of the reference curve, the melt apparent extension viscosities of any setting conditions can be calculated through eqs. (4) and (5):

$$\dot{\epsilon} = \frac{v_0}{L} \cdot \lambda_r b_i \cdot \ln(\lambda_r b_i) \quad (4)$$

$$\eta_{el,i} = \frac{v_{0,r} \eta_{el,r}}{v_{0,i}} \frac{\ln(\lambda_r)}{b_i \ln(\lambda_r b_i)} \quad (5)$$

Here, the melt apparent extensional viscosities of LDPE at temperature of  $170^{\circ}\text{C}$  and extrusion flow rate of  $45 \text{ mm/s}$  ( $b = 0.627$ ) are determined by this





**Figure 8** Melt apparent extensional viscosity versus strain rate (170°C, melt drawing velocity 45 mm/s).

method. Similarly, eqs. (4) and (5) should also be based on the assumption of Newtonian viscosity. As shown in Figure 8, the calculations and the measurement data of the melt apparent extensional viscosity of the LDPE are close to each other. This presents that the melt spinning master-curve analysis becomes a useful way to obtain the data of extensional strain rate and viscosities indirectly. When either the temperature or the melt drawing velocity is too high or too low, the measurements cannot be performed regularly because the melts stick or wind-up to the wheels, one may use the data known to plot the master-curves, explore the principles of  $b$ , and then calculate the melt apparent extensional viscosities by this method. In other words, it is an effective way to expand the measurements range of melt spinning measurements.

### CONCLUSIONS

The effects of temperature, extension strain rate, and melt drawing velocity on the extensional rheological properties of a LDPE melt were significant. The results showed that the draw-down force ( $F$ ) increased with an increase of the draw ratio and melt drawing velocity ( $v_0$ ), while decreased with a

rise of temperature; the melt apparent extensional viscosity decreased with increasing extension strain rate and with a rise temperature.

The melt spinning curves of the LDPE under various temperatures and melt drawing velocities were plotted as master-curves. Linear relationship between the scaling factor  $b$  and temperature, as well as linear relationship between  $\log b$  and  $\log v_0$  have been explored. It was found that the calculations and the measurement data of the melt extensional viscosity of the LDPE are close to each other.

According to the value of  $b$  and the data of reference curve, the melt apparent extensional viscosities of any setting conditions can be calculated. Hence, it might be concluded that the master-curves analysis proves to be an effective way to enlarge the range of melt spinning technique.

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