

Rheological and Thermal Properties of Single-Site Polyethylene Blends

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ABSTRACT: Branched polyethylenes, low-density polyethylenes (LDPE1 and LDPE2) or long-chain-branched very low density polyethylenes (VLDPE2), were blended with very low density polyethylenes containing short branches (VLDPE1 and VLDPE3). The rheological and thermal measurements of the pure copolymers and their blends (VLDPE1-LDPE1, VLDPE1-LDPE2, VLDPE1-VLDPE2, and VLDPE2-VLDPE3) were taken by controlled stress rheometry and differential scanning calorimetry, respectively. The shear-thinning effect became stronger with increasing long-chain-branched polymer compositions when it was correlated with the flow behavior index, and the extent of shear thinning was different for each blend set. Stronger shear thinning and a linear composition dependence of the zero-shear viscosity were observed for the VLDPE1-LDPE1 and VLDPE1-LDPE2 blends. These blends followed the log ad-

ditivity rule, and this indicated that they were miscible in the melt at all compositions. In contrast, a deviation from the log additivity rule was observed for the VLDPE1-VLDPE2 blend compositions with 50% or less VLDPE2 and for the VLDPE3-VLDPE2 blends with 50% or more VLDPE2. The thermal properties of the blends were consistent with the rheological properties. VLDPE1-LDPE1 and VLDPE1-LDPE2 showed that these blends were characteristic of a single-component system at all compositions, whereas the phase separation (immiscibility) was detected only for VLDPE1-VLDPE2 blends with 50% or less VLDPE2 and for VLDPE3-VLDPE2 blends with 50% or more VLDPE2. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1549–1557, 2005

Key words: blends; miscibility; polyethylene (PE); rheology

INTRODUCTION

Studies of the rheological properties of polyethylenes (PEs) and their blends have attracted great attention because of the interest in determining the relationships of the morphology, processability, and properties of these blends. In particular, melt rheology gives viscosity/shear-rate data that are important for optimizing conditions during the processing of a polymer.^{1,2} Linear low-density polyethylenes (LLDPEs) and low-density polyethylenes (LDPEs) are widely used in industry to manufacture various products, including films, sheets, and pipes. The rheological and processing behavior of PEs mainly depends on parameters such as the weight-average molecular weight (M_w), molecular weight distribution (MWD), comonomer content,³ and long-chain-branching (LCB) content and distribution.^{4–8} A chain structural parameter, LCB is known to have a large impact on polymer

rheological properties because polymers with LCB demonstrate excellent processing properties.^{4,5}

A breakthrough in polyolefin technology, the use of single-site catalysts (metallocenes) for the polymerization of olefins with predictable structural, physical, and mechanical properties emerged nearly a decade ago.⁹ The single-site nature of these types of catalysts allows the efficient control of the molecular structure and leads to the formation of ethylene copolymers with narrow MWDs and relatively homogeneous comonomer distributions. Thus, this novel technology has been particularly useful for the production of well-defined LLDPEs because the α -olefin comonomer is incorporated more uniformly than it is with conventional catalysts. Metallocene- or single-site-catalyzed LLDPEs have been made with short branches and with long branches, and many are commercially available. The characterization of the rheological properties of these PEs and their blends is a concern for manufacturers.

Studies of the rheological properties of various types of metallocene polyethylenes (m-PEs)^{10–15} and their blends have been reported.^{16–25} To improve the rheological and processing behavior, many researchers have blended long-branched m-PE into other polymers. The dynamic viscoelastic and steady-state flow properties, die swell measurements, and melt strengths of these blends have been investigated. The steady-state flow properties are directly related to the

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TABLE I
Properties of the Polymers

| Property | VLDPE1 ^a | VLDPE2 ^b | VLDPE3 ^c | LDPE1 ^d | LDPE2 ^d |
|--------------------------------------|---------------------|---------------------|---------------------|--------------------|--------------------|
| Comonomer | Butene | Octene | Octene | | |
| Catalyst type ^e | M | S | ZN | P | P |
| MFI (°/min ³) | 27.0 | 1.0 | 1.0 | 7.0 | 22.0 |
| Density (g/cm ³) | 0.901 | 0.908 | 0.912 | 0.919 | 0.918 |
| M_w | 58,000 | 96,700 | 120,000 | 474,000 | 89,000 |
| M_w/M_n | 2.65 | 2.86 | 3.80 | 23.3 | 4.4 |
| Comonomer content (mol) | 6.3 | 2.4 | 4.2 | | |
| T_m (°C) _n ^f | 92.7 | 105.4 | 123.0 | 106.5 | 103.9 |
| T_c (°C) _n ^f | 76.6 | 90.3 | 100.5 | 87.8 | 87.1 |

M_n = number-average molecular weight; T_c = crystallization temperature.

^a Ref. 28

^b Ref. 29

^c Ref. 30

^d Data were taken from chemical data sheets published by the manufacturer.

^e ZN = Ziegler–Natta catalyst; S = constrained geometry single-site catalyst; M = metallocene; P = peroxide.

^f T_c and T_m were obtained at scanning rates of 10°C/min.

processing properties, whereas dynamic rheological behavior can be used to separate viscous-like and elastic-like behavior. It has been suggested that the shear sensitivity of m-PEs can be readily controlled through the selective incorporation of LCB. A synergistic effect for the melt strength and other rheological properties has also been observed for LCB-rich m-PE blends.^{16–22} The rheological properties of a blend are sensitive not only to the molecular structure but also to the phase behavior. The effect of the blend phase morphology on the rheological properties has also been investigated. Utracki and Schlund^{26,27} extensively studied various rheological properties of LLDPEs and their blends with LLDPE and LDPE. According to their findings; LLDPE–LLDPE blends demonstrate some miscibility, whereas LLDPE–LDPE blends are thermodynamically immiscible. For the latter blends, the possibility of the presence of a compatible mixture is suggested.

We prepared four sets of binary blends of very low density polyethylenes (VLDPEs) with short-chain branching, produced by metallocene or Ziegler–Natta catalysts, and LDPEs or VLDPEs with LCB. The aim of blending these PEs was to study the miscibility, rheology, and crystallization, which are useful properties for film applications. In this article, we address the dynamic rheological behavior of these blends. In addition, the melting of the blends was examined with differential scanning calorimetry (DSC) to study phase behavior in the solid state and infer miscibility in the melt state. Some steady-state flow experiments were performed to complement the dynamic rheology.

EXPERIMENTAL

Blend preparation

Table I lists the characteristics of the polymers used in this study. The 1-butene and 1-octene copolymers and

LDPEs were commercial-grade PEs, and they were supplied by Qenos Engineering Plastics, Ltd. (Altona, Australia). These polymers were selected because they contained overlapping regions of melting or molecules with common unbranched segments. The following four blend sets were prepared: VLDPE1–LDPE1, VLDPE1–LDPE2, VLDPE1–VLDPE2, and VLDPE3–VLDPE2. These blends with various compositions (by weight) were prepared by melt extrusion (190°C) with an Axon BX-12 single-screw extruder (Axon Australia Pty., Ltd., Mudgeeraba, Australia) with a Gateway screw 12.5 mm in diameter (length/diameter = 26:1). The hot strands of the blends were quenched in room-temperature water, dried, and finally granulated. The details of the operation conditions have been reported elsewhere.³¹ In these blends, the first components, VLDPE1 and VLDPE3, contained only short-chain branches, whereas the second components, LDPE1, LDPE2, and VLDPE2, had both short- and long-chain branches.

Melt rheology

Pellets of the blends and pure polymers were molded into circular disks 25 mm in diameter and 2 mm thick at 200°C with a heated press. A Rheometrics SR 200 dynamic stress rheometer with 25-mm-diameter parallel-plate geometry with constant gap spacing was employed to measure the steady-shear rheological properties of the blends. All rheological tests were performed at 180°C within the shear rate ($\dot{\gamma}$) range of 10^{-2} – 10^2 s⁻¹. Purified nitrogen was purged through the test compartment to prevent oxidation and degradation. This instrument required only a small volume of materials to reach rapid temperature equilibrium.

Data analysis

The flow behavior index (n) was calculated from a power-law equation:

$$\tau = K(\dot{\gamma})^n \quad (1)$$

where τ is the shear stress and K is a constant.³² The slope of the plot of $\log \tau$ versus $\log \dot{\gamma}$ represents n , which is an indicator of the extent to which the polymer deviates from Newtonian behavior ($n = 1$ for Newtonian fluids).

The zero-shear viscosity (η_0) of the blends and pure polymers was calculated with the following modified Cross–Bueche equation:³³

$$\frac{\eta_0}{\eta} = 1 + (\alpha\dot{\gamma})^m \quad (2)$$

where η is the viscosity at $\dot{\gamma}$, α is the characteristic relaxation time related to the molar mass for a linear polymer solution, and m is a measure of the shear thinning of the melt. Iwakura and Fujimura³⁴ revealed that α is related to the size of the apparent flow unit for polymer melts. The parameters η_0 , α , and m were obtained via curve fitting with the Solver function in Microsoft Excel.

DSC

A PerkinElmer DSC7 was used under a nitrogen purge (15 mL min⁻¹) to study the thermal behavior of these blends and pure polymers after different thermal treatments. Sample masses of 3–4 mg were encapsulated in aluminum pans with a crimper. After the samples were melted at 180°C for 5 min, the samples were continuously cooled to 10°C at a rate of 10°C min⁻¹. The DSC melting curves were then obtained by the heating of the samples from 10 to 180°C at a rate of 10°C min⁻¹. A baseline scan was performed with a matched empty pan. The calorimeter was calibrated for temperature and heat flow with indium and zinc standards, and the calibration was regularly checked against the onset melting temperature (T_m) of indium.

RESULTS AND DISCUSSION

Flow curves and n

Logarithmic plots of τ versus $\dot{\gamma}$ for the blends obtained at 180°C are displayed in Figure 1(a–d). All the flow curves display a linear relationship within the studied range of $\dot{\gamma}$, suggesting that the power-law equation can be used to express the relationship between τ and $\dot{\gamma}$. The tangent of the plot of τ versus $\dot{\gamma}$ gives n , and the value of n indicates the extent to which the polymer deviates from Newtonian behavior. Clearly, the ob-

served tangent of τ versus $\dot{\gamma}$ was less than unity for all the blends, and this indicated that the blends behaved as pseudoplastic non-Newtonian fluids at 180°C. During the shearing, the polymer chains became disentangled and oriented themselves in the shear direction and thereby exhibited more non-Newtonian behavior.³²

Illustrated in Figure 2 is a plot of the variation of the n values with the blend composition for all the blend sets. High n values were observed for these blends, and this may be due to the moderate $\dot{\gamma}$ range used during the rheological measurements. Figure 2 also shows that the n values gradually shifted to lower values with the addition of the second component containing some LCB. However, the extent of the shift changed for the different sets of blends, and the reasons for the observed behavior are given later.

LDPE blends

The LDPEs and VLDPE1 had different physical properties and performances because of the differences in their molecular structures. LDPE1 and LDPE2 were made through a high-pressure process and had short-chain branches and long-chain branches. Conversely, VLDPE1 was an ethylene–butene copolymer prepared with a metallocene catalyst and contained mainly short-chain branches.²⁸ As the LDPE1 content increased, n of the VLDPE1–LDPE1 blends decreased smoothly, and this indicated the beginning of shear-thinning behavior. Shear thinning was characterized by n values below unity, and the smaller n was, the stronger the shear-thinning effect was.¹⁸ This shear-thinning behavior was due to high elastic deformation accompanying the viscous flow of a polymer fluid. That is, under the action of an external force, macromolecular coils oriented with the external force, and this led to decreased viscosity.

Shear thinning became more pronounced with increasing LCB content as the LDPE composition increased.¹² As mentioned previously, LDPE1 had many long-chain branches. These branches were defined as rheologically significant; that is, their length exceeded the critical molar mass for chain entanglement.¹⁴ LCB increased segmental molecular entanglements and reduced the polymer hydrodynamic volume. These two factors competed with each other in determining the rheological properties of the polymer. At very low $\dot{\gamma}$ values, LDPE1 had a higher viscosity than its linear counterpart as a result of increased chain entanglements. However, LDPE was easier to disentangle than a linear or short-branched PE because of its smaller hydrodynamic volume. Therefore, LDPE1 containing LCB was expected to show a more evident shear-thinning effect.¹²

Similar behavior was also observed for n of the VLDPE1–LDPE2 blend series, even though LDPE2

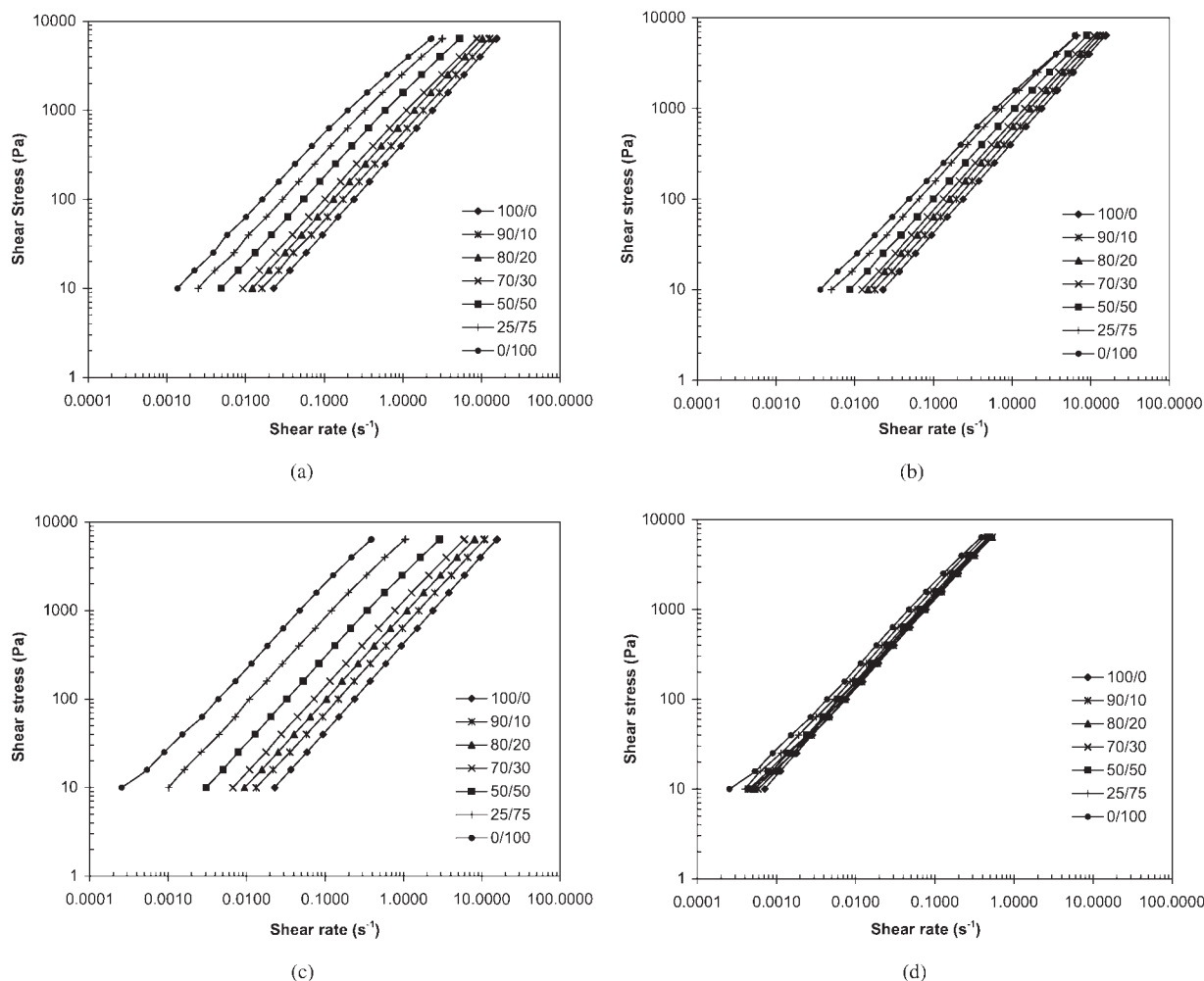


Figure 1 Logarithmic plots of τ versus $\dot{\gamma}$ for (a) VLDPE1–LDPE1, (b) VLDPE1–LDPE2, (c) VLDPE1–VLDPE2, and (d) VLDPE3–VLDPE2 blends at 180°C. The first number of the ratio indicates the amount of VLDPE1 or VLDPE3 (the lines are not model fits; they have been drawn to guide the eye).

had lower M_w and MWD values than LDPE1 (89,000 vs 474,000 g mol^{-1} for M_w , and 4.4 vs 23.3 for MWD). Because both types of blends exhibited similar shear-thinning behavior, the difference in M_w and MWD appeared to be less important than LCB in controlling the shear-thinning behavior of these blends. Therefore, the slightly different shear-thinning behaviors of the two sets of blends could probably be attributed to the small difference in the LCB content and distribution between LDPE1 and LDPE2.

VLDPE2 blends

VLDPE2 was a single-site-initiated ethylene–octene copolymer with long-chain branches, which was produced with Dow constrained geometry catalyst technology. The LCB content in VLDPE2 ranged from 0.01 to 3/1000 backbone carbon atoms,^{35,36} which was much lower than that in LDPEs. Thus, pure VLDPE2 showed higher n values than the LDPEs, although a

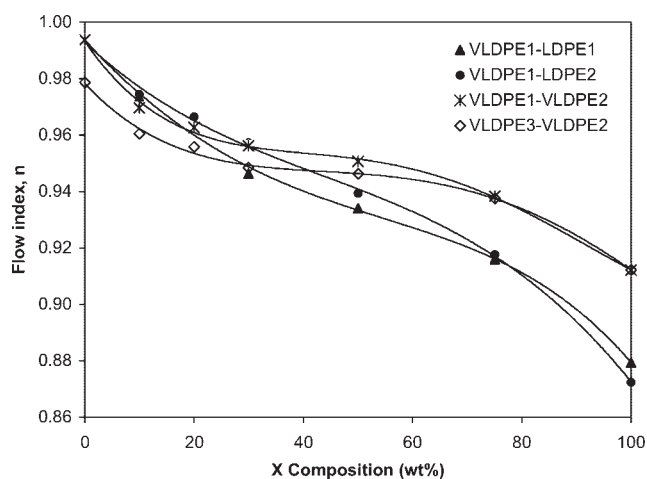


Figure 2 n versus the blend composition for VLDPE1–LDPE1, VLDPE1–LDPE2, VLDPE1–VLDPE2, and VLDPE3–VLDPE2 blends. The X composition indicates the second component (the lines are not model fits; they have been drawn to guide the eye).

similar trend of shear-thinning behavior was found for the two blend series, as shown in Figure 2. The higher n values for VLDPE2 blends, compared with those of the LDPE blends, indicated the presence of a weaker shear-thinning effect than that of the VLDPE1–LDPE blends.

Both sets of VLDPE1–VLDPE2 and VLDPE3–VLDPE2 blends had the same second component (VLDPE2), which contained a small amount of LCB. However, different n values could still be observed for the two sets of blends. Moreover, slightly stronger shear-thinning characteristics were seen for VLDPE3–VLDPE2. VLDPE3 had a higher M_w value of 120,000 g mol⁻¹, and so the average M_w value of the PEs in the VLDPE3–VLDPE2 blends was higher than that for the blends containing VLDPE1, which had a lower M_w value of 58,000 g mol⁻¹. As previously discussed, shear thinning is related to chain disentanglement and orientation along the shear flow. In blends containing high- M_w VLDPE3, the flow resistance of the blends decreased rapidly, and relative movements of intermolecular segments became easier, as $\dot{\gamma}$ increased. This implied that when the relative M_w and $\dot{\gamma}$ values were higher, the shear-thinning effect became stronger with the same amount of LCB.

Effect of $\dot{\gamma}$ on the melt viscosity

Over the explored range of $\dot{\gamma}$, all sets of the blends exhibited a decrease in the melt viscosity with increasing $\dot{\gamma}$, and this indicated that these blends were pseudoplastic non-Newtonian fluids at 180°C. At very low $\dot{\gamma}$ values, the chains were in a random coil arrangement and were entangled because of the thermal motion of chain segments; hence, the polymers showed the highest viscosity at low $\dot{\gamma}$ values. As $\dot{\gamma}$ increased, intermolecular entanglements were partially disrupted, and this allowed molecules to orient along the shear direction. Therefore, the resistance to flow, that is, the viscosity, decreased. At higher $\dot{\gamma}$ values, a more significant decrease in the blend viscosity was observed, especially for blends with more LCB.

The melt viscosity became a constant at η_0 . η_0 is of special interest for polymer characterization because it is greatly influenced by the molecular structure of the polymer and makes rheological behavior understandable at the molecular level.¹⁸ At zero shear, the rheological response depends on the size of the macromolecular random coils and specific interactions among the macromolecules.³⁷ Among the available models, we found that the modified Cross–Bueche equation [eq. (2)] gave a good fit to the viscosity data. Hence, the η_0 values of the pure polymers and the corresponding four sets of blends were calculated with eq. (2) and a curve-fitting technique. Figure 3 displays the η_0 values plotted against the blend composition. The graphs of η_0 versus the compositions of the VLDPE1–

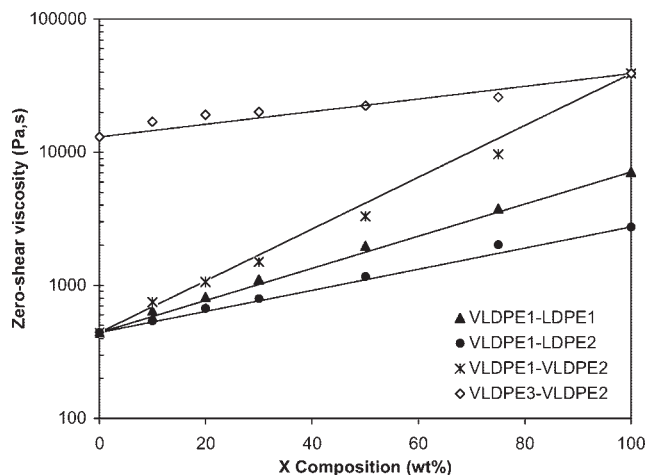


Figure 3 η_0 versus the blend composition for VLDPE1–LDPE1, VLDPE1–LDPE2, VLDPE1–VLDPE2, and VLDPE3–VLDPE2 blends. The X composition indicates the second component.

LDPEs blends approximately followed the log additivity rule, and this suggested that these blends were miscible in the melt. Cho et al.²³ also reported that the complex melt viscosity of LLDPE–LDPE blends followed the log additivity rule of mixtures at any value of $\dot{\gamma}$, and so the blends were miscible in the melt state. However, the VLDPE1–VLDPE2 blends containing high VLDPE2 contents demonstrated a negative deviation from the log additivity rule, but the VLDPE3–VLDPE2 blends with low VLDPE2 contents demonstrated a positive deviation from the log additivity rule; this indicated that the blends could be immiscible at these compositions. Similar conclusions were drawn from DSC studies after an analysis of the melting and crystallization behavior of the blends, as explained in a later section.

Figure 3 further illustrates that for the VLDPE1–LDPE1 blends, the logarithm of η_0 of the blends increased linearly with the addition of long-chain-branched LDPE1, and this indicated increasing melt strength. Also, as the LDPE2 content increased, the VLDPE1–LDPE2 blends showed enhanced melt viscosity to a smaller extent than the VLDPE1–LDPE1 blends because of the lower M_w of LDPE2 (89,000 vs 474,000 g mol⁻¹). Fox and Flory^{38,39} proposed that above the critical entanglement molar mass, the relationship between η_0 and M_w for linear polymers at low $\dot{\gamma}$ values is given by

$$\eta_0 = KM_w^{3.4} \quad (3)$$

M_w of VLDPE2 (96,700 g mol⁻¹) was close to that of LDPE2 (89,000 g mol⁻¹) but significantly lower than that of LDPE1 (474,000 g mol⁻¹). Thus, it was expected that η_0 of the VLDPE1–VLDPE2 blends would be slightly higher than that of the VLDPE1–LDPE2

blends but much lower than that of the VLDPE1–LDPE1 blends. In addition, Yan et al.¹² studied the influence of LCB on the rheological properties of PEs with approximately the same M_w and molar MWD values at very low $\dot{\gamma}$ values. The viscosity increased with increasing LCB density. Because VLDPE2 had a much lower LCB concentration than the LDPEs as mentioned previously, we expected that the η_0 values of the VLDPE1–VLDPE2 blends would be lower than those of the VLDPE1–LDPE2 blends. However, in contrast to the theoretical analysis prediction, the observed experimental η_0 values were higher, as illustrated in Figure 3. This behavior was probably attributable to the significantly different MWDs of VLDPE2, LDPE1, and LDPE2 (2.86, 23.3, and 4.4, respectively). Thus, the broader MWD of LDPE1 (23.3) could result in better flowability and hence reduce its viscosity to be lower than that of VLDPE2. In addition, the differences in the LCB distributions of VLDPE2 and LDPEs arose for another reason. Goyal et al.⁵ reported that the branching distribution in LDPE had a significant effect on the melt strength behavior, which in turn affected the processing behavior considerably. These different magnitudes of η_0 for VLDPE2, LDPE1, and LDPE2 were confirmed by their different melt flow indices (MFIs; 1.0, 7.0, and 22.0 dg min⁻¹, respectively).

Figure 3 also shows that the η_0 values of the VLDPE3–VLDPE2 blends exhibited the highest values of the four sets of blends. VLDPE3 was an ethylene–octene copolymer produced with a conventional Ziegler–Natta catalyst, and it had only short-chain branches.³⁰ Because η_0 of a polymer is proportional to its molar mass to the 3.4th power [eq. (3)], the blends containing VLDPE3 exhibited higher η_0 values on account of the higher molar mass of VLDPE3. The higher η_0 values indicated higher melt strength and higher bubble stability, which are favorable for polymer processability.¹⁸

Effect of the composition on the melt viscosity

The melt viscosity obtained with the four τ values in increasing order (10, 100, 1000, and 6393 Pa) at a constant temperature (180°C) is presented in Figure 4 as a function of the second component composition. These tests were performed to investigate the effect of τ and the blend composition on the melt viscosity. The dependence of the logarithmic melt viscosity on the composition for VLDPE1–LDPE blends at the four τ values approximately followed the log additivity rule, and this confirmed that the first two sets of blends were completely miscible in the melt state. The same conclusion was obtained by an investigation of the η_0 data, as mentioned previously. It is suggested that a substantial phase change in the structure of the melts did not take place over the entire composition range.

However, at lower τ values, the shear viscosity of the VLDPE1–VLDPE2 blends with high VLDPE2 contents and the VLDPE3–VLDPE2 blends with low VLDPE2 contents demonstrated negative and positive deviations from the log additivity rule, respectively. This implied immiscibility in these cases. As τ ($\dot{\gamma}$) increased, the molecules in the blends with long-chain branches became readily disentangled; hence, the blends showed a nearly linear relationship for the viscosity, and this resulted in an improvement in the miscibility for these blends. There was a larger viscosity increase for the blends with a high second component content that had more LCB. For each set of blends, the melt viscosity decreased with increasing τ , as expected; however, the extent of the decrease varied. In addition, at higher τ values, that is, at higher $\dot{\gamma}$ values, the variation of the melt viscosity with the blend composition became minimal. This was because long-chain branches became disentangled at high τ values.

From the viewpoint of microrheology, flow occurs when polymer molecules slide past each other. Therefore, flowability depends on the mobility of molecular chains and entanglements. For polymer blend melts, the compatibility and miscibility between the phases are important factors affecting the rheological characteristics. Along with the mixing methods and conditions, they determine the behavior of dispersion and the distribution of the components in the blends.

Thermal analysis

The conformation of the miscibility behavior of these blends was obtained by an analysis of the melting endotherm characteristics. DSC melting curves were obtained after the blends were cooled from the melt at 10°C min⁻¹. The VLDPE1–LDPE1 and VLDPE1–LDPE2 blends showed only one crystallization and melting peak, which changed smoothly as the composition varied, and this indicated the presence of only one crystal morphology for all compositions. The composition dependence with T_m for all the blend sets is plotted in Figure 5. A gradual change in T_m with the VLDPE1 composition can be clearly seen in Figure 5 for the VLDPE1–LDPE and VLDPE1–LDPE2 blends. This indicates that there was cocrystallization between the polymers, and so these blends were consistent with a single-component system. Additionally, the miscibility studies conducted for the fractionated blends prepared by a thermal fractionation technique in a DSC instrument gave the same results, and this suggested complete or partial miscibility at all compositions.⁴⁰

The VLDPE1–VLDPE2 blends showed different behavior, but a broad, single melting and crystallization peak was observed in the DSC curves.³¹ No change in T_m was observed for blends containing high VLDPE2

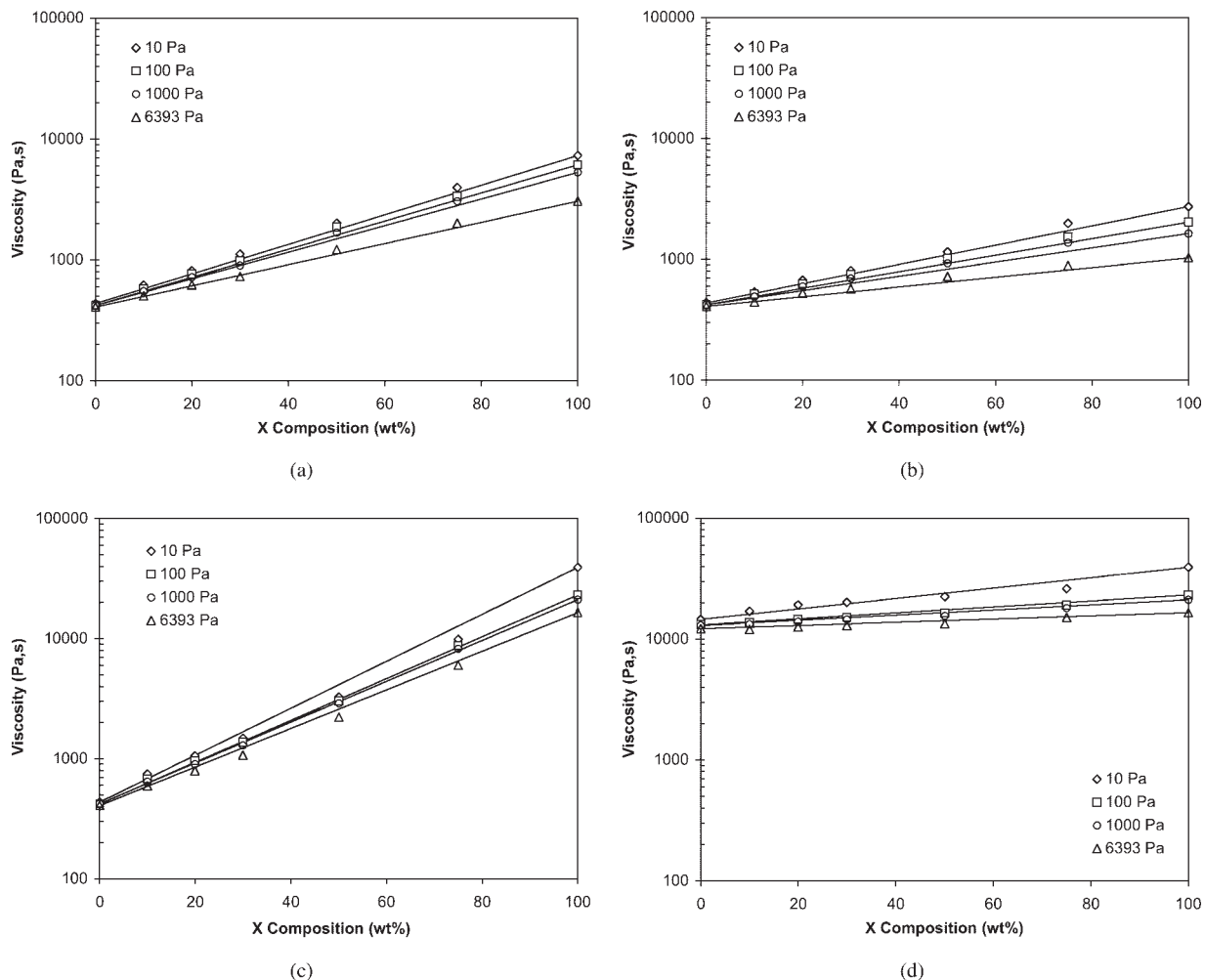


Figure 4 Melt viscosity versus the blend composition for (a) VLDPE1–LDPE1, (b) VLDPE1–LDPE2, (c) VLDPE1–VLDPE2, and (d) VLDPE3–VLDPE2 blends at τ values of 10, 100, 1000, and 6393 Pa. The X composition indicates the second component.

contents, whereas a decrease in T_m was noticed with 50% or less VLDPE2; this indicated that the blends could cocrystallize only at these compositions. Conversely, the T_m changes shown in Figure 5 for VLDPE3–VLDPE2 blends demonstrated changes only for compositions with more than 50% VLDPE2, and this suggested some cocrystallization for these compositions. In addition, this behavior was observed for rapidly cooled samples.⁴¹ Quenched and cooled samples are expected to preserve the melt structure because phase separation is favored during slow cooling. Thus, the thermal data, in conjunction with our previous studies,^{31,40} implied some cocrystallization and, therefore, some melt miscibility for all the blends. However, the extent of cocrystallization and melt miscibility was different, as discussed previously, for each blend set. These data agreed with the rheological measurements.

CONCLUSIONS

Rheological and thermal measurements of VLDPE1–LDPE1, VLDPE1–LDPE2, VLDPE1–VLDPE2, and

VLDPE2–VLDPE3 binary blends were performed. LDPE1, LDPE2, and VLDPE2 had some LCB, and VLDPE1 and VLDPE3 had only short-chain branches. The shear flow of all blends obeyed the power law. It was observed by n that a shear-thinning effect became stronger as the long-chain-branched polymer composition increased, and the extent of shear thinning was different for each blend set. A stronger shear-thinning effect and a linear composition dependence of η_0 were observed for the VLDPE1–LDPE1 and VLDPE1–LDPE2 blends. These blends followed the log additivity rule, and this indicated that they were miscible in the melt at all compositions. In contrast, a deviation from the log additivity rule was observed for VLDPE1–VLDPE2 blend compositions with 50% or less VLDPE2 and for VLDPE3–VLDPE2 blends with 50% or more VLDPE2. The thermal properties of the blends were consistent with the rheological properties. VLDPE1–LDPE1 and VLDPE1–LDPE2 were consistent with single-component systems at all compositions, whereas phase separation (immiscibility) was detected only for VLDPE1–VLDPE2 blends with 50%

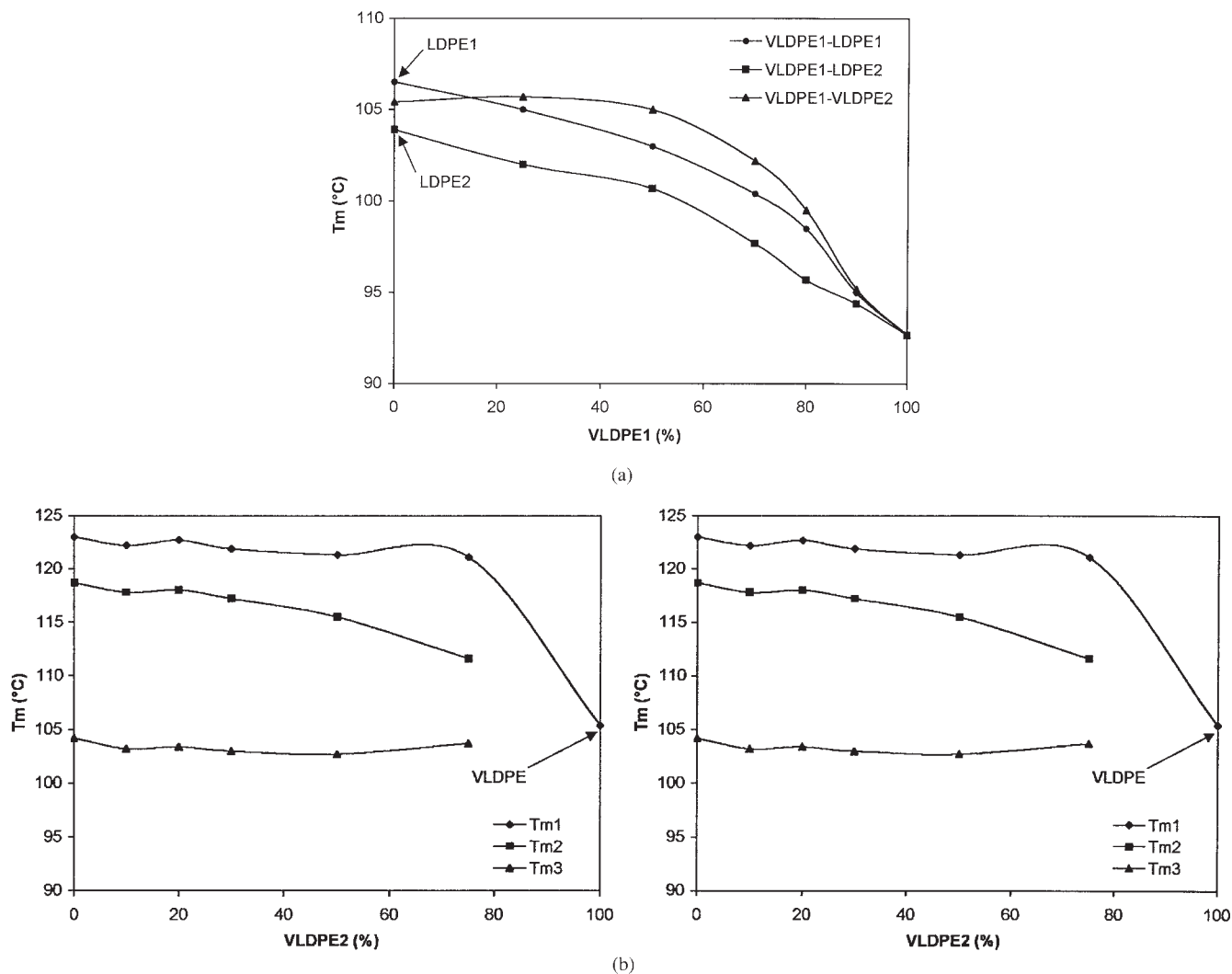


Figure 5 Composition dependence of T_m of the blends: (a) the change in T_m of LDPE1, LDPE2, and VLDPE2 for the VLDPE1-LDPE1, VLDPE1-LDPE2 and VLDPE1-VLDPE2 blends and (b) the change in three T_m 's of VLDPE3 in the VLDPE2-VLDPE3 blend. T_{m1} represents the highest melting peak temperature (the lines are not model fits; they have been drawn to guide the eye).

or less VLDPE2 and for VLDPE3-VLDPE2 blends with 50% or more VLDPE2. Finally, the results showed that the addition of LDPE to m-PE with no LCB and the addition of m-PE with a low amount of LCB to PEs with no LCB increased the shear-thinning behavior and provided better processability at high $\dot{\gamma}$ values.

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