Polymer 42 (2001) 3867–3874

polymer

www.elsevier.nl/locate/polymer

Effect of composition distribution on miscibility and co-crystallization phenomena in the blends of low density polyethylene with conventional and metallocene-based ethylene–butene copolymers

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Received 27 June 2000; received in revised form 15 August 2000; accepted 19 September 2000

Abstract

Three ethylene–butene copolymers (two metallocene-based and one conventional) having different composition distributions were blended with low density polyethylene (LDPE) in a wide proportion range. The miscibility of the blend melts was studied with the rheological method. It is found that zero-shear viscosity of all the blends does not obey the logarithmic additivity rule, indicating the immiscible state of the blend melts. The blends were rapidly quenched from the melts and co-crystallization phenomena were investigated by differential scanning calorimetry (DSC). The obtained results show that composition distribution has a great influence on co-crystallization. In the blends of the conventional ethylene–butene copolymer, which has a broad composition distribution, part of the co-crystals may segregate from the crystals of both LDPE and ethylene copolymer and exist as a separated population. This suggests that there exist three phases in the melts. In contrast, the blends of the metallocene-based ethylene–butene copolymers with a narrow composition distribution are only composed of two phases together with some exchange between the two components. It is also observed that broader composition distribution leads to more ethylene–butene copolymer transferred into LDPE. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Composition distribution; Miscibility; Co-crystallization

1. Introduction

Co-crystallization phenomenon is frequently observed in the blends of different types of polyethylene [1–9]. It is believed that co-crystallization is produced due to the thermodynamically miscible parts of two components in the blends having similar crystallization rate [10–12]. This means that the miscibility of the components in melt plays an important role in the co-crystallization phenomenon, though it is a kinetic process. The miscibility of the blend melt and the crystallization rate strongly depend on the molecular structure of the polymers such as branch content, molecular shape and molecular weight [13–18]. Among these factors, the branch content of ethylene copolymers may be the most important one. As a result, when one of the components is composed of a series of fractions with different branch contents, i.e. the intermolecular composition distribution is inhomogeneous, the composition distribution may have a great influence on co-crystallization [19,20]. In fact, the ethylene/α-olefin copolymers produced with Ziegler–Natta catalysts generally have a broad composition distribution [21], even though the structure of the copolymers from metallocene catalysts is also not very homogeneous [22,23]. Tashiro et al. observed different co-crystallization degrees in the blends of high density polyethylene (HDPE) with two linear low density polyethylene (LLDPE) samples (LLDPE1 and LLDPE2) having a close composition [16]. No explanation was given for this phenomenon. However, it could be seen from this paper that these two LLDPE samples were prepared by two different methods: one from the hydrogenation of polybutadiene and the other with heterogeneous Ziegler–Natta catalyst. The DSC melting curves of the former were much narrower than the latter, indicating a more homogeneous composition distribution [16]. To our knowledge, most of the ethylene copolymers used in the literature for the study of co-crystallization were not well characterized in the composition distribution, and there has been no systematic report about the influence of composition distribution on co-crystallization.

For the blends of LDPE with HDPE, it is often observed

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PII: S0032-3861(00)00756-4

Table 1
Some characteristics of polymer samples

Samples	Branches content (CH/1000C)		Density (g/cm^3)	M_w ($\times 10^{-4}$)	M_w/M_n
	Short[a]	Long[b]			
A	1.9	0	0.947	11.10	2.28
B	5.8	0	0.931	8.01	2.72
C	2.9	0	0.949	13.86	6.49
LDPE	11.7	1.6	0.923	9.65	4.85

[a] Branches containing ≤8 carbon atoms (via ^{13}C-NMR).

[b] Branches containing >8 carbon atoms (via ^{13}C-NMR).

that the linear part of LDPE is incorporated into the crystals of HDPE and co-crystallization occurs in HDPE crystals, leading to the decrease in the melting temperatures of both LDPE and HDPE [24]. However, co-crystallization can also occur in other forms. For example, co-crystals may segregate from both HDPE and LDPE and exist as a separate part (showing a third intermediate melting peak between the melting temperatures of two pure components) [25]. Recently, Wignall et al. reported that co-crystals can also occur within the LDPE lamellae by incorporating HDPE molecules [26]. Therefore, two questions are raised: Why can co-crystallization occur in different forms? How do the polymer structure and crystallization conditions affect the forms of co-crystallization? So far, no answer has been given to these two questions in the publications.

In the present work, ethylene–butene copolymers with different composition distributions, which were prepared with metallocene and conventional Ziegler–Natta catalysts, were blended with LDPE in a wide range of blending ratios. The miscibility in the melt of the blends and the co-crystallization phenomena were studied and the observed differences between these copolymers were correlated to their composition distributions.

2. Experimental procedure

2.1. Materials

LDPE was blended with three different ethylene–butene copolymers. Some characteristics of these polymers are listed in Table 1. Samples A and B prepared with metallocene catalyst were donated by RIPP SINOPEC. Sample C, which was prepared with heterogeneous Ziegler–Natta catalyst, was supplied by Qilu Petrochemical Corporation. LDPE prepared by free radical polymerization under high pressure was commercially purchased.

2.2. Preparative temperature rising elution fractionation (TREF)

Preparative TREF apparatus was used to collect a sufficient amount of polymer fractions. About 2 g of polymer was dissolved in xylene at a concentration of 0.005 g/ml at 130°C. This solution was deposited on an inert support, sea sand (particle diameter: 0.3–0.6 mm) packed in a steel column. The length and the internal diameter of the column are 1.0 and 40 mm, respectively. The column was cooled to room temperature at a rate of 1.5°C/h. Then, the deposited polymer was heated stepwise and eluted with xylene. The polymer fractions were recovered by evaporating the xylene solvent and drying in a vacuum oven. Because a small amount of antioxidant 1010 had been added, the total recovery of polymer was around 105%.

2.3. Characterization of composition distribution with DSC

The samples of ethylene–butene and LDPE were first heated to 170°C and kept for 10 min, then were quickly transferred into an oil bath of 140°C. The temperature of the oil bath decreases stepwise, and at each temperature the samples were maintained for 12 h under nitrogen gas atmosphere. The temperatures of the oil bath were 140, 135, 130, 125, 120, 115, 105, 100, 95, 90, 85 and 80°C. Then, the treated samples were scanned with DSC at a heating rate of 5°C/min.

2.4. Dynamic rheological testing

The polymer samples were molded into 2 mm thick disks with a diameter of 30 mm under 160°C and 15 MPa. The dynamic rheological properties were carried out on a Rheometric Science ARES-9A rheometer. Parallel plates with gap 1.0 mm and diameter 25 mm were used. The temperatures for testing were 170°C and the angular frequency range was from 0.1 to 300 rad/s. The strain and time sweeps were first performed before dynamic testing to ensure that the frequency sweeps were within the linear viscoelastic and stable region.

2.5. Preparation of the blends

LDPE and ethylene–butene copolymers were dissolved in xylene (1% w/v) at 130°C and stirred for 2 h. Then, the hot xylene solution of the polymer blends was poured into a large amount of ethanol to precipitate the blends, followed by filtering and drying under vacuum at 60°C for two days. The pure components went through the same procedure. For

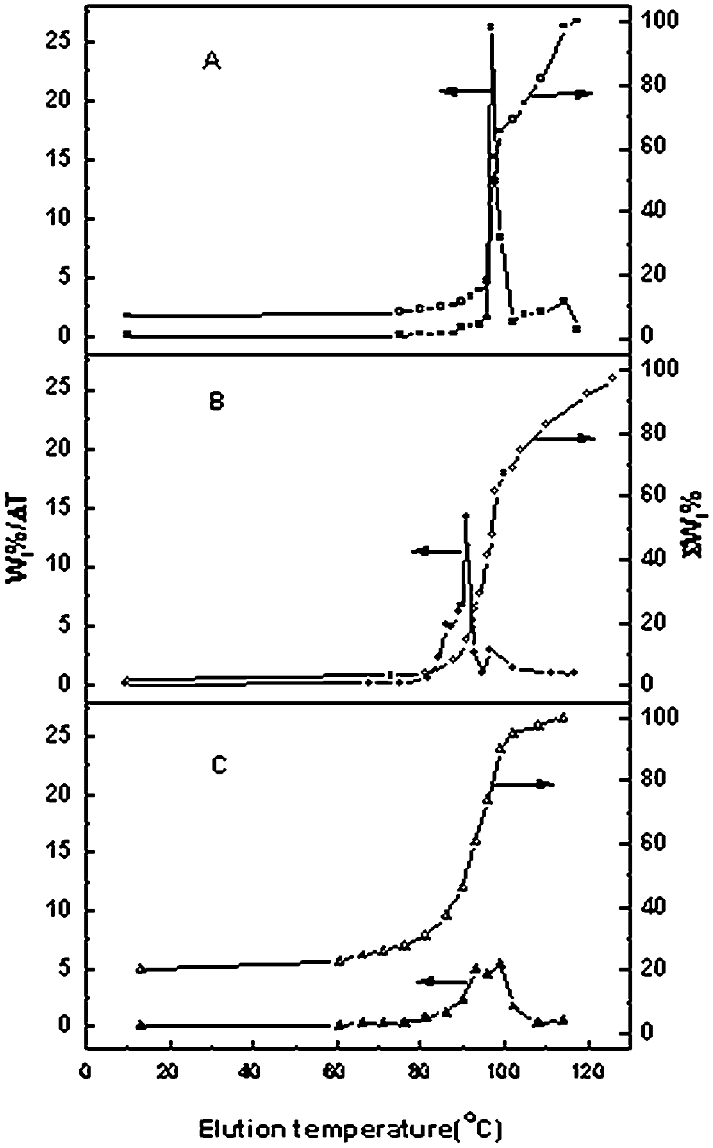


Fig. 1. TREF curves of various ethylene–butene copolymers.

the purpose of convenience, all blends were designated with a letter and a number, which referred to ethylene–butene copolymers and the proportion of the ethylene copolymers, respectively.

2.6. Thermal treatments and DSC measurement

The blends were weighted and wrapped in aluminum pans for DSC measurement. The aluminum pans were sealed in glass tubes full of N_2 and placed into an oil bath at 170°C for 30 min, then rapidly quenched with liquid nitrogen. The melting curves of the thermally treated samples were recorded on a Perkin–Elmer DSC-7 calorimeter. The heating rate applied was 10°C/min, and the temperature was calibrated with standard substance Indium at the same heating rate.

3. Results and discussion

3.1. Composition distribution of pure components

Fig. 1 illustrates the TREF curves of samples A, B and C. TREF fractionates the ethylene copolymers based on comonomer content [27,28]. The higher the comonomer content, the lower the elution temperature. From the peak height, peak width and peak number in $W_i\%/\Delta T$–T curves of Fig. 1, one can compare the composition distribution of these three samples. The higher and narrower peaks, and the smaller number of peaks suggest a narrower composition distribution. It is observed that the peak height decreases in the order $A > B > C$ whereas the peak width exhibits a reverse order $A < B < C$. This result shows that the metallocene-based ethylene–butene copolymers A and B have a more homogeneous composition distribution than the

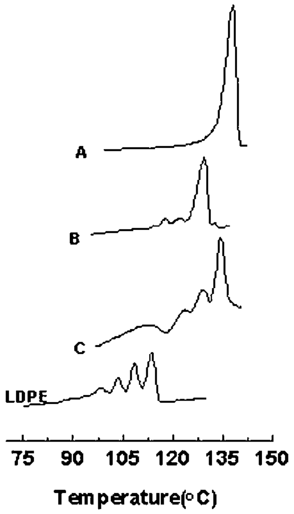


Fig. 2. Melting curves of different pure components after stepwise crystallization.

conventional sample C. Moreover, it is found from the cumulative curves in Fig. 1 that as high as 20 wt% of sample C is eluted at room temperature, and this quantity is much higher than that of samples A and B, indicating that sample C contains more highly branched fractions than samples A and B.

The composition distribution of ethylene copolymers can also be qualitatively investigated by DSC and this method shows better resolution than TREF [22,29]. Fig. 2 shows the DSC melting curves of various pure components after stepwise crystallization from 140 to 70°C at an interval of 5°C. Under this crystallization condition, the crystallization of ethylene copolymers is mainly controlled by the composition (thermodynamic factor) instead of kinetic factors, thus the polymer fractions with different comonomer contents will not co-crystallize. The larger the comonomer content, the lower the crystallization and melting temperatures. Only a single peak appears in the melting curve of sample A, indicating a relatively homogeneous composition distribution of this polymer. In the melting curve of sample C it is observed that four peaks distribute in a wide temperature range (from 100 to 135°C). This shows that sample C has a much broader composition distribution than sample A, though they have similar densities. Sample B has an intermediate composition distribution between sample A and C, since there exist several small peaks besides a major peak in its melting curve. The result obtained with the DSC method is in accordance with that of TREF. The DSC curve of LDPE reveals that the molecular structure of LDPE is also inhomogeneous.

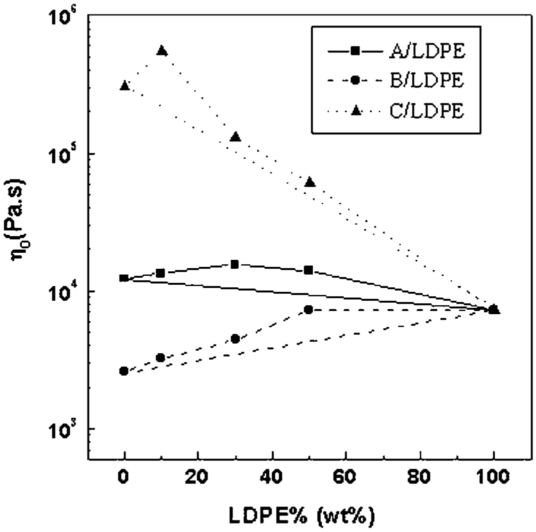


Fig. 3. The plot of logarithmic zero-shear viscosity versus the proportion of LDPE in the blends.

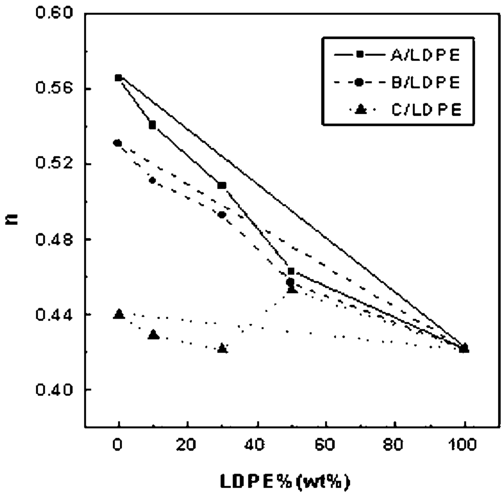


Fig. 4. The plot of values of n versus the proportion of LDPE in the blends.

3.2. Rheological results

The complex viscosity (η) of various blends at different frequencies was determined with a dynamic rheometer under 170°C. It is found that all experimental data can be fitted by the Cross model [30]:

$$\eta = \frac{\eta_0}{[1 + \tau^* \gamma]^{1-n}}, \tag{1}$$

where η_0 is the zero-shear viscosity, τ^* a representative relaxation time and n an exponent.

It is generally accepted that the zero-shear viscosity of a miscible blend without specific interactions or free volume variation should obey the logarithmic additivity rule defined as [31]:

$$\log \eta_0 = \sum w_i \log \eta_0^i. \tag{2}$$

Fig. 3 is the plot of log η_0 versus the proportion of LDPE in the blends. It is observed that the zero-shear viscosity of all the blends exhibits a positive deviation from the logarithmic additivity rule, indicating the immiscible state of

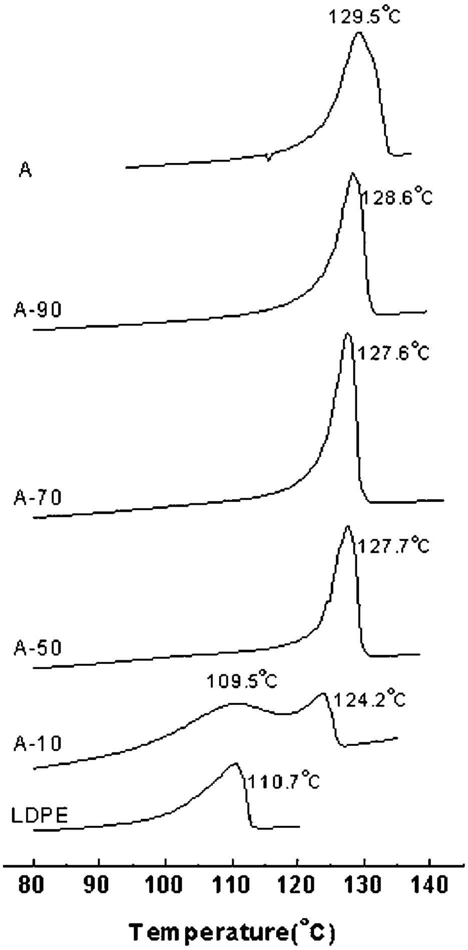


Fig. 5. Melting curves of rapidly quenched A/LDPE blends.

these blend melts. The obtained values of *n* are also plotted versus the proportion of LDPE in the blends (Fig. 4). All the blends show a negative deviation except for the blend C-50. This unusual change will be discussed together with the result of co-crystallization.

3.3. The occurrence of co-crystallization

The blends were heated to 170°C and then rapidly quenched with liquid nitrogen. This thermal treatment was applied for two purposes. Firstly, in such a procedure the crystallization is mainly controlled by kinetic factors and co-crystallization phenomena can be readily observed. Secondly, the morphology of the blend melt is solidified and the co-crystallization behavior can be correlated with the phase behavior of the melt [19]. Figs. 5–7 show the melting curves of the rapidly quenched blends, and the data of melting temperature and fusion heat are listed in Table 2.

In the rapidly quenched blends of LDPE with samples A and B, it is found that the melting temperatures of both components are lower than that of pure LDPE and those of ethylene–butene copolymers, respectively. This indicates that the most linear part of LDPE is incorporated into the lamellae of ethylene–butene copolymers, thus reducing the stability of the lamellae of ethylene–butene copolymers and leaving more branched parts in the LDPE [9]. On the other hand, crystallization kinetics experiments have revealed that the crystallization of the ethylene–butene copolymers becomes faster after blending with LDPE [32]. This was attributed to the transfer of the highly branched fractions of ethylene–butene copolymers into LDPE. The above results show that samples A and B are not completely immiscible with LDPE, though the presence of liquid–liquid phase separation is evidenced by rheological experiment. There are some exchanges between LDPE and these two ethylene copolymers, i.e. some less branched fractions of LDPE were incorporated into ethylene copolymers and a part of the highly branched ethylene copolymers is transferred into LDPE.

In contrast, a broad melting peak is observed at the low temperature region in the blend C-70, and in the blend C-50 this peak is further separated into two melting peaks at 106.3 and 115.5°C. Moreover, it is found that the high melting peak temperatures of the blends C-90, C-70 and C-50 are higher than that of the pure sample C, while the low peak temperatures are lower than that of pure LDPE. It is strange that the melting peak temperature becomes higher after blending, and this phenomenon is rarely reported. From the third intermediate melting peak between the melting peaks of LDPE and sample C, we can judge that a part of the co-crystals segregate from the crystals of both sample C and LDPE and exist as a separated population in the blend C-50.

Since the samples in Figs. 5–7 are directly quenched from the melt state, the co-crystallization behavior of these blends can be correlated with the miscibility of their melts. Only two melting peaks are observed in the blends of LDPE with samples A and B, indicating two phases in the melts of these blends. On the contrary, three endotherms appear in some of the blends of LDPE with sample C (for instance, C-50), which correspond to LDPE crystals, segregated co-crystals and ethylene–butene copolymer crystals. This shows that there exist three phases in the melt of the blend of LDPE with sample C at certain proportions. As reported above, it is observed that in the blend containing 50 wt% sample C, the value of *n* in the rheological experiment suddenly changes from the usual negative deviation to positive deviation at this proportion (Fig. 5(b)). This unusual change may also imply the presence of ternary phases in this blend. Therefore, the metallocene-based and conventional ethylene–butene copolymers exhibit different miscibility with LDPE. This difference may originate from their different composition distributions and can be illustrated as in Scheme 1. Scheme 1 shows the exchange between LDPE and ethylene–butene (E–B) copolymers. Both LDPE and E–B copolymer are viewed as compositionally heterogeneous and the stacks in this scheme are designated for differently branched fractions. LDPE and the metallocene-based

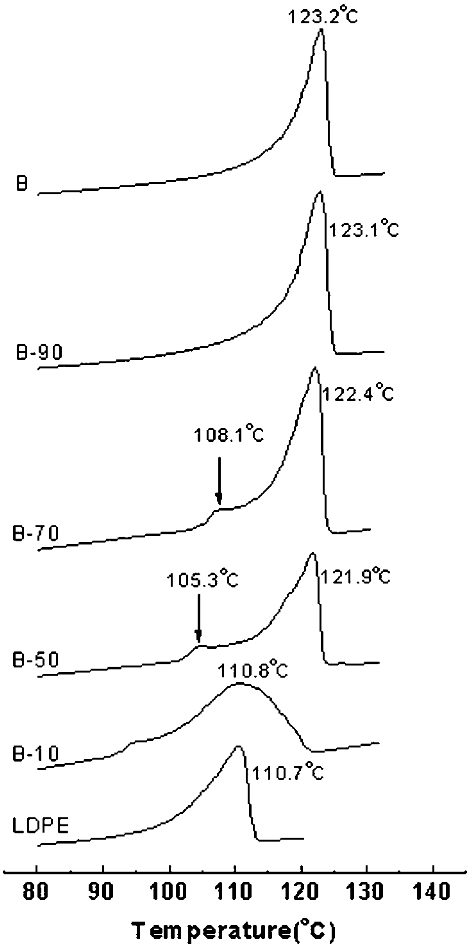


Fig. 6. Melting curves of rapidly quenched B/LDPE blends.

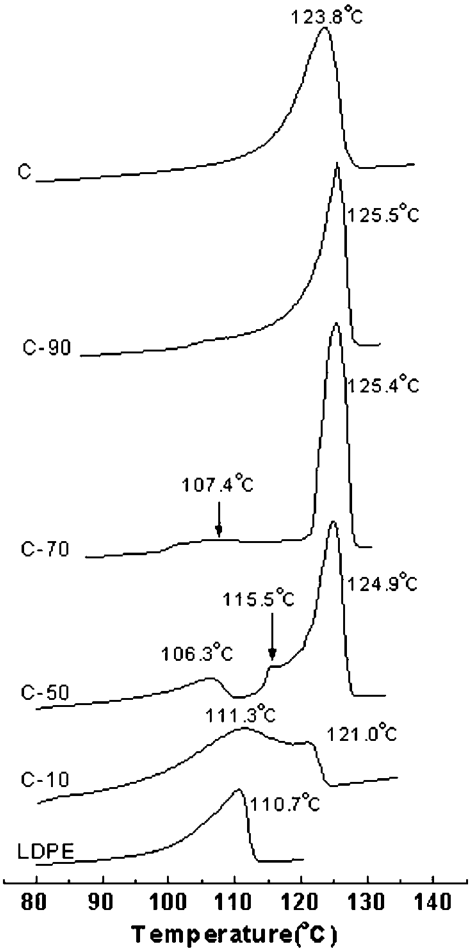


Fig. 7. Melting curves of rapidly quenched C/LDPE blends.

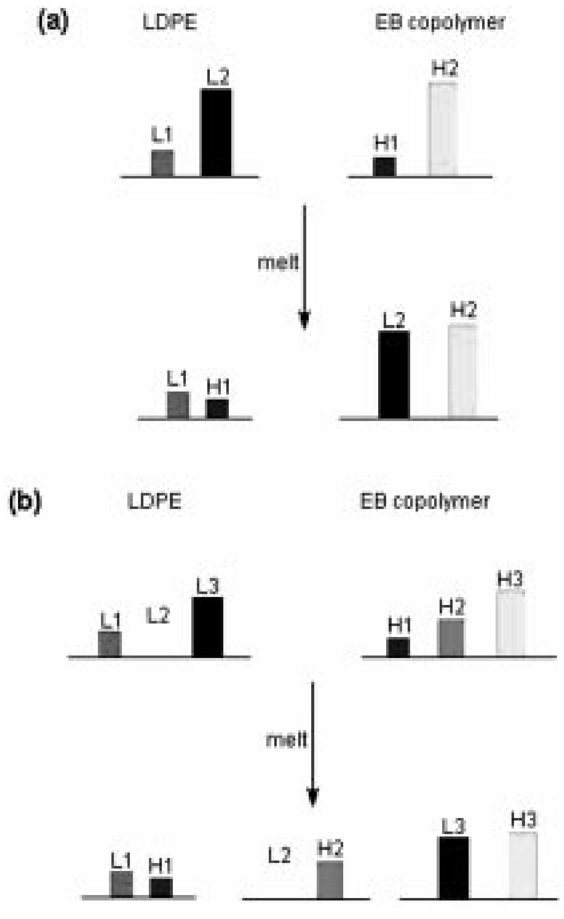
samples A and B can be considered to consist of two parts for simplicity: L1 (highly branched part) and L2 (less branched part) for LDPE, and H1 (highly branched part) and H2 (less branched part) for samples A and B. There are two phases, in the blend melts of LDPE with samples A and B, which are composed of L1 and H1, L2 and H2, respectively, due to the exchange between the two components (Scheme 1(a)). Nevertheless, in the blends of sample C with LDPE both components must be viewed to be composed of three parts for simplicity, and the blend melts (at least for the blend C-50) are ternary blend systems [15,33,34] instead of a binary blend system (Scheme 1(b)). The highly branched fractions (L1), intermediately branched fractions (L2) and the less branched fractions (L3) of LDPE are miscible with the corresponding fractions H1, H2 and H3 of sample C, respectively. After the blends are quenched, they exhibit different co-crystallization phenomena because of the difference in miscibility. Based on these analyses, it is very clear that the composition distribution of the components has a great influence on the form of occurrence of co-crystallization, though only three ethylene copolymers are used to blend with LDPE in the present work and definite conclusions cannot be drawn.

The TREF result has revealed that sample C contains much more highly branched fractions than the metallocene-based samples A and B. These highly branched fractions can severely interfere with the crystallization of the less branched fractions [35]. After blending with LDPE, these highly branched fractions are transferred into the separated co-crystals and the crystals of LDPE. The loss of these fractions leads to the disappearance of the interference effect, and thus the melting temperatures of the sample C increase accordingly. On the contrary, the metallocene-based copolymers A and B contain few highly branched fractions and the interference to the crystallization of the less branched fractions is not remarkable. The transfer of the highly branched fractions of samples A and B into LDPE hardly change the melting temperature of the high temperature peaks. In fact, the melting temperatures of the high temperature peaks for the quenched blends of samples A and B are always lower than that of corresponding pure ethylene copolymers due to the concentration dilution effect [36].

Table 2
DSC data of the quenched samples (the superscripts H and L denote high temperature peak and low temperature peak, respectively)

Samples	T_m^L/T_m^H (°C)	$\Delta T_m^{L\,a}/\Delta T_m^{H\,b}$ (°C)	$\Delta H_f^L/\Delta H_f^H$ (J/g) Experimental	$\Delta H_f^L/\Delta H_f^H$ (J/g) Calculated[d]	$\Delta(\Delta H_f^H)^c$ (J/g)
LDPE	110.7/–	0/–	81.8/0	–	–
A	–/129.5	–/0	–/152.7	–	–
A-90	–/128.6	–/−0.9	0/145.3	8.2/137.4	7.9
A-70	–/127.6	–/−1.9	0/134.2	24.5/106.9	27.3
A-50	–/127.7	–/−1.8	0/112.0	40.9/76.4	35.6
A-10	109.5/124.2	− 1.2/−5.3	75.1/–[e]	73.6/15.3	–
B	–/123.2	–/0	–/128.7	–	–
B-90	–/123.1	–/−0.1	0/128.1	8.2/115.8	12.3
B-70	108.1/122.4	− 2.6/−0.8	2.2/106.2	24.5/90.1	15.9
B-50	105.3/121.9	− 5.4/−1.3	3.1/98.2	40.9/64.4	33.8
B-10	110.8/–	+ 0.1/–[e]	62.1/–[e]	73.6/12.9	–
C	–/123.8	–/0	–/162.2	–	–
C-90	105.8/125.5	− 4.9/+1.7	0.2/153.0	8.2/146.0	7.0
C-70	105.6/125.4	− 5.1/+1.6	9.9/121.1	24.5/113.5	7.6
C-50[f]	106.3/124.9	− 4.4/+1.2	22.4/110.7	40.9/81.1	29.7
C-10	111.0/121.0	+ 0.3/−2.8	85.1/–[e]	73.6/16.2	–

[a] Difference between the melting temperatures of low peak and pure LDPE.
[b] Difference between the melting temperatures of high peak and pure ethylene copolymer.
[c] Difference between the experimental and calculated ΔH_f^H.
[d] Calculated assuming completely segregated crystals.
[e] It was not determined because of not well-separated peaks, and the fusion enthalpy was included in low temperature peak.
[f] The fusion enthalpy of the intermediate peak at 115.5°C was included in the high temperature peak.



Scheme 1.

3.4. Semi-quantitative estimation of the exchange of the components

The exchange of the components in the blends can be semi-quantitatively estimated from the change of the fusion enthalpy. It is found that the experimental data of fusion enthalpy corresponding to the high temperature peaks (ΔH_f^H) are invariably larger than the theoretical values calculated assuming completely segregated crystals. The differences between the experimental and calculated data of the high temperature peaks ($\Delta(\Delta H_f^H)$) are approximate to the theoretical values of fusion enthalpy corresponding to the low temperature peaks. This indicates that most of the LDPE is incorporated into the crystals of ethylene copolymers.

On the other hand, the values of fusion enthalpy for the low temperature peaks increase in the order A < B < C at any proportion, which is the same as the composition distributions. The fusion enthalpy of the low temperature peaks is contributed by two parts: the highly branched part of LDPE (L1) and the highly branched part of ethylene copolymer (H1). Since most of the LDPE is transferred into the ethylene copolymers, the contribution of the highly branched part of LDPE is very small and the highly branched part of ethylene copolymer is mainly responsible for the lower temperature peaks. Therefore, one can see that the quantity of ethylene–butene copolymer transferred into LDPE rises as the composition distribution becomes broader. This result is easily understandable. The broader the composition distribution, the more the highly branched fractions in the ethylene–butene copolymers, thus more ethylene–butene is incorporated into the crystals of LDPE.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (Grant No.: 59703002).

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