Nonisothermal Crystallization Kinetics of Ethylene–Butene Copolymer/Low-Density Polyethylene Blends

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ABSTRACT: Nonisothermal crystallization kinetics of the blends of three ethylene–butene copolymers with LDPE was studied using differential scanning calorimetry (DSC) and kinetic parameters such as the Avrami exponent and the kinetic crystallization rate (Z_c) were determined. It was found that the pure components and the blends have similar Avrami exponents, indicating the same crystallization mechanism. However, the crystallization rate of the blends was greatly influenced by LDPE. The Z_c of all the blends first increases with increasing LDPE content in the blends and reaches its maximum, then descends as the LDPE content further increases. The crystallization rate also depends on the short-chain branching distribution (SCBD) of the ethylene–butene copolymers. The Z_c of the pure component with a broad SCBD is smaller, but its blends have a larger crystallization rate due to losing highly branched fractions after blending with LDPE. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 123–129, 2001

Key words: ethylene–butene copolymer; nonisothermal crystallization kinetics; blend; LDPE

INTRODUCTION

The solid-state structure in the blends of different types of polyethylene, such as HDPE/LDPE, HDPE/LLDPE, and LLDPE/LDPE, has received great research interest due to the theoretical importance and the wide practical applications of these systems. The occurrence of cocrystallization in these blends has been reported by various authors.[1–8] It is generally believed that cocrystallization is produced due to thermodynamically miscible parts of two components having a similar crystallization rate.[9,10] Therefore, it is of great importance to study the crystallization kinetics of these blends, since the degree of cocrystallization is determined by the crystallization rate of the two components. Studies on the isothermal crystallization of polyethylene blends have appeared in many publications.[11,12] However, the degree of cocrystallization also strongly depends on the crystallization conditions. The isothermal crystallization rate can only be correlated to the degree of cocrystallization in an isothermal condition. In fact, the blends usually undergo a nonisothermal crystallization process, especially in practical processing. As a result, a study on the nonisothermal crystallization process of polyethylene blends is meaningful. On the other hand, in these blends, both components are crystallizable. So far, there are few reports on the nonisothermal crystallization of such a system, although the crystallization of polymer blends composed of one crystallizable polymer and one amorphous polymer has been widely investigated.

Table I   Some Characteristics of Polymer Materials

Samples	Content of Counit (mol %)	Density (g/cm^3)	M_w ($\times 10^{-4}$)	M_w/M_n	Melting Temperature (°C)
mPE1	0.38	0.947	11.10	2.28	133.2
G	0.58	0.949	13.86	6.49	130.1
mPE3	1.16	0.931	8.01	2.72	127.6
LDPE	2.66	0.923	12.40	6.80	110.4

In this article, three ethylene–butene copolymers, two metallocene-based copolymers, and one conventional copolymer were each blended with LDPE. The kinetic parameters, such as the crystallization rate and the Avrami exponent, were determined from differential scanning calorimetry (DSC) crystallization exotherms. The effect of the polymer structure and the composition of the blends on the kinetic parameters is discussed.

EXPERIMENTAL

Materials

Two ethylene–butene copolymer samples (mPE1 and mPE3) prepared with a metallocene catalyst were supplied by SINOPEC. One ethylene–butene copolymer sample (G), prepared with a conventional Ziegler–Natta catalyst, was a commercial product of Qilu Petrochemical Co. (Linzi, China). LDPE prepared by free-radical polymerization under high pressure was purchased from the Shanghai Petrochemical Co. (Shanghai, China). Some characteristics of these four polymers are listed in Table I.

Preparation of Blends

The blends were prepared by dissolving the ethylene–butene copolymers and LDPE in xylene (1% w/v) at 130°C for 2 h and precipitating into alcohol, followed by filtering and drying under a vacuum at 50°C for 48 h. The LDPE content in the blends was 10, 30, 50, and 90 wt %, respectively.

Thermal Measurements

DSC measurements were made on a Perkin–Elmer DSC-7 calorimeter with a sample weight of about 2–3 mg. The temperature and melting enthalpy were calibrated by the standard substance, indium. The samples were encapsulated into aluminum pans and heated from room temperature to 150°C at a rate of 10°C/min under argon and kept at 150°C for 3 min, then cooled at a scanning rate of 10°C/min and the crystallization thermograms recorded.

Determination of Kinetic Parameters

The kinetic parameters of nonisothermal crystallization were determined, based on the simplified assumption that crystallization occurs under constant temperature. In this case, the Avrami equation can be used[13]:

$$1 - X = \exp(-Z_t t^n) \text{ or } \log[-\ln(1 - X)]$$
$$= n \log t + \log Z_t \quad (1)$$

where $X = X_t/X_E$ is the degree of polymer transformation; X_t, the degree of crystallinity after time t of the crystallization process; and X_E, the maximum degree of crystallinity as a result of crystallization.

The Avrami exponent (n) and crystallization rate (Z_t) can be obtained from the slope and intercept of the line in the plot of $\log[-\ln(1 - X)]$ versus $\log Z_t$. Considering the effect of the cooling rate, Z_t is corrected by the cooling rate,[14] $\log Z_c = \log Z_t/(dT/dt)$, and one can get Z_c (the kinetic crystallization rate).

Dynamic Rheological Testing

The dynamic rheological properties were carried out on a Rheometric Science ARES-9A rheometer. Parallel plates with a gap of 1.0 mm and diameter of 25 mm were used. The temperature for testing was 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.
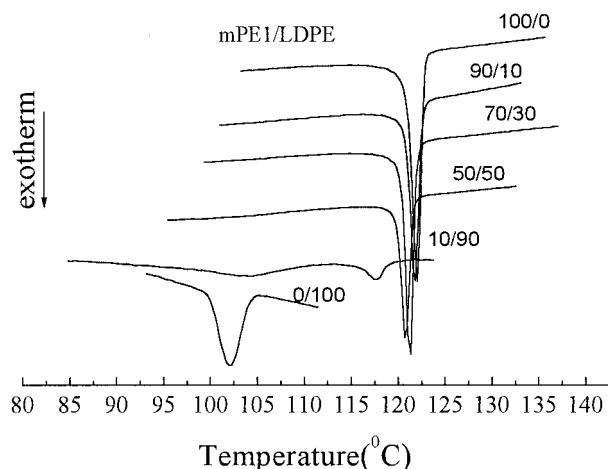
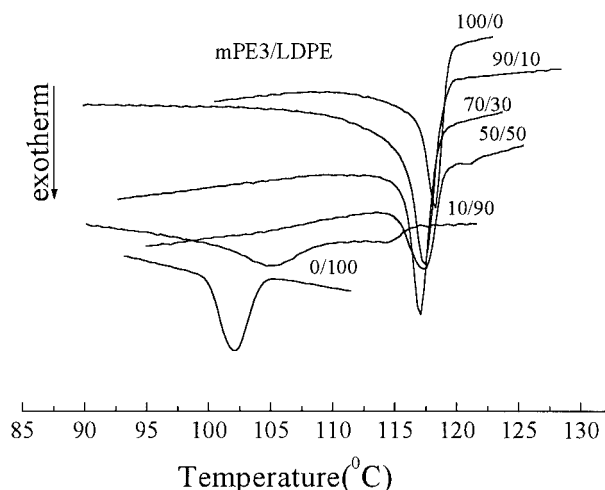**Figure 1** DSC crystallization exotherms of mPE1, LDPE, and their blends.

Figure 3 DSC crystallization exotherms of mPE3, LDPE, and their blends.

RESULTS AND DISCUSSION

Appearance of Crystallization Exotherms

The crystallization exotherms of the pure components and blends are shown in Figures 1–3 and the values of the parameters determined are given in Table II. These crystallization exotherms are quite similar in appearance. All DSC traces show only one crystallization peak except those of the blends containing 90 wt % LDPE.

For all the blends, the crystallization peak temperature (T_c) decreases with increasing of the contents of LDPE in the blends. While the content of LDPE in the blends reaches 90 wt %, there is
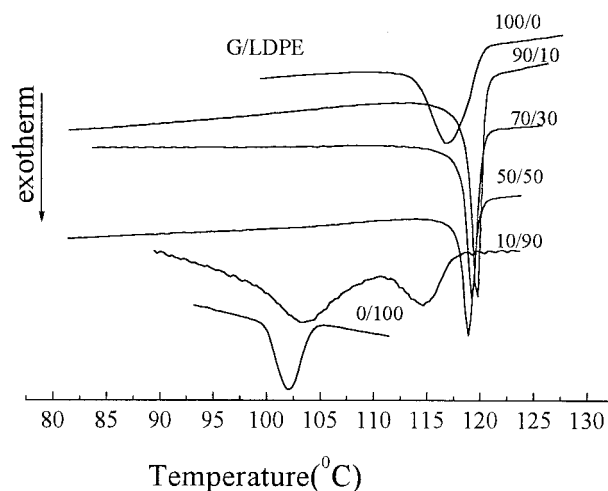

Figure 2 DSC crystallization exotherms of G, LDPE, and their blends.

an abrupt decrease in the crystallization peak temperature. This behavior has been attributed to a possible interplasticizing action caused by some molecules of LDPE acting as a diluent within the crystalline regions of HDPE.[1,15] Compared with the crystallization peak temperatures of the pure components, the blends of mPE1 and mPE3 have lower crystallization peak temperatures, but the crystallization peak temperatures of the blends of G are higher than that of pure sample G, except for the blend containing 90 wt % LDPE.

The addition of LDPE also affects the width of the crystallization peak at half-height ($w_{1/2}$), varying with different samples. The width of the crystallization peak at half-height ($w_{1/2}$) of the G/LDPE blends is always smaller than that of the pure polymer G, but the change is just the reverse for the mPE3/LDPE blends. In the mPE1/LDPE blends, the width of the crystallization peak at half-height ($w_{1/2}$) is larger than that of the pure polymer mPE1 in some compositions and is smaller in other compositions.

Avrami Exponent

For all samples, there is a good linear relationship when $\log[-\ln(1 - X)]$ is plotted versus $\log t$, as shown in Figures 4–6, indicating that, at this cooling rate, the simplified assumption that crystallization occurs under constant temperature is satisfied. From the slope and intercept of the lines, one can determine the Avrami exponent and the kinetic crystallization rate (Z_c).

Table II   Parameters of Crystallization Kinetics

Blend Ratio	Crystallization Peak Temperature (T_c) (°C)	$w_{1/2}$ (°C)[a]	Avrami Exponent (n)	Crystallization Rate (Z_c)
mPE1/LDPE				
100/0	122.1	1.2	2.15 ± 0.04	0.76 ± 0.03
90/10	122.0	1.2	2.33 ± 0.09	0.64 ± 0.04
70/30	121.4	1.2	1.96 ± 0.05	1.22 ± 0.03
50/50	121.0	0.9	2.07 ± 0.06	1.09 ± 0.04
10/90H[b]	117.9	1.8	2.06 ± 0.03	0.31 ± 0.02
10/90L[c]	104.6	10.4	1.97 ± 0.04	0.01 ± 0.02
G/LDPE				
100/0	117.4	4.2	2.12 ± 0.05	0.06 ± 0.02
90/10	119.7	1.2	3.04 ± 0.07	0.22 ± 0.03
70/30	119.4	1.4	2.32 ± 0.04	0.50 ± 0.02
50/50	119.2	1.4	2.15 ± 0.08	0.58 ± 0.04
10/90H[b]	114.8	3.3	2.28 ± 0.02	0.07 ± 0.02
10/90L[c]	103.4	6.0	1.90 ± 0.09	0.04 ± 0.02
mPE3/LDPE				
100/0	118.2	1.6	2.21 ± 0.02	0.34 ± 0.01
90/10	117.4	2.2	1.78 ± 0.08	0.27 ± 0.04
70/30	117.2	1.6	1.96 ± 0.04	0.36 ± 0.02
50/50	117.7	2.3	2.41 ± 0.03	0.12 ± 0.02
10/90H[b]	113.8	2.6	2.14 ± 0.04	0.10 ± 0.03
10/90L[c]	104.8	4.2	2.15 ± 0.06	0.05 ± 0.02
LDPE	102.1	2.5	2.54 ± 0.05	0.08 ± 0.04

[a] Width of crystallization peak at half-height; the error is within ±0.1°C.
[b] High-temperature crystallization peak.
[c] Low-temperature crystallization peak.

The fractional values of the Avrami exponent for all pure components and blends are given in Table II. Gupta et al.[16] reported that the regular change of the Avrami exponent with the blend composition from a value of about 3 corresponding to HDPE to a value of 2 corresponding to LLDPE was observed in the nonisothermal crystallization
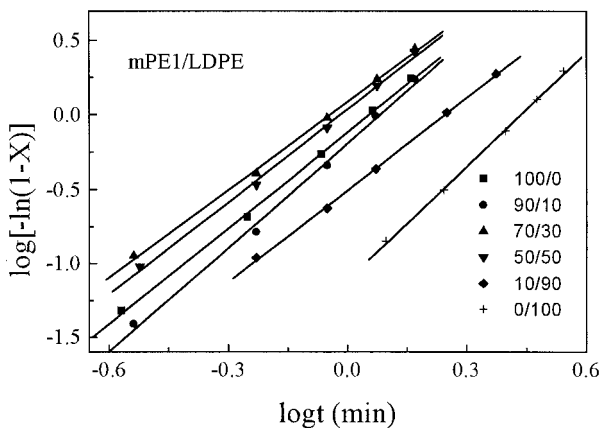

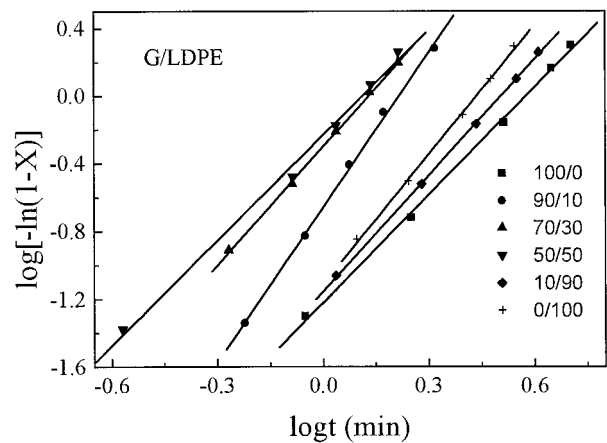**Figure 4** Plot of $\log[-\ln(1 - X)]$ versus $\log t$ for mPE1/LDPE blends.

Figure 5 Plot of $\log[-\ln(1 - X)]$ versus $\log t$ for G/LDPE blends.
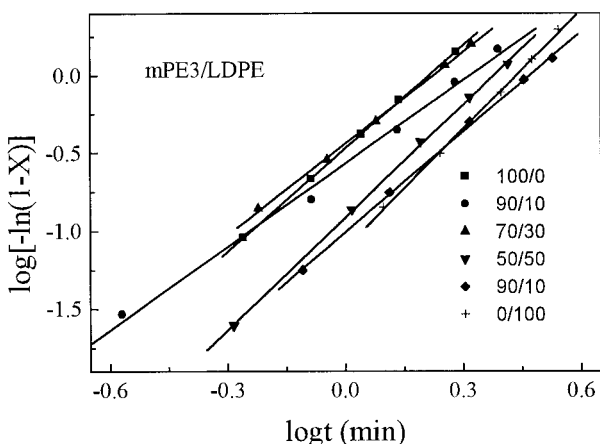
Figure 6 Plot of $\log[-\ln(1 - X)]$ versus $\log t$ for mPE3/LDPE blends.

of the HDPE/LLDPE blends. But in our samples, there is no regular change of the Avrami exponent with composition. This may be due to the similar Avrami exponents of LDPE and ethylene–butene copolymers. The similar Avrami exponents of the blends indicate that the addition of LDPE hardly changes the crystallization growth and nucleation behavior of ethylene–butene copolymers. It was found that the Avrami exponents of all the blends are between 2 and 3, suggesting that crystallites are two-dimensional and nucleation may be between instantaneous and sporadic. Similar results were reported in the HDPE/LLDPE blends. The crystallites with sheaflike, rodlike, or disklike morphology were observed by SALS and TEM.[12,16]

Kinetic Crystallization Rate (Z_c)

The cooling rate has an important effect on the kinetic crystallization rate (Z_c). At a low cooling rate, the faster the cooling rate, the larger the Z_c. When the cooling rate is beyond a critical rate, Z_c hardly changes, irrespective of the cooling rate and polymer structure.[14,17] We chose a cooling rate of 1°C/min so that the variation of Z_c with the blend composition can be observed.

In examining the variation of Z_c with the composition of the blends, one can see that in the initial stage Z_c increases with increase of the LDPE content, then Z_c reaches its maximal value, at which the blending proportions are 70/30, 70/30, and 50/50 for mPE1/LDPE, mPE3/LDPE, and G/LDPE, respectively (Fig. 7). Beyond these proportions, Z_c decreases. This shows that the blends have a larger crystallization rate than

that of the pure components at some blend compositions.

The crystallization of polymer/polymer blends has been studied so far by many investigators, but few have reported that the crystallization rate of a polymer became larger after blending. Martuscelli et al.[18] found that the addition of poly(vinyl methyl ether) could accerelate the crystallization of isotactic polystyrene. It is believed that poly(vinyl methyl ether) is miscible with isotactic polystyrene in the melt state. On the one hand, the addition of poly(vinyl methyl ether) decreases the nucleation rate of isotactic polystyrene. On the other hand, due to the lower glass transition temperature of poly(vinyl methyl ether), the blends have lower glass transition temperatures than that of pure isotactic polystyrene; thus, the mobility of isotactic polystyrene segments is enhanced and the activation free energy (ΔF^*) of the transport process is decreased, which leads to the enhancement in the spherulitic growth rate of isotactic polystyrene. When the latter factor overcomes the former one, the blends may exhibit a larger crystallization rate than that of the corresponding pure components. This explanation is applicable based on the assumption that the blends are miscible in the melt state. However, rheological experiments reveal that all the blends in the present work are phase-separated in the melting state.

Figure 8 shows the variation of the zero-shear viscosity (η_0) with the compositions of the blends. It was found that the zero-shear viscosity of the blends does not obey the logarithmic mixture rule,[19] indicating that LDPE is immiscible with all three ethylene–butene copolymers in the melting state.
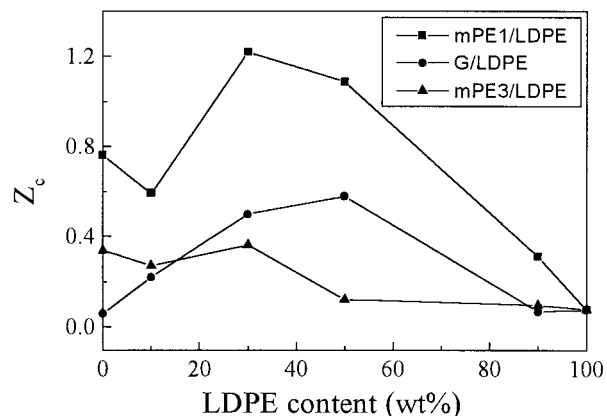

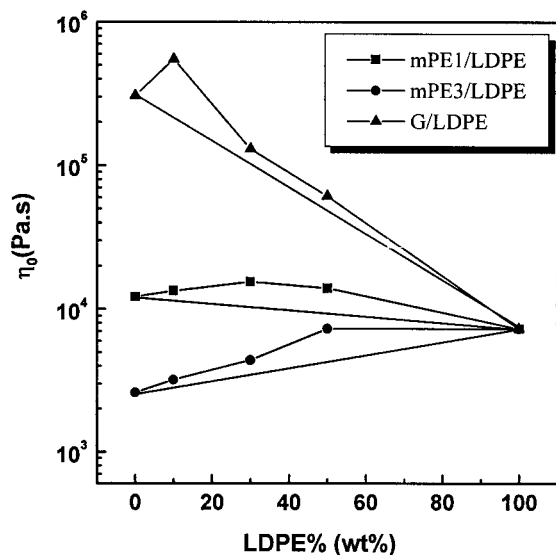**Figure 7** Variation of Z_c with composition of the blends.

Figure 8 Variation of zero-shear viscosity (η_0) with composition of the blends.

Therefore, the larger crystallization rate of ethylene–butene copolymers/LDPE blends than that of the pure components may follow another mechanism. In all these blends, the cocrystallization phenomenon is observed using the DSC method and it is found that cocrystallization can occur in different forms.[20] In the mPE1/LDPE and mPE3/LDPE blends, some more branched fractions of ethylene copolymers are transferred into LDPE and some less branched fractions of LDPE are incorporated into the ethylene copolymers, while in the G/LDPE blends some more branched parts of sample G and some less branched LDPE form separated cocrystals, which is reflected by an intermediate melting peak between the melting peaks of the LDPE and ethylene copolymer. The occurrence of cocrystallization shows that LDPE and various ethylene–butene copolymers are not completely immisicible, but partly miscible, although phase-separation is observed. Thus, the phenomenon that the crystallization of the ethylene copolymers is accelerated after blending with LDPE may result from the loss of more branched fractions in the ethylene copolymers, which have a slower crystallization rate and can reduce the crystallization rate of the less branched fractions.[21] At a large proportion of LDPE, the crystallization of the ethylene–butene copolymers may be suppressed by LDPE, leading to decrease in the crystallization rate.

The above mechanism can also satisfactorily explain the differences in the crystallization rate among these ethylene–butene copolymers and their blends with LDPE. It can be seen from Figure 7 that the Z_c of three pure ethylene–butene copolymers decreases in the order mPE1 > mPE3 > G, but the blends of G have a larger Z_c than that of the blends of mPE3 when the blends contain 30 or 50 wt % LDPE. Our previous work showed that sample G, which is prepared with a conventional Ziegler–Natta catalyst, has a broad short-chain branching distribution.[20] This means that sample G contains more highly branched fractions. Thus, sample G has a slower crystallization rate when compared with the metallocened-based samples mPE1 and mPE3, although its density is close to the density of mPE1 and higher than the density of mPE3. After blending with LDPE, ethylene–butene copolymers lose their highly branched fractions. Due to the different forms of crystallization and more highly branched fractions for the conventional sample G, the G/LDPE blends show a more marked increase in the crystallization rate and the crystallization temperature relatively to the pure sample G.

CONCLUSIONS

The above results show that the simplified assumption that crystallization occurs under a constant temperature is suitable for nonisothermal crystallization of these ethylene–butene copolymers/LDPE blends. The addition of LDPE has little effect on the Avrami exponents, but increases the crystallization rate of the ethylene–butene copolymers, which is the result of the loss of highly branched fractions in the ethylene–butene copolymers. The crystallization rate of the blends also depends on the short-chain branching distribution of the ethylene–butene copolymers. The more highly branched the fractions, the larger the increase in the crystallization rate after blending.

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