Crystallization Kinetics of High-Density Polyethylene/Linear Low-Density Polyethylene Blend

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SYNOPSIS

This article presents crystallization kinetics studies on a cocrystallizing polymer high-density polyethylene (HDPE)/linear low-density polyethylene (LLDPE) blend. The non-isothermal crystallization exotherms obtained by differential scanning calorimetry (DSC) were analyzed to investigate the effect of cocrystallization on kinetics parameters, namely the Avrami exponent and activation energy. The regular change of Avrami exponent with blend composition from a value of about 3 corresponding to HDPE to a value of 2 corresponding to LLDPE is observed. A sheaf-like crystalline growth with variation of nucleation depending on blend composition is concluded from these results of DSC exotherm analysis in conjunction with the small-angle light scattering observations. The observed variation of activation energy of crystallization with blend composition suggests the role of interaction of side chains and comonomer units present in the LLDPE. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The properties of linear polyethylene could be engineered to a great extent by the incorporation of various types of comonomer in the main chain, as in the case of linear low-density polyethylene (LLDPE). Due to their superior mechanical properties, ease of processability, environmental stress cracking resistance, and thin film forming properties, LLDPE is a better alternative to various other grades of polyethylenes. Furthermore, the compatibility of LLDPE with other grades of polyethylene provides a scope of developing new materials by blending different grades of polyethylene.

Studies on blends of LLDPE with high-density polyethylene (HDPE),[1,2] medium-density polyethylene (MDPE),[3,4] low-density polyethylene (LDPE),[3,4] and ultra-high molecular weight polyethylene (UHMWPE)[5] have been reported by various authors,[1-7] many of whom have recognized that LLDPE cocrystallizes with various grades of polyethylene.[6,7] The cocrystallization of the two components of a blend has an additional advantage of

modification of mechanical properties and thus has generated interest in its study. In our previous article,[6] we reported a study of cocrystallization of LLDPE with HDPE in a binary blend revealing the effect of blending ratio on the nucleation rate, crystallinity, and crystallite size distribution.

In this article, we report the cocrystallization kinetics behaviour of an HDPE/LLDPE blend. The kinetics parameters like the Avrami exponent and the activation energy have been evaluated from differential scanning calorimetry (DSC) crystallization exotherms. A regular variation of the Avrami exponent with blending ratio was observed, which is discussed in terms of the effects of the cocrystallization.

EXPERIMENTAL

Materials

The HDPE (Hostalen GF 7745F) used for this study was a product of Polyolefin Industries Ltd., Bombay, India. The LLDPE (Dowlex 2740 E), an octene based polymer, was a product of Dow Chemicals, U.S.A. The properties of these two polymers are listed in Table I.

Table I   Characteristic Properties of HDPE and LLDPE

Property	HDPE	LLDPE
$[\eta]$ at 115°C in decalin (dl/g)	1.10	1.50
Melting temperature (°C)	131	126
Melt flow index (g/10 min)	0.75	1.00
Density (g/cc)	0.952	0.925
Tensile stress at yield (MPa)	24.5	19.3
$CH_3/100C$	1.81	3.00
Crystallinity (%)	46	36

Blend Preparation

The solid chips of HDPE and LLDPE were mixed in a tumble mixer to form a uniform composition throughout the batch size. This uniformly mixed feed was then melt blended in a single screw extruder (Betol 1820) with L/D ratio of 17 and screw speed of 22 rpm. The temperature profile of the extruder was kept as 160°C at the feed zone, 200°C at the compression zone, and 210°C at the metering zone and at the die-end. The extruded strands were cooled in water maintained at 30°C and subsequently granulated after allowing a maturation time of 8 h.

Test Specimens

Test specimens were cut from compression-moulded sheets for light scattering measurements. Compression moulding was done at 165°C at a pressure of 300 kg/cm², followed by cooling at ambient condition.

Measurements

DSC measurements were made on a Perkin Elmer DSC-7 thermal system on a sample size of about 10 mg. The crystallization exotherms were recorded at the cooling rates of 0.5, 2, 5, 10, and 20°C/min. All the plots presented were normalized to unit weight of the sample.

Small-Angle Light Scattering

The Hv light scattering patterns were recorded on an optical bench-type small-angle light scattering photometer comprised of a polarizer and an analyser He–Ne laser source. Hv designates the directions of polarizer and analyzer in the horizontal and vertical position, respectively.

DETERMINATION OF KINETICS PARAMETERS

Following the procedure based on the Avrami equation for crystallization kinetics and the Arrhenius equation for the rate constant enables the evaluation of the crystallization kinetics parameters from the DSC exotherm recorded under nonisothermal conditions.

The Avrami equation[8] describing crystallization of polymeric materials under isothermal condition may be expressed as follows:

$$\alpha = 1 - \exp(-kt^n) \qquad (1)$$

where α is the extent of crystallization for the elapsed time t and k is the rate constant. The Arrhenius expression for the rate constant is:

$$k = A \exp(-E/RT) \qquad (2)$$

where A is the preexponential factor and E is the activation energy of the crystallization process.

The rate equation for the isothermal crystallization process could be written as:

$$\alpha' = d\alpha/dt = nkt^{(n-1)}(1 - \alpha). \qquad (3)$$

The nonisothermal crystallization process may be assumed to be comprised of infinitesimally small isothermal crystallization steps.[9,10] Therefore, the variables of the Avrami equation under a nonisothermal condition for the entire process will represent average values of all the corresponding constituents of isothermal crystallization steps. The Avrami equation is essentially a representation of crystallization as a function of time without involving temperature as a variable. In the case of crystallization in a nonisothermal condition, the rate equation may be modified as follows for the case of linear variation of temperature represented as follows:

$$T = T_o + \beta t \qquad (4)$$

where, T_o is the onset temperature and T is temperature after time t and β is the heating rate. Note: In the case of the cooling cycle, β will be negative and eq. (4) will be

$$T = T_o + (-\beta)t,$$

At peak crystallization exotherm (i.e., peak maxima), the derivative of the rate eq. (3) should be equal to zero.

$$\alpha'' = d\alpha'/dt = 0. \tag{5}$$

On combining eqs. (2), (3), and (4) and applying the condition specified in eq. (5), the following relationship is obtained:

$$\frac{\alpha'}{(1 - \alpha)} = nAe^{-E/[R(T_o+\beta t)]} t^{(n-1)}. \tag{6}$$

On differentiation

$$\frac{\alpha''(1 - \alpha) + (\alpha')^2}{(1 - \alpha)^2} = nAe^{[-E/R(T_o+\beta t)]}$$

$$\times \left[\frac{-E\beta}{R(T_o + \beta t)^2} t^{(n-1)} + (n - 1)t^{(n-2)} \right]. \tag{7}$$

On, putting $\alpha'' = 0$

$$\frac{\alpha'^2}{(1 - \alpha)^2} = nAe^{E/R(T_o+\beta t)} t^{(n-1)}$$

$$\times \left[-\frac{E\beta}{R(T_o + \beta t)^2} + \frac{n - 1}{t} \right]. \tag{8}$$

On substituting from eqs. (4) and (6) and on rearrangement, the equation takes the form:

$$\frac{\alpha' t}{(1 - \alpha)} = (n - 1) - \frac{E\beta t}{RT^2}. \tag{9}$$

Equation (9) represents the crystallization behaviour at the temperature corresponding to the peak (i.e., maximum) of the nonisothermal exotherm. We may use the suffix "p" to denote the peak temperature and replacing the parameter t by corresponding temperature difference (i.e., $\beta t = T_p - T_o$)

$$\frac{\alpha'_p(T_p - T_o)}{\beta(1 - \alpha_p)} = (n - 1) - \frac{E(T_p - T_o)}{RT_p^2}. \tag{10}$$

Equation (10) thus suggests that the plot of $\alpha'_p[(T_p - T_o)/\beta(1 - \alpha_p)]$ as a function of $[(T_p - T_o)/T_p^2]$ would be linear with slope and intercept equal to E/R and $(n - 1)$, respectively.

Thus the activation energy E and Avrami exponent n can be determined from the experimental data of the crystallization exotherm recorded under linearly varying temperature. The quantity α was evaluated from the ratio of the area under the crys-

tallization exotherm per unit mass of the sample. α_p is the extent of crystallization at the peak maximum and is determined as the fractional area under the exotherm from its onset temperature T_o to the peak temperature T_p to the total area under the crystallization exotherm. The exotherm peak temperature T_p is determined as the point of intersection of the tangents by the two sides of the exotherm. The temperature of onset of the crystallization T_o is determined as a point where the exotherm initially departs from the base line.

RESULTS AND DISCUSSION

The crystallization exotherms for HDPE, LLDPE, and their blend at 50/50 composition are shown in Figures 1–3 and values of the relevant parameters determined from them are given in Table II. These crystallization exotherms are quite similar in appearance but differ quantitatively with cooling rate such that as the cooling rate decreases the peak temperature increases and the extent of crystallization (i.e., peak area) decreases.

Cocrystallization

As discussed in our previous paper,[6] the single peak character of the exotherm is obviously an indication of cocrystallization of HDPE and LLDPE. It was shown[6] that the variations in the exotherm as a function of blending ratio were attributable to the effect of blending on nucleation and growth of crystallization and the subsequently developed morphology and crystallinity. The cocrystallization of HDPE and LLDPE is reported by other authors[2] also. However, Hu et al.[2] have reported that HDPE/LLDPE blend yields a doublet exotherm under certain conditions of crystallization, that is, when the melts of the blend of HDPE and LLDPE are allowed to crystallize slowly. This doublet type exotherm is attributed to the formation of individual crystallites of the two components. The present results show the single-peak character of the exotherm even at the slowest cooling rate, 0.5°C/min, implying insignificant effect of time of crystallization in the studied range on the crystallization tendency of HDPE and LLDPE.

Avrami Exponent and Activation Energy

The plots of $[\alpha'_p(T_p - T_o)/\beta(1 - \alpha_p)]$ versus $[(T_p - T_o)/T_p^2]$ are shown in Figure 4 for HDPE,
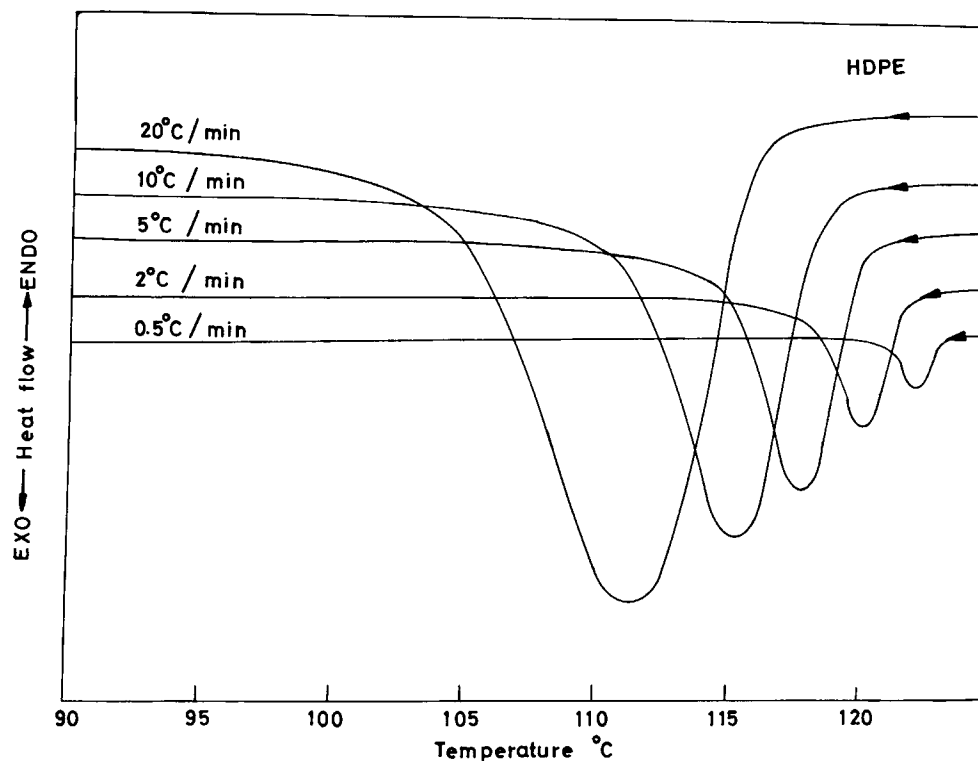
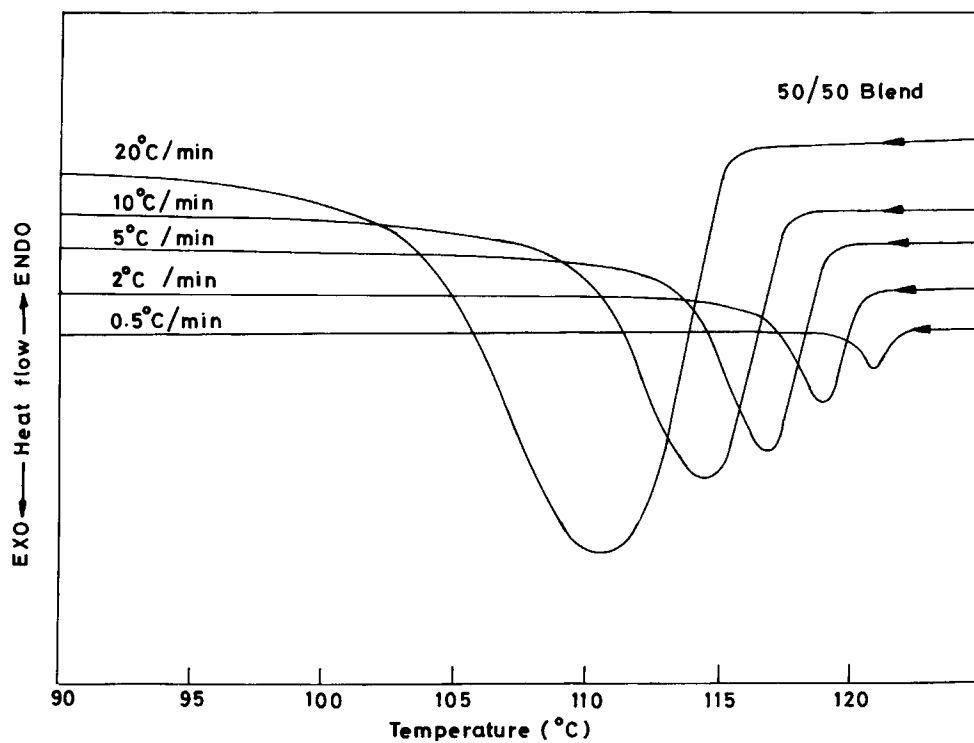**Figure 1**   Crystallization exotherm of HDPE at different heating rates.

Figure 2   Crystallization exotherm of 50/50 HDPE/LLDPE blend at different heating rates.
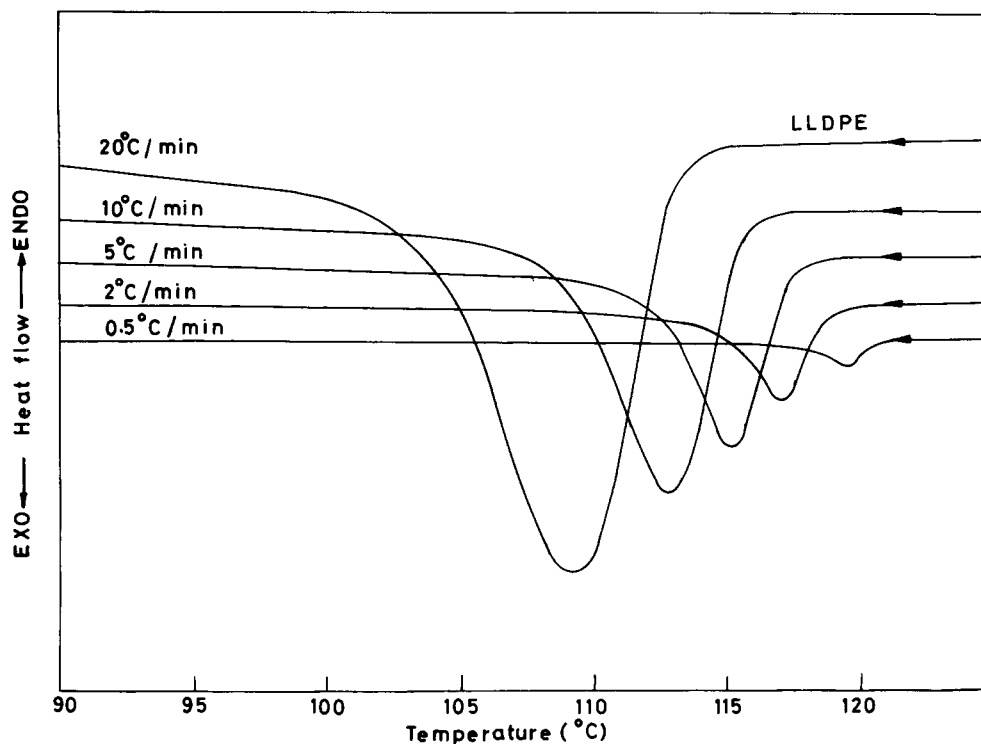
Figure 3 Crystallization exotherm of LLDPE at different heating rates.

LLDPE, and their blend at one composition, 50/50 wt %. These plots are linear with intercept and slope related to Avrami exponent n and activation energy E, according to eq. (10). Values of n and E obtained for HDPE, LLDPE, and their blend at the various blending ratios, are listed in Table III. Avrami exponent and activation energy for the two polymers HDPE and LLDPE differ considerably as follows: $n = 2.94$ and $E = 30$ kcal/mol for HDPE and $n = 1.72$ and $E = 11$ kcal/mol for LLDPE.

The presently observed values of the Avrami exponent for various samples vary from 1.72 to 2.94, which may be rounded off to the nearest integral values only for the pure components HDPE and LLDPE to represent the differences in their crystallization growth and nucleation behaviour. However, for the blend there is a continuous variation of the value of n with blending ratio that cannot be represented by any single integral value; hence they are to be discussed for their fractional values. The fractional values of the Avrami exponent would represent an average contribution of simultaneous occurrence of various types of nucleation and growth of crystallization, each conforming to different integral values of the exponent n.

The fractional values of the Avrami exponent are

not unusual in the literature.[11-15] Hey et al.[13,14] reported that fractional values of n show better fit to time-dependent crystallization than the integral values. For polyethylene they have reported[13,14] the values of n in the range of 2.7 to 3.5, which are slightly lower than the values 2.8 to 3.8 reported by Rabesiaka and Kovacs.[15] Furthermore, these values of n between 3 and 4 were reported[15] in terms of spherulitic growth from instantaneous nucleation for the case of $n = 3$. The lower values of n between 2 and 3 were attributed to simultaneous occurrence of tridimensional growth of crystallites from instantaneous nuclei ($n = 3$) and two dimensional growth of crystallites from instantaneous nucleation ($n = 2$).

The nearest integral values of the Avrami exponent for HDPE and LLDPE may imply two possibilities: HDPE forms tridimensional crystallites with instantaneous nucleation ($n = 3$) and LLDPE forms two-dimensional growth with instantaneous nucleation ($n = 2$); and/or HDPE forms two-dimensionally growing crystallites from sporadic nucleation ($n = 3$) and LLDPE forms two-dimensionally growing crystallites from instantaneous nucleation ($n = 2$).

The continuous linear variation of the Avrami

Table II Characteristic Parameters of DSC Crystallization Exotherms of HDPE, LLDPE, and Their Blends on Different Cooling Rates

Sample (wt % HDPE : LLDPE)	Cooling Rate (°C/min)	α_p	t_p (min)	T_o (°C)	T_p (°C)
100 : 0	20	0.418	1.63	111.4	90.0
	10	0.394	2.23	115.4	99.1
	5	0.376	5.26	117.9	106.3
	2	0.374	9.26	120.0	109.5
90 : 10	20	0.401	1.56	112.1	90.0
	10	0.358	2.10	115.7	100.0
	5	0.356	4.40	118.0	107.5
	2	0.331	6.24	120.5	111.7
75 : 25	20	0.409	1.28	111.5	90.0
	10	0.384	2.27	115.4	102.5
	5	0.332	4.23	117.6	106.3
	2	0.330	6.84	119.7	111.2
65 : 35	20	0.420	1.60	110.9	92.5
	10	0.387	2.69	114.8	98.8
	5	0.339	3.82	117.2	103.8
	2	0.360	6.42	119.5	111.8
50 : 50	20	0.406	1.38	110.2	90.0
	10	0.320	2.56	114.5	100.7
	5	0.339	3.86	116.9	104.1
	2	0.334	4.48	118.9	111.2
30 : 70	20	0.445	1.35	110.3	90.0
	10	0.353	2.34	114.3	100.8
	5	0.392	4.05	116.6	106.8
	2	0.302	6.26	118.5	110.9
20 : 80	20	0.405	1.64	110.5	90.0
	10	0.344	1.95	114.0	87.5
	5	0.342	3.80	116.6	106.8
	2	0.302	9.60	118.5	110.9
0 : 100	20	0.417	1.36	109.2	90.0
	10	0.337	1.78	112.7	99.1
	5	0.295	3.75	115.1	106.2
	2	0.267	5.74	117.0	109.5

exponent, as shown in Figure 5, with blending ratio for HDPE/LLDPE blend may be attributed largely to the effect of differences in nucleation and not to the differences in the type of growth, owing to the cocrystallization of the two components. The decrease of n with increasing LLDPE content of the blend suggests the increasing favour for instantaneous nucleation in the presence of LLDPE.

The values of Avrami exponent may be expressed as comprised of two parts: the contribution due to nucleation; and the contribution due to growth. Considering the crystalline growth to be identical owing to the cocrystallization of two components of the blend, the observed difference of the Avrami ex-

ponent may be essentially attributed to the difference in nucleation behaviour. Let us attribute a value varying from 0 to 1 for the contribution due to nucleation to the total value of n, such that the sporadic nucleation contributes a value of 1 and instantaneous nucleation contributes a value 0. The remaining portion of n, 1.94 for HDPE and 1.72 for LLDPE, would thus represent the contribution due to growth process that may be taken to be equal to its nearest integral value, 2 for both HDPE and LLDPE.

The systematic changes from sporadic to instantaneous nucleation with increasing LLDPE content of the blend may account for the variation of the
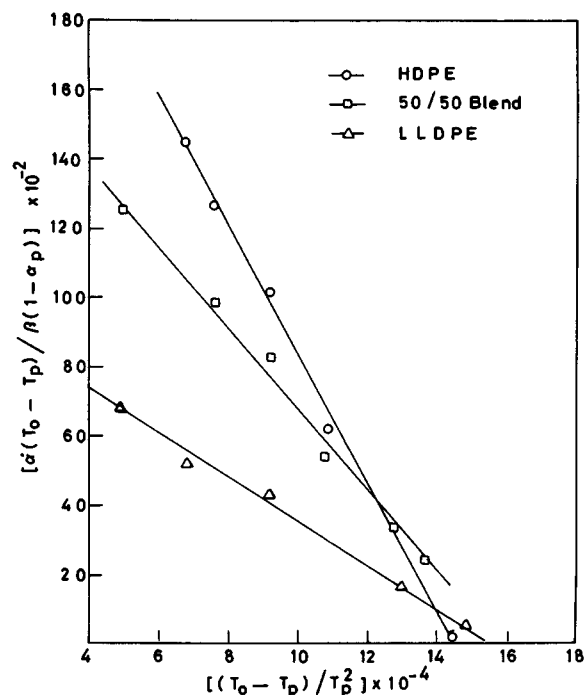
Figure 4 Plot of $[\alpha'_p(T_p - T_o)/\beta(1 - \alpha_p)]$ versus $(T_p - T_o)/T_p^2$ for HDPE, LLDPE, and 50/50 HDPE/LLDPE blend.

Figure 5 Variation of Avrami exponent and activation energy with composition.

nucleation dependent component of n. Thus the measured Avrami exponent n may be expressed as:

$$n = n_{\text{nucleation}} + n_{\text{growth}}$$

where $n_{\text{nucleation}}$ and n_{growth} represent components dependent on nucleation and growth, respectively.

The observed variation of the Avrami exponent with blend composition (Fig. 5) may thus be con-

Table III   Avrami Exponent and Activation Energy for HDPE, LLDPE, and Their Blends

Sample (wt % HDPE : LLDPE)	Avrami Exponent (n)	Activation Energy (E), kcal/mol
100 : 0	2.94	29.06
90 : 10	2.73	26.10
75 : 25	2.65	23.75
65 : 35	2.40	24.00
50 : 50	2.30	20.50
30 : 70	2.10	16.50
20 : 80	1.93	14.10
0 : 100	1.72	11.74

sidered to be comprised of two parts: the blend composition invariant part and the blend composition variant part.

The blend composition invariant part of the Avrami exponent is equal to 2 that is attributed to the two-dimensional growth of crystallites for HDPE, LLDPE, and their blends. Whereas, the blend composition variant part of the Avrami exponent ranges from 1 to 0 and corresponds mostly to sporadic nucleation for HDPE, and a combination of sporadic and instantaneous nucleation for HDPE/LLDPE blend, and corresponds mostly to instantaneous nucleation for LLDPE. The combination of the two types of nucleation thus accounts for the overall fractional value of the Avrami exponent for the blend.

Variation of activation energy with blend composition (Fig. 5) is quite similar to the variation of Avrami exponent. The lower activation energy for crystallization of LLDPE than HDPE seems to be due to the storage of some of the thermal energy by the crystallites owing to the presence of greater repulsive force exerted by the bulky pendant groups expected to be present at the crystalline boundary.[6] Formation of cocrystallites enhances this repulsive force due to greater abundance of the bulky groups

at the crystallite boundaries and thus reduces its activation energy with increasing LLDPE content of the blend.

Small-Angle Light Scattering

The small-angle light scattering patterns of HDPE, LLDPE, and their blend at 50/50 composition are
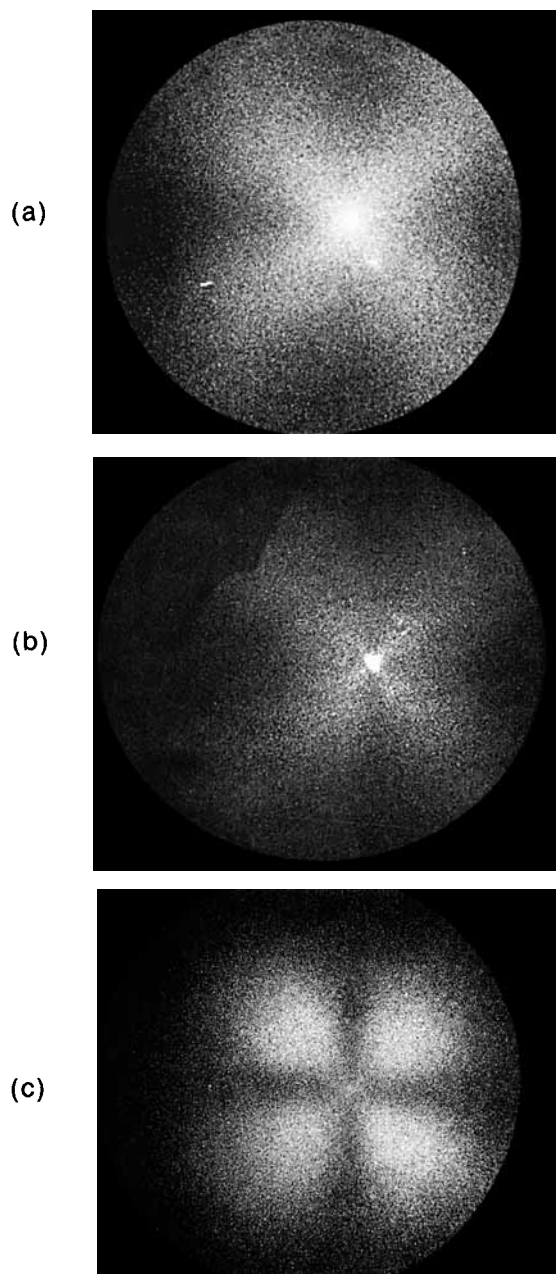
(a)

(b)

(c)

Figure 6 Small-angle light scattering pattern of (a) HDPE, (b) 50/50 HDPE/LLDPE blend, and (c) LLDPE.

shown in Figure 6. These four-lobe patterns observed in all the cases are attributable to the sheaf-like crystallites and/or distorted spherulites present in these systems.[16,17] The other blend compositions also show similar scattering patterns. Thus the variation of the Avrami exponent seems attributable more to the type of nucleation because the crystalline growth is not much varying with the blend composition.

CONCLUSION

HDPE and LLDPE in their blend form a strong cocrystalline mass, which produces neat singlet crystallization exotherms in DSC experiments. The blending of HDPE with LLDPE produces pronounced effects on the crystallization kinetics parameters, the Avrami exponent and activation energy. The Avrami exponent and activation energy for crystallization of HDPE systematically decreased with increasing LLDPE content of the blend from 2.94 to 1.72 for the Avrami exponent and from 30 to 11 kcal/mol for activation energy. The Avrami exponent, which has an inherent component as a contribution due to both nucleation and growth characteristics of the crystallization process, is interpreted as being comprised of two parts: the nucleation dependent part varying from 0 to 1 for the extreme cases and the growth dependent part being constant for the case of growth of cocrystallized structure, being represented by a fractional value close to 2 for both HDPE and LLDPE. For the case of the blend, the observed variation of n is thus attributed to the variation of the nucleation process depending on the blending ratio. The similarity of the growth of crystallite structure for all the compositions of the blend is supported by the small-angle light scattering measurements.

The linear decrease in activation energy with increasing LLDPE content of the blend is apparently due to the increase in destabilizing effect on the crystallites by the pendant groups of LLDPE that are largely present at the crystallite boundaries.

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