

Rheological and thermal properties of m-LLDPE blends with m-HDPE and LDPE

Chenyang Liu, Jin Wang, Jiasong He*

State Key Laboratory of Engineering Plastics, Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 15 January 2002; accepted 4 March 2002

Abstract

The dynamic and steady state behavior of metallocene linear low density polyethylene (m-LLDPE) blended with metallocene high density polyethylene (m-HDPE) and with low density polyethylene (LDPE) were measured in parallel plate rheometer at 160, 180, and 200 °C. The composition dependence of zero shear viscosity η_0 , the characteristic relaxation time τ_0 and the characteristic frequency ω_0 of m-LLDPE/m-HDPE blends show a linear variation in the whole range of weight fraction, which indicates that m-LLDPE/m-HDPE blends are miscible blend. At the same time, m-HDPE showing a 'dissident' rheological behavior should possess a certain very low degree of LCB. Two calculation methods of LCB verify this point. In contrast, the composition dependence of zero shear viscosity η_0 of m-LLDPE/LDPE blends shows a positive deviation from the log-additivity rule, which can be well fitted by using the immiscible blend equation of Utracki. The characteristic relaxation time τ_0 and the characteristic frequency ω_0 have a sharp variation with the small amounts of LDPE in the blends, which also indicates a phase separation in the system. The thermal properties of m-LLDPE/m-HDPE blends are very similar to a single-component system. However, m-LLDPE/LDPE blends are immiscible in both melt and crystal states. DSC results are consistent with the rheological properties of these two series of blends. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Metallocene polyethylene; Rheology; Blends

1. Introduction

The application of metallocene catalysts has opened the possibility of designing polyethylene chain structure at a molecular level and thus tailoring product properties [1–4]. Different from the conventional Ziegler–Natta catalysts, metallocene catalysts produce polyethylenes with narrow molecular weight distributions (MWDs). While the metallocene polyethylenes have superior physical and mechanical properties, compared to those produced using conventional catalysts with the same average molecular weights, they often have poor processabilities due to high viscosities. In practice, this disadvantage can be seen in the extrusion as a high melt pressure and a high motor load. Consequently, the market penetration has been much slower than predicted earlier.

For a given average molecular weight, the long chain branching (LCB) and MWD are primary factors controlling the rheological and processing behavior of polyethylenes

[5,6]. Recently, the effect of LCB on the linear viscoelastic behavior of polyethylene and the determination of the LCB level in metallocene polyethylenes by using rheological data [7–10] are the focus of polyethylenes rheology. Metallocene polyethylene, such as high density polyethylene (HDPE) or linear low density polyethylene (LLDPE), which possesses low amounts of long-chain branching, displays rheological features in dynamic viscosity, relaxation time, elastic modulus, activation energy of flow and melt strength. Based on the effect of temperature on dynamic viscosity, the relation of the zero shear viscosity and the intrinsic viscosity, and the difference between the locations of the peaks in 'viscosity MWD' and GPC MWD, three methods were proposed to evaluate the levels of LCB. On the other hand, one of the most important developments in the field of metallocene polyolefin design in recent years is the production of polyolefin with a bimodal MWD. Mainly produced by operating two polymerization reactors under different conditions in series, this material is a polymer blend consisted of two 'fractions' with average molecular weights which differ significantly. The potential danger of inhomogeneities within the material even in case of an identical chemical composition of both high and low

* Corresponding author. Tel.: +86-10-6261-3251; fax: +86-10-6255-9373.

E-mail address: hejs@sklep.icas.ac.cn (J. He).

Table 1
Characteristics of the polyethylenes studied

Sample	Density (g/cm ³)	MI (g/10 min)	Branch degree (%)	M_w	M_w/M_n
m-LLDPE ^a	0.928	1.7	2.7	45 700	2.1
m-HDPE	0.947	2.2	0.0	83 100	2.0
LDPE	0.920	7.1	5.5	102 000	6.8

^a Metallocene catalyzed ethylene and 1-butene copolymer.

molecular weight fractions had been reported [11]. The negative effects of inhomogeneity include processing problems like surface distortion and even melt fracture as well as a significant deterioration of the mechanical and optical performance of these products. All the while, polyolefin blend has attracted considerable interest both in the research community and in industry. Therefore, a better understanding and detailed description and prediction of blend properties [12–14] are necessary. However, the physical properties of 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, HDPE–low density polyethylene (LDPE), is not fully understood yet [15,16]. The rheological properties of polymers are not only sensitive to the molecular structure but also to phase behavior. An important application of rheology in polymer science is as a tool for the determination of molecular structure and phase behavior [10,17,18].

In the paper, two series of binary blends involving m-LLDPE with m-HDPE and LDPE were prepared and tested by rheological and DSC methods. Although the rheological properties of m-LLDPE and m-HDPE are well documented, the effects of blending m-LLDPE with m-HDPE and with LDPE are relatively unexplored. The objective of this paper is to present the influence of LCB introduced by blending method on the viscoelastic properties of m-LLDPE and the miscibility of blends which have different molecular structure.

2. Experimental

2.1. Materials characterization and blending

The m-PE materials studied, m-LLDPE and m-HDPE were supplied as pellets by Research Institute of Petroleum Processing, SINOPEC. The LDPE was supplied by Yanshan Petrochemical Corporation, China. The molecular parameters of materials, M_w , M_w/M_n , were measured on a PL-210 high-temperature GPC instrument. The GPC was calibrated with narrow MWD polystyrene standards that covered the molecular weight region from 10^3 to 10^7 . In addition to this, well-characterized polyethylene samples were used as in-house standards. The samples were dissolved in *o*-dichlorobenzene and measurement was carried out at 135 °C. The level of SCB of the samples was determined by FTIR on 0.15 mm melt-pressed disks.

All the molecular and physical parameters are listed in Table 1.

Two series of blending samples were prepared with m-LLDPE: series I with m-HDPE and series II with LDPE, respectively. Codes and composition of blends are given in Table 2. The polymers were mixed for 5 min in Haake Rheomix600 mixer at 160 °C. Before the preparation of mixtures, the polymers were stabilized by addition of 0.5% Irganox 1010 antioxidant to prevent the thermooxidative degradation.

2.2. Rheological measurements

Dynamic and steady shear rheological measurements were carried out on a Rheometrics SR 200 dynamic stress rheometer. After blending, the samples were melt pressed at 160 °C into 1 mm thick disk using a CS-183 Mini-Max Molder. The measurements were then run with 25 mm parallel plate geometry and a 1 mm sample gap. Thermal stability of samples during the rheological testing was checked by a time sweep, where the selected samples gave a stable G' signal for at least 90 min at 200 °C. The dynamic viscoelastic properties were determined with frequencies from 0.1 to 500 rad/s, using strain values determined with a stress sweep to lie within the linear viscoelastic region. Measurements were carried out in nitrogen atmosphere at three different temperatures 160, 180 and 200 °C.

2.3. Thermal analysis

The blends were analyzed using a Perkin–Elmer DSC-7 for crystallization and melting studies. The samples were dried at 80 °C for 24 h before DSC measurements. Experiments were carried out with 6–10 mg of sample under dry nitrogen. All samples were first heated to 180 °C at a rate of 10 °C/min, held at 180 °C for 2 min, and then cooled at a rate of 10 °C/min to 40 °C and held at 40 °C for 2 min. They were then scanned from 40 to 180 °C at a rate of 10 °C/min. Crystallization and melting temperatures were obtained from the cooling and second-heating thermograms, respectively.

3. Results and discussion

3.1. Rheological properties of m-LLDPE/m-HDPE blends

Fig. 1 shows for m-LLDPE/m-HDPE blends the variation of the viscosity η versus shear rate $\dot{\gamma}$ as well as the complex

Table 2
Rheological properties of the polyethylene blends

Sample code	Polymer cont (wt%)			η_0 (Pa s)			τ_0 (s) 180 °C	ω_0 (rad/s) 180 °C	E_a (kJ/mol)
	m-LLDPE	m-HDPE	LDPE	160 °C	180 °C	200 °C			
I.0	100	0		2400	1730	1240	0.021	3.2	30.1
I.20	80	20		3600	2200	1700	0.041	2.1	31.9
I.40	60	40		4600	3100	2100	0.089	1.1	33.3
I.60	40	60		6800	4500	3100	0.21	0.57	33.0
I.80	20	80		9200	6240	4190	0.43	0.31	33.6
I.100	0	100		14300	10000	6900	0.91	0.17	30.8
II.0	100		0	2400	1730	1240	0.021	3.2	30.1
II.20	80		20	4100	2700	1860	0.12	0.41	33.5
II.40	60		40	5500	3500	2400	0.29	0.20	35.2
II.60	40		60	7100	4400	2700	0.36	0.19	41.6
II.80	20		80	7900	4700	2800	0.46	0.18	44.6
II.100	0		100	6900	3900	2300	0.42	0.25	46.5

viscosity η^* versus frequency ω at 180 °C. For each blend, one can observe that the low shear rate viscosity plateau broadly spans to 10^{-2} s^{-1} and that the Cox–Merz rule [19] is quite well verified. Both observations allow the determination of the zero shear viscosity η_0 with satisfactory accuracy. Among the various available models, we found that the Cross equation gave a reasonably good fit to viscosity data

$$\eta = \eta_0 / [1 + (\tau_0 \dot{\gamma})^{1-n}] \quad (1)$$

where η_0 is the zero shear viscosity, τ_0 the relaxation time related to the longest relaxation time, and n is an exponent. The fitted values of η_0 and τ_0 are included in Table 2.

Fig. 1 also shows a gradual increase in viscosity of blends with an increase in m-HDPE content in the whole range of shear rate, due to m-HDPE has a high molecular weight but a similar MWD, compared to m-LLDPE in Table 1. The zero shear viscosity linearly increases from $1.7 \times 10^3 \text{ Pa s}$ of

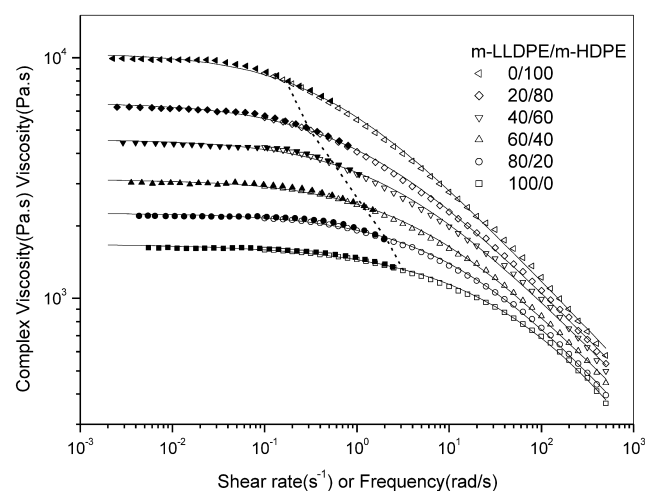


Fig. 1. Shear rate dependence of viscosity (solid) and frequency dependence of complex viscosity (open) for the blends of m-LLDPE/m-HDPE at 180 °C. The solid lines represent the fitting of experimental data to Cross equation. The dash line connects the position of the characteristic frequency ω_0 .

m-LLDPE to $1 \times 10^4 \text{ Pa s}$ of m-HDPE. It is clear in Fig. 2 that good straight line dependence of $\log \eta_0$ versus w_2 was obtained for m-LLDPE/m-HDPE blends at 160, 180 and 200 °C. The additivity of $\log \eta_0$ indicates a lack of specific influences in the blends of series I and probable miscibility.

$\log \tau_0$ gradually increases from 0.021 s of m-LLDPE to 0.91 s of m-HDPE with increasing m-HDPE content, and $\log \omega_0$ (which will be described in detail later) decreases from 3.2 rad/s of m-LLDPE to 0.17 rad/s of m-HDPE, as shown in Fig. 3. Indeed, a clear linear correlation is obtained for both parameters, which indicates that series I blends are miscible. The onset of frequency dependence of viscosity (non-Newtonian, shear-thinning behavior) can be defined as a characteristic frequency ω_0 , at which $\eta(\omega_0) = 0.8\eta_0$ [20]. Because of the practical importance of shear-thinning behavior in polymer melt rheology, some attempts have been made to correlate critical parameters for the onset of non-Newtonian behavior with molecular structure. Recent experiments [5] have exhibited that ω_0 are well correlated

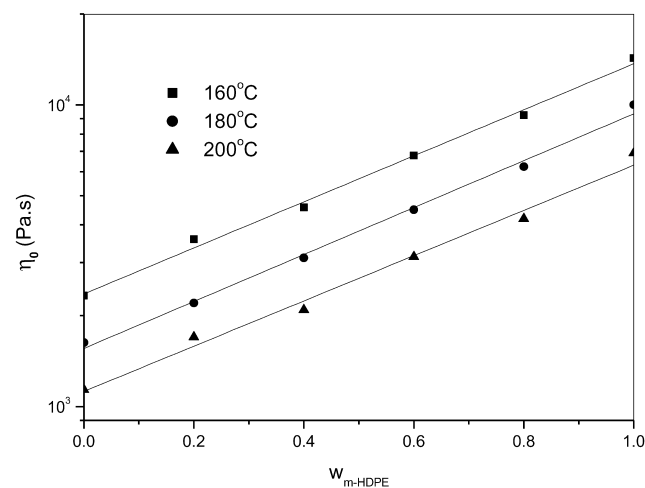


Fig. 2. The composition dependence of zero shear viscosity η_0 for the blends of m-LLDPE/m-HDPE at different temperatures. The solid lines are determined by a linear fit.

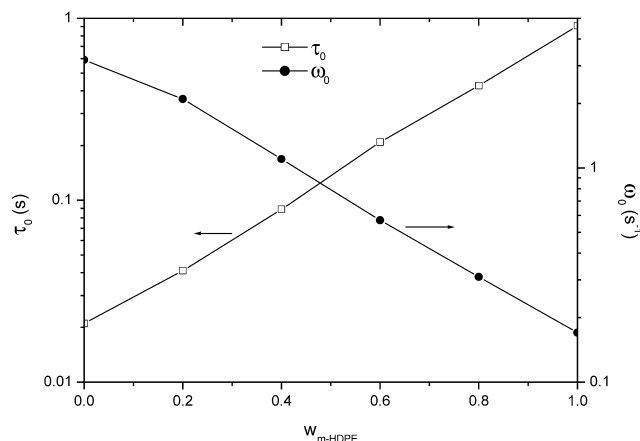


Fig. 3. The composition dependence of the characteristic relaxation time τ_0 and the characteristic frequency ω_0 for the blends of m-LLDPE/m-HDPE at 180 °C.

with the polydispersity index M_w/M_n : the slope of the plots $\log \omega_0 - \log M_w/M_n$ attains a value of -3.3 for the metallocene polymer and -3.0 for the conventional one. The correlation of ω_0 and polydispersity cannot be observed in Fig. 3. The polydispersity of blends is always wider than that of the component, but for the blends of series I, ω_0 only decreases with increasing m-HDPE fraction (the dash line connects the position of the characteristic frequency ω_0 in Fig. 1), which indicates that m-HDPE enhances the pseudo-plasticity (shear-thinning) of the blend. Several researchers [7,21] have also reported lower ω_0 for slightly long chain branched metallocene polyethylenes.

Why does m-HDPE have a stronger shear-thinning behavior? Recently, the polyethylenes rheology studies are mainly focused on the effect of molecular structure of polyethylene on its linear viscoelastic behavior and the determination of the LCB level in metallocene polyethylenes by using rheological data [7–10]. In the condition of similar molecular weight, polydispersity and short chain branching (SCB), the rheological features of the LCB can be summarized as follows: (a) higher dynamic viscosities at low frequencies; (b) higher relaxation times; (c) higher values of elastic modulus; (d) higher activation energy of flow; (e) higher melt strength, as well as strain hardening in extensional flow.

In the present investigation, except for the absence of extensional rheological data, the m-HDPE having above-mentioned (a)–(d) ‘dissident’ rheological behavior possesses a certain very low degree of LCB. (a) The viscosity and the weight average molecular of linear polyethylene at 190 °C should be in agreement with Ref. [22]: $\eta_0 = 3.40 \times 10^{-15} M_w^{3.6}$. The η_0 of m-HDPE has a little higher deviation from the exponent correlation. (b) The values of τ_0 against η_0 should show a linear correlation for linear polyethylene reported in Refs. [9,23], but τ_0/η_0 of m-HDPE here is much larger than that of m-LLDPE, and a smaller ω_0 value of m-HDPE means a more pseudo-plasticity behavior. (c) Figs. 4 and 5 show that m-HDPE

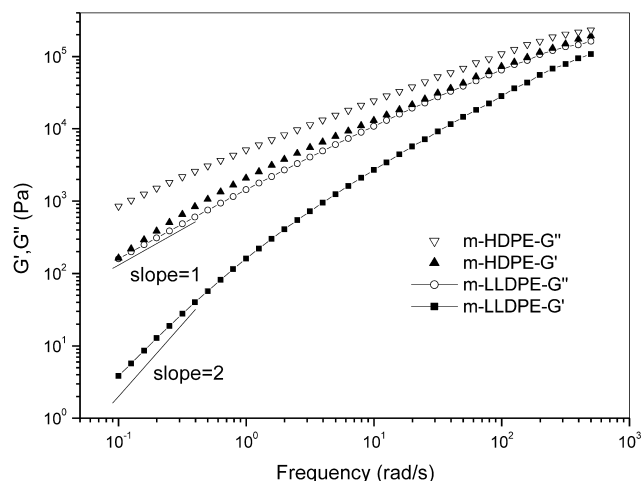


Fig. 4. The comparison of storage and loss modulus at 180 °C for m-LLDPE and m-HDPE.

has a higher values of elastic modulus and that the value of G' increases gradually with increasing fraction of m-HDPE. (d) Vega et al. [7] recommended the calculation of an ‘LCB index associated to activation energy of flow’ by subtracting the activation energy of flow of a linear polymer from that of polymer with LCB

$$I_{LCB} = \frac{(E_a)_{LCB} - (E_a)_l}{(E_a)_l} \quad (2)$$

where $(E_a)_{LCB}$ is the activation energy of flow of a low LCB PE such as m-HDPE, and $(E_a)_l$ which equals 24.0 kJ/mol is the activation energy of flow of a linear PE. The value of the I_{LCB} of m-HDPE is 0.28 by using Eq. (2).

In a recent article, Garcia-Franco [24] correlated the level of LCB in polymer with a rheological measurement of the gel-like behavior of a polymer. Because all the LCB polyethylenes exhibit a plateau in the loss angle δ , as a function of frequency, they believe this to be caused by

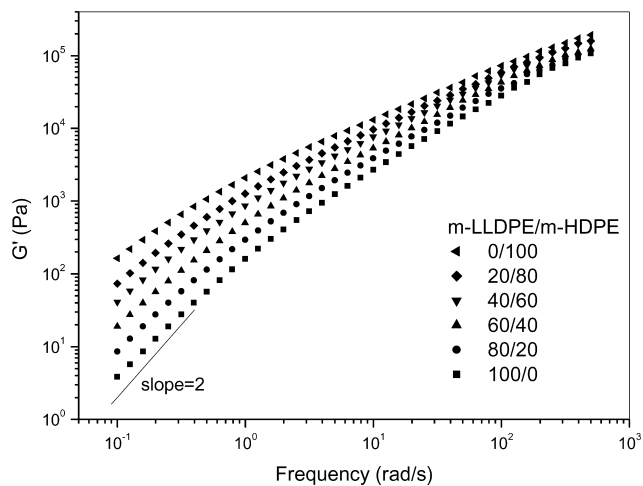


Fig. 5. The composition dependence of storage modulus for m-LLDPE/m-HDPE blends at 180 °C.

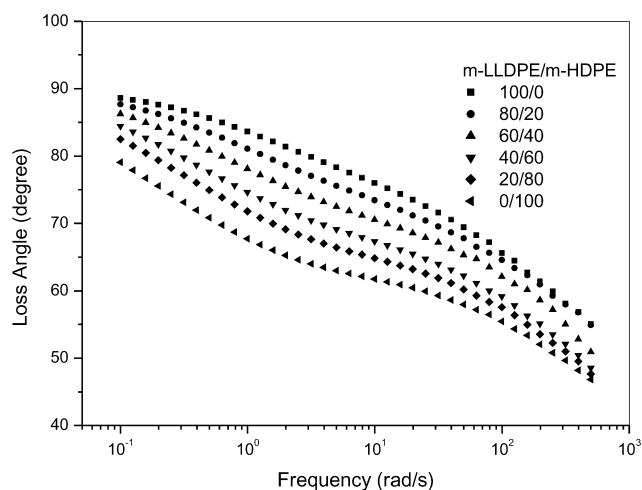


Fig. 6. The composition dependence of loss angle for m-LLDPE/m-HDPE blends at 180 °C.

only a modification of the relaxation behavior due to the presence of the LCB. Fig. 6 shows the effect of increasing m-HDPE content on the loss angle δ for the series I blends, which is similar to the effect of different amount of LCB. The LCB amount of m-HDPE is 0.3 LCB/ 10^4 C by using the relation of the network relaxation exponent n and LCB amount/ 10^4 C [24], because the values of n for m-HDPE is about 0.66. Some researchers [6,8] suggested the LCB in the polyethylene to be the result of copolymerization of ethylene with vinyl-ended macromonomers that are the polymer chains terminated by β -hydride elimination mechanism in metallocene polymerization.

The abnormal rheological behaviors verify that m-HDPE should possess a certain very low degree of LCB. The linear variation of viscoelastic properties of m-LLDPE/m-HDPE blends in the whole range of weight fraction indicates that these blends are miscible ones. Thus the addition of m-HDPE having an amount of LCB to m-LLDPE will exhibit higher zero shear rate viscosity and more significant shear-thinning, which will provide better performance in blow molding, vacuum forming or even film production.

3.2. Rheological properties of m-LLDPE/LDPE blends

The viscosity curves of m-LLDPE/LDPE blends at 180 °C are presented in Fig. 7. It can be seen that at low shear rate the viscosities of all blends are much higher than that of m-LLDPE and that the m-LLDPE/LDPE-20/80 has the highest zero shear rate viscosity in all composition. However, at high frequency the viscosities of all blends are lower than that of m-LLDPE, and the viscosity decreases with the addition of LDPE. The rheological properties are due to the higher M_w and wider polydispersity of LDPE than that of m-LLDPE. Rheological parameters of blends series II are also listed in Table 2.

In Fig. 8, $\log \eta_0$ versus w_2 is shown for m-LLDPE/LDPE blends at 160, 180 and 200 °C. The zero viscosity of

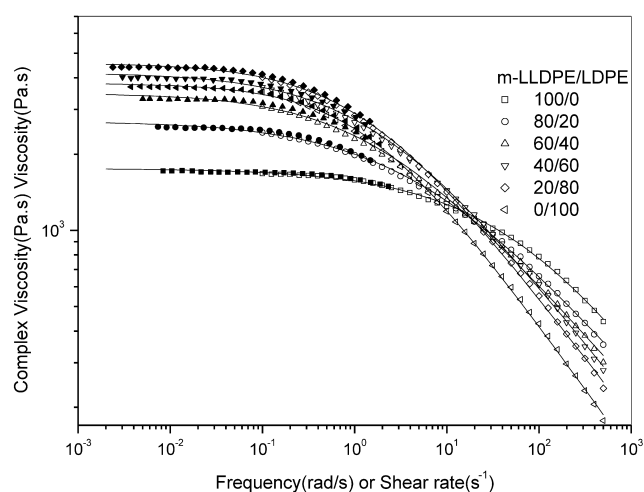


Fig. 7. Shear rate dependence of viscosity (solid) and frequency dependence of complex viscosity (open) for the blends of m-LLDPE/LDPE at 180 °C. The solid lines represent the fitting of experimental data to Cross equation.

m-LLDPE/LDPE blends has a large positive deviation from log-additivity rule, which is a result of immiscible blends [25]. Munoz-Escalona et al. [26] have reported that for blends of two metallocene HDPEs, the data of complex viscosity at 0.01 Hz have a positive deviation from log-additivity rule. They suggested that a decrease of free volume fraction of blends lead to the positive deviation blend (PDB) behavior.

On the other hand, Utracki [17] brought forward an equation allowing one to predict or to interpret the concentration dependence of immiscible blend viscosity

$$\log \eta = \log \eta_L + \Delta \log \eta^E \quad (3)$$

in which the first term is negative deviation blend caused by interlayer slip

$$\log \eta_L = -\log[1 + \beta(\phi_1 \phi_2)^{1/2}] - \log(\phi_1/\eta_1 + \phi_2/\eta_2) \quad (4)$$

where β is the interlayer slip factor. In the blend system, w_i equals ϕ_i because both components have a similar density. The second term of $\Delta \log \eta^E$ is an excess term to be derived from the concept of the emulsion-like behavior of polymer blend. This excess term must be zero at $w_i = 0$ and reach maximum at the phase inversion concentration, $w_i = w_{il}$

$$\Delta \log \eta^E = \eta_{\max} \left\{ 1 - \left[(\phi_1 - \phi_{1I})^2 / (\phi_1 \phi_{2I}^2 + \phi_2 \phi_{1I}^2) \right] \right\} \quad (5)$$

in which η_{\max} is a parameter determining magnitude of the PDB effect. Utracki [27] reported that two LLDPE blends manifested miscible blends, however, another LLDPE/LDPE blends behaved as immiscibility but a ‘compatible’ mixture of emulsion type.

The curves in Fig. 8 are the results of fitting the data of m-LLDPE/LDPE blends to Utracki’s equation, and their parameter values are listed in Table 3. The values of β are very small indicating that the interlayer slip effect can be omitted. As temperature increases, both values of w_{2I} and

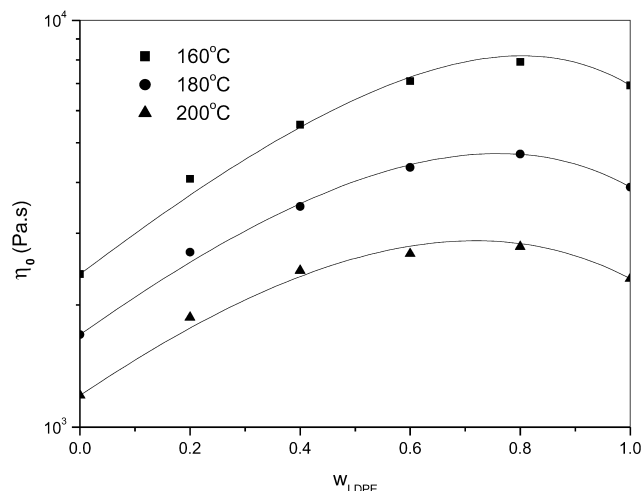


Fig. 8. The composition dependence of zero shear viscosity η_0 for the blends of m-LLDPE/LDPE at different temperatures. The solid lines represent the fitting of the immiscible blend equation.

η_{\max} decrease, which demonstrating that the site where this excess term reaches maximum closes to the m-LLDPE and that PDB effect becomes weak. It is probable that immiscibility of m-LLDPE/LDPE becomes weak.

For blend series II, $\log \tau_0$ and $\log \omega_0$ at 180 °C versus w_2 are plotted in Fig. 9. Both the values of τ_0 and ω_0 have a sharp change with a small amount of LDPE in the blend. As the weight fraction of LDPE beyond 40%, the values of τ_0 and ω_0 reach a relatively steady plateau, which also indicates inhomogeneity and suggests a phase separation in the system.

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, HDPE–LDPE, is not fully understood yet [15,16]. Rheological measurement is not only sensitive to the molecular structure of polymer, such as molecular weight, MWD, SCB and LCB, but also to the phase behavior of polymer blends. In the present study, LDPE, different from m-LLDPE in the molecular structure, has high degree of branch (55 methyl groups/1000 carbon atoms, both SCB and LCB). Recently, Choi et al. [28] reported the effects of branching characteristics of LDPE on its melt miscibility with HDPE by using molecular simulation. Phase separation in LDPE/HDPE blends in the melt was predicted for high branch contents in their simulations, and the cut-off value for the segregation was found to be

Table 3
Parameters used for curve fitting of data in Fig. 8

Temperature (°C)	$\lambda = \eta_1/\eta_2$	w_{2l}	β	η_{\max}	r^2
160	0.35	0.61	0.012	0.269	0.998
180	0.44	0.58	0.010	0.236	0.996
200	0.54	0.56	0.011	0.185	0.994

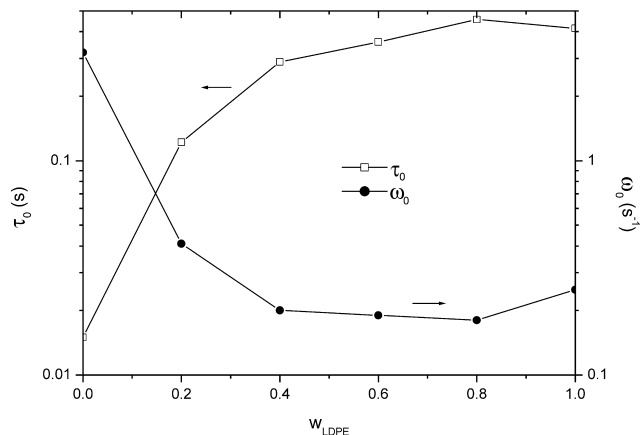


Fig. 9. The composition dependence of the characteristic relaxation time τ_0 and the characteristic frequency ω_0 for m-LLDPE/LDPE blends at 180 °C.

around 30 branches per 1000 long chain carbons. Our results presented here are consistent with their prediction. So m-LLDPE/LDPE blends behave as well-stabilized emulsions, i.e. these blends represent a ‘compatible’ system of industrial importance.

3.3. DSC analysis

The curves of the DSC melting scans of m-LLDPE/m-HDPE and m-LLDPE/LDPE are plotted in Figs. 10 and 11, respectively. The thermal analysis results are summarized in Table 4. Blends of m-LLDPE/m-HDPE show only one crystallization and melting temperature peak, indicating the existence of one type of crystal species on all compositions. It would appear, therefore, that cocrystallization of m-LLDPE and m-HDPE took place. Fig. 12 also shows a gradual increase in crystalline melt temperature from 127.0 to 134.1 °C for the m-LLDPE/m-HDPE blends with an increase in m-HDPE content. It indicates that the blends of m-LLDPE and m-HDPE are very similar to a single-component system.

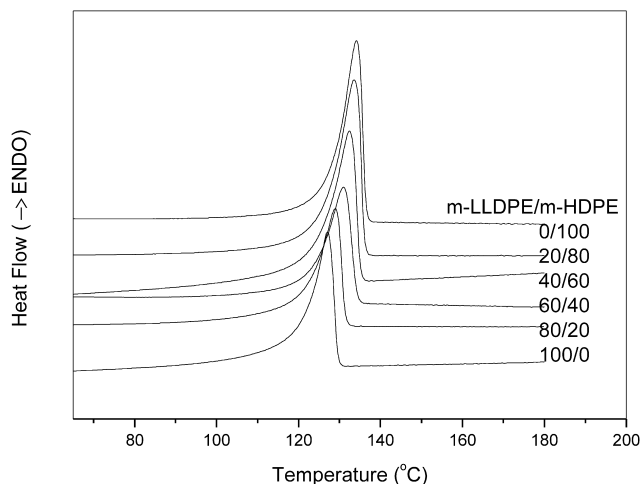


Fig. 10. DSC traces for m-LLDPE/m-HDPE blends.

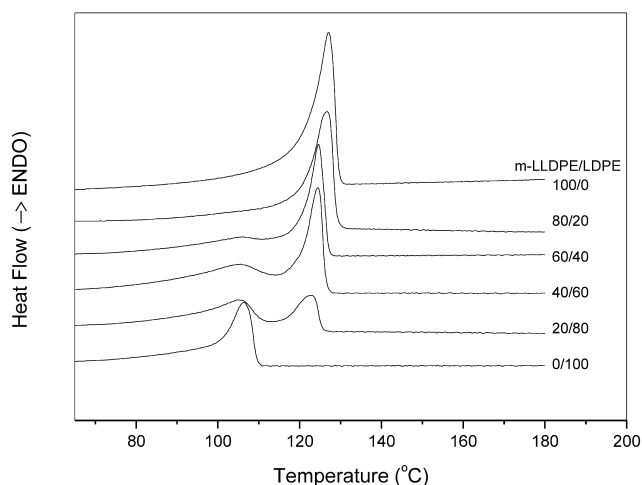
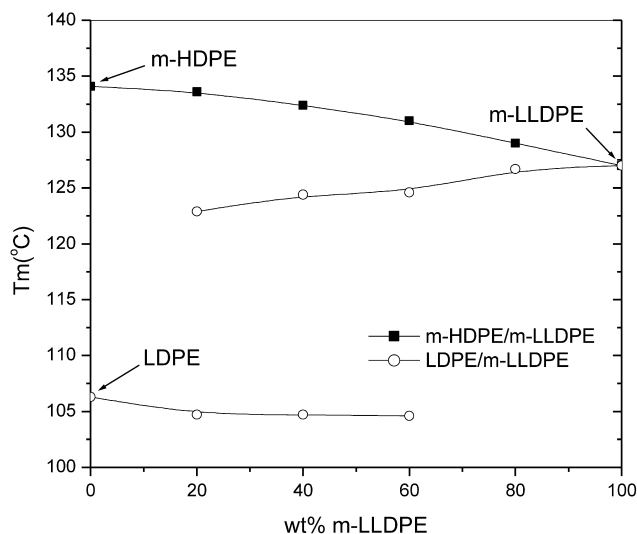


Fig. 11. DSC traces for m-LLDPE/m-LDPE blends.

Blends of m-LLDPE/LDPE-60/40, 40/60, 20/80 show two distinct peaks, as shown in Fig. 11. No cocrystallization phenomenon is observed in the case of m-LLDPE/LDPE blends. This is perhaps due to the high degree of branching of LDPE. In the polymer blend melt, when the temperature decreases, the polyethylene component, which is in the structure of emulsion in the melt, enters into the near growing crystal nucleus, leading to liquid–solid phase separation. Fig. 12 also shows that the melting points of both m-LLDPE and LDPE are depressed by the other component instead of closing to each other. It is possibly due to the following effects [29]:

1. The kinetic effect of one solid phase, which may obstruct or make irregular the growth of the lamellar crystallites or the spherulites of the other phase.
2. Thermal perturbations due to different rates of crystallization between m-LLDPE and LDPE.

Conclusively, the thermal properties of m-LLDPE/m-HDPE blends are very similar to a single-component system. However, m-LLDPE/LDPE blends are immiscible

Fig. 12. The composition dependence of melting temperature T_m for m-LLDPE/m-HDPE blends and m-LLDPE/LDPE blends.

in both melt and crystal state. These results are consistent with the rheological properties of two series blends presented in Sections 3.1 and 3.2.

4. Conclusions

Zero shear viscosity of m-LLDPE/m-HDPE blends agrees well with the log-additivity rule at different temperature. The characteristic relaxation time and the characteristic frequency also vary linearly with increasing m-HDPE fraction. These results confirm that the system is miscible blends. The thermal properties of m-LLDPE/m-HDPE blends are also very similar to a single-component system. At the same time, HDPE showing a dissident rheological behavior should possess a very low degree of LCB. Both different calculation methods of LCB verify this point. In contrast to m-LLDPE/m-HDPE blends, zero shear viscosity of m-LLDPE/LDPE blends has a positive deviation from the log-additivity rule, which can be well fitted by using the

Table 4
Thermal analysis data of polyethylene blends

Sample code	Melt temperature in first scan (°C)		Crystallization temperature (°C)		Melt temperature in second scan (°C)	
I.0		126.9		111.7		127.0
I.20		128.4		112.8		129.0
I.40		129.9		113.9		131.0
I.60		131.8		115.2		132.4
I.80		133.0		116.8		133.6
I.100		133.8		117.0		134.1
II.0	126.9	–	111.7	–	127.0	–
II.20	125.8	–	110.7	–	126.6	–
II.40	124.7	104.8	110.0	90.6	124.6	104.6
II.60	124.8	104.7	108.3	95.0	124.4	104.7
II.80	123.2	104.7	105.7	93.6	122.9	104.7
II.100	–	106.6	–	89.0	–	106.3

immiscible blend equation of Utracki. The characteristic relaxation time and the characteristic frequency have a sharp variation with the small amount of LDPE in the blends. The authors believe that the system is immiscible blends, which behaves as a well-stabilized emulsion. The thermal properties of m-LLDPE/LDPE blends are consistent with the rheological properties. Finally, the results show that the addition of m-HDPE having an amount of LCB to m-LLDPE will provide better performance in blow molding, vacuum forming or even film production.

Acknowledgements

The authors greatly appreciate the financial support for this work by the Core Research for Knowledge Innovation of the Chinese Academy of Sciences (Grant No. KJCX 2-203).

References

- [1] Hamielec AE, Soares JBP. *Prog Polym Sci* 1996;21:651.
- [2] Brichinger HH, Fischer D, Mulhaupt R, Rieger B, Waymouth RM. *Angew Chem Int Ed Engl* 1995;34:1143.
- [3] Todo A, Kashiwa N. *Macromol Symp* 1996;101:301.
- [4] Fu Q, Chiu FC, McCreight KW, Guo MM, Tseng WW, Cheng SZD, Keating MY, Hsieh ET, Lauriers PJ. *J Macro Sci: Phys* 1997;B36:41.
- [5] Munoz-Escalona A, Lafuente P, Vega JF, Santamaria A. *Polym Engng Sci* 1999;39:2292.
- [6] Yan D, Wang WJ, Zhu S. *Polymer* 1999;40:1737.
- [7] Vega JF, Santamaria A, Munoz-Escalona A, Lafuente P. *Macromolecules* 1998;31:3639.
- [8] Malmberg A, Liimatta J, Lehtinen A, Lofgren B. *Macromolecules* 1999;32:6687.
- [9] Shroff RN, Mavridis H. *Macromolecules* 1999;32:8454.
- [10] Wood-Adams PM, Dealy JM, deGroot AW, Redwine OD. *Macromolecules* 2000;33:7489.
- [11] Gahleitner M. *Prog Polym Sci* 2001;26:895.
- [12] Krishnamoorti R, Graessley WW, Dee GT, Walsh DJ, Fetters LJ, Lohse DJ. *Macromolecules* 1996;29:367.
- [13] Economou IG. *Macromolecules* 2000;33:4954.
- [14] Wignall GD, Alamo RG, Ritchson EJ, Mandelkern L, Schwahn D. *Macromolecules* 2001;34:8160.
- [15] Schipp C, Hill MJ, Barham PJ, Cloke VM, Higgins JS, Oiarzabal L. *Polymer* 1996;37:2291.
- [16] Agamalian M, Alamo RG, Kim MH, Londono JD, Mandelkern L, Wignall GD. *Macromolecules* 1999;32:3093.
- [17] Utracki LA. *J Rheol* 1991;35:1615.
- [18] Nesarikar AR. *Macromolecules* 1995;28:7202.
- [19] Cox WP, Merz EH. *J Polym Sci* 1958;28:619.
- [20] Graessley WW. *Adv Polym Sci* 1974;16:1.
- [21] Hatzikiriakos SG, Kazatchkov IB. *J Rheol* 1997;41:1299.
- [22] Raju VR, Smith GG, Marin G, Knox JR, Graessley WW. *J Polym Sci Phys Ed* 1979;17:1183.
- [23] Aguilar M, Vega JF, Sanz E, Martinez-Salazar J. *Polymer* 2001;42:9713.
- [24] Garcia-Franco CA, Srinivas S, Lohse DJ, Brant P. *Macromolecules* 2001;34:3115.
- [25] Utracki LA. *Polymer alloys and blends*. Munich: Hanser, 1989.
- [26] Munoz-Escalona A, Lafuente P, Vega JF, Munoz ME, Santamaria A. *Polymer* 1997;38:589.
- [27] Utracki LA, Schlund B. *Polym Engng Sci* 1987;27:1512.
- [28] Fan ZJ, Williams MC, Choi P. *Polymer* 2002;43:1497.
- [29] Datta NK, Birley AW. *Plast Rubber Process Appl* 1982;2:237.