

Rheological, Thermal, and Morphological Properties of Low-Density Polyethylene/Ultra-High-Molecular-Weight Polyethylene and Linear Low-Density Polyethylene/Ultra-High-Molecular-Weight Polyethylene Blends

Yang Chen, Huawei Zou, Mei Liang, Pengbo Liu

The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, People's Republic of China

Correspondence to: H. Zou (E-mail: hwzou@163.com) or M. Liang (E-mail: liangmeiww@163.com)

ABSTRACT: The dynamic rheological behavior of low-density polyethylene (LDPE)/ultra-high-molecular-weight polyethylene (UHMWPE) blends and linear low-density polyethylene (LLDPE)/UHMWPE blends was measured in a parallel-plate rheometer at 180, 190, and 200°C. Analysis of the log–additivity rule, Cole–Cole plots, Han curves, and Van Gurp curves of the LDPE/UHMWPE blends indicated that the blends were miscible in the melt. In contrast, the rheological properties of LLDPE/UHMWPE showed that the miscibility of the blends was decided by the composition of LLDPE. The differential scanning calorimetry results and scanning electron microscopy photos of the LLDPE/UHMWPE blends were consistent with the rheological properties, whereas with regard to the thermal and morphological properties of LDPE/UHMWPE blends, the results reveal three endothermic peaks and phase separation, which indicated a liquid–solid phase separation in the LDPE/UHMWPE blends. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 945–953, 2013

KEYWORDS: compatibilization; differential scanning calorimetry (DSC); rheology; phase behavior; polyolefins

Received 1 July 2012; accepted 18 July 2012; published online 28 September 2012

DOI: 10.1002/app.38374

INTRODUCTION

The study of blends of ultra-high-molecular-weight polyethylene (UHMWPE) with conventional polyolefins is of continued interest. It has been well documented that a number of physical properties and the processability of polyolefins can be improved by blending.¹ One of the most important developments in the field of polyolefin design in recent years is the production of polyolefins with a bimodal molecular weight distribution. Mainly produced by the operation of two polymerization reactors under different conditions in series, this material is a polymer blend consisting of two fractions with average weights that differ significantly. The potential danger of inhomogeneities within the material, even in the case of identical chemical compositions of both high and low-molecular-weight fractions, has been reported.²

Polyethylene (PE)–PE miscibility has been a topic of great academic and commercial interest for the past decade because of its relevancy to the understanding of the processing and performance properties of blends containing different types of PE.

Therefore, a better understanding and detailed description and prediction of the blend properties are necessary. However, a consensus has not yet been achieved on the liquid–liquid miscibility of such blends. For example, different groups of researchers have presented completely opposite views, ranging from total phase separation^{3,4} to complete homogeneity^{5,6} for blends composed of high-density polyethylene (HDPE) and low-density polyethylene (LDPE) and for those composed of HDPE and linear low-density polyethylene (LLDPE),^{7,8} but there have been few reports on the miscibility of LDPE/UHMWPE and LLDPE/UHMWPE blends.

PE is produced in many forms, and each has different properties because of their structural variations. UHMWPE is a simple supermolecular polymer, which was developed in recent decades. Typical LDPE contains short-chain branches (1–3 per 100 backbone carbon atoms) and long-chain branches (0.1–0.3 per 100 backbone carbon atoms). LLDPE is produced by the copolymerization of ethylene with an α -olefin such as hexene, and it can have a wide range of branch contents, depending on

Table I. Characteristics of the PE Studied

Sample	Density (g/cm ³)	Melt index (g/10 min) ^a	Branching degree (branches per 1000 carbons)	M_w (g/mol)
LDPE 2210 H	0.919	1.8	16.3	8.2×10^4
LLDPE DFDA7042	0.918	2	34.8	9.6×10^4
UHMWPE	0.937	Not measurable ^b	—	2.5×10^6

M_w , weight-average molecular weight.

^aUnder the conditions of 190°C and 2.16 kg.

^bClose to zero and hard to measure.

the catalyst and concentration of the added comonomer. The properties of the individual species can be altered by mixing the components. However, the understanding of the mechanical and melt flow properties of such blends is handicapped by the absence of a consensus concerning the melt miscibility of the components.

In crystallizable polymer blends, miscibility studies are complicated because of the crystallization effect.¹ The concept of polymer miscibility generally applies to amorphous materials or melts, and it is essential to analyze the polymer miscibility in the melt state and cocrystallization in the solid state.

Dynamic rheological tests have unique advantages in the characterization of polymer viscoelastic properties. They are also effective for the investigation of the morphology property relationships of multicomponent polymer blends. However, to the best of our knowledge there have been no studies on the detection of the phase behavior of LDPE/UHMWPE and LLDPE/UHMWPE blends by dynamic rheometry. In this study, two series of blends were prepared and tested by rheological, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) methods. The objective of this article is to present the miscibility and phase behavior results of the two series of blends.

EXPERIMENTAL

Materials and Sample Preparation

Materials. The materials used in this study were LDPE, with the trademark 2210 H, and LLDPE, with the trademark DFDA 7042; they were supplied as pellets by Lanzhou Petrochemical Corp. (Lanzhou Gansu China). UHMWPE was supplied as a powder by Beijing Second Subsidiary Additive Factory (Beijing China). All of the molecular and physical parameters are listed in Table I.

Sample Preparation. In this study, LDPE/UHMWPE and LLDPE/UHMWPE blends were prepared by melt blending. The polymers were blended in a mixer (Rheomix 600, Haake, Germany) at 190°C for 10 min with compositions of 100/0, 90/10, 80/20, 70/30, and 60/40 w/w, respectively; these blends were named LU0, LU10, LU20, LU30, and LU40, respectively, for the LDPE/UHMWPE blends and LLU0, LLU10, LLU20, LLU30, and LLU40, respectively, for the LLDPE/UHMWPE blends. Then, the melt blends were compression-molded into desired disks at 170°C for melt rheological measurements. In the preparation of all the blends, the polymers were stabilized by the addition of 0.5 wt % antioxidant to prevent thermooxidative degradation.

Dynamic Rheological Measurements

Dynamic rheological measurements were carried out in a dynamic rheometer (Bohlin Gemini 2000, Malvern, British) in

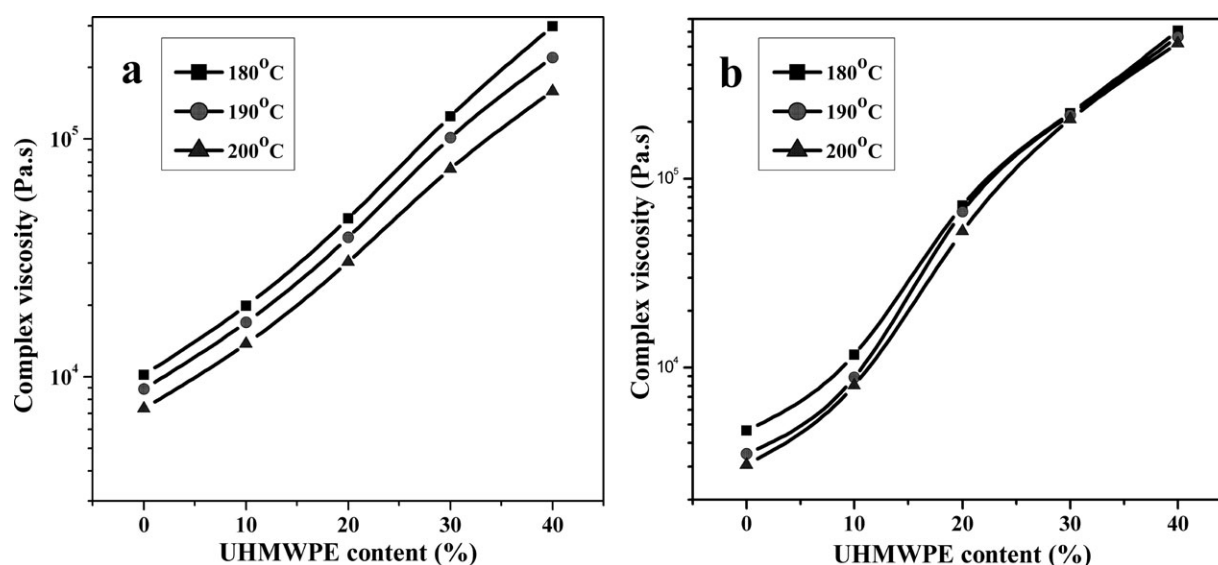


Figure 1. Composition dependence of complex viscosity (0.01 Hz) for the blends at different temperatures: (a) LDPE/UHMWPE and (b) LLDPE/UHMWPE.

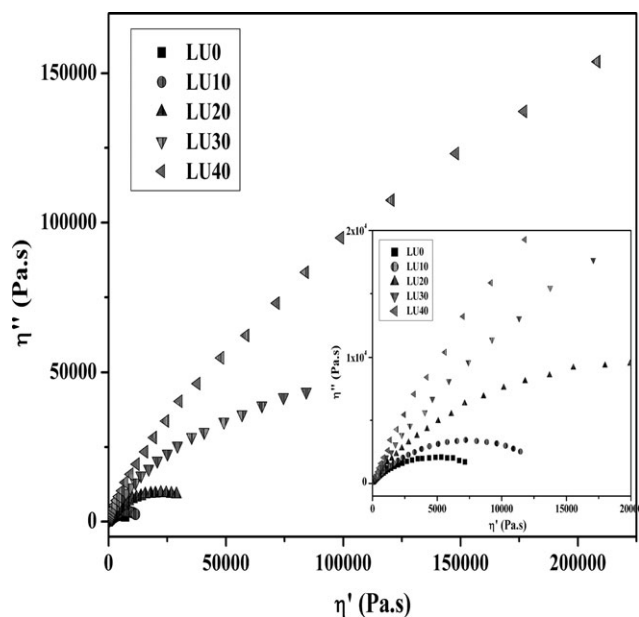


Figure 2. Cole–Cole plots for the blends of LDPE/UHMWPE at 200°C.

constant-strain mode. The diameter of the plate was 25 mm, and the gap was about 1 mm. All of the samples were tested in the frequency range from 0.01 to 100 Hz at 180, 190, and 200°C, respectively. To keep the response in the linear viscoelastic region, the applied strain was controlled at 1%. The thermal stability of the samples during rheological testing was checked by a time sweep, and all of the tests were completed within 10 min.

DSC

The melting and crystallization behavior of each blend was determined using a differential scanning calorimeter (DSC; DSC-204, Netzsch, Germany). Experiments were carried out with 6–10-mg samples under dry nitrogen. All samples were first heated to 165°C at a rate of 10°C/min and held at 165°C for 5 min; they were then cooled at a rate of 10°C/min to 50°C and held at 50°C for 3 min. They were then scanned from 50 to 165°C at a rate of 10°C/min. The crystallization and melting temperatures were obtained from the cooling and second-heating thermograms, respectively.

SEM

The samples were cryogenically fractured in liquid nitrogen, and then, all of the surfaces were gold-coated to enhance the image

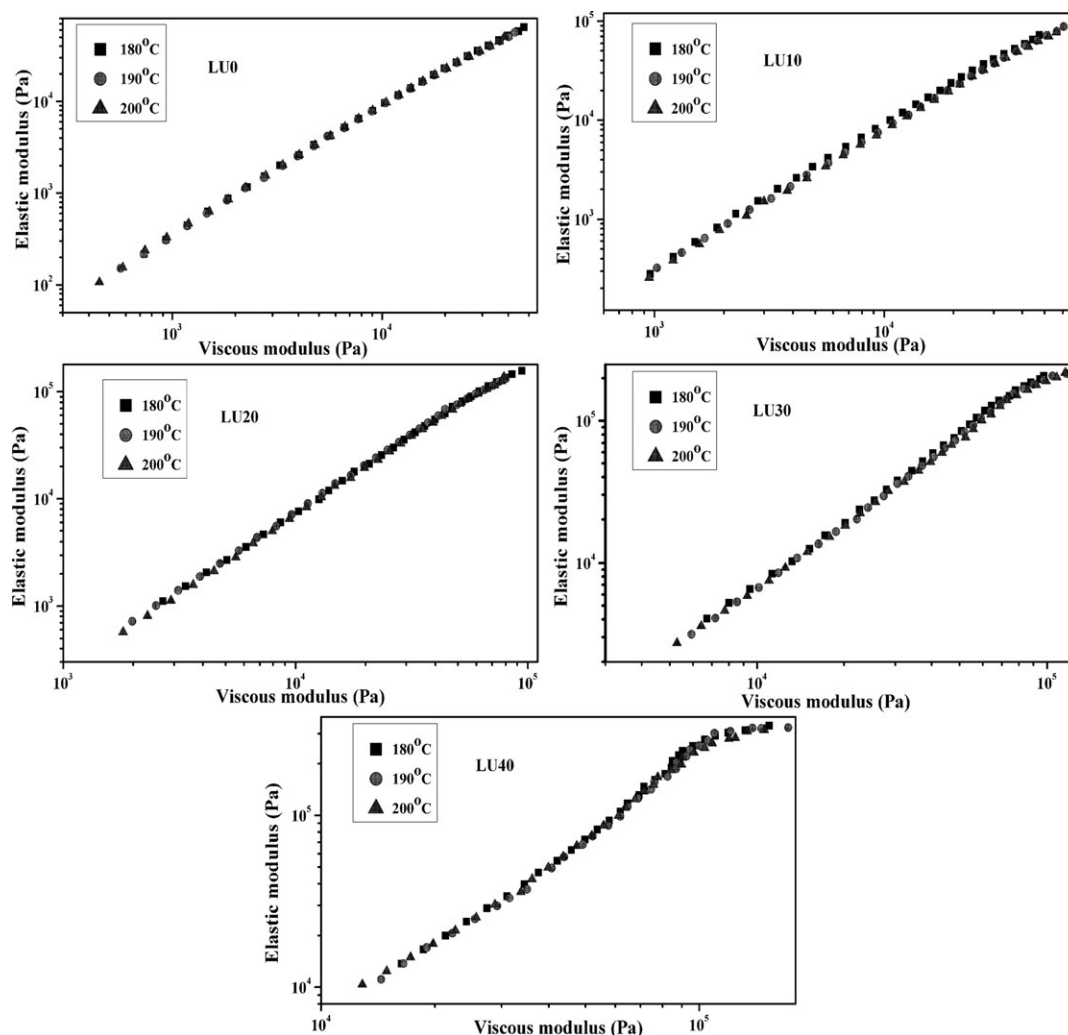


Figure 3. Han curves for the blends of LDPE/UHMWPE at different temperatures.

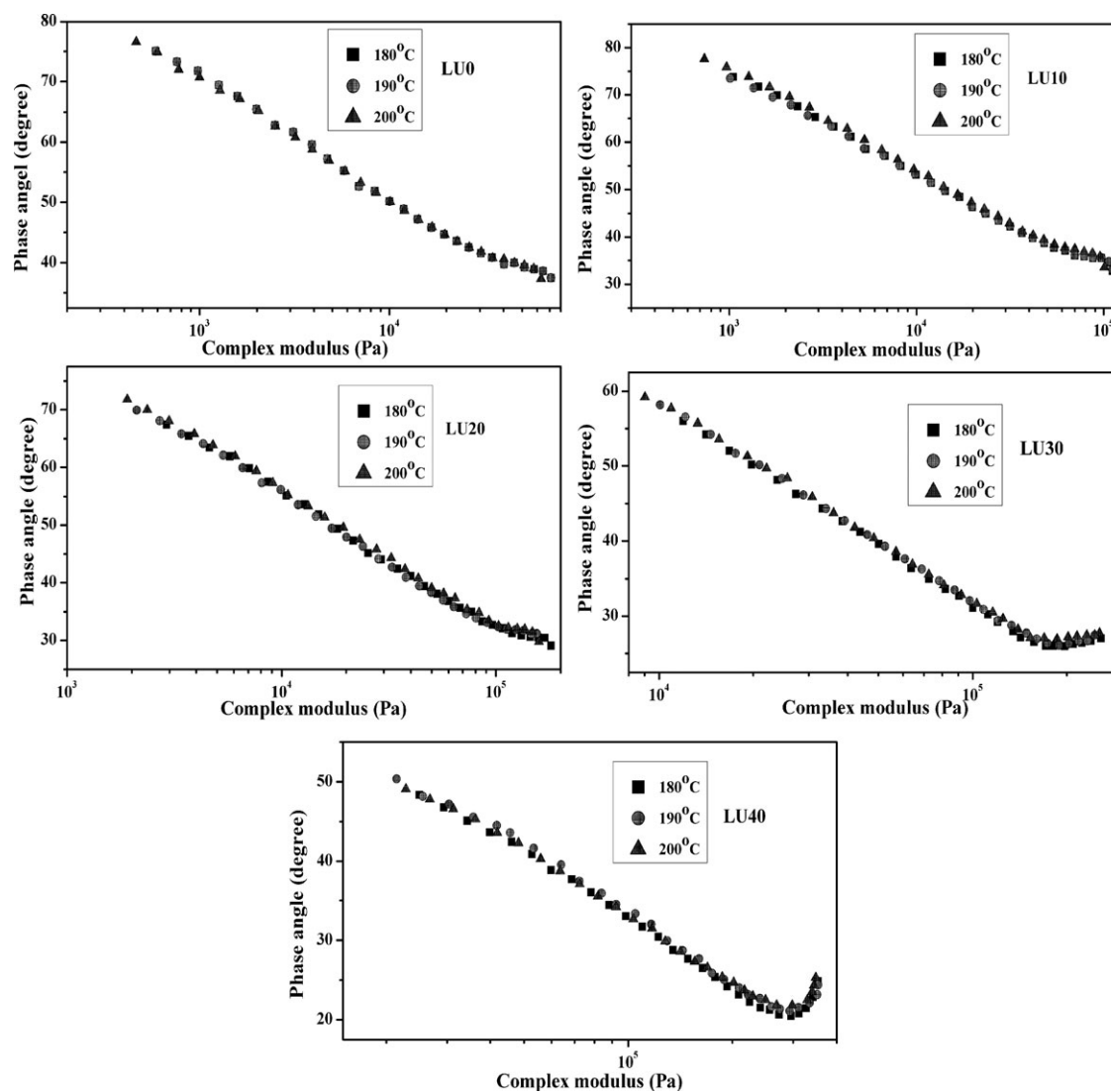


Figure 4. Van Gurp curves for the blends of LDPE/UHMWPE at different temperatures.

resolution and to prevent electrostatic charging. The morphology of the fracture surfaces was observed by a scanning electron microscope (SEM; JSM-5900, JOEL, Tokyo, Japan) instrument at an acceleration voltage of 5 kV.

RESULTS AND DISCUSSION

Rheology Properties of the LDPE/UHMWPE Blends

Figure 1(a) shows the variation of complex viscosity for the LDPE/UHMWPE blends at 0.01 Hz versus the UHMWPE content at 180, 190, and 200°C. It also shows a gradual increase in the viscosity of the blends with increasing UHMWPE content. It is clear that almost a straight-line dependence of $\log \eta_{(0.01 \text{ Hz})}$ (the value of complex viscosity at 0.01 Hz) versus the UHMWPE content was obtained for the LDPE/UHMWPE blends at 180, 190, and 200°C. The additivity of $\log \eta_{(0.01 \text{ Hz})}$ indicated a lack of specific influence in the blends and probable miscibility.

The rheological data were analyzed with Cole–Cole plots, which represented the relationship between the imaginary viscosity

(η'') and the real viscosity (η'). Although it is an empirical method, it has been widely used to analyze the melt miscibility of polymer blends.^{9,10} A smooth, semicircular shape of the plotted curves suggests good compatibility, that is, phase homogeneity in the melt, and any deviation from this shape shows a heterogeneous dispersion and phase separation due to immiscibility.

The Cole–Cole plots at 200°C of the LDPE/UHMWPE blends are shown in Figure 2 and at 180, 190, and 200°C, the Cole–Cole plots showed similar trends. It appeared that all of the blends were miscible, as was evident from the smooth, semicircular shape of the plots. However, the diagnosis of the miscibility of the five samples from merely the shape of the Cole–Cole dependence could be misleading, and other supporting rheological data were required to strengthen the hypothesis.

The validity of the observation based on the Cole–Cole plots appearance was further supported by the $\log G'$ (elastic modulus) versus $\log G''$ (viscous modulus) plots, which were compared to further investigate the miscibility of the blends. Han

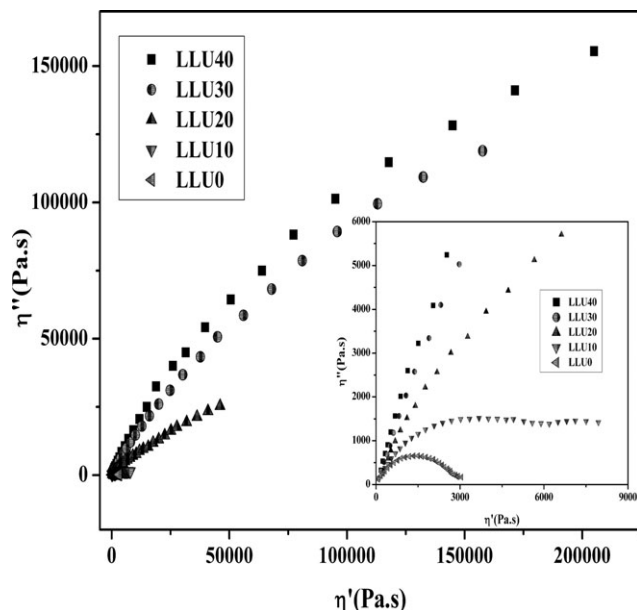


Figure 5. Cole–Cole plots for the blends of LLDPE/UHMWPE at 200°C.

curves, presented as curves of G' versus G'' in logarithmic scale, were proposed by Han and Chuang¹¹ and have often been used to detect phase separation in polymer blends. For a homogeneous polymer system, the Han curve is independent of the temperature and is generally linear. Han curves of the LDPE/UHMWPE blends at 180, 190, and 200°C are presented in Figure 3. As shown, all of the blends exhibited single-phase behavior as the plots were generally linear and independent of the temperature; thus, we believe that the LDPE/UHMWPE blends we studied were miscible. This suggests that the results of the Han curves were consistent with the previous rheological results. We also found that all of the values of the slopes of the Han curves were lower than those of a monodisperse polymer system (viz., 2 for Han curves, according to the linear viscoelastic theory) because of the polydispersity of the system. Moreover, the rheological properties at high frequencies were a reflection of the relaxation of chain segments. The transition of the Han curves at high frequencies with higher contents of UHMWPE indicated a longer relaxation time of the chain segments, which may have been caused by a different number of UHMWPE chains diffused into the LDPE chains.

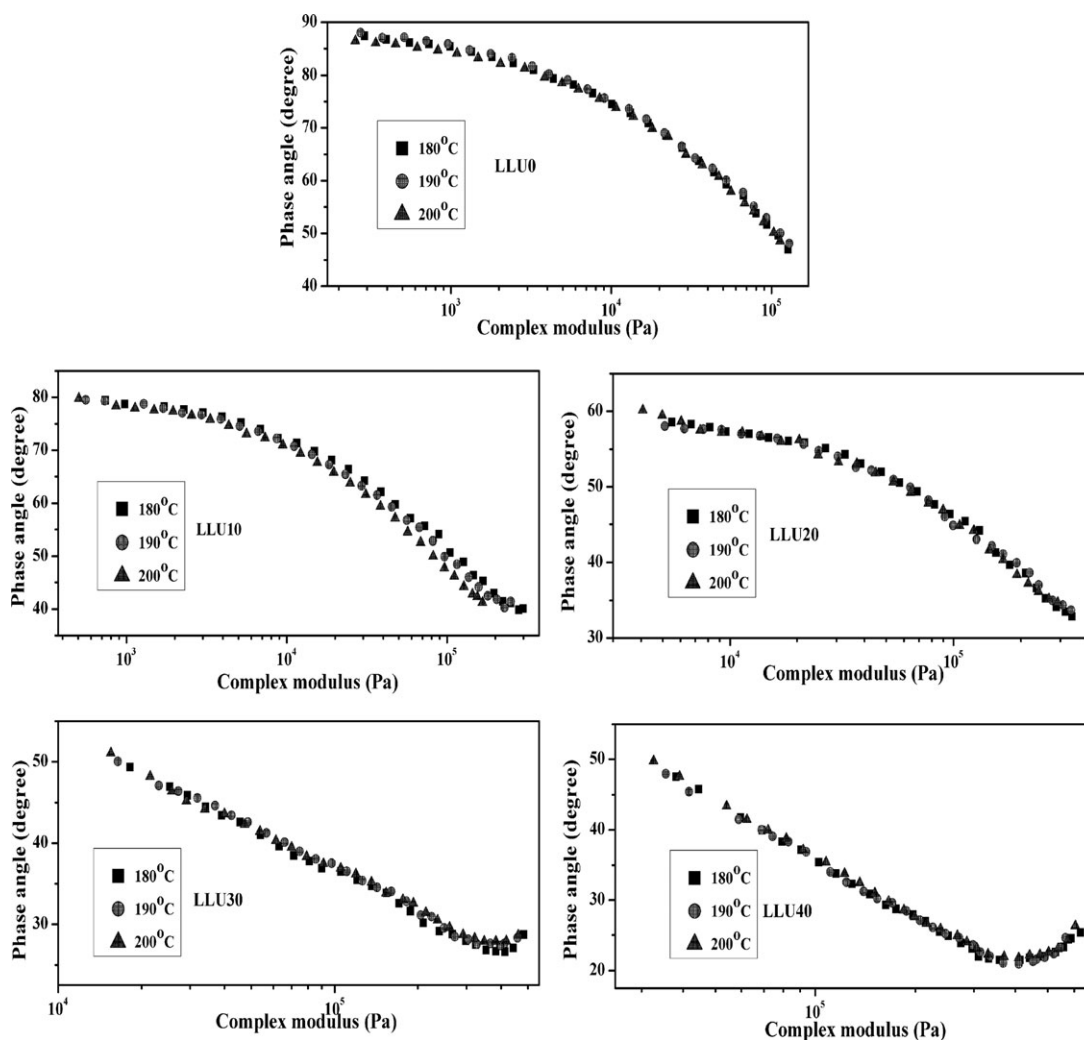


Figure 6. Van Gurp curves for the blends of LLDPE/UHMWPE at different temperatures.

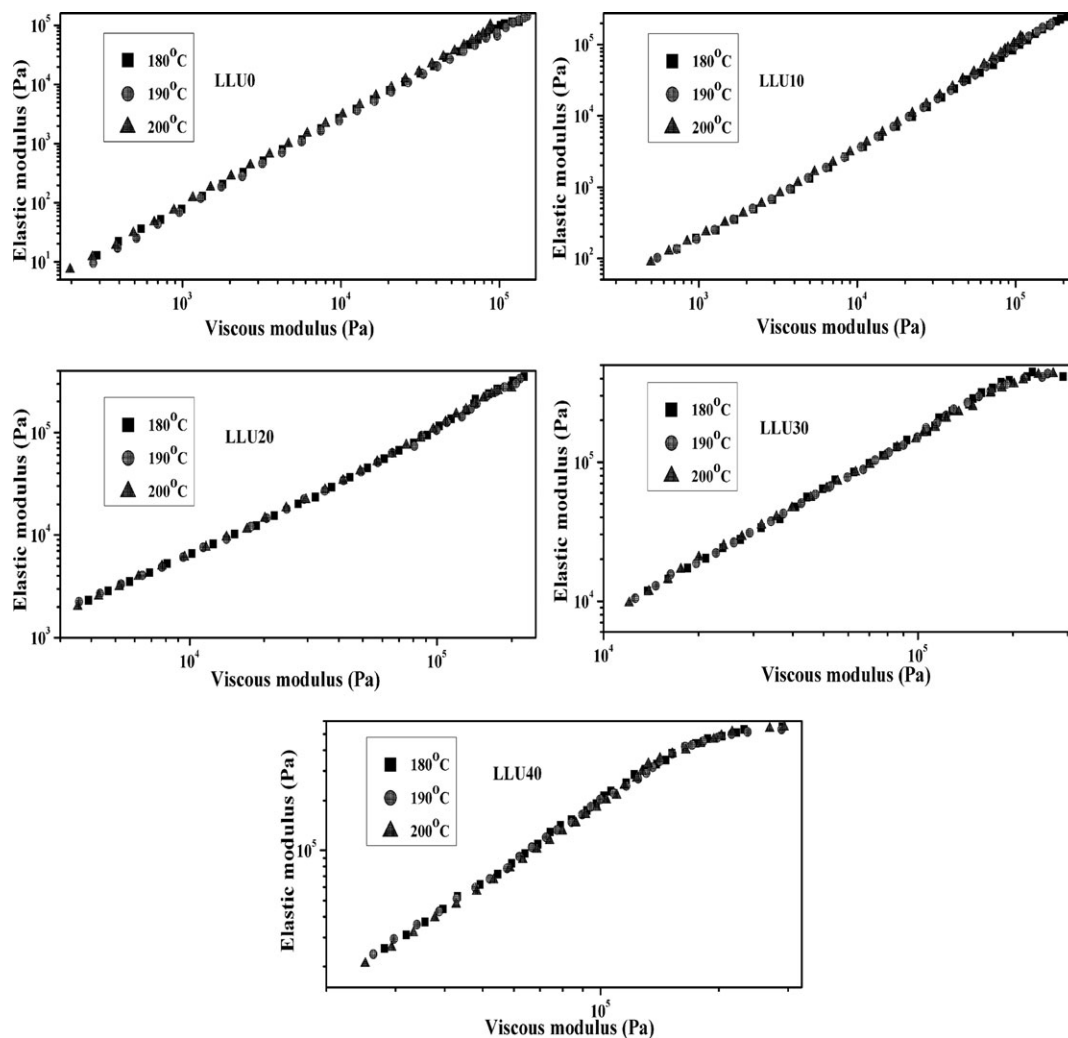


Figure 7. Han curves for the blends of LLDPE/UHMWPE at different temperatures.

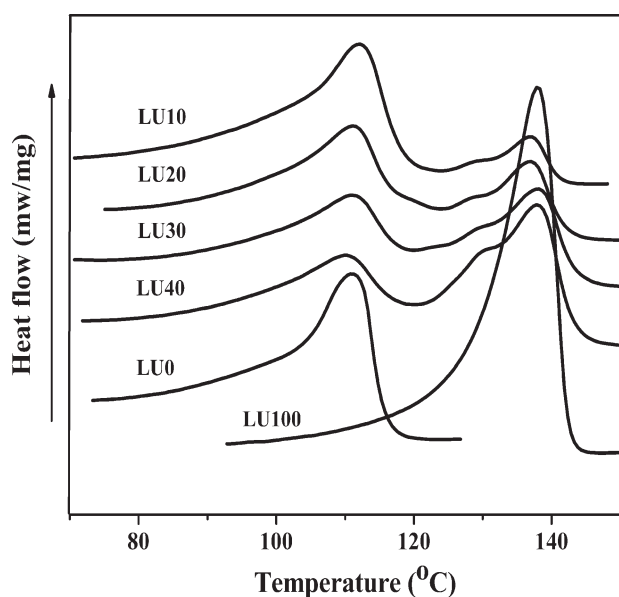


Figure 8. Melting curves for the blends of LDPE/UHMWPE.

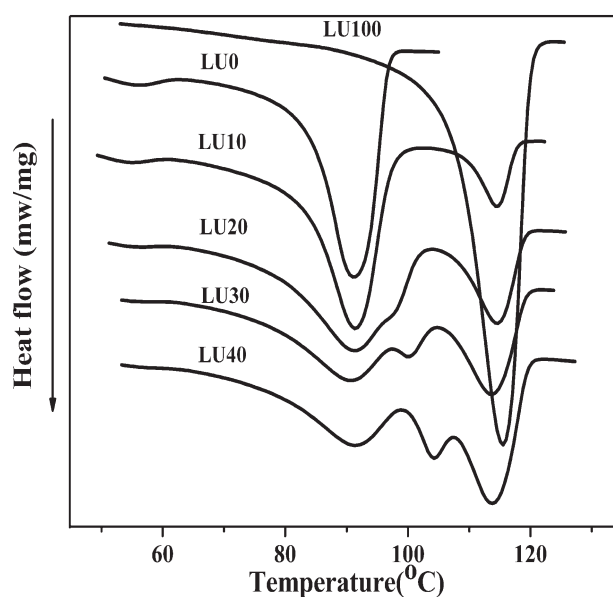


Figure 9. Crystallization curves for the blends of LDPE/UHMWPE.

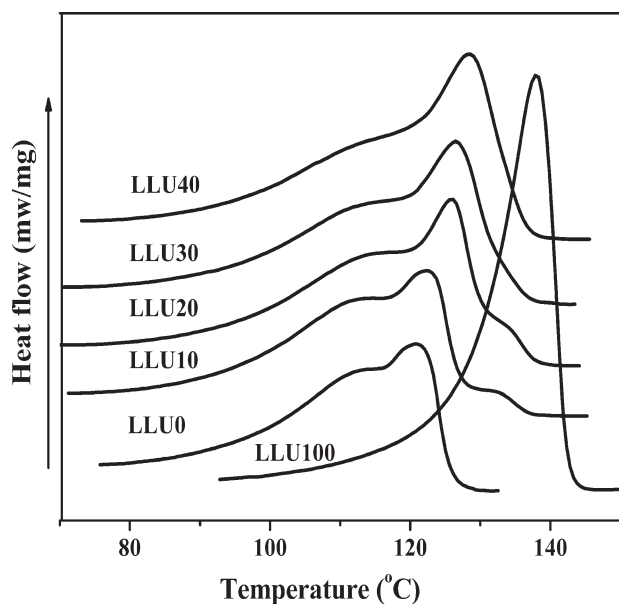


Figure 10. Melting curves for the blends of LLDPE/UHMWPE.

Although use of Cole–Cole plot and Han curve for assessing the polymer blends’ miscibility is quite common, there is little published data^{12,13} on the use of the Van Gorp’s plot. Van Gorp and Palmen¹³ presented in a rarely noticed publication an approach for the verification of the time–temperature superposition principle (TTS). They plotted the phase angle of the measured rheological data versus the corresponding absolute value of the complex shear modulus and found that the isothermal frequency curves merged into a common line when the TTS held. This way of verifying the TTS principle for a given polymer sample is based on the exclusion of the temperature-dependent characteristic elementary time and the quantities deduced from the characteristic time according to the scaling laws.¹⁴ Equivalent conclusions were also drawn by others, for example, by Mavridis and Shroff,¹⁵ who used the loss tangent instead of the phase angle itself.

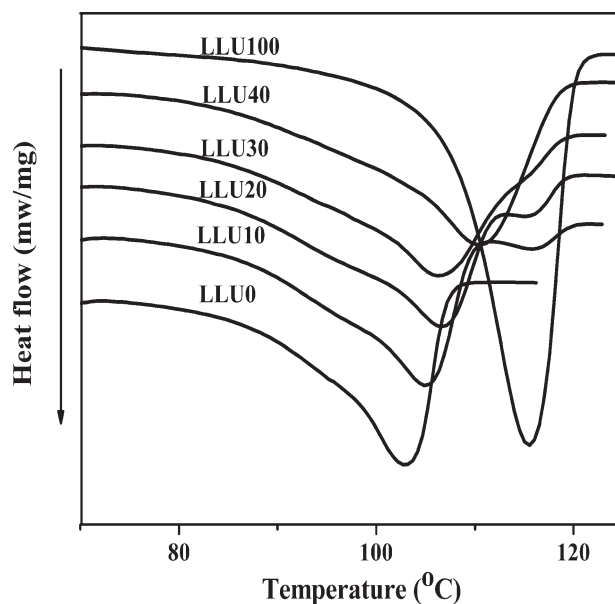


Figure 11. Crystallization curves for the blends of LLDPE/UHMWPE.

As shown in Figure 4 the TTS held for all of the LDPE/UHMWPE blends we studied; this indicated that all of the blends were homogeneous or miscible in the melt. This agreed with the trends observed in the Cole–Cole plots and Han curves. We concluded that the LDPE/UHMWPE blends we studied were miscible in the melt state.

In addition, the transition of Van Gorp curves at high frequencies with higher contents of UHMWPE may also have indicated a higher entanglement density; that is, a higher number of UHMWPE chains diffused into the LDPE.

Rheological Properties of the LLDPE/UHMWPE Blends

Figure 1(b) shows the variation of complex viscosity at 0.01 Hz versus the UHMWPE content at 180, 190, and 200°C for the LLDPE/UHMWPE blends. It also shows a gradual increase in the viscosity of blends with increasing UHMWPE content. It

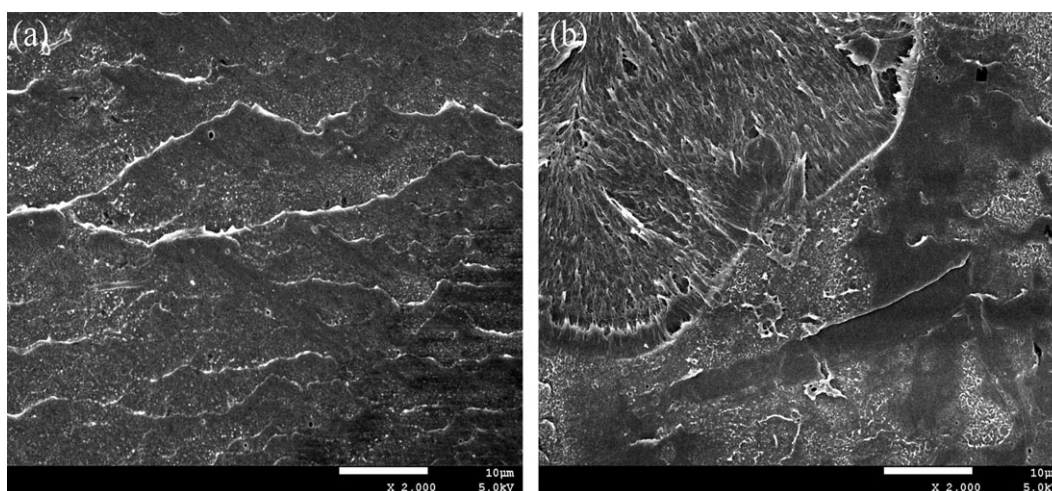


Figure 12. SEM photos for the LDPE/UHMWPE blends: (a) LU10 and (b) LU40.

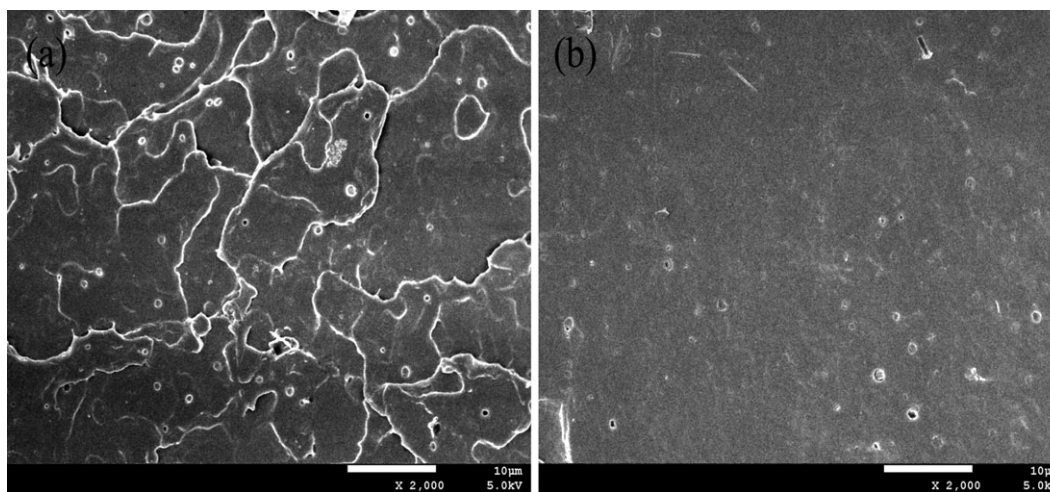


Figure 13. SEM photos for the LLDPE/UHMWPE blends: (a) LLU10 and (b) LLU40.

was clear that a straight-line dependence of $\log \eta_{(0.01 \text{ Hz})}$ versus the UHMWPE content was not obtained compared to that of the LDPE/UHMWPE blends at 180, 190, and 200°C. The additivity of $\log \eta_{(0.01 \text{ Hz})}$ indicated that the blends were probably phase separated or partial miscible.

The Cole–Cole plots at 200°C of the LLDPE/UHMWPE blends are shown in Figure 5 and at 180, 190, and 200°C, the Cole–Cole plots showed similar trends. It appeared that at 180, 190, and 200°C, LLU0, LLU30, and LLU40 were miscible; this was evident from the smooth, semicircular shape of the plots, whereas for LLU10 and LLU20, especially LLU10, there was a clear deviation in each plot, which indicated the immiscibility of the sample.

As can be seen from Figure 6 the TTS held for the samples LLU0, LLU30, and LLU40. LLU20 showed a weak deviation, whereas the deviation was particularly notable for sample LLU10. The deviation indicated morphological changes taking place in the melt during the experiment. This indicated that LLU0, LLU30, and LLU40 were homogeneous or miscible in the melt, but LLU10 and LLU20 were nonhomogeneous or phase-segregated. This result agreed with the trends observed in the Cole–Cole plots.

Han curves of the four samples at 180, 190, and 200°C are presented in Figure 7. As shown, all of the samples exhibited single phase behavior as the plots were generally linear and independent of the temperature; thus, we believe that the blends were miscible in the melt state. Combining this with the previous rheological results, we conjectured that because of the identical chemical structures in the interface, the Han curves were less sensitive than Cole–Cole plots and TTS for this two-phase morphology.

The phase behavior of polyolefin blends is a crucial issue. However, the physical properties of those components are too similar to enable the detection of such phase separation directly in the melt; the phase behavior of many common binary blends as, for example, not only HDPE/LDPE^{3–6} and HDPE/LLDPE^{7,8} but also LDPE/UHMWPE and LLDPE/UHMWPE, are not fully

understood yet. Rheological measurement is not only sensitive to the molecular structure of polymer but also to the phase behavior of polymer blends. Choi et al.¹⁶ and Hussein et al.¹⁷ reported the effects of the branching characteristics of LDPE and LLDPE on their melt miscibilities with HDPE with molecular simulation. The phase separation in HDPE/LDPE blends in the melt was predicted for high branch contents in their simulations, and the cutoff value for the segregation was found to be around 30 branches per 1000 long-chain carbons. The HDPE/LLDPE blends were found to microphase separate when the branch content of LLDPE exceeded 30 branches per 1000 carbons. At 40 branches per 1000 carbons, the two polymers displayed partial microphase separation, and complete microphase separation was observed at 60 branches per 1000 carbons. The branch contents of the LDPE and LLDPE we studied in this work were 16.3 branches (15.4 short-chain branches) and 34.8 per 1000 long-chain carbons, respectively, so the rheological results presented here were consistent with their prediction.

DSC Analysis

The melting and crystallization curves of LDPE/UHMWPE are plotted in Figures 8 and 9, respectively. The LDPE/UHMWPE blends showed three endothermic peaks, as shown in Figures 8 and 9. In melting studies of mixtures of linear and branched PEs, some investigators^{18,19} have reported that DSC experiments revealed three endothermic peaks. An intermediate peak between the HDPE and LDPE peaks has been associated with the fusion of a cocrystal formed from linear and branched PEs.

Figure 9 also shows that the crystallization temperatures of both LDPE and UHMWPE were depressed by the other components instead of being close to each other. In the polymer blend melt, when the temperature decreased, thermal perturbations due to different rates of crystallization between LDPE and UHMWPE, the PE component, which is in the structure of an emulsion in the melt, entered into the near growing crystal nucleus, and led to liquid–solid phase separation.²⁰

The melting and crystallization curves of LLDPE/UHMWPE are plotted in Figures 10 and 11, respectively. On the other hand,

the pure LLDPE (LLU0) showed a bimodal and relatively broad peak because of its branching. The bimodal response was composed of a low-temperature shoulder and a high-temperature peak. This phenomenon was actually the result of an overlap of two peaks resulting from reorganization during scanning.²¹ The difference between the behavior of UHMWPE and LLDPE was a result of the branching because LLDPE has short-chain branching and UHMWPE has a linear structure. The blends of LLU30 and LLU40 showed similar melting and crystallization peaks as LLU0; this suggested a single crystal population or cocrystallization in these blends. However, LLU10 and LLU20 showed multiple peaks. The high-temperature peak was attributed to the cocrystallization of linear fractions of LLDPE and UHMWPE, whereas the broad shoulder at lower temperatures represented the melting of lamellae formed by the branched LLDPE chains.

Conclusively, although the LDPE/UHMWPE blends were miscible in melt state, because of different rates of crystallization between LDPE and UHMWPE, liquid–solid phase separation formed. The thermal properties of the LLDPE/UHMWPE blends were consistent with the rheological properties, and the results show that the extent of phase separation was found to be dependent on the content of LLDPE.

SEM. As shown in Figure 12 the UHMWPE chains could not be dispersed well in LDPE by melt blending, but there was no rheological characteristic signal for this two-phase-like morphology at low frequency. Combining this with the DSC results, we concluded that although the LDPE/UHMWPE blends were miscible in the melt state, because of different rates of crystallization between LDPE and UHMWPE, liquid–solid phase separation formed.

As revealed by Figure 13 LLU10 showed phase separation, whereas LLU40 showed good miscibility. This was consistent with the rheological and thermal properties, which showed that the system had partial microphase separation and the extent of phase separation was dependent on the content of LLDPE.

CONCLUSIONS

Analysis of the log–additivity rule, Cole–Cole plots, Han curves, and Van Gorp's plot confirmed that the LDPE/UHMWPE blends we studied were miscible in the melt. However, the thermal properties and morphology of the blends were not consistent with the rheological properties, which showed liquid–solid phase separation due to different rates of crystallization between LDPE and UHMWPE. In contrast to those of the LDPE/UHMWPE blends, the rheological properties of the LLDPE/UHMWPE blends showed that the system displayed partial microphase separation. The DSC results and SEM photos of the LLDPE/UHMWPE blends were consistent with the rheological properties, which showed that the system showed partial microphase separation and the extent of phase separation was dependent on the content of LLDPE.

Specifically, the two-phase-like morphology in the melt blends could be detected by the failure of TTS, log–additivity, and Cole–Cole plots but could not be detected by the Han curves.

ACKNOWLEDGMENTS

The authors thank the National Natural Science Foundation of China (contract grant numbers 50903049 and 50903053), the Applied Basic Research Programs of Science and Technology Commission Foundation of Sichuan Province (contract grant number 2009JY0031), and Provincial Science and Technology Pillar Program of Sichuan (contract grant number 2010GZ0176, China) for financial support, and the Analytical and Testing Center of Sichuan University for providing DSC and dynamic rheology measurements.

REFERENCES

- Vadhari, P.; Kyu, T. *Polym. Eng. Sci.* **1987**, *27*, 202.
- Gahleitner, M. *Prog. Polym. Sci.* **2001**, *26*, 895.
- Hill, M. J.; Barham, P. J.; Keller, A. *Polymer* **1992**, *33*, 2530.
- Hill, M. J.; Barham, P. J. *Polymer* **1992**, *33*, 4099.
- Alamo, R. G.; Londono, J. D.; Mandelkern, L.; Stehling, F. C.; Wignall, G. D. *Macromolecules* **1994**, *24*, 411.
- Alamo, R. G.; Graessley, W. W.; Krishnamoorti, R.; Lohse, D. J.; Londono, J. D.; Mandelkern, L.; Stehling, F. C.; Wignall, G. D. *Macromolecules* **1997**, *30*, 561.
- Agamalian, M.; Alamo, R. G.; Kim, M. H.; Londono, J. D.; Mandelkern, L.; Wignall, G. D. *Macromolecules* **1999**, *32*, 3093.
- Hill, M. J.; Puig, C. C. *J. Appl. Polym. Sci.* **1997**, *65*, 1921.
- Kim, H. K.; Rana, D.; Kwag, H.; Choe, S. *Korea Polym. J.* **2001**, *8*, 34.
- Kwag, H.; Rana, D.; Choe, K.; Rhee, J.; Woo, T.; Lee, B. H.; Choe, S. *Polym. Eng. Sci.* **2000**, *40*, 1672.
- Han, C. D.; Chuang, H. K. *J. Appl. Polym. Sci.* **1985**, *30*, 4431.
- Reichert, P.; Hoffmann, B.; Bock, T.; Thomann, R.; Mulhaupt, R.; Friedrich, C. *Macromol. Rapid Commun.* **2001**, *22*, 519.
- Van Gorp, M.; Palmen, J. *Rheol. Bull.* **1998**, *67*, 5.
- Trinkle, S.; Friedrich, C. *Rheol. Acta.* **2001**, *40*, 322.
- Mavridis, H.; Shroff, R. N. *Polym. Eng. Sci.* **1992**, *32*, 1778.
- Fan, Z. J.; Williams, M. C.; Choi, P. *Polymer* **2002**, *43*, 1497.
- Abu-Sharkh, B. F.; Giri, A. M.; Hussein, I. A. *Eur. Polym. J.* **2004**, *40*, 1177.
- Fonseca, C. A.; Harrison, I. R. *Thermochim. Acta.* **1998**, *313*, 37.
- Clampitt, B. H. J. *Polym. Sci. Part A Polym. Chem.* **1965**, *3*, 671.
- Liu, C.; Wang, J.; He, J. *Polymer* **2002**, *43*, 3811.
- Arnal, M. L.; Sanchez, J. J.; Muller, A. J. *Polymer* **2001**, *42*, 6877.