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

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SYNOPSIS

Binary blend of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), prepared by melt mixing in an extruder, in the entire range of blending ratio, is studied for crystallization behavior by differential scanning calorimetry (DSC) and X-ray diffraction measurements. Cocrystallization was evident in the entire range of blend composition, from the single-peak character in both DSC crystallization exotherms and meltingendothermsandtheX-raydiffractionpeaks.AdetailedanalysisofDSCcrystallization exotherms revealed a systematic effect of the addition of LLDPE on nucleation rate and the subsequently developed crystalline morphology, which could be distinguished in the three regions of blending ratio, viz., the "HDPE-rich blend," "LLDPE-rich blend," and the "middle range from 30–70% LLDPE content." Variations in crystallinity, crystallite size, and d spacing are discussed in terms of differences in molecular structure of the components.

INTRODUCTION

With the introduction of linear-low density polyethylene (LLDPE), the scenario of utilization and future scope of the conventional grades of polyethylene, viz. high-density polyethylene (HDPE) and low-density polyethylene (LDPE), has considerably changed over the years. Owing to its superior properties, LLDPE has completely replaced other grades of polyethylenes in certain applications or has been used as blend with the other polyethylenes. Studies published in recent years clearly indicate the advantages of incorporation of LLDPE in the mechanical properties of various blends, viz., HDPE/LLDPE blend,[1] LDPE/LLDPE blend,[2] and ultra-high molecular weight polyethylene (UHMWPE)/LLDPE blend.[3]

The LLDPE molecules have linear sequences of polyethylene interspersed by relatively bulkier unit of a comonomer (e.g., octene, butene, etc.). These linear sequences are sufficiently long for the formation of crystalline structure similar to that of HDPE. However, the crystallization and morphology of LLDPE may differ from HDPE in terms of crystallite size, size distribution, and degree of crystallinity. The crystal structure, however, may not differ since both represent the ordered arrangement of long molecular chains of similar chemical structure. It is reported[4] that the spherulites of LLDPE become less developed, more uniform in size, and tend to progressively deteriorate with decreasing average length of uninterrupted polyethylene sequence, i.e., with increasing concentration of comonomer. These sequences of polyethylene of LLDPE may cocrystallize with HDPE. Such crystallization may modify the morphology due to the additional entity, viz., the comonomer present in LLDPE, for example, by restricting the growth of crystal size and/or modifying the crystal boundary region where the structure would be different from the amorphous phase of polyethylene due to the presence of the comonomers. The cocrystallization may therefore by expected to influence mechanical properties. Vadhar and Kyu[3] have found that in the blend of LLDPE and UHMWPE, the mechanical properties were profoundly affected by the mixing technique used. They also observed from their differential scanning calorimetry results that cocrys-

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tallization of the two components depends on the conditions of mixing, such that poor mixing results in separate crystallization while good mixing allows cocrystallization. Thus cocrystallization seems to play an important role in controlling the mechanical properties of such blends.

In this article we present a study on crystallization behavior of HDPE/LLDPE blend in the range of blending ratio extending from 100% HDPE to 100% LLDPE contents, with an emphasis on the cocrystallization of LLDPE with HDPE. Changes in crystallization behavior and the resulting morphology as a function of blending ratio are studied through differential scanning calorimetry and X-ray diffraction. Variations in the DSC crystallization exotherms are clearly distinguished for the two steps of crystallization, viz., the nucleation and growth. The ultimate crystalline morphology, which is governed by the relative rates of these two steps of crystallization, is shown to differ in the three regions of blend compositions, viz., the HDPE-rich blend, the LLDPE-rich blend, and the middle region.

EXPERIMENTAL

Materials

HDPE (Hostalene GF 7745F) used was a product of Polyolefin Industries Ltd., Bombay, India, and the LLDPE based on octene comonomer (Dowlex 2740E) was a product of Dow Chemicals, U.S.A. Some important properties of these two polymers are listed in Table I.

Blend Preparation

Blends were prepared by melt mixing in a single-screw extruder (Betol 1820) of L/D ratio 17, using temperature profile as 160°C at the feed zone, 200°C at the compression zone, and 210°C at the metering zone and the die end. The screw speed was kept at 22 rpm. The extruded strands were cooled in water at 30°C and subsequently granulated after allowing a maturation time of 8 h. Injection molding was

Table I   Characteristics of Raw Materials

Property	HDPE	LLDPE
Melt flow index (g/10 min)	0.75	1.00
Density (g/cm³)	0.952	0.924
Melting peak temperature (°C)	131	126
Tensile yield stress (MPa)	24.5	19.3

Table II   Nomenclature and Composition of Samples

Designation	Composition (wt %)	
	HDPE	LLDPE
HDPE	100	0
B1	90	10
B2	75	25
B3	65	35
B4	50	50
B5	30	70
B6	20	80
LLDPE	0	100

done, subsequently keeping identical extruder conditions. The various samples thus prepared are designated as shown in Table II.

Measurements

Crystallization exotherms and melting endotherms were recorded on a Perkin-Elmer differential scanning calorimeter (Model DSC-7) at cooling and heating rates of 10°C/min in nitrogen atmosphere. Powdered samples of about 10 mg were used. All the samples were first run through a heating cycle from ambient to 160°C and then through a cooling cycle after 2 min at 160°C. Furthermore, using the software provided in the instrument, the thermograms were normalized to constant weight and recorded in all cases.

X-ray diffraction measurements were made on a Rigaku diffractometer using CuK_α radiation at a scanning speed of 5°/min in the 2θ range for 10–40°. Crystallinity, d spacing, and crystallite thickness were calculated as per the procedure described elsewhere.[5]

ANALYSIS PROCEDURE

Changes in the crystallization exotherm can be correlated with the changes in crystallization behavior and the resulting morphology by the analysis procedure, based on the parameters defined now and illustrated in Figure 1.

1. S_i, the initial slope of the exotherm (represents the slope of the higher temperature side of the exotherm for this measurement during cooling) depends on the rate of the process occurring in the initial stage of crystallization,
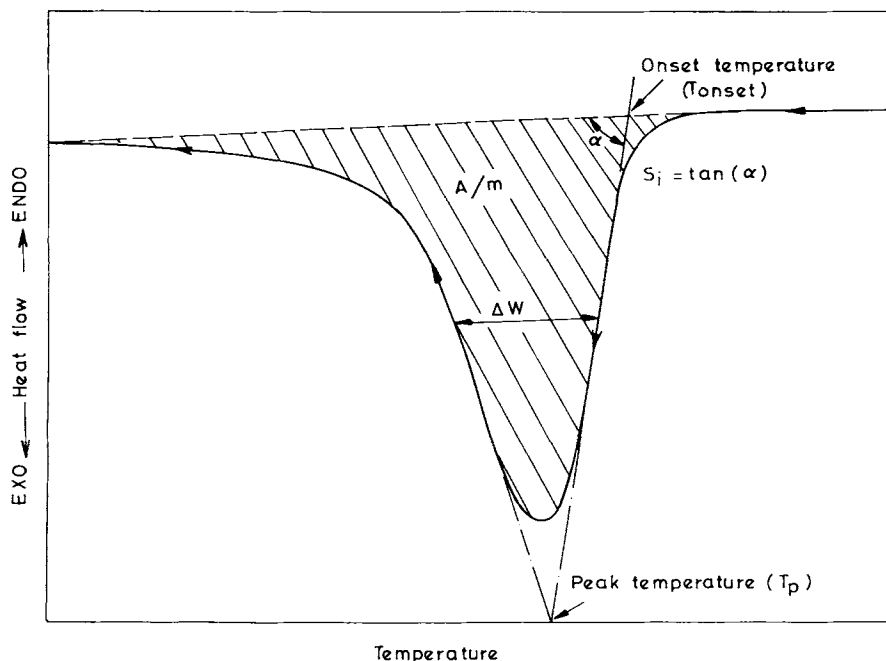
Figure 1 Schematic diagram of crystallization exotherm recorded during cooling cycle.

viz., the nucleation. Thus an increase of S_i implies an increase of rate of nucleation and vice versa.

2. Δw, the width of the exotherm peak at half height, is dependent on crystallite size distribution. The greater the Δw, the wider would be the crystallite size distribution.

3. A/m, the ratio of area (A) under the exotherm and mass (m) of the sample, is proportional to the degree of crystallinity.

4. T_p, the exotherm peak temperature, determined as the point of intersection of the tangents by the two sides of the exotherm. An increase of T_p may imply an increase of the rate of the process and vice versa.

5. T_{onset}, the temperature of onset of the crystallization, may be interpreted in a similar way as T_p. However, the rates of variation of T_p and T_{onset} may differ owing to the differences in the initial slope (S_i). Hence T_{onset} may be associated with nucleation process, while T_p is associated with overall crystallization process.

A self-check of the consistency of this analysis procedure is inherent in the mutually opposite trends of variation of S_i and Δw, i.e., an increase of S_i (or rate of nucleation) should result in a decrease of Δw (or the narrow distribution of crystallite size), and vice versa. This analysis procedure has been used previously for polypropylene-based blends.[6-9]

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

The crystallization exotherms of HDPE and LLDPE show single peaks (Fig. 2) around 111 and 107°C, respectively. The height and area of the peak, for these curves normalized to identical sample weight, are higher for HDPE than LLDPE, as expected due to higher crystallinity of the former.

The crystallization exotherms of the HDPE/ LLDPE blend, shown in Figure 2, are similar to those of the individual components and are gradually varying in area and position on temperature scale with varying LLDPE content of the blend. The single-peak character in these exotherms of the blend is an indication of cocrystallization in view of the findings of other authors[3,10] for the blends of LLDPE with other grades of polyethylene.

The melting endotherms of these samples, presented in Figure 3, also show single-peak character at all the compositions of the blend, which further supports the cocrystallization in this blend. Subsequent discussion on the effect of blending ratio on crystallization behavior is based on the analysis of crystallization exotherms, since they are recorded on samples crystallized afresh from the melt with all previous history of crystallization washed away.

Variations of these parameters of the crystallization exotherms as function of LLDPE content of the blend are shown in Figure 4. The temperatures
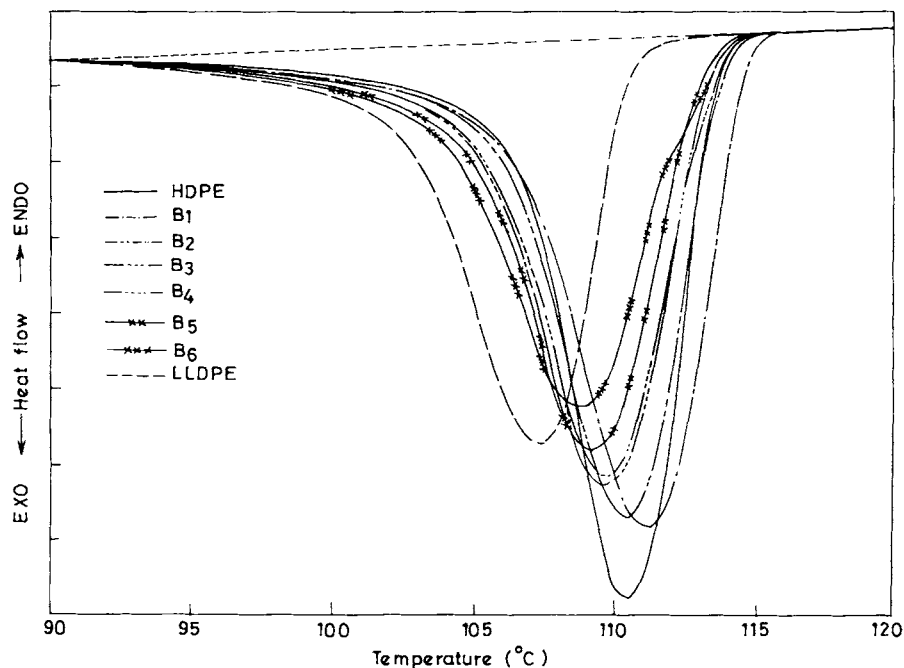
Figure 2 DSC crystallization exotherms of HDPE, LLDPE, and their blends.

T_p and T_{onset} increase, with respect to the values for HDPE, on 10% addition of LLDPE and then decrease continuously with increasing LLDPE content of the blend. However, the variations of T_p and T_{onset} are quite inappreciable in the range of 30–70% LLDPE content, i.e., the middle region of blend composition where the two phases are in equal (or approximately equal) proportion. Thus the variation of T_p and T_{onset} may be viewed to differ in the three regions of blend composition: (i) HDPE-rich blend (i.e., 0–30% LLDPE content), (ii) the middle region (i.e., 30–70% LLDPE content), and (iii) LLDPE-rich blend (i.e., 70–100% LLDPE content).

The initial slope S_i of the exotherm decreases
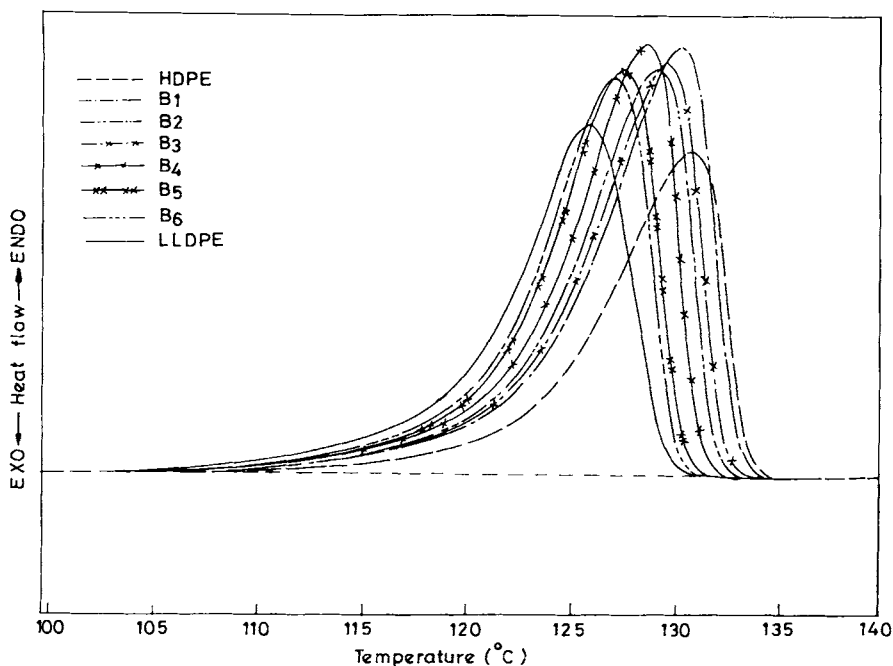

Figure 3 DSC melting endotherms of HDPE, LLDPE, and their blends.

with increasing LLDPE content continuously in the whole range up to 80% LLDPE content. At 80% LLDPE content the S_i of the blend is much lower than that of pure LLDPE. This region of LLDPE-rich blend is not well explored here owing to the lack of samples in this range of blend composition, hence the variations of crystallization parameters are not emphasized and the curves in this region are drawn by dotted lines (Fig. 4). The difference of values of S_i of LLDPE and HDPE indicates a slower rate of nucleation of LLDPE than HDPE, and the addition of LLDPE decreases the rate of nucleation of HDPE continuously up to 80% LLDPE content.

Variation of half-width, Δw, of the exotherm is opposite to that of S_i, which fulfills the aforesaid requirement of self-consistency. The decreasing rate of nucleation gives rise to creation of nuclei at different times, which ultimately grow into crystallites of widely differing sizes. In the range of HDPE-rich blends, the 10% LLDPE addition seems to show
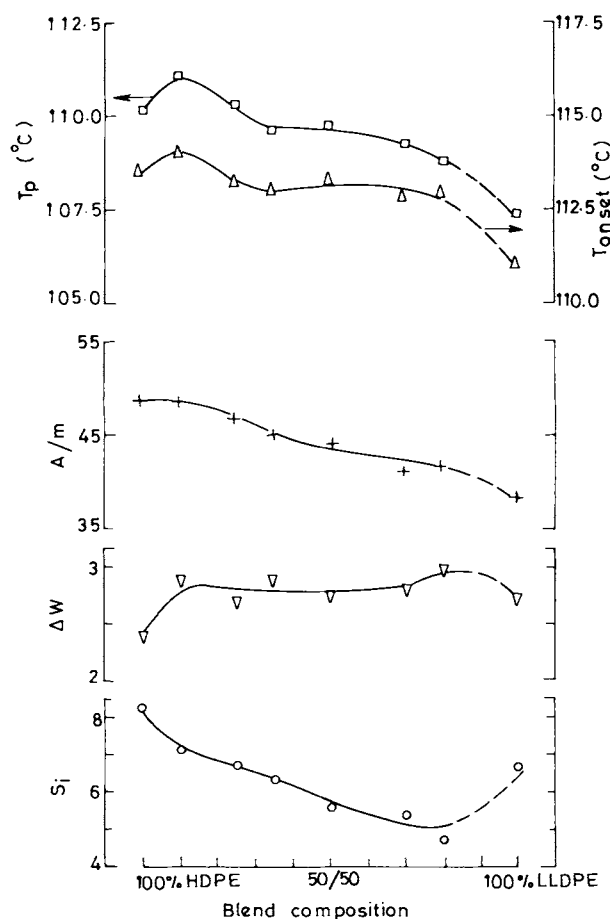

Figure 4 Plot of the various parameters determined from DSC crystallization exotherm as a function of blend composition. S_i, Δw, and A/m are in arbitrary units.

greater effect on S_i and Δw (as the curves are steeper in this region) than the subsequent additions. In the T_p and T_{onset} curves also the data points at 10% LLDPE content are relatively higher than others.

The decrease of T_p and T_{onset} may also be viewed as the decrease of the rates of the respective processes. The decrease of both the parameters related with nucleation, viz., T_{onset} and S_i, are mutually consistent. The variation of T_p indicates a decrease of overall crystallization rate. Thus the decrease of both nucleation and crystallization rates must result in a decrease of degree of crystallinity with increasing LLDPE content of the blend, which is clearly supported by the observed variation of A/m in Figure 4. However, the decrease of A/m is quite insignificant in the region 0–10% LLDPE content, which seems an effect of somewhat enhanced rate of crystallization implied by higher value of T_p at this blend composition.

Hu et al.,[10] on the other hand, report a continuous decrease of Δw and T_p with increasing LLDPE content in the entire range of blending ratio for HDPE/LLDPE blend. This differs from the present results, particularly, at low LLDPE content (i.e., 10% LLDPE). The trend of decrease of T_c with increasing LLDPE content, reported by Hu et al.,[10] is qualitatively similar to the variation of T_p in the present data except at this low LLDPE content composition. On the other hand the variation of Δw differs from that observed by Hu et al.[10] They find a continuous decrease while we find initially a rapid increase and then a gradual increase. Our trend of variation of Δw is fully in agreement with the variation of S_i, required by the previously stated conditions of consistency, viz., an increase of S_i should be accompanied by a decrease of Δw. The reason for this difference of results is not clear, except that the exotherms were recorded at different cooling rates in the two studies, and the LLDPE is octene based in the present work and butene based in the work of Hu et al.[10]

Thus, on the basis of these DSC results, the overall picture of the crystalline morphology in the three regions of blend composition may be described as follows.

In HDPE-rich blend the addition of LLDPE slows down the nucleation rate while the overall crystallization rate is slightly higher at 10% LLDPE containing blend than in HDPE. As a result, the decrease of crystallinity is apparent only when LLDPE content is higher than 10%. The crystallite size distribution increases with increasing LLDPE content. The situation at 10% LLDPE content is somewhat unique, as the changes in crystallization

behavior are sharper when one goes from 0 to 10% LLDPE composition of the blend.

In the middle region of blend composition (30–70% LLDPE content), nucleation rate (i.e., the parameter S_i) decreases continuously while overall crystallization rate (i.e., the parameter T_p and T_{onset}) remains almost unchanged. This is accompanied by continuous decrease of crystallinity and increase of crystallite size distribution with increasing LLDPE content.

In LLDPE-rich blend the variations of morphology may be described by considering LLDPE as the reference system and HDPE as inclusion. Addition of HDPE increases the overall crystallization rate while the nucleation rate first decreases sharply and then increases slightly after 20% addition of HDPE. The crystallinity initially shows a higher value at 20% HDPE content than for pure LLDPE and then becomes stable, while the crystallite size distribution increases up to 20% HDPE addition and then decreases on further addition of HDPE.

X-Ray Diffraction

The x-ray diffraction patterns of HDPE, LLDPE, and their blend at various compositions are shown in Figure 5. The diffraction patterns of LLDPE and HDPE have similar features, viz., the two sharp maxima at $2\theta = 21.4°$ (110 reflection) and 24.0° (200 reflection) and a small maxima around $2\theta = 20.0°$. Similar diffraction pattern of HDPE is reported[11,12] in the literature, while the diffraction pattern for LLDPE is rare in the literature. Hence, the presently observed resemblance of the two diffraction patterns may be emphasized. There is, however, slight difference in the d spacing of LLDPE and HDPE; the former has higher d spacing.

Blending of HDPE and LLDPE produces no change in the overall shape of the diffraction pattern. However, some gradual changes in crystallinity, crystallite size, and d spacing are found with variation of LLDPE content of the blend. The d spacing, calculated by Bragg's equation, for the two promi-
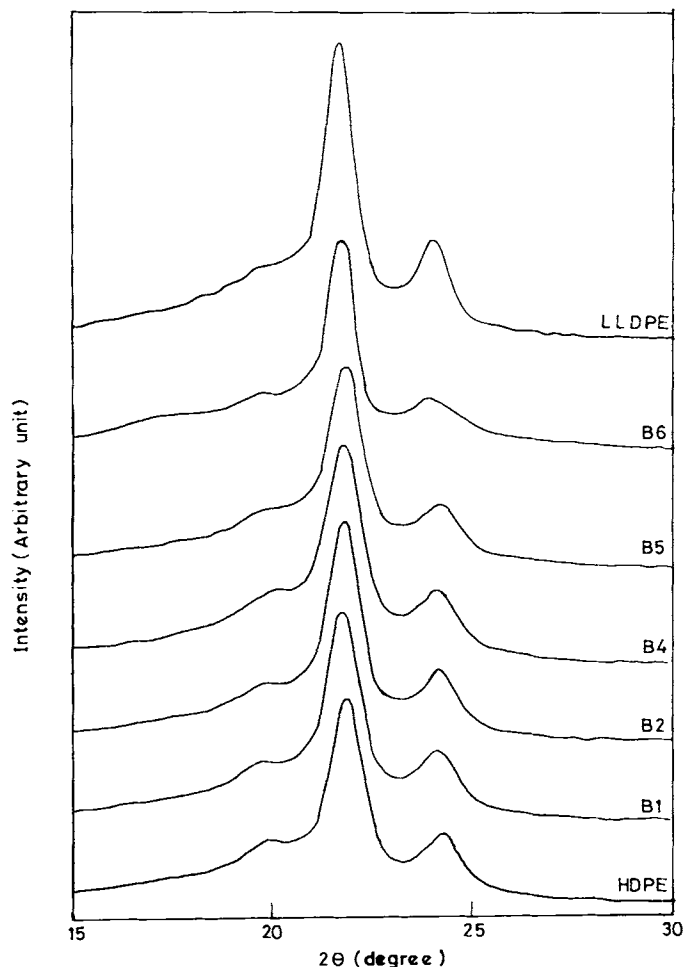

Figure 5 X-ray diffraction patterns of HDPE, LLDPE, and their blends.

nent reflections [(110) and (200)] are smallest for HDPE and largest for LLDPE, while its value gradually increases with increasing LLDPE content of the blend, as shown in Figure 6. The total increase in d spacing is less than 0.1 Å, which is not ignorable as it is quite systematic and regular over the whole range. Such small variations in d spacing have been reported by other authors[3,10] for the blends of different grades of polyethylene undergoing cocrystallization. The variation of d spacing with blending ratio for HDPE/LLDPE blend[10] and UHMWPE/LLDPE[3] are reported linear or slightly nonlinear depending on the mixing technique used.

Crystallite size, calculated by Scherrer's equation from the half-width of 110 diffraction peak, varies as shown in Figure 6. An increasing trend of crystallite size with increasing LLDPE content is discernible despite the large scatter of data points. Role of LLDPE in increasing crystallite size of the cocrystals is difficult to visualize. However, the decrease of nucleation rate, as shown by the DSC re-
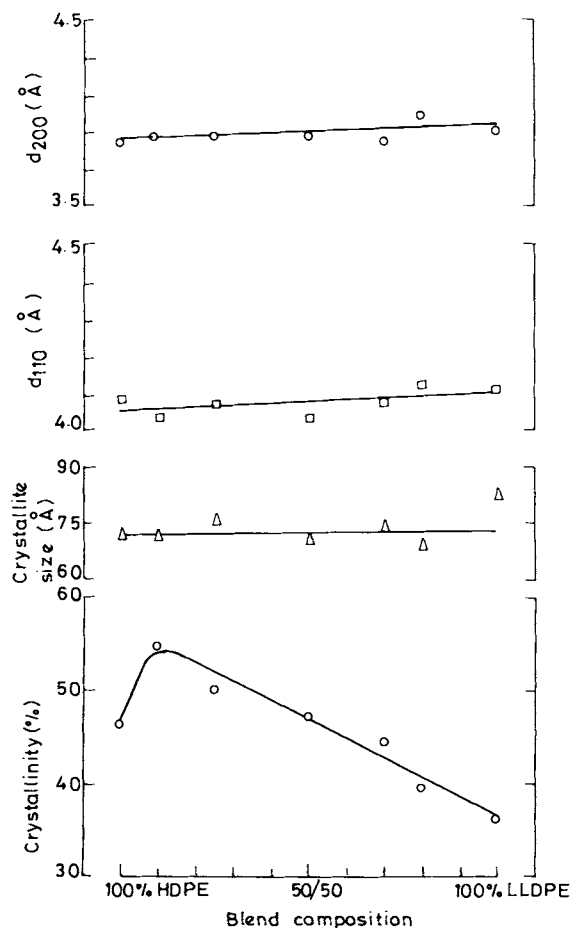

Figure 6   Plot of X-ray crystallinity parameters vs. blend composition.

sults, might be responsible for the formation of large crystallites (with wide size distribution) to account for this observed trend in crystallite size variation, inferred from X-ray measurements.

It may be emphasized that any peak broadening, which should have shown a decrease of crystallite size, of the X-ray diffraction maxima does not occur on blending. This is an argument in favor of co-crystallization, as also used by other authors[3] for UHMWPE/LLDPE blend. Since if the two components form separate crystals, then their diffraction maxima will be slightly different on the 2θ scale and overlap to give rise to apparent peak broadening. Such an effect is not present in these diffraction maxima, which show either no change or slight decrease of peak width, thus supporting the occurrence of cocrystallization.

The crystal structure of the cocrystallized HDPE and LLDPE would contain only polyethylene-type linear sequences of both the components. The side group (i.e., octene in this case) containing segments of LLDPE would remain outside the cocrystalline regions. These molecular segments of LLDPE at the boundary of the crystallites would differ from those of HDPE in their mobility, hence they would exert different types of forces on the crystalline region. These forces due to segmental mobility at the boundary of the crystallites would cause fluctuations and may result in an increase of d spacing with increasing LLDPE content, as is actually observed. This increase of d spacing, however, is accompanied by slight increase or no significant variation of crystallite size.

Crystallinity shows an increase initially on adding 10% LLDPE and then decreases with increasing LLDPE content as shown in Figure 6. The decrease of crystallinity may be attributed to the obstruction of mobility of HDPE chains by the LLDPE chains, which might reduce the ease of crystallization. At low LLDPE content (i.e., 10%), the LLDPE seems to ease the mobility of HDPE chains owing to the increased free volume due to the presence of bulky octene groups, which helps in crystallization and thus results in increase of crystallinity. At higher LLDPE content, the bulky comonomer units' role of obstructing the segmental mobility predominates over their free volume increasing mechanism. Hence the rate of crystallization decreases with increasing LLDPE content, at LLDPE content higher than 10%. Furthermore, the trend of variation of X-ray crystallinity (Fig. 6) is qualitatively similar to the variation of the DSC crystallinity parameter A/m (Fig. 4), except in the low LLDPE content region. The difference in DSC and X-ray crystallinity, es-

pecially in the low LLDPE content region, might be due to the different crystallization condition employed in the two cases. In DSC the crystallization occurred at a constant cooling rate (i.e., 0°C/min) while the samples used for X-ray measurements crystallized at slow cooling at ambient temperature after molding.

CONCLUSION

These DSC and X-ray diffraction results show that cocrystallization of HDPE and LLDPE occurs at all compositions of their blend prepared by melt mixing in a single-screw extruder. The evidences for cocrystallization are apparent as the single-peak character of the DSC crystallization exotherms and melting endotherms and the absence of peak broadening in X-ray diffraction.

The effect of LLDPE on the crystallization behavior of HDPE is quite sharp at 10% LLDPE content, where the nucleation rate is considerably lowered and overall crystallization rate is enhanced while the crystallinity increases (as in X-ray diffraction data) or remains unchanged (as in DSC results). The effects of LLDPE on crystallization differ in the three ranges of blend composition, as discussed. In HDPE-rich blend the addition of LLDPE slows down the nucleation rate and enhances the overall crystallization rate, such that the ultimate crystallinity and crystal size distribution depends on the mutual compromise of the two effects. On the other hand, in the LLDPE-rich blend, addition of HDPE increases the overall crystallization rate, while the nucleation rate first decreases and then increases above 20% HDPE content. Fur-

thermore, the presence of the comonomer in LLDPE (viz., octene in this case) tends to increase the Bragg's spacing corresponding to both (110) and (200) reflections, which also supports the cocrystallization of LLDPE and HDPE.

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