

Miscibility Behavior of Metallocene Polyethylene Blends

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ABSTRACT: Very-low-density polyethylenes (VLDPEs) with short branches, formed by metallocene or Ziegler–Natta catalysts, were blended with low-density polyethylenes (LDPEs) or VLDPEs with long branches. The crystallization and melting behavior of these blends were examined by differential scanning calorimetry (DSC). The blends of metallocene-catalyzed VLDPE1 and LDPEs showed a smooth change in both crystallization and melting peak temperatures, indicating that there was co-crystallization and, hence, partial miscibility at all compositions. However, the blends of VLDPE1 and long-chain branched VLDPE2 co-crystallized at 50% or less VLDPE2 content, whereas Ziegler–Natta-catalyzed VLDPE3–VLDPE2 blends showed co-crystallization at 50% or higher VLDPE2 compositions. It is concluded that either complete or partial miscibility has occurred between the two polyethylenes in each of the blends with VLDPE2. Nevertheless, VLDPE2 did not cause a significant change in the morphology of VLDPE1, perhaps because of the reduced number of long branches present in VLDPE2 compared with LDPEs. The molar masses or melt flow indices of the polyethylenes were not significant in controlling the morphology; only the distribution of branches along the chains was important. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2227–2236, 2001

Key words: co-crystallization; long branches; morphology; polyethylene blends; single-site catalyst

INTRODUCTION

Long-chain branching is an important structural parameter in processing of polymers because the polyethylenes with long-chain branches have good melt properties and therefore efficient processability.¹ Low-density polyethylene (LDPE) is a polymer with both long- and short-chain branches and is often blended with linear low-density polyethylenes (LLDPE) to achieve a balance of processing properties of LLDPE films. LLDPE, by itself, provides superior mechanical and thermal properties for these films,² but poor

melt properties that cause processing difficulties.^{3,4} Therefore, it is believed that the long-chain branches present in LDPE give better melt strength to these films by increasing the extensional strain characteristics of the melt. Speed has shown that the processing behavior of blown LLDPE films can be significantly improved by addition of up to 30% (w/w) LDPE.⁵ In addition the blending of LDPE into LLDPE is also found to improve the optimal properties of LLDPE films.^{6,7}

LLDPEs melt at higher temperatures [typically, the temperature of melting (T_m) = 125 °C] than LDPEs (typically T_m = 110 °C), though LLDPEs have a very broad melting range.^{8,9} The densities of LLDPEs are generally in the range of 0.91 to 0.93 g cm⁻³. The polyethylenes that have densities between 0.89 and 0.91 g cm⁻³ are called very-low-density polyethylenes (VLDPE) and those with den-

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sities of 0.89 g cm^{-3} and below are called ultra-low-density polyethylenes (ULDPE).¹⁰

Recently, a group of new polyethylenes has been introduced into the market. They are mainly produced by metallocene or single-site catalysts and are shown to have superior properties compared with conventional polyethylenes. Because of the single-site nature of the catalysts, they have a narrower molecular weight distribution and a more uniform distribution of co-monomers than conventional LLDPEs.^{11,12} The metallocene- or single-site-catalyzed grade LLDPEs have been made with short branches¹³ as well as with some long branches.^{12,14,15} The co-monomer distribution of short-chain branched LLDPEs may coincide with those of LDPEs because the short branches relate to both of these polymers. On the other hand, LLDPEs containing both short- and long-chain branches offer the opportunity to prepare blends between polyethylenes with similar short-chain branch content and distribution, while introducing the long branches. Therefore, the blends of long-chain branched LLDPEs may become important as they are for LDPEs.^{16,17} These polymers also exhibit properties similar to those of LDPEs, despite the lower amount of long-chain branches present in long-branched LLDPEs.

Generally, the properties of blends are determined by the morphologies present in the blends, and extensive studies have been carried out on the crystallization and morphology of Ziegler–Natta-catalyzed LLDPE and LDPE blends. The blend of LLDPE and LDPE is not a simple mixture, and the two polyethylenes are not necessarily miscible, even in the melt. They are shown to have biphasic morphology at all compositions, even after different thermal treatments,¹⁸ and to exhibit an upper critical solution temperature phase diagram.¹⁹ The small differences in the branching between polyethylenes result in liquid–liquid phase separation, and the blends are more miscible only when the branch contents are similar.²⁰

The crystallization and morphology of blends of metallocene- or single-site-catalyzed polyethylenes have also been studied.^{21–35} Hill et al.²¹ studied the phase behavior of lightly branched metallocene polyethylene (m-PE) blends. The m-PE–LDPE blends containing low LDPE contents show liquid–liquid phase separation at medium temperatures ($125\text{--}170 \text{ }^\circ\text{C}$), whereas they are homogeneous in the high and low temperature range. Furthermore, the phase behavior of these

blends was similar to that of conventional copolymer blends with similar branch content. The crystallization behavior of blends of metallocene- or single-site-catalyzed polyethylenes and high-density polyethylenes (HDPE) has been investigated by several researchers^{22–28} and it was found that crystallization behavior was strongly dependent on the content and distribution of branching of m-PE. Blends, prepared with m-PE containing low octene co-monomer contents ($<2.0 \text{ mol}\%$), were miscible at all compositions, whereas a nonmiscible domain was observed for blends of higher co-monomer contents.^{23,28} Lee et al. also reported that similar branched m-PE and HDPE were miscible only at a composition of 20% and Ziegler–Natta-catalyzed LLDPE–HDPE blends gave better miscibility than blends of metallocene-catalyzed LLDPE and HDPE because of the heterogeneity in co-monomer distribution of Ziegler–Natta-catalyzed LLDPE.^{24–26} However, the morphology of blends is markedly dependent on the crystallization conditions, and there is a controversy over the miscibility of polyethylene blends at all concentrations.

In the present work, polyethylene blends containing different branching densities and branch lengths were studied. In particular, VLDPEs with short-chain branches, formed by metallocene or Ziegler–Natta catalysts, have been blended with film-grade LDPEs or long-chain branched VLDPE. The melting and crystallization behaviors of blends in relation to miscibility and morphology were investigated by differential scanning calorimetry (DSC).

EXPERIMENTAL

All materials used in this study are commercially available and the properties of these polymers are given in Table I. 1-Butene, 1-octene copolymers, and LDPEs were supplied by Kemcor Australia Ltd., Dow Plastics, and Orica Pty Ltd., respectively. To investigate the effect of different branch density and branch length on morphology, the following four sets of blends were prepared (VLDPE1–LDPE1, VLDPE1–LDPE2, VLDPE1–VLDPE2, and VLDPE3–VLDPE2). In these four systems, all first components (VLDPE1 and VLDPE3) have only short-chain branches, whereas all second components (LDPE1, LDPE2, and VLDPE2) have both short- and long-chain branches.

Table I Properties of Polymers Used in This Study^a

Property	VLDPE1	VLDPE2	VLDPE3	LDPE1	LDPE2
Co-monomer	Butene	Octene	Octene	—	—
Catalyst type ^b	M	S	ZN	Autoclave	Autoclave
MFI (dg min ⁻¹)	27.0	1.0	1.0	7.0	20.0
Density (g cm ⁻³)	0.901	0.908	0.912	0.919	0.918
M_w/M_n	2.65 ^c	2.0 ^d	3.8 ^d	—	—
Co-monomer content (mol %)	6.3 ^e	9.5	12.9 ^f	—	—

^a All data were taken from chemical data sheets published by the manufacture.

^b ZN = Ziegler–Natta catalyst, S = constrained geometry single-site catalyst, and M = metallocene.

^c Ref. 42.

^d Ref. 38.

^e Ref. 28.

^f Ref. 41.

Preparation of Blends

The blends were prepared by melt mixing the polymers in an Axon BX-12 single-screw extruder (Axon Australia Pty. Ltd.) with a Gateway screw of diameter 12.5 mm and length:diameter ratio of 26:1. The temperature profile was 140, 195, 200–170°C, for feeding, compression, metering and die-end zone, respectively. The screw speed was 60 rpm. The hot strands were quenched in room temperature water, dried, and finally granulated. Blends were mixed in various proportions, that is, 10, 20, 30, 50, and 75% (by weight).

Differential Scanning Calorimetry

A Perkin Elmer Series DSC7 calorimeter, purged with nitrogen (15 mL min⁻¹), was used to study the thermal behavior of pure polymers and blends. Measurements were made on approximately the same sample masses (3–4 mg), which were sealed in aluminum pans. All samples were held in the melt at 180°C for 5 min to eliminate any effects of previous thermal memory before cooling. Samples were then cooled from 180 to 10°C and again heated to 180°C. A cooling and heating rate of 10 °C min⁻¹ was used. The melting temperature (T_m), crystallization temperature (T_c), heat of fusion (ΔH_m), and the heat of crystallization (ΔH_c) of pure polymers and blends were measured. A baseline scan was performed with an empty pan. The calorimeter was calibrated for temperature and heat flow using indium as a standard.

Data Analysis

The excess heat of fusion (ΔH_f^e) was calculated from

$$\Delta H_f^e = \Delta H_{f,\text{exp}} - \sum X_i \cdot \Delta H_{f,i} \quad (1)$$

where X_i is the weight fraction of component i ($i = 1, 2$); $\Delta H_{f,\text{exp}}$ and $\Delta H_{f,i}$ are measured heats of fusion for the blends and pure polymers, respectively.³⁶

RESULTS AND DISCUSSION

VLDPE1–LDPE Blends

Specific heat crystallization and melting curves for the blends of VLDPE1–LDPE1 and pure polymers are shown in Figures 1 and 2, respectively, and the corresponding crystallization and melting temperature values are listed in Table II. The crystallization curves show single exotherm, which shifts to lower temperatures with increasing VLDPE1 content. The melting endotherms are rather complex with up to three peaks present in most of the blends, with the highest peak corresponding to the melting of LDPE1. Also, a melting temperature depression is observed with decreasing LDPE1 content in all blends. The blends, except the 25:75 blend, show a shoulder on the higher temperature side of the main peak, at a temperature that increases with increasing LDPE1 content. In addition, there is a broad peak on the low temperature side of the main peak whose temperature increases with increasing LDPE1 composition. The smooth increase in peak temperatures from VLDPE1 to LDPE1 suggests that there may be some co-crystallization in the blends. The increase in melting temperature of co-crystallites with increasing LDPE1 amount could be because the co-crystallites thickness increases when the LDPE1 content is increased.

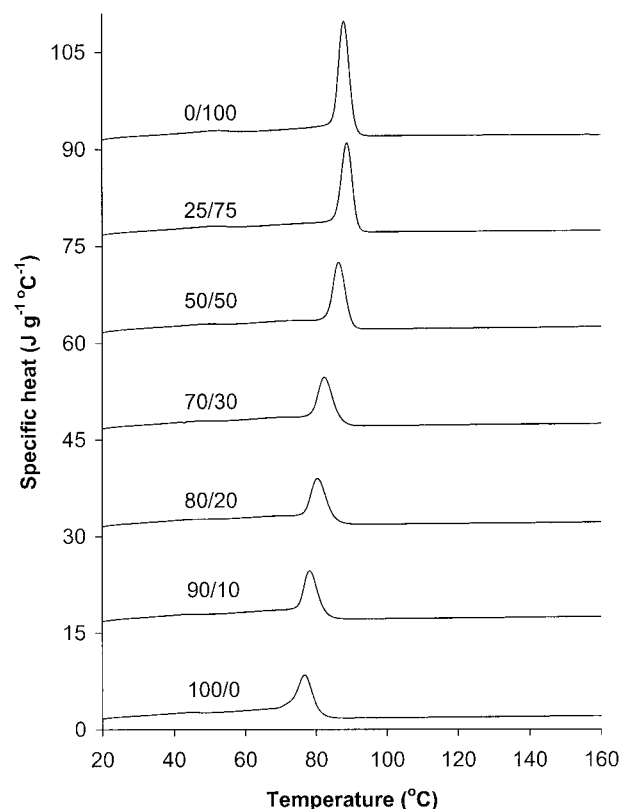


Figure 1 DSC specific heat crystallization curves for VLDPE1-LDPE1 blends and the pure polymers. An adapted scale is drawn by adding 15 units to the each curve. The first number of the ratio indicates the VLDPE1 amount.

Furthermore, the formation of a higher temperature shoulder peak at 50% or less LDPE1 content suggests that the LDPE1 has limited ability to form one co-crystallized phase. Thus, these blends show morphologies that are indicative of crystallization from a mixed melt, and these results are in agreement with the data reported by Hill and co-workers²¹ on a similar type of VLDPE1-LDPE blend system.

A similar behavior is also found from the analysis of crystallization and melting curves of VLDPE1-LDPE2 blends (Figures 3 and 4 and Table III), and these results suggest that long-chain branches could be introduced into short chain-branched VLDPE1 by blending with LDPEs. LDPE2 has a higher melt flow index (MFI, 20 dg min⁻¹) so there is a small difference in the average molar mass of the polyethylenes in VLDPE1-LDPE2 blends compared with the blends containing LDPE1, which has very low MFI (1 dg min⁻¹). Because both types of blends exhibit similar morphologies, the molar masses

and melt viscosity differences seem to be unimportant in controlling the morphology of these blends.

VLDPE1 Blends with Long-Chain Branched VLDPE2

VLDPE2 has been produced by the Dow constrained geometry catalyst technology (CGCT).¹⁴ This polyolefin plastomer differs from VLDPE1 in the type of co-monomer and the incorporation of long-chain branches on the polymer backbone.¹⁵ It is expected to have a more controlled distribution of short-chain branches as well as long-chain branches because of the single-site nature of the catalyst used. VLDPE2 shows a much broader exotherm (Figure 5, top curve) compared with LDPEs, which also contains short-chain as well as long-chain branches.

The specific heat crystallization curves of blends of VLDPE1-VLDPE2 (Figure 5) show a single exotherm for all blends. A shoulder peak on

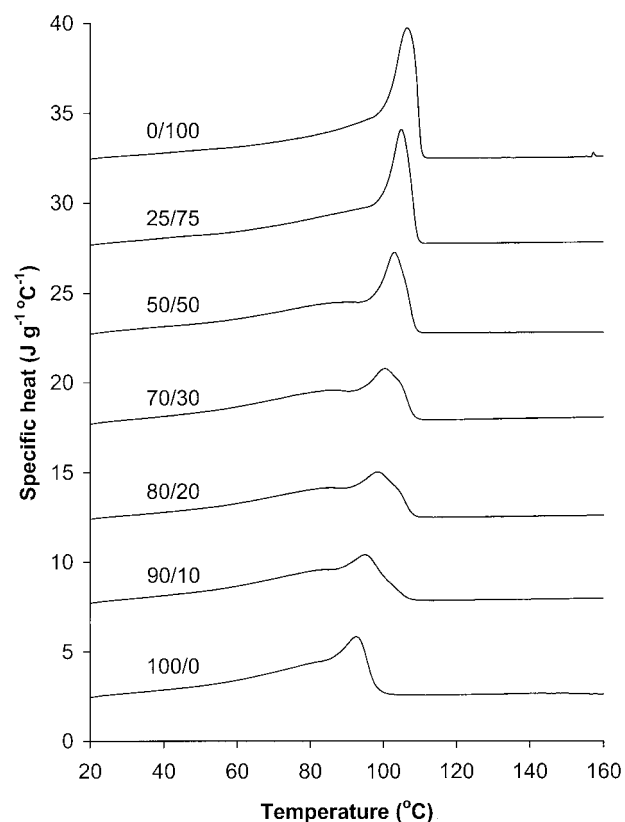


Figure 2 DSC specific heat melting curves for VLDPE1-LDPE1 blends and the pure polymers. An adapted scale is drawn by adding 5 units to the each curve. The first number of the ratio indicates the VLDPE1 amount.

Table II Crystallization and Melting Characteristics of VLDPE1-LDPE1 Blends and Pure Polymers

Composition	Crystallization ^a					Melting			
	T_{c1} (°C)	ΔH_c (J g ⁻¹)	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	T_{m1} Onset (°C)	ΔH_m (J g ⁻¹)	Calculated ΔH (J g ⁻¹)	ΔH_f^e (J g ⁻¹)
VLDPE1-LDPE1									
0/100	87.8	118.2	106.5	—	—	99.1	118.8	118.8	0.0
25/75	88.8	112.0	105.0	93.5	—	98.4	112.6	111.1	1.5
50/50	86.3	105.2	103.0	90.3	106.1	95.3	105.4	103.5	1.9
70/30	82.3	95.7	100.4	86.2	104.7	88.6	96.2	97.3	-1.1
80/20	80.3	94.5	98.5	85.8	104.2	82.1	94.7	94.3	0.4
90/10	78.0	86.7	95.0	84.2	102.2	76.0	87.2	91.2	-4.0
100/0	76.6	87.3	92.7	79.6	—	78.2	88.1	88.1	0.0

^a A shoulder at low temperature.

the low temperature side of the main peak is also seen for the blends containing 20–50% VLDPE2. The corresponding melting curves, Figure 6, again display three melting peaks in most blends; a broad lower temperature peak and a sharper

main melting peak with a shoulder on its higher temperature side. The peak on the lower temperature side of the main peak is much more apparent in these blends compared with those of the VLDPE1-LDPE blends. In particular, when the

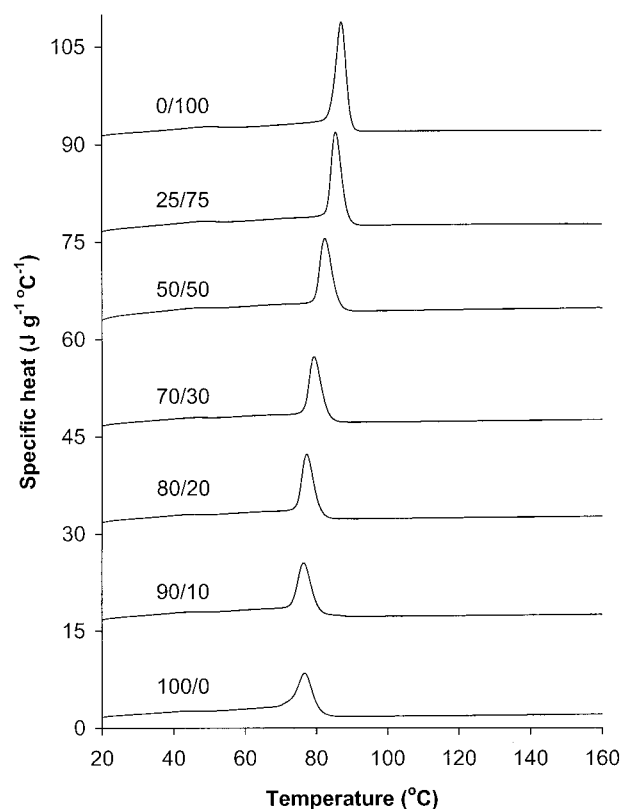


Figure 3 DSC specific heat crystallization curves for VLDPE1-LDPE2 blends and the pure polymers. An adapted scale is drawn by adding 15 units to the each curve. The first number of the ratio indicates the VLDPE1 amount.

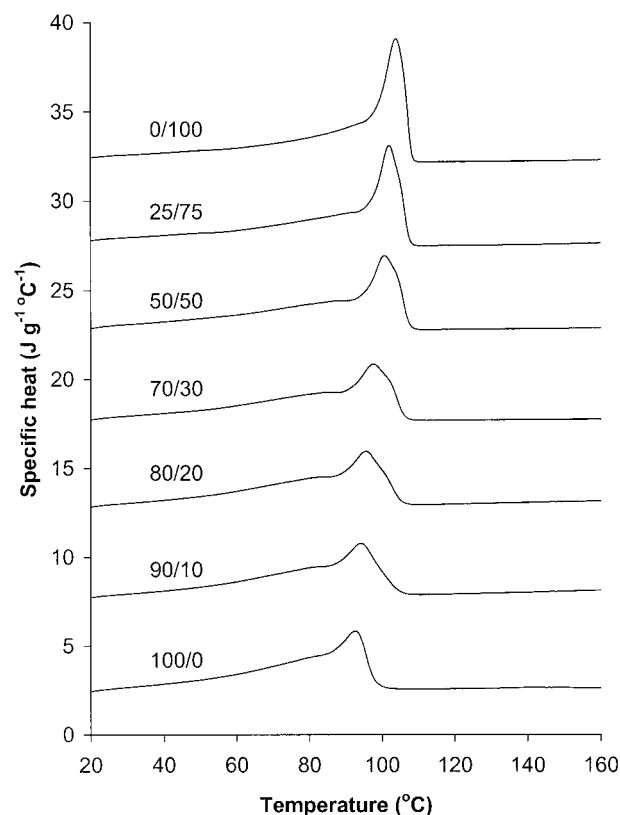


Figure 4 DSC specific heat melting curves for VLDPE1-LDPE2 blends and the pure polymers. An adapted scale is drawn by adding 5 units to the each curve. The first number of the ratio indicates the VLDPE1 amount.

Table III Crystallization and Melting Characteristics of VLDPE1-LDPE2 Blends and Pure Polymers

Composition	Crystallisation ^a		Melting						
	T_{c1} (°C)	ΔH_c (J g ⁻¹)	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	$T_{m1\text{ onset}}$ (°C)	ΔH_m (J g ⁻¹)	Calculated ΔH (J g ⁻¹)	ΔH_f^e (J g ⁻¹)
VLDPE1-LDPE2									
0/100	87.1	114.4	103.9	—	—	96.8	116.5	116.5	0.0
25/75	85.5	104.1	102.0	91.5	105.5	95.5	110.8	109.4	1.4
50/50	82.5	98.7	100.7	88.7	104.2	92.7	101.1	102.3	-1.2
70/30	79.3	89.9	97.7	85.6	101.8	86.9	91.1	96.6	-5.5
80/20	77.1	88.0	95.7	83.9	100.5	83.5	89.5	93.8	-4.3
90/10	76.3	87.5	94.4	82.7	—	80.5	88.1	91.0	-2.9
100/0	76.6	87.3	92.7	79.6	—	78.2	88.1	88.1	0.0

^a A shoulder at low temperature.

VLDPE2 content is 20%, the height of both the broad lower temperature peak and the main melting peak is almost the same. This result suggests that when small amounts of VLDPE2 (<50%) are blended with VLDPE1, some sequences of com-

mon length of VLDPE1 and VLDPE2 co-crystallize. In addition, blends of <50% VLDPE2 show an increase in the main melting peak and the broad peak temperatures as VLDPE2 content is raised. The increase in the main melting peak is

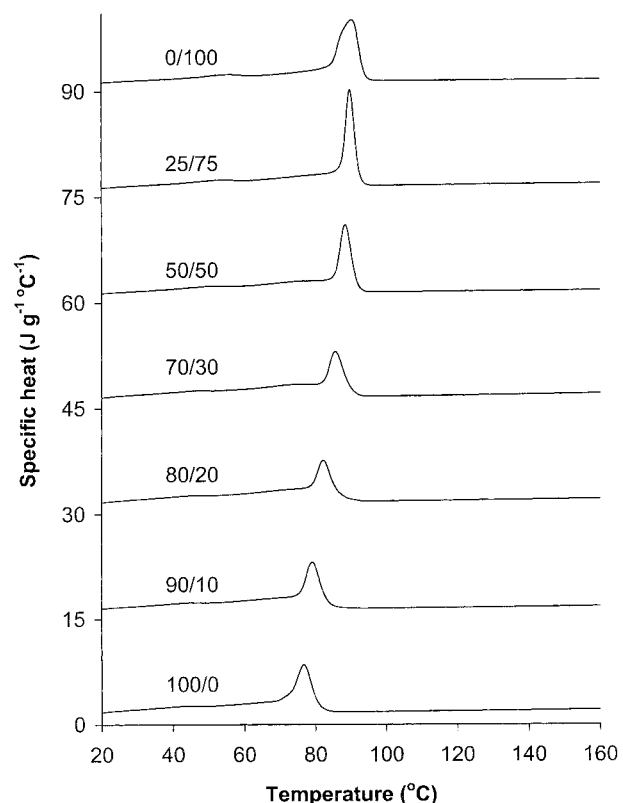


Figure 5 DSC specific heat crystallization curves for blends of VLDPE1 and long-chain branched VLDPE2 and the pure polymers. An adapted scale is drawn by adding 15 units to the each curve. The first number of the ratio indicates the VLDPE1 amount.

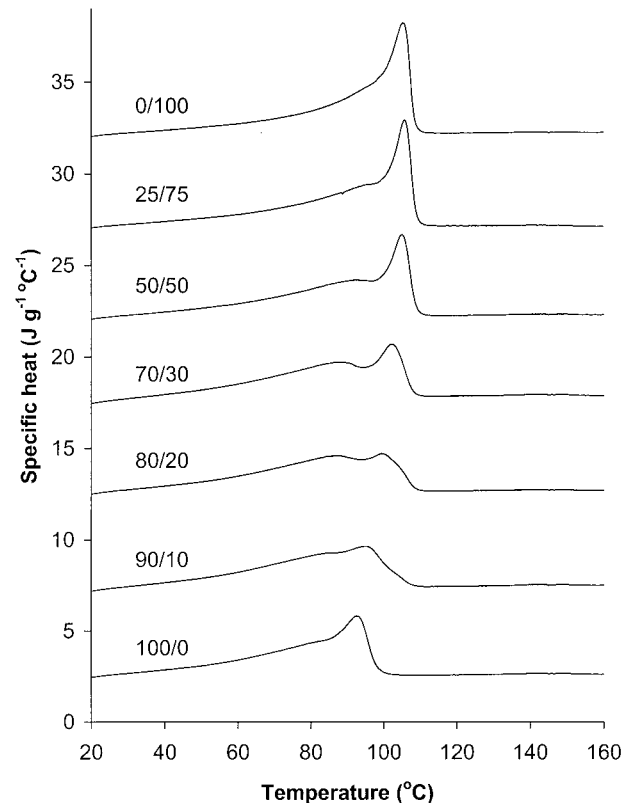


Figure 6 DSC specific heat melting curves for blends of VLDPE1 and long-chain branched VLDPE2 and the pure polymers. An adapted scale is drawn by adding 5 units to the each curve. The first number of the ratio indicates the VLDPE1 amount.

an indication of co-crystallization. Nevertheless, separate crystallization is observed for the blends containing $\geq 50\%$ VLDPE2 content. The approximately constant main melting peak that is associated with melting of the crystalline phase formed by pure VLDPE2 indicates that these blends crystallized separately. Schellenberg et al. also noticed the phase separation of HDPE-VLDPE2 blends of $\geq 50\%$ weight concentrations.²³

These results imply that it is more difficult for long-chain branches in VLDPE2 to be introduced into VLDPE1 by blending with VLDPE2 compared with the blends of VLDPE1 and LDPEs. This result could be because of the different molecular structures between VLDPE2 and LDPEs, where the longer segments between branches in LDPEs more easily form co-crystals with VLDPE1 because the distribution of branches in the LDPE is more heterogeneous. Conversely, because of the more uniform distribution of branches, absence of longer interbranch segments in the molecular chains, and low amount of long-chain branches present in VLDPE2, the co-crystallization between VLDPE1 and VLDPE2 might be difficult. Thus, it can be concluded that the miscibility of these metallocene- or single-site-catalyzed polyethylene blends not only depends on the blend composition but also on the distribution of branches in the polyethylene with long-chain branches. Similar results have been found for the blends of HDPE and LLDPE, which are produced by single-site catalysts.^{22, 23, 28} Moreover, because the MFI of VLDPE1 and VLDPE2 are 27 and 1 dg min⁻¹, respectively, there is a large difference in the average molar mass of the polyethylenes in the blends. However, the crystallization temperatures of these blends are not significantly different from those of the VLDPE1-LDPE blends.

VLDPE3 Blends With Long Chain-Branched VLDPE2

The crystallization and melting curves of VLDPE3-VLDPE2 blends are shown in Figures 7 and 8, respectively. VLDPE3 is a Ziegler-Natta-catalyzed ethylene-octene copolymer produced by conventional LLDPE catalyst technology.³⁷ VLDPE3 has only short-chain branches and both VLDPE3 and VLDPE2 have the same MFI (1.0 dg min⁻¹). When the VLDPE2 content is below 50%, the crystallization peak temperatures are unchanged. However, the crystallization peak temperatures show a decrease for the blends contain-

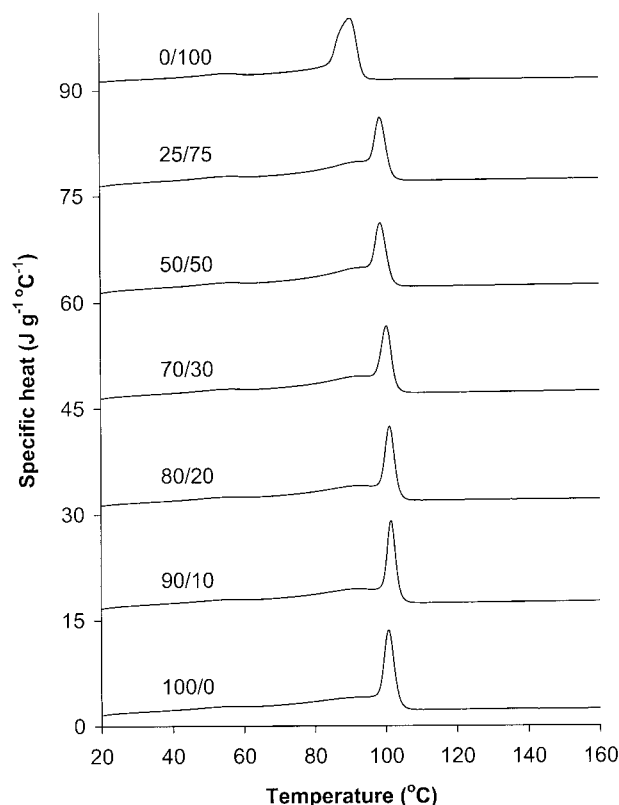


Figure 7 DSC specific heat crystallization curves for blends of VLDPE3 and long-chain branched VLDPE2 and the pure polymers. An adapted scale is drawn by adding 15 units to the each curve. The first number of the ratio indicates the VLDPE3 amount.

ing $\geq 50\%$ VLDPE2. These results suggest that two polymers may have crystallized independently when the VLDPE2 content is $< 50\%$ and co-crystallized when VLDPE2 content is $\geq 50\%$.

The pure VLDPE3 exhibits a triple exotherm, and it has been proposed that the phenomenon of multiple melting peaks is due to either the melting of α , β , γ crystalline phases or the melting and reorganization of a single crystalline phase.^{38, 39} As seen previously for VLDPE1-VLDPE2 blends, there are also three melting peaks in the VLDPE3-VLDPE2 blends. The highest melting peak temperatures are unchanged, apart from a dilution effect, as the proportion of the branched VLDPE2 is increased. The broad lower temperature peak is almost the same as the melting peak temperatures of the two pure polymers (T_{m3} of VLDPE2 and T_{m3} of VLDPE3). However, when the VLDPE2 content is $\geq 50\%$, the middle melting peak temperature (T_{m2}) shifts toward lower temperatures. When the VLDPE2 content is $< 50\%$, the values of T_{m2} are almost the same. The same

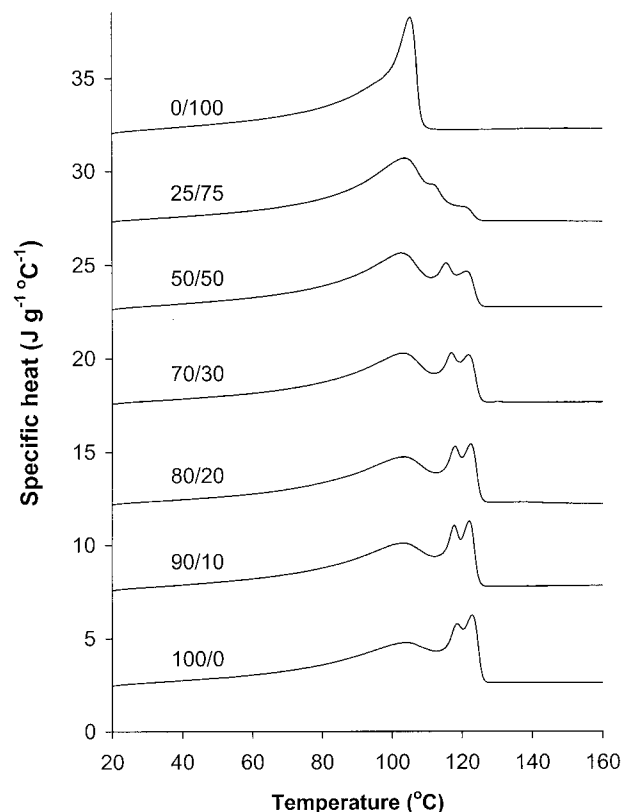


Figure 8 DSC specific heat melting curves for blends of VLDPE3 and long-chain branched VLDPE2 and the pure polymers. An adapted scale is drawn by adding 5 units to the each curve. The first number of the ratio indicates the VLDPE3 amount.

trend is also seen in the crystallization temperatures. These results indicate that a part of the blends of VLDPE3-VLDPE2 co-crystallize only at $\geq 50\%$ VLDPE2. This result has also been ob-

served in similar types of blends containing VLDPE2.⁴⁰

An attempt was made to better understand the thermal behavior of these blends by obtaining excess heat of fusion values (ΔH_f^e). The ΔH_f^e values were calculated using the eq.1,³⁶ and the values are given in Tables II–V. The ΔH_f^e values show insignificant deviation for all blends at all compositions, indicating that the one polymer in a blend did not prevent or enhance crystallization of the other polymer in a blend.

The onset crystallization temperatures (T_o) as a function of the blend composition are given in Figure 9. The T_o values represent the crystallization rate of the fastest crystallizing component in the blends. All curves show a deviation of the linearity, indicating the involvement of different crystallization mechanisms during the cooling process. A significant variation of T_o with the composition is observed for all VLDPE1–LDPE blends, confirming that co-crystallization had been taken place between these blends and therefore, the two polymers are either partially or completely miscible. For the VLDPE1–VLDPE2 blends with $\geq 50\%$ VLDPE2, an almost constant T_o is observed, whereas for $< 50\%$ VLDPE2 blends, the T_o decreases dramatically, approaching that of the pure VLDPE1. The opposite trend is found in the VLDPE3–VLDPE2 blends. Therefore, the co-crystallization began to occur, when VLDPE2 was $< 50\%$ in the VLDPE1–VLDPE2 blends, whereas the blends with $\geq 50\%$ VLDPE2 were co-crystallized in VLDPE3–VLDPE2 blends. The miscibility of long-chain branched VLDPE2 blends is thus composition dependent, and they can be either completely immiscible or partially

Table IV Crystallization and Melting Characteristics of VLDPE1–VLDPE2 Blends and Pure Polymers

Composition	Crystallization ^a			Melting						
	T_{c1} (°C)	T_{c2} (°C)	ΔH_c (J g ⁻¹)	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	$T_{m1 \text{ onset}}$ (°C)	ΔH_m (J g ⁻¹)	Calculated ΔH (J g ⁻¹)	ΔH_f^e (J g ⁻¹)
0/100	90.3	—	101.5	105.4	—	—	96.3	103.6	103.6	0.0
25/75	89.8	—	99.1	105.7	95.2	—	98.8	101.6	99.7	1.9
50/50	88.5	78.3	99.0	105.0	92.8	—	97.3	101.2	95.9	5.3
70/30	85.6	75.6	96.0	102.2	88.0	105.2	91.6	97.8	92.8	5.0
80/20	82.1	71.7	94.1	99.5	87.1	103.9	77.7	94.2	91.2	3.0
90/10	79.0	—	90.4	95.2	84.2	101.7	62.1	92.4	89.7	2.7
100/0	76.6	—	87.3	92.7	79.6	—	78.2	88.1	88.1	0.0

^a A shoulder at low temperature.

Table V Crystallization and Melting Characteristics of VLDPE3-VLDPE2 Blends and Pure Polymers

Composition	Crystallization ^a			Melting						
	T_{c1} (°C)	T_{c2} (°C)	ΔH_c (J g ⁻¹)	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	$T_{m1 \text{ onset}}$ (°C)	ΔH_m (J g ⁻¹)	Calculated ΔH (J g ⁻¹)	ΔH_f^e (J g ⁻¹)
VLDPE3-VLDPE2										
0/100	90.3	—	101.5	—	—	105.4	96.3	103.6	103.6	0.0
25/75	94.8	—	103.7	121.1	111.6	103.7	78.6	104.0	105.3	-1.3
50/50	98.6	92.5	102.2	121.3	115.5	102.7	77.1	102.3	107.6	-5.3
70/30	100.1	92.7	106.0	121.9	117.2	103.0	111.1	107.5	109.5	-2.0
80/20	100.8	92.5	103.1	122.7	118.0	103.4	112.6	104.3	110.4	-6.1
90/10	101.3	92.4	106.4	122.2	117.8	103.2	113.1	106.6	111.3	-4.7
100/0	100.5	92.2	109.2	123.0	118.7	104.2	112.6	112.2	112.2	0.0

^a A shoulder at low temperature.

miscible. It can also be seen from these data that the crystallization would have occurred far from equilibrium, probably because of the effects of the different content of long-chain branches in the blend systems. Further morphological investigations will be carried out using microscopic techniques such as scanning electron microscopy (SEM).

CONCLUSIONS

The thermal analysis of blends of VLDPE1 or VLDPE3 with short-chain branches and LDPEs or VLDPE2 with long-chain branches has shown that

there is co-crystallization between the two polyethylenes in most blends. Both the VLDPE1-LDPE1 and VLDPE1-LDPE2 blends showed a smooth change in both crystallization and melting peak temperatures, indicating that there may be a co-crystallization and hence miscibility at all compositions. The presence of similar morphologies of these LDPE blends also indicates that the molar masses or melt flow indices are not significant in controlling the morphology. However, the blends of VLDPE1 and long-chain branched VLDPE2 were co-crystallized at $\leq 50\%$ VLDPE2 content, whereas Ziegler-Natta-catalyzed VLDPE3-VLDPE2 blends showed the co-crystallization at $\geq 50\%$ VLDPE2 compositions. The long-chain branches present in VLDPE2 are relatively few in number compared with LDPEs and, therefore, VLDPE2 does not cause a significant effect on the morphology of VLDPE1. However, the long-chain branches in VLDPE2 are expected to contribute more to the rheologic characteristics than the morphology.

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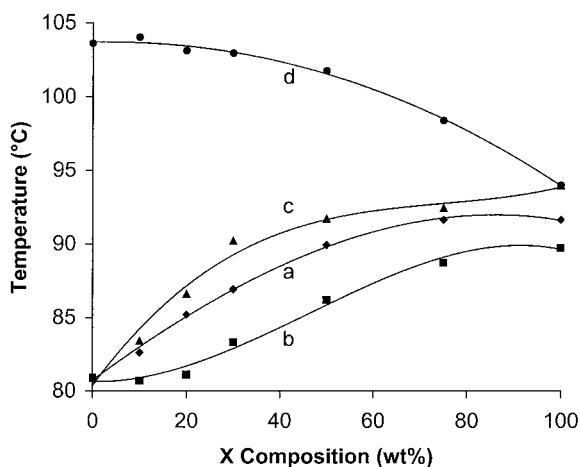


Figure 9 The plots of onset crystallization temperature (T_o) versus blend composition: (a) VLDPE1-LDPE1; (b) VLDPE1-LDPE2; (c) VLDPE1-VLDPE2; and (d) VLDPE3-VLDPE2. The symbol X indicates LDPE1, LDPE2, and long-chain branched VLDPE2 compositions.

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