

# Rheological Behaviors and Molecular Weight Distribution Characteristics of Bimodal High-Density Polyethylene

Hong-Wang Shen, Tao Luan, Bang-Hu Xie, Wei Yang, Ming-Bo Yang

College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu 610065, Sichuan, People's Republic of China

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**ABSTRACT:** A series of bimodal high density polyethylene (PE) with different molecular weight distributions (MWDs) were prepared by melt blending, and the fitting multipeaks on Gaussian were used to analyze the MWD curves, and the ratio of the areas under unimodal curves was as a tool to characterize the MWD; the phase behaviors and rheological behaviors were studied by dynamic rheological. The results showed that homogeneous bimodal high density PEs could be successfully prepared via melt blending, and the bimodal characteristic could be adjusted as expected. For samples with the MWD peak positions

unvaried, the storage modulus, complex viscosity, and zero-shear viscosity decreased rapidly with the value of  $A_{L/U}$  increasing. Especially in the low frequency region, the loss modulus surpassed the storage modulus ( $G'' > G'$ ) when  $A_{L/U} > 10.17$  and the dynamic cross-point  $G_x$  appeared and increased with increasing  $A_{L/U}$ , with an increasing extent much larger than that due to the width of MWD. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1543–1549, 2011

**Key words:** polyethylene; blending; bimodal MWD; dynamic rheological behavior

## INTRODUCTION

It is always an important topic that adjustment of the molecular structure to improve the properties of polyethylene (PE) in academia and in industry. Except for the average molecular weight, the molecular weight distribution (MWD) is also an important factor in determining the properties of PE materials. For conventional polymers with unimodal MWD, generally, a contradiction exists between the mechanical properties and processabilities. For example, better physical and mechanical properties can be obtained by increasing the average molecular weight, which, at the same time, leads to poor processabilities due to high viscosities.<sup>1–4</sup> In the recent years, a type of PE with bimodal MWD, composed of higher molecular weight and lower molecular weight fractions, exhibits good processability and excellent mechanical properties. The high-molecular weight fractions endows the resin good mechanical properties, and the low-molecular weight fractions are beneficial to improve the processability, resulting in a good balance between the mechanical properties and processability.<sup>5–7</sup>

Usually, there are several methods for the production of multimodal or broad MWD resins: melt blending, reactor in series configuration, or single reactor with dual site catalysts.<sup>8–11</sup> Essentially, these methods are identical: BPE is the blend of two types of PEs with different average molecular weight and MWD. Generally, it is difficult and expensive to produce BPE with different MWD characteristics by the latter two in the laboratory, instead of the melt blending. Krumme et al.<sup>12,13</sup> have had prepared HDPE with bimodal molecular weight distribution by solution blending and discussed the isothermal crystallization. But the studies about the influence of the bimodal MWD characteristics on material properties (include melt rheological properties) were still scarce.<sup>14,15</sup>

For the BPE products, the component homogeneity is a precondition for excellent properties, which are closely related to the miscibility of two types of PEs. The rheological property is one of important properties for polymers and sensitive to the miscibility of blends, and it has been used to study the miscibility of blends consisting of different grades of PEs. Some common methods include the Han-plots, Cole–Cole plots, and Log-additive composition plots.<sup>16–21</sup>

The influences of the average molecular weight and MWD on the rheological properties, phase behavior, and the miscibility of blends have been reported.<sup>22–25</sup> Shan et al.<sup>23</sup> synthesized in-reactor blends of PE/poly(ethylene-co-1-octene) resin with bimodal MWD and bimodal short branching distribution using a two-step polymerization process and discussed on the effect of

Correspondence to: B.-H. Xie (xiebangh@tom.com).

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the component content and the molecular weight on the phase behavior and rheological properties. But only a few publications focus on the influences of the positions and intensities of two peaks in the MWD curves of BPEs on the material properties.

In this work, a series of BPEs, with basically identical peak positions but different peak intensities in the MWD curves, were prepared by the method of melt blending of two types of HDPEs, and the phase behaviors and rheological behaviors were studied. The MWD curves were processed by the method of Gaussian fit multipeaks, and the ratio of areas under the obtained curves was used as a tool to characterize bimodal MWD.

## EXPERIMENTAL

### Materials

The bimodal PE-100 was produced as pellets by Shanghai Petrochemical Co, with  $M_w = 590$  kg/mol, density of  $0.949$  g/cm<sup>3</sup>, and a melt flow rate (measured at 190°C and 21.6 kg) of 6.38 g/10 min. The unimodal PE-2911 was supplied as pellets by Fushun Petrochemical Co, with  $M_w = 170$  kg/mol, density of  $0.960$  g/cm<sup>3</sup>, and a melt flow rate (measured at 190°C and 2.16 kg) of 20.0 g/10 min.

### Sample preparation

The binary blends of PE-100 and PE-2911, with the mass ratio of PE-100/PE-2911 100/0, 96/4, 92/8, 88/12, and 84/16, and marked as  $S_0$ ,  $S_1$ ,  $S_2$ ,  $S_3$ , and  $S_4$ , respectively, were prepared by blending in TSSJ-25 corotating twin-screw extruder twice,  $L/D = 33$ . The temperature profiles were 130, 160, 180, 210, 210, and 205°C for the feed zone, the compression zone, the metering zone, the exhaust zone, and the pumping zone, respectively.

### Characterization

High temperature gel permeation chromatograph (GPC)

The average molecular weight and polydispersity index (PDI) of raw materials and the extrudates were obtained by GPC (Model PL-GPC 220, UK) using 1,2,4-trichlorobenzene as a solvent at 160°C. The calibration of the data was performed using standard polystyrene samples.

### Dynamic rheological test

The linear viscoelastic properties of the blends in the melt state were measured using Rheometer System Gemini 200, measurement of the storage ( $G'$ ) and loss ( $G''$ ) moduli as well as the complex viscosity ( $\eta^*$ ) were made using parallel mode. The samples

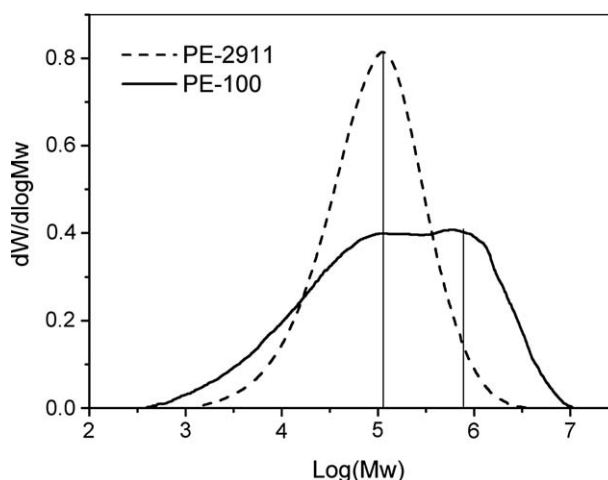


Figure 1 MWD curves of PE-2911 and PE-100.

were melt-pressed at 200°C into 25 mm × 1-mm circular disks. To determine the linear viscoelastic region of blends, dynamic strain sweeps were carried out between 0.1 and 10% strain at 10 Hz at 220°C. Dynamic frequency sweeps were performed over the 0.01–100 Hz at 220°C and 1% strain.

## RESULTS AND DISCUSSION

### MWD characteristics and compositions of the blends

Figure 1 showed the MWD curves of PE-2911 and PE-100 obtained from GPC test. It can be seen that the MWD curve for PE-2911 was unimodal, while that for PE-100 was bimodal: The lower peak position of PE-100 was almost the same to the peak position of PE-2911 ( $\log M_{Mw} = 5.05$ ), and the other peak position was obviously higher ( $\log M_{Mw} = 5.90$ ). For brevity, in this work, we named the peak at relatively lower molecular weight as the lower peak, while the peak at relatively higher molecular weight as the upper peak at axis of abscissa ( $\log M_{Mw}$ ). The MWD curve of PE-100, especially the bimodal characteristic, just had little change after extrusion; moreover, this MWD curve and that of other blends ( $S_1$ ,  $S_2$ ,  $S_3$ , and  $S_4$ ) had shown continuous and regular changes, as illustrated in Figure 2. The molecular parameters were listed in Table I, indicating that the weight-average molecular weight ( $M_w$ ) decreased, but the number-average molecular weight ( $M_n$ ) increased gradually with increasing in the content of PE-2911, and the changes were slight.

As can be shown in Figure 2, the increase in the peak intensity of the lower peak for all the blends was found to follow the increase in the content of PE-2911, while the peak intensity of the upper peak presented a reverse trend. Noted that the peak positions showed no significant change, and the overall characteristics of the MWD curves were basically the same.

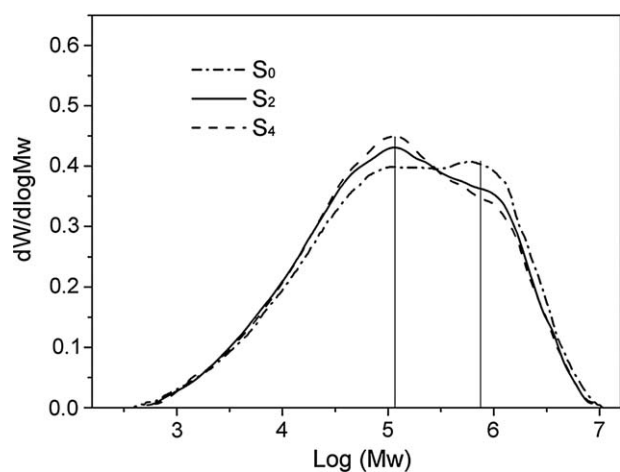


Figure 2 MWD curves of  $S_0$ ,  $S_2$ , and  $S_4$ .

At present, there are rare approaches to characterize the bimodal MWD characteristic. The PDI is not sufficient in this case (as be shown from Table I,  $Mw/Mn$  for this series of BPEs ranged only from 23.06 to 28.20), what is more important, PDI could not reflect the differences in the important structural characteristics, such as the relative intensity of two peaks. In fact, BPE is essentially blends of two kinds of PEs with different unimodal MWD. Therefore, detailed analysis of the two unimodal PE MWD characteristics would be beneficial to the characterization of the bimodal MWD characteristics. Wang et al.<sup>25</sup> synthesized bimodal PE, and the result of fitting multi-peaks on Gaussian presented the peak 1 and peak 2 MWD curves. In this work, the fitting multi-peaks on Gaussian by using the Origin 7.5 soft package was used to analyze the MWD curves of BPEs.

Figure 3 showed the fitting multi-peaks on Gaussian result of the  $S_2$  MWD curve. All the Gaussian fitting data of BPE MWD curves were quite good, and the fitting correlation coefficient  $R^2$  was more than 0.99. For any BPE, the result presented two unimodal MWD curves, called as lower peak fraction (LPF) curve and upper peak fraction (UPF) curve, whose peak positions were close to the lower peak and higher peak position on the bimodal MWD curve, respectively. Table II displayed the average value of the molecular parameters related to curves  $LPF_i$  and  $UPF_i$  ( $i = 0-4$ ) of all the blends. It showed that BPEs ( $S_0-S_4$ ) were composed of LPF fraction with  $Mw = 424$  kg/mol,  $Mw/Mn = 23.5$ , and UPF fraction with

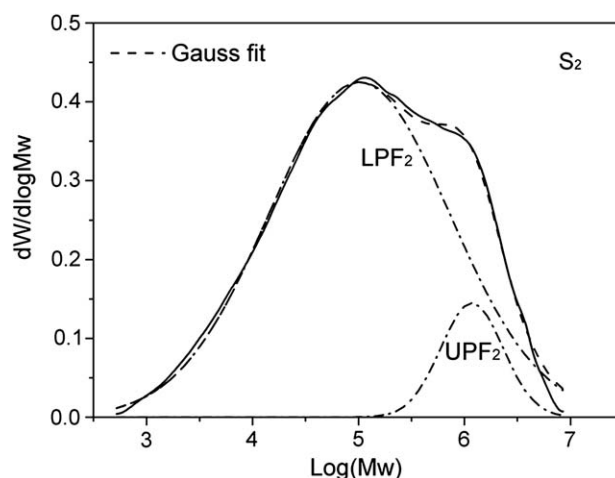


Figure 3 Fitting multi-peaks on Gaussian of  $S_2$  MWD curve.

$Mw = 1463$  kg/mol,  $Mw/Mn = 1.74$ , and a series of BPEs could be prepared by adjusting the mass proportion of LPF and UPF. In other words, it was believed that any BPE was the two unimodal PEs (LPF/UPF) blends, and the ratio of the area under LPF and UPF curves determined the weight proportion, defined as  $A_L/A_U$  here. All  $A_L/A_U$  were listed in Table I.  $A_L/A_U$  might reflect concisely the bimodal characteristics, and it represented corresponding BPEs ( $S_0-S_4$ ) in the following discussion.

### Melt miscibility

#### Log-additive composition plots

In Figure 4, the complex viscosity  $\eta^*$  versus weigh content of PE-2911 were plotted for BPEs at different frequencies. For partially miscible or immiscible blends, the  $\eta^*$  versus composition curve may exhibit positive or negative deviation from linearity owing to the phase morphologies.<sup>26,27</sup> Here,  $\eta^*$  of the BPEs shows good linearity with increasing content of PE-2911 at different frequencies, there was no obvious deviation from linearity, indicating that PE-100 and PE-2911 were melt miscible for the BPE blends.

#### Cole-Cole plots

The plot of  $\eta''$  versus  $\eta'$ , named Cole-Cole plots, are commonly used to analyze the miscibility of polymer

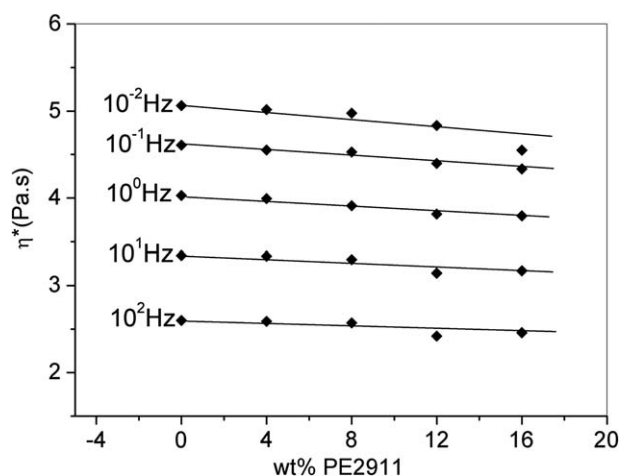
TABLE I  
The Molecular Parameters of BPE Blends

Samples	$A_{L/U}$	$\bar{M}_{Mw}$ (kg/mol)	$\bar{M}_{Mn}$ (kg/mol)	$\bar{M}_{Mw}/\bar{M}_{Mn}$
$S_0$	4.15	590.0	20.90	28.20
$S_1$	4.40	572.8	21.31	26.88
$S_2$	8.48	556.0	21.74	25.88
$S_3$	10.17	539.3	22.19	24.30
$S_4$	11.14	522.5	22.66	23.06

TABLE II  
The Average Value of Molecular Parameters of LPF<sub>i</sub> and UPF<sub>i</sub> ( $i = 0-4$ )

Fractions	$M_w^P$ (kg/mol)	$\bar{M}_{Mw}$ (kg/mol)	$\bar{M}_{Mn}$ (kg/mol)	$\bar{M}_{Mw}/\bar{M}_{Mn}$
LPF	94.4	424	18	23.5
UPF	1110	1463	841	1.74

$M_w^P$ , the molecular weight at the peak position.

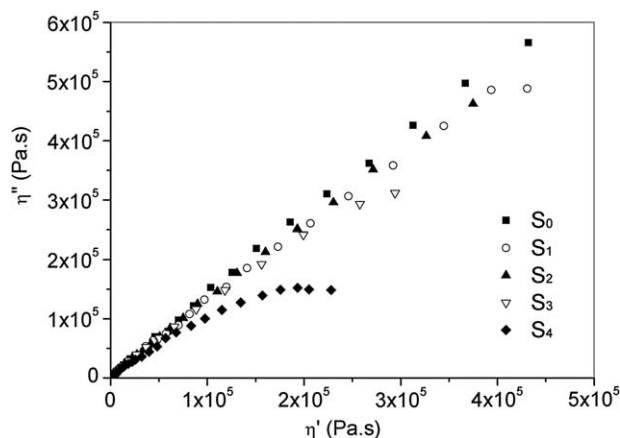


**Figure 4** The composition dependence of  $\eta^*$  for the blends at different frequency. The solid line represent the link line between  $\eta^*$  of  $S_0$  and PE-2911.

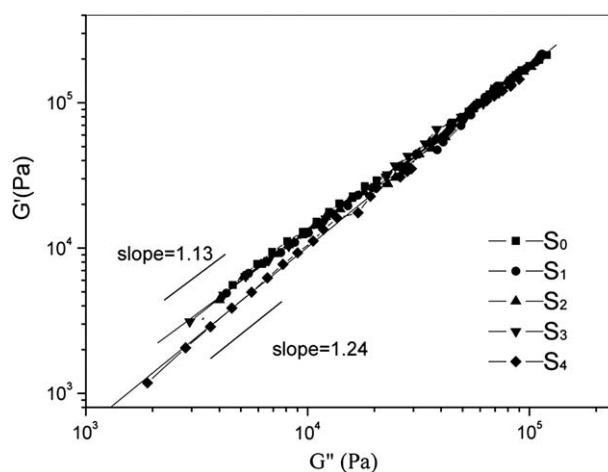
blends. Smooth, semicircular-shaped Cole–Cole plots imply miscibility between the components, while phase separation represents bimodal plots.<sup>28–30</sup> Plots of  $\eta''$  versus  $\eta'$  for BPE blends were shown in Figure 5. In the range of scanning frequency, all the plots were smooth. The  $S_0$  plot was a straight line, while for  $S_1$ – $S_4$ , the slopes of the plots gradually decreased with increasing PE-2911 content, and the plots exhibited deviations from linearity at high frequency. Especially in  $S_4$ , a semicircular-shaped Cole–Cole plot was present. The reason for the poorly semicircular-shaped Cole–Cole plots here at the range of 0.01–100 Hz might be the large average molecular weight of the samples. These results also showed that there was no sufficient evidence in the immiscibility of the components.

#### Han plots

$G'$  versus  $G''$  plots, called Han-plots, are also used to investigate the miscibility of polymer blends. Distinct differences exist between Han-plots of homogenous



**Figure 5** The Cole–Cole plots of BPEs.



**Figure 6**  $G'$  versus  $G''$  plots of BPEs.

polymer and multiphase polymer system. Han-plots for the former were independent of the composition, showing the same slope and very good linearity, but that for the latter were dependent of the composition and different slopes.<sup>31–33</sup> Figure 6 showed the  $G'$  versus  $G''$  plots for the BPE blends. All  $G'$  kept a good linear with  $G''$ , and the regions of  $S_0$ – $S_3$  plots overlapped each other with the slope of 1.13. For the  $S_4$  plot, slight separation existed compared to others, and the slope was 1.24 probably because of its large differences in the molecular weight and the melt viscosity of the LPF and UPF. Despite this, it was believed that the two components were melt miscible in BPE blends.

In a word, the two components were melt miscible in all BPE blends, and they could not take place obvious phase separation.

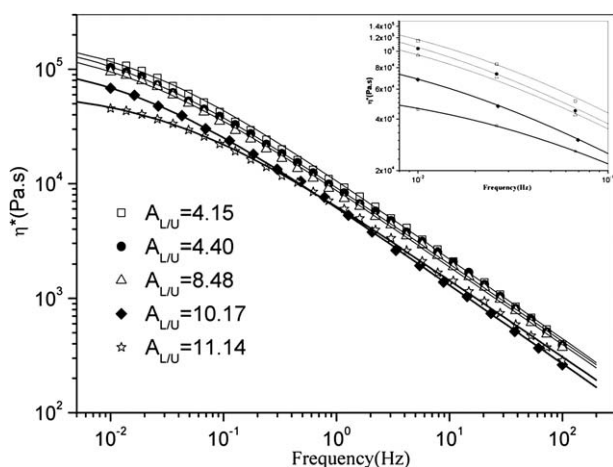
#### Dynamic rheological properties

The Cross model was a modification of the power law to include parameters to account for the Newtonian behavior of the polymer at the low frequency. The equation of the Cross model was shown as<sup>34</sup>:

$$\eta = \eta_0[(1 + |\lambda\dot{\gamma}|^m)]^{-1} \quad (1)$$

where  $\eta_0$  is the zero shear viscosity,  $\lambda$  is the characteristic time, and  $m$  is the rate index.

Figure 7 showed the variation of complex viscosity ( $\eta^*$ ) versus frequency at 220°C for the BPEs, and the Cross model fits with the experimental data well. The results were listed in Table III. As shown, a decrease in  $\eta^*$  can be observed with an increase in  $A_{L/U}$ . Shear-thinning behavior was observed for all the BPEs and  $m$  was almost the same, indicating that the  $A_{L/U}$  had little influence on it. The parameter of interest for this study was the zero shear viscosity. At low frequency, a Newtonian viscosity plateau might occur, and the viscosity generally approached



**Figure 7** The solid lines represent the fitting of experimental data  $\eta^*$  versus frequency to Cross equation. The partial enlarged figure was in the top right corner.

a constant value and was independent of the frequency.<sup>7</sup> It should be noted that these BPE samples did not exhibit distinguishable plateaus but a transition zone between Newtonian plateau and power-law zone because of the high molecular weight and broad MWD. Wood-Adams et al.<sup>22</sup> also reported that PE with broad MWD showed wider transition zones between Newtonian plateau and power-law zone.  $\eta_0$  decreased rapidly with increasing in  $A_{L/U}$ , especially for  $A_{L/U} = 8$ . The characteristic time  $\lambda$  is the reciprocal of the shear rate at which the zero-shear viscosity occurs and characterizes the frequency or time dependence of the elasticity. With  $A_{L/U}$  increasing, the  $\lambda$  significant decreased, especially for  $A_{L/U} > 10$ .

Dynamic storage ( $G'$ ) and loss ( $G''$ ) modulus of materials reflect the melt elasticity and viscosity, respectively. The frequency dependence of  $G'$  and  $G''$  reflects the movement of molecular chains. The case that the storage modulus overcomes the loss modulus ( $G' > G''$ ) is defined as an elasticlike behavior, while it is defined as an viscoulike behavior when the loss modulus overcomes the storage modulus ( $G'' > G'$ ). From Figure 8, the dynamic cross-point, defined as  $G_x$ , separates the viscoulike and elasticlike behaviors.<sup>3</sup>

**TABLE III**  
Rheological Properties Parameters of BPEs with Different  $A_{L/U}$

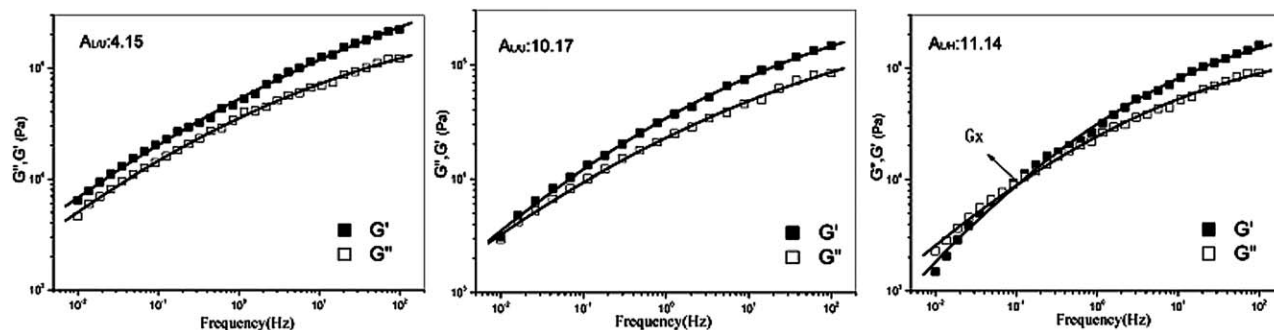
$A_{L/U}$	$\eta_0$ ( $10^4$ Pa s)	$\lambda$ (s)	m
4.15	23.067	90.073	0.691
4.40	20.230	88.552	0.674
8.48	18.030	83.031	0.674
10.17	12.359	72.646	0.689
11.14	6.592	28.125	0.675

Figure 8 presented the storage and loss modulus for BPEs with different  $A_{L/U}$  values. As can be seen, BPEs showed an elasticlike behavior ( $G' > G''$ ) in the whole frequency range when  $A_{L/U} < 10.17$ . At low frequency, the storage and loss modulus get closer and closer with increasing  $A_{L/U}$ . The cross-point  $G_x$ ,  $G_x = 3117$  Pa, was observed when  $A_{L/U} = 10.17$  (the frequency was about  $10^{-2}$  Hz), and when  $A_{L/U} = 11.14$ ,  $G_x = 9263$  Pa (the frequency was about  $10^{-1}$  Hz). That is, when the frequency was smaller than  $10^{-1}$  Hz, BPEs showed a viscoulike behavior ( $G'' > G'$ ). Usually, the  $G_x$  is regarded to be related to PDI, and the  $G_x$  decreased as PDI increased. For LLDPE series, Utracki proposed<sup>16</sup>:

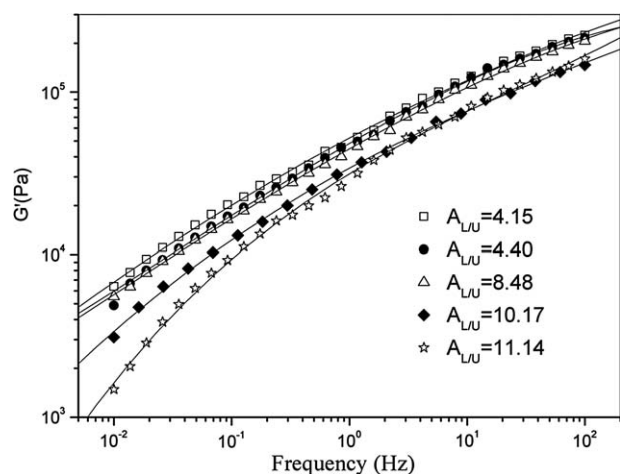
$$G_x = 8.4 \times 10^5 (\overline{M}_w/\overline{M}_n)^{-1.385} \quad (2)$$

Vega<sup>3</sup> applied the equation to HDPE and found it worked well. Meanwhile, some reports put forward that it was applicable in given condition. For PE, the  $G_x$  was affected by structures such as branching, cross-linking, degradation, and so on, and, in these cases, the equation was not always suitable.<sup>35</sup> Here, the  $G_x$  also increased as PDI decreased, and the slight decrease of PDI caused great increase of  $G_x$ . When the  $A_{L/U}$  was from 10.17 to 11.14, PDI decreased slightly, but the  $G_x$  became threefold. However, estimated by the equation, the increased amplitude would be less than 10%. Considering that there were limited differences in the structures of the samples, the large change in the  $G_x$  might be mainly caused by the increasing of  $A_{L/U}$ .

Comparison of the changes in the storage modulus with frequency can also provide more insight into the



**Figure 8** The comparison of  $G'$  and  $G''$  at 220°C for the BPEs.



**Figure 9** The  $A_{L/U}$  dependence of  $G'$  for BPEs at 220°C. The solid lines represent the fitting of experimental data by Fit Polynomil.

polymer microstructure. Figure 9 showed the  $A_{L/U}$  dependence of  $G'$  for BPEs in the frequency and the solid lines were fitting curves. The storage modulus all decreased with increasing  $A_{L/U}$ . When the frequency was more than  $10^0$  Hz, there were slight changes, because in the high frequency range, the chain segments were main, and the differences between the chain segments were less than those between the molecular chains. When the frequency was less than  $10^0$  Hz, there were great decrease in the storage modulus and greater and greater with the decreasing in the frequency, because the elastic behavior reflected the molecular chains entanglement. In the low frequency range, the  $A_{L/U}$  showed little effect on the storage modulus when  $A_{L/U} < 8.48$ , however, the storage modulus significantly decreased with increasing of  $A_{L/U}$  when  $A_{L/U} > 8.48$  that was to say, when the content of LPF was up to some value, the molecular chains entanglement would significantly decrease, and the melt elasticity and the storage modulus decreased more significantly.

However, the effect of  $A_{L/U}$  on the loss modulus was less, especially in the low frequency range. This was also the reason of the viscouslike behavior for BPEs with higher  $A_{L/U}$ .

In addition, the loss factor,  $\tan \delta = G''/G'$  describes the recovery characteristics of the melt after deformation. A larger  $\tan \delta$  indicates that the polymer material possesses poorer recovery characteristics, because the chains relax slowly after being stressed. So, as  $A_{L/U}$  increased, the loss factor increased and the recovery of BPEs decreased. The loss factors were almost the same at high frequency, while there were large differences between the loss factors in the low frequency range. When  $A_{L/U} > 10.17$ , the  $\tan \delta$  would be more than 1, thus, the loss modulus overcame the storage modulus, and the chains relaxed very slowly after being stressed.

## CONCLUSIONS

1. A series of BPEs whose MWD curves had shown invariable peak positions and relative change in the peak intensity were conveniently prepared by the method of melt blending. The result of fitting multi-peaks on Gaussian presented two unimodal curves (LPF and UPE), and the ratio of the area  $A_{L/U}$  can be used as a tool to characterize the bimodal MWD characteristics.
2. The changes in  $A_{L/U}$  significantly affect the dynamic rheological properties of BPEs, especially in the frequency less than  $10^0$  Hz. The complex viscosity, zero-shear viscosity, and storage modulus all rapidly decreased with the increase in  $A_{L/U}$ , and the melt elasticlike behavior transformed gradually to the viscouslike behavior; moreover, the frequency when the transformation took place was higher and higher, and  $G_x$  increased sharply.

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