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# Morphology of HDPE/LDPE blends with different thermal histories

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High-density and low-density polyethylene (HDPE and LDPE) were melt-blended with the intent of building a morphological model from the unit cell level as a function of weight content and heat treatment. The compression-moulded sheets were slowly and rapidly cooled to compare the extremes in crystallization conditions. Based on the *d*-spacings, there is no apparent distortion on the unit cell level for either heat treatment. The addition of LDPE caused the crystallite size to decrease from 265 Å for the HDPE homopolymer to 130 Å for the LDPE. This is indicative of separate crystallite formation since a co-crystal would necessarily have the same size regardless of LDPE weight content. The high branch content of the LDPE seems to suppress crystallite growth of the rapidly cooled blends as the 25 wt% HDPE blend and LDPE have the same crystallite dimensions. Although two phases are present, there is a noticeable shift of both the HDPE and LDPE peaks towards one another, indicating some interaction on the molecular level. The lamellae that comprise the crystalline phase decrease in population and thickness as the LDPE content increases.

**(Keywords: polyethylene blends; morphology; thermal history)**

## INTRODUCTION

Interest in the blending of polyethylenes stems from the need to understand conditions of phase segregation and miscibility as well as to improve particular properties over those of the one-component system. Traditionally, different branch content polyethylenes are blended in order to improve the toughness or processability. Other microstructural features such as molecular weight and molecular weight distribution also influence the mechanical properties. The morphology of the branched and linear polyethylenes both in the blend and homopolymer reflect the combined effect of thermal history and microstructure.

The effects of branching content and molecular weight are important when a copolymer, such as linear low-density polyethylene (LLDPE) or highly branched low-density polyethylene (LDPE), is mixed with the linear chains of high-density polyethylene (HDPE). In this vein, considerable research has been devoted to phase segregation and/or miscibility of LLDPE with LDPE and HDPE as well as HDPE/LDPE blends in solution[1-9]. A blend of HDPE with LLDPE containing 18 short-chain branches per thousand carbon atoms[1] showed co-crystallization based on the presence of a single d.s.c. peak and the lack of peak broadening in wide-angle X-ray diffraction. At the lamellar level, these two materials formed a co-lamellar entity as evidenced by Raman–LAM (Longitudinal Acoustic Mode) studies. Again, the long period varied linearly with composition without any maximum or minimum value. The resulting spherulitic structure decreased in size with increasing LLDPE content. However, when the samples were allowed to crystallize isothermally, phase segregation occurred. Two melting temperatures were present with the higher corresponding to the isothermally crystallized material and the lower to the quenched crystals. This indicates the importance in separating out thermodynamic and kinetic effects on phase segregation.

A study devoted to time-dependent phase segregation focused on a 50/50 HDPE/LDPE solution blend[2]. This composition was assumed to be miscible as substantiated by a single endothermic d.s.c. peak. The morphology was spherulitic and uniform. This blend exhibited two morphologies after isothermal crystallization particular to each component. After quenching from the crystallization temperature, a fine S-shaped lamellar morphology characteristic of the LDPE was dispersed within the larger sheets of HDPE lamellae. The thicker lamellae were assumed to be HDPE, since LDPE crystallization was restricted at the chosen crystallization temperature. A parallel study[3] focused on the ranges of miscibility as a function of composition and temperature in order to construct a phase diagram. It was found that above 50 wt% HDPE the systems were monophasic. Transmission electron micrographs revealed a banded spherulitic morphology at this composition and higher, but a double morphology at lower HDPE content in which the lamellae were thinner and more unevenly dispersed.

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Solution-blended high- and low-density polymers exhibit composition-dependent miscibility, while melt blends of HDPE with LDPE typically exhibit biphasic behaviour[4,7]. When the materials are crystallized, the relatively linear chains of HDPE permit the formation of spherulites. In contrast, branches of LDPE are excluded to an increasing extent beyond the methyl branch length. These branches are found in the interlamellar phase. The degree of exclusion from the lamellae depends on the regularity of the intermolecular branch point spacing to a greater extent than the type of branch[10–12]. The branches excluded to the interlamellar region increase the strain on the crystal, decreasing the thickness and lowering the melting temperature. It is assumed that these branches also act as barriers to chains of HDPE and subsequent co-crystallization.

The purpose of this work was to develop a tie between the observed mechanical properties and morphology of an HDPE and LDPE blended in the melt. Research on melt-blended polyethylenes has not yet proposed an explanation for the observed relationship between the morphology which develops in both phase-segregated and miscible materials and the mechanical behaviour. In this paper, a morphological picture of the blends as a function of blend ratio and thermal history will be constructed, beginning on the unit cell level and moving to domain characterization. In a subsequent investigation[13], the effects of tensile deformation will be described and a morphological deformation model proposed.

## EXPERIMENTAL

### *Materials*

The high-density (LF603-00) and low-density (NA820) polyethylene were supplied by Quantum Chemical Company from whom the molecular weight averages, densities and branching contents shown in *Table 1* were also obtained. The weight average molecular weight of both polyethylenes was 120000. HDPE/LDPE blends of 75/25, 50/50 and 25/75 wt% as well as pure HDPE and LDPE were prepared at a screw speed of 60 rev min$^{-1}$ in a twin-screw extruder with a temperature profile of 177–190–191–189–195–207°C. It is acknowledged that a screw speed of 60 rev min$^{-1}$ is relatively low for a twin-screw extruder but it is part of a series of extrusions to determine compatibility and/or miscibility as well as mechanical properties as a function of shear rate. The pellets were then compression-moulded into sheets of 2.8 mm thickness at a temperature of 180°C and pressure of 3000 psi for 5 min followed by 15 min at $30 \times 10^3$ psi. Sheets were water-quenched by running cold water through the platens for 8 min. Slow cooling was accomplished by turning off the heaters and removing the plaque when the platens had reached 30°C. The duration of this cooling cycle was on the order of 6 h.

**Table 1** Polyethylene sample characteristics used in study of melt-blended high- and low-density polyethylenes. All data supplied by Quantum Chemical Company

| Material | Density (g cm$^{-3}$) | PDI[a] | $CH_3$/ 1000C | $C_2H_5$/ 1000C | $C_4H_7$/ 1000C |
|---|---|---|---|---|---|
| LF603-00 (HDPE) | 0.959 | 8.2 | 0.1 | – | – |
| NA820 (LDPE) | 0.916 | 8.4 | 1 | 5.2 | 8.6 |

[a] Polydispersity index

### *Wide-angle X-ray diffraction* (*WAXD*)

Samples were examined in a Phillips diffractometer at an accelerating voltage of 40 kV and amperage of 30 A using CuK$\alpha$ radiation to determine changes in *d*-spacings and half-widths as a function of composition and heat treatment. All materials were scanned at a rate of 0.01 $2\theta$ s$^{-1}$ between 5 and 50° in reflectance mode. Corrections were made for Lorentzian scattering, background and polarization effects. The *d*-spacings were calculated from the Bragg equation using the peaks corresponding to reflections along the (110) and (200) planes and by assuming an orthorhombic unit cell with an *a*-axis of 7.417 Å, *b*-axis of 4.945 Å and *c*-axis of 2.547 Å. The half-widths were used to determine the crystallite size from the Debye–Scherrer equation using a constant value of 1.0 (ref. 14).

### *Density measurements*

The density of the compression-moulded plaques was measured using an isopropanol–distilled water density gradient column at 23°C. Five samples were taken from the centre of the plaques. The crystallinity was calculated from the Chiang–Flory[15] relationship, in which the densities of the crystalline and amorphous phases were assumed to be 1.000 g cm$^{-3}$ and 0.853 g cm$^{-3}$, respectively[16].

### *Differential scanning calorimetry* (*d.s.c.*)

Samples used for thermal analysis were removed from the centre of the compression-moulded plaques and weighed between 5 and 10 mg. Each was scanned in a Perkin–Elmer model 7000 DSC instrument at 10°C min$^{-1}$ between 30 and 175°C. From the normalized area under the curve the per cent crystallinity was calculated based upon a perfect crystal heat of fusion of 290 J g$^{-1}$ (ref. 17).

### *Microscopy*

The morphology was examined first at the optical level by cutting 10 $\mu$m sections from the compression-moulded plaque using a Jung Frigocut 2800E at $-20$°C. The sections were etched in a 5% w/w potassium permanganate and *o*-phosphoric acid solution for 1 h (ref. 18) and then washed and placed between a glass slide and cover slip. Samples for transmission electron microscopy (TEM) were prepared by staining a piece of the compression-moulded plaque in a 0.2 g/10 ml solution of $RuCl_3 \cdot 3H_2O$ in sodium hypochlorite for 2 h at room temperature. Samples were then embedded in epoxy, trimmed and stained in the vapour phase for 20 min to increase contrast and hardness. Microtoming was done with a diamond knife at room temperature using an RMC MT-6000 Ultramicrotome. Sections ranged in thickness from approximately 80 to 150 nm, depending upon the necessary mass thickness contrast. Samples were viewed in a JEOL 100SX TEM at 100 kV excitation voltage.

## RESULTS

The development of a molecular model begins with the smallest measurable entities and builds to those observable on the micrometre level. To understand the blends' mechanical behaviour a visible model of the morphology from the smallest to the largest features was constructed. This study begins by using techniques which are capable of probing molecular dimensions, such as WAXD, and concludes with an examination of the blends at the micrometre level.

### *Unit cell and crystallite dimension determination*

The intensity–2θ plots are shown in *Figures 1* and *2*. The slowly cooled materials (*Figure 1*) have sharper peaks than the rapidly cooled materials (*Figure 2*) at 21.5°, 24.5° and 30° 2θ, corresponding to the (110), (200) and (020) reflections. From examination of the amorphous scattering peak centred at around 19.5° 2θ it is seen that the peak is broader in the rapidly cooled materials for all compositions. These two results lend credence to the qualitative conclusion that the rapidly cooled blends contain smaller crystallites which are less populous than in the slowly cooled blends.

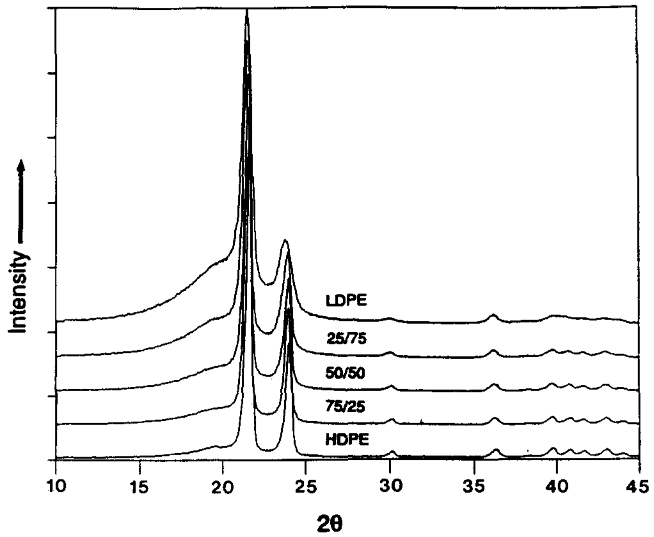

**Figure 1** Wide-angle X-ray diffraction intensity *versus* 2θ plots for slowly cooled blends scanned from 10° to 45° 2θ

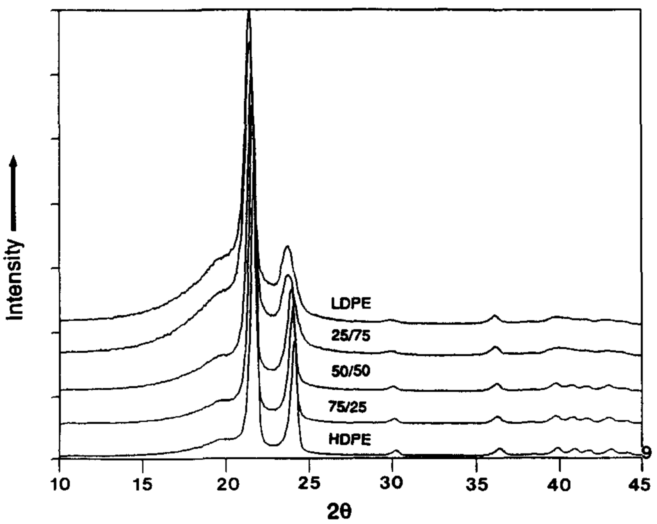

**Figure 2** Wide-angle X-ray diffraction intensity *versus* 2θ plots for rapidly cooled blends scanned from 10° to 45° 2θ

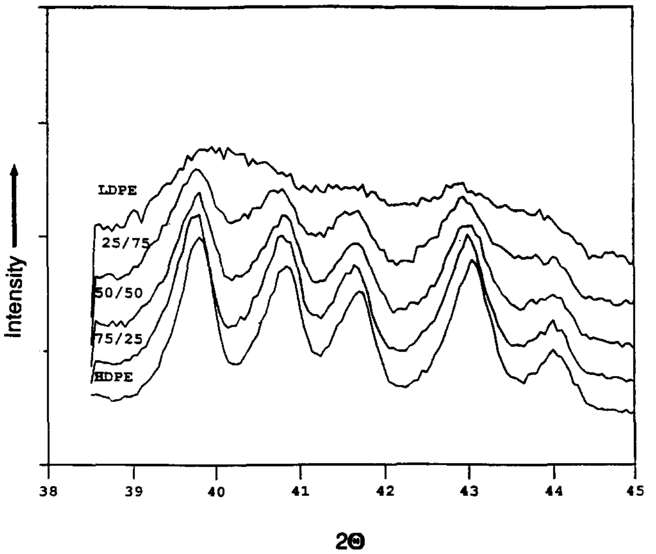

**Figure 3** Intensity *versus* 2θ plots for 2θ values between 38° and 45° for the slowly cooled blends. The change in small *d*-spacings is more evident than in the full intensity scan

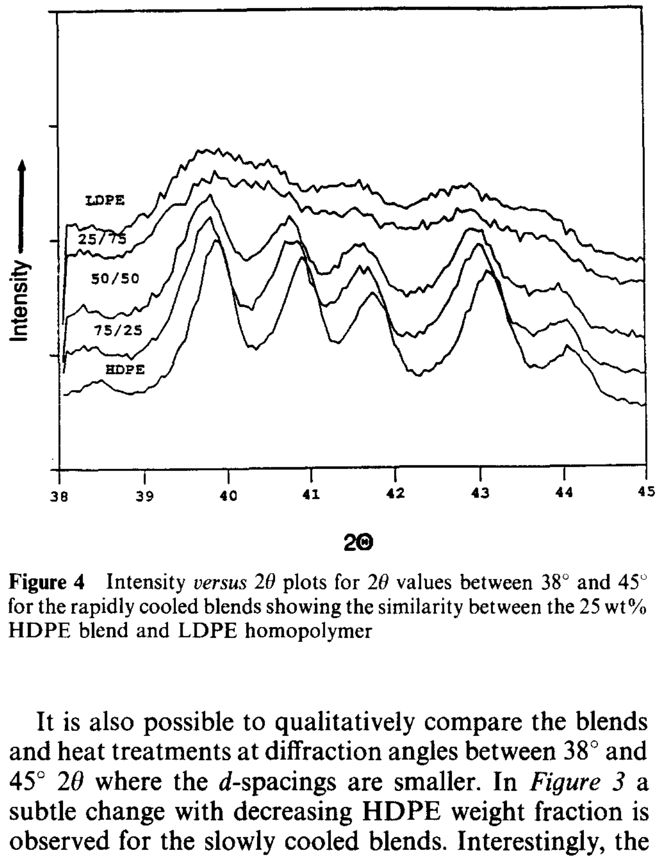

**Figure 4** Intensity *versus* 2θ plots for 2θ values between 38° and 45° for the rapidly cooled blends showing the similarity between the 25 wt% HDPE blend and LDPE homopolymer

It is also possible to qualitatively compare the blends and heat treatments at diffraction angles between 38° and 45° 2θ where the *d*-spacings are smaller. In *Figure 3* a subtle change with decreasing HDPE weight fraction is observed for the slowly cooled blends. Interestingly, the rapidly cooled 25 wt% HDPE blend and LDPE show very similar shapes (*Figure 4*). The distortion on the unit cell level for the blend and homopolymer is not seen on the other side of the composition when the HDPE is the dominant phase. It is possible that the similarity may extend to dimensions 50 times greater, i.e. the lamellar size scale.

In order to quantitatively gauge the similarity in molecular dimensions with increasing weight percentage of LDPE, the *d*-spacings for the (110) and (200) reflections were calculated. The *d*-spacings were evaluated at 2θ values around 21.5° for the (110) reflection and 24° for the (200), and showed only a slight compositional dependence (*Figure 5*) in the slowly cooled blends. This is in agreement with results obtained for HDPE/LLDPE blends[1,20]. Specifically, the $d_{110}$ values for the slowly cooled HDPE and LDPE are 4.11 Å and 4.13 Å, respectively. The rapidly cooled materials had larger *d*-spacings than the slowly cooled materials (*Figure 6*). For the rapidly cooled HDPE the *d*-spacing from the (110) reflection was 4.09 Å and that of the LDPE 4.17 Å. Therefore, although the $d_{110}$ value for the blends remains constant at 4.12 Å, regardless of heat treatment, the rapidly cooled homopolymers exhibit a more significant difference than the slowly cooled ones. Rapid cooling may cause the unit cell distortions since the crystallization proceeds at a rate faster than diffusion of the chains. When crystallized, the interlamellar region may be more highly strained, as is the unit cell, which causes expansion measured from certain crystallographic planes.

The difference between the *d*-spacings measured from the (200) reflection of the homopolymers is less exaggerated. That is, the HDPE and LDPE *d*-spacings for the slowly cooled materials are 3.71 Å and 3.75 Å, respectively, while those for the rapidly cooled materials are 3.70 Å and 3.76 Å. For each of the slowly cooled blends and the 75 and 50 wt% rapidly cooled blends the $d_{200}$ spacing is 3.72 Å while that of the 25 wt% rapidly cooled blend is 3.76 Å. Whether or not the LDPE and 25 wt% blend have the same structure on the unit cell level cannot, however, be judged. Since both the 75 and 25 wt% HDPE blends have the same *d*-spacings, this statement would automatically preclude the inherent dissimilarities between the HDPE-rich and HDPE-poor blends. Therefore, the difference of 0.03 Å between the homopolymers and blends is probably insignificant and one may say that the blends and the homopolymers do not look very different at the unit cell level.

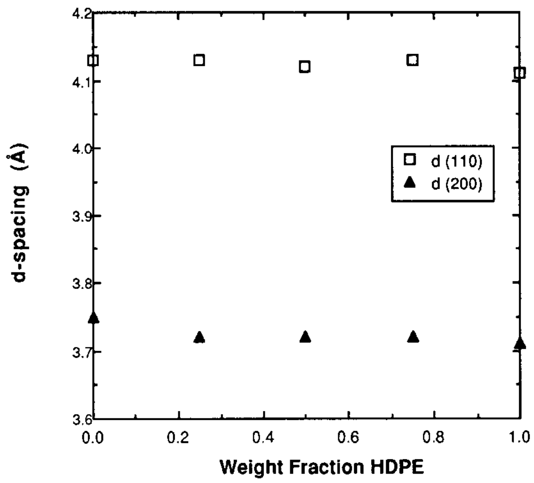

**Figure 5** The *d*-spacings calculated from Bragg's law as a function of the weight fraction of HDPE for the (110) and (200) reflections of the slowly cooled blends

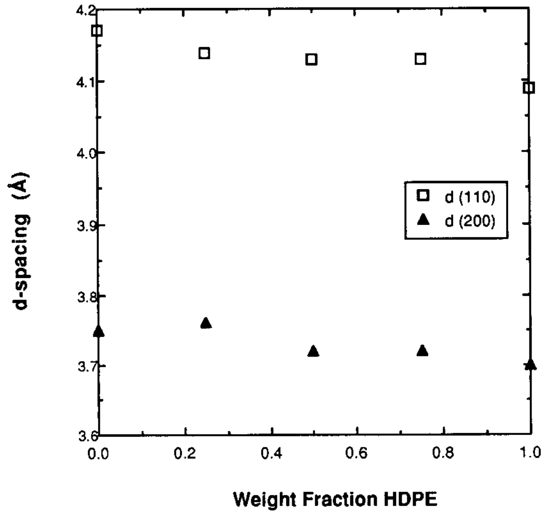

**Figure 6** The *d*-spacings calculated from Bragg's law as a function of the weight fraction of HDPE for the (110) and (200) reflections of the rapidly cooled blends

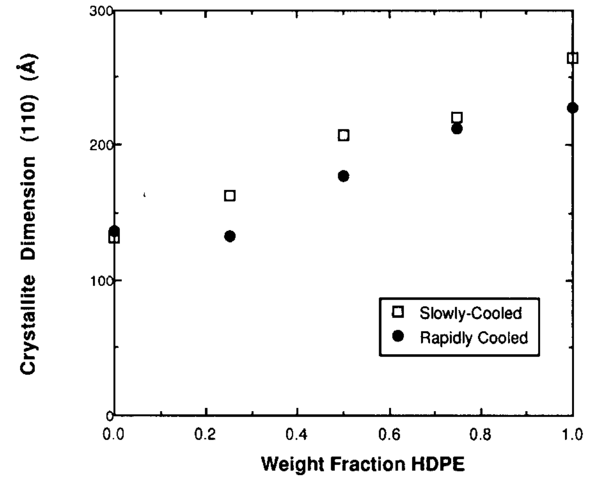

**Figure 7** Crystallite dimension measured from the half-width of the (110) reflection at approximately 21.5° $2\theta$ for both the rapidly and slowly cooled blends

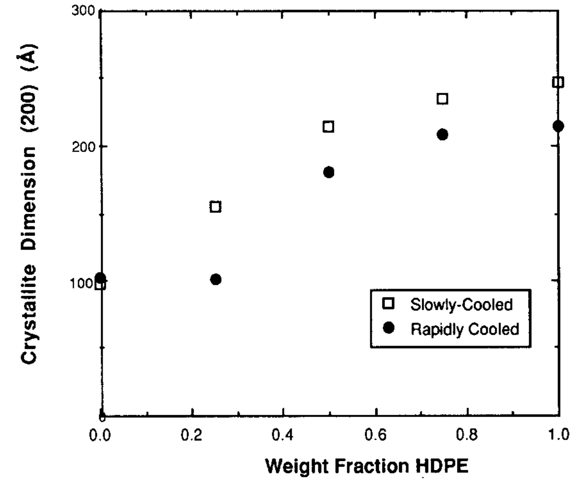

**Figure 8** Crystallite dimension measured from the half-width of the (200) reflection at approximately 24° $2\theta$ for both the rapidly and slowly cooled blends

The proximity of the peaks for the homopolymers makes it difficult to resolve them in the blends. However, if two types of crystals are formed then the peaks lying close to one another will broaden[1,20]. Broadening necessarily leads to a decrease in crystallite dimensions calculated from the Debye–Scherrer equation. From the intensity–$2\theta$ plots, the crystallite dimensions were calculated from the half-widths of the (110) and (200) reflections (*Figures 7* and *8*). The (110) reflection corresponds to the diagonal in the *a–b* plane. Here, a linear decrease is found in this dimension for the slowly cooled materials from the HDPE (265 Å) to the 75 wt% HDPE blend and then trails off smoothly to a value of 131 Å for the LDPE homopolymer. In contrast, the rapidly cooled materials show a smooth decrease as a function of composition from the HDPE (228 Å) to the 25 wt% HDPE blend. The latter blend and LDPE achieve the same dimension of 135 Å along the (110) crystallographic direction. The same is also found for the (200) dimension where the minimum observed for both the 25 wt% HDPE blend and LDPE is 120 Å. The (200) reflection corresponds to the direction perpendicular to both the growth (020) and thickness (002) directions. Although the blends may not be differentiated from each other or the homopolymers on the unit cell level, there are distinct trends observed for the crystallite dimensions. Additionally, it seems clear that separate crystallization of the low- and high-density has occurred.

The WAXD technique provides information concerning the unit cell and dimensions on the order of 100–300 Å. Also, one may judge whether or not the HDPE/LDPE blends co-crystallize. Another technique to determine miscibility on the angstrom level is d.s.c. It is possible to make a qualitative determination of the lamellar size distribution and thickness as well as to measure the heats of fusion and melting temperatures.

### *Miscibility and lamellar size evaluation using d.s.c.*

The d.s.c. endotherms of the slowly cooled and rapidly cooled materials are shown in *Figures 9* and *10*, respectively. All compositions for both heat treatments show two peaks. At HDPE contents of 25 and 50 wt%, the LDPE phase is strongly evident. However, the LDPE peak of the 75 wt% HDPE blend is negligible in comparison to that of the HDPE. This is due to the fact that the LDPE cannot readily crystallize at temperatures where the HDPE has begun to crystallize[1,8]. As the minor and less crystalline phase, the LDPE in the blend crystallizes around the already solidified HDPE to a lesser extent than the pure homopolymer. The HDPE phase may act as a nucleating agent of the low-density phase but little co-crystallization occurs.

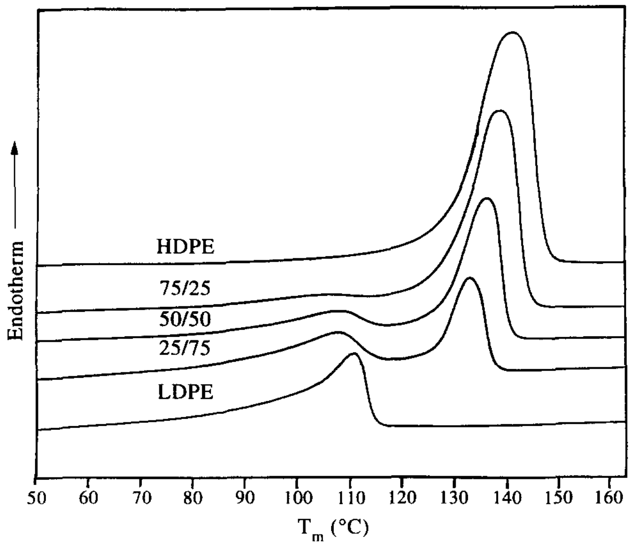

**Figure 9** Differential scanning calorimetry endotherms for the plaques of the slowly cooled blends scanned at 10°C min$^{-1}$ in which the biphasic nature of the system is evidenced by two peaks

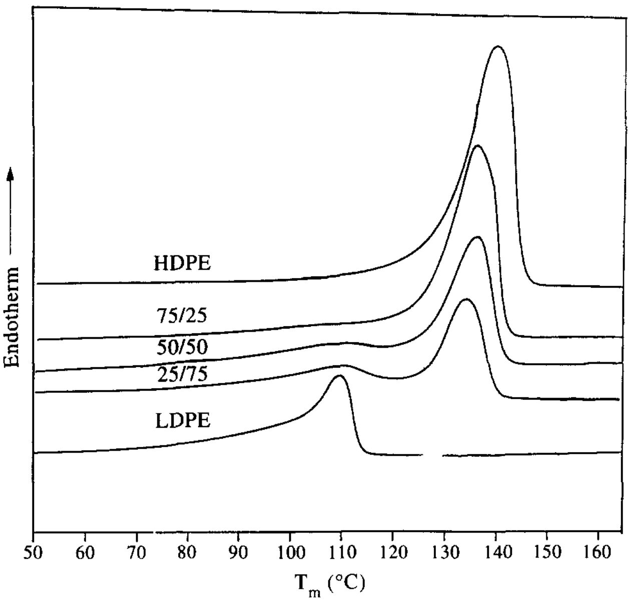

**Figure 10** Differential scanning calorimetry endotherms for the plaques of the rapidly cooled blends scanned at 10°C min$^{-1}$. As for the slowly cooled blends, two peaks are evident, reflecting the phase segregation in this system

**Table 2** Area ratios for slowly and rapidly cooled blends calculated from peak areas of endotherms for each component. Here $A_{1bl}$ is the area under the endotherm for the high-density polyethylene in the blend and $A_1$ is the area for the pure homopolymer. Likewise, $A_{2bl}$ is the area for the low-density polyethylene in the blend and $A_2$ is that for the pure LDPE homopolymer

| | Slowly cooled | | Rapidly cooled | |
|---|---|---|---|---|
| Material | $A_{1bl}/A_1$ | $A_{2bl}/A_2$ | $A_{1bl}/A_1$ | $A_{2bl}/A_2$ |
| HDPE | 1 | – | 1 | – |
| 75/25 | 0.71 | 0.06 | 0.69 | 0.01 |
| 50/50 | 0.43 | 0.24 | 0.45 | 0.11 |
| 25/75 | 0.21 | 0.37 | 0.19 | 0.33 |
| LDPE | – | 1 | – | 1 |

If this is indeed the case, then the two homopolymers will crystallize in accordance with their weight fraction in the blend. The area due to the LDPE or HDPE in the blend divided by the area under the endotherm of the homopolymer should then be equal to its weight fraction in the blend. In *Table 2*, the area ratios of the component in each blend to the homopolymer are shown. The HDPE ratios are very close to their weight fractions whereas the LDPE ratios are considerably less. The LDPE, therefore, is strongly affected by the presence of the HDPE while the HDPE may crystallize independently of the LDPE. The effect of heat treatment is also obvious when considering both the 25 and 50 wt% HDPE blends in that the values for the rapidly cooled materials are much lower than those of the slowly cooled material. The peaks of the endotherms were also used in this comparison and yielded the same results.

The melting peaks of both phases vary linearly with composition (*Figure 11*). The decrease is consistent with the idea that the crystallite perfection for each phase is diminished in the presence of the second due to a diluent

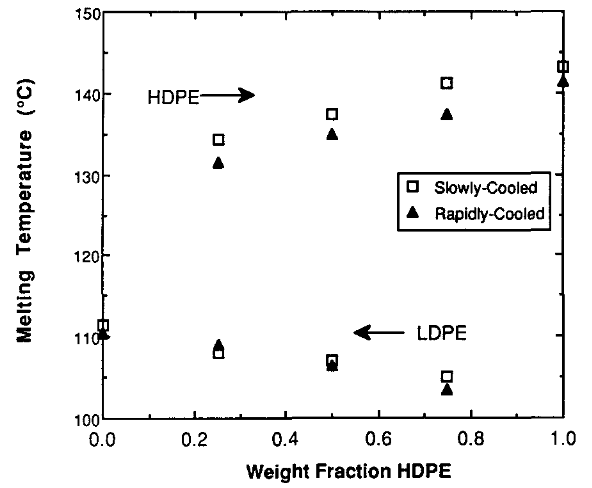

**Figure 11** Melting temperatures of HDPE and LDPE phases as a function of weight fraction HDPE for both the slowly and rapidly cooled blends

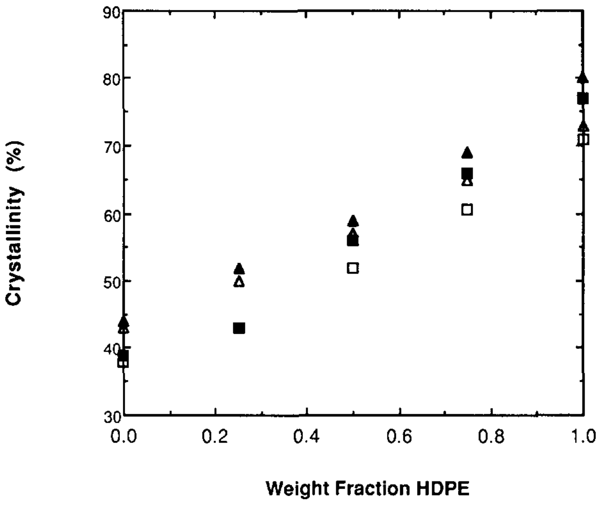

**Figure 12** Crystallinity as a function of weight fraction of HDPE in the blends calculated from density and d.s.c. measurements. Solid symbols correspond to the slowly cooled samples and open symbols to the rapidly cooled samples: ■, □, d.s.c. data; ▲, △, density data

effect[7]. A single intermediate melting peak would be observed only in the presence of a material with which one or the other materials could form a co-crystalline phase[1,6,9]. Although there is a shift in the peaks towards one another, this seems to be only a phase of intermediate density and not necessarily a co-crystalline material. It seems likely that each component, as it increases in weight concentration in the blend, assumes a more perfect crystalline form and this is then reflected in both the melting temperatures and the endotherms.

*Figure 12* depicts the total percentage crystallinity measured from the densities and heats of melting. The density values are slightly higher than those calculated from the heat of melting. This is due to the assumption that the material consists of only the amorphous and crystalline phases. Since the interlamellar region also contributes to the crystalline density, the total crystallinity is overestimated. The crystallinity decreases linearly as a function of HDPE weight content. The values for the slowly cooled materials are higher than those of the rapidly cooled materials with the exception of the pure LDPE which is the same for both heat treatments. A number of possibilities exist as to why the LDPE is insensitive to the thermal history. It could be that the thermal treatments are not extreme enough to affect the structure. Additionally, the broad molecular weight distribution results in the formation of many small crystallites at both cooling rates, which are subject to melting and recrystallization upon heating. This is derived from basic considerations of diffusion-controlled crystallization in which the more highly branched LDPE is less sensitive to thermal treatment than the HDPE.

A rudimentary correlation of the d.s.c. peak half-widths with the lamellar distribution may be done since wider peaks reflect a larger lamellar distribution. When comparing the widths of the HDPE peaks in the blends in *Figures 9* and *10*, it is seen that the difference between thermal treatments is slight. The widths of the 75 wt% HDPE peaks are the same, again indicative of the suppression of LDPE crystallization and the dominance of the HDPE in determining the morphology. Both the 50 and 25 wt% HDPE blends have HDPE peaks sharper in the slowly cooled than in the rapidly cooled materials. When comparing the LDPE, however, the slowly cooled LDPE peak is wider than that of the rapidly cooled LDPE. This is an indication of the wide molecular weight distribution.

### *Morphology via optical microscopy and TEM*

Optical microscopy was attempted to further elucidate the morphology. The 10 $\mu$m slices of both slowly cooled and rapidly cooled compression-moulded plaques showed no definable differences between the blends. Most notable was the absence of spherulites and axialites in the HDPE and LDPE, although there was a morphological gradient from the edges of the plaque towards the centre. This can be described as a transcrystalline region 20 $\mu$m thick adjacent to a uniform bulk morphology. Compression-moulded plaques may be expected to show this gradient since there is a higher nucleation density and more rapid crystallization occurs on the surfaces than in the bulk. Since no spherulites were discernible it was assumed that the high crystallinity (75%) of the slowly cooled HDPE must be due to a high population of lamellae. The HDPE homopolymer was dissolved in xylene at 135°C, filtered, and then remelted to determine whether or not processing contributed to the lack of spherulitic formation. In this case, small spherulites 5–10 $\mu$m in diameter were seen. It can be said then, that this is one contributing factor to the lack of spherulite formation.

In *Figure 13a* is a microtomed section of the slowly cooled HDPE plaque. Here, no spherulitic morphology is apparent but instead a dense population of lamellae with thicknesses of 250 Å dominate the picture. The lamellae are also twisted such that one may be viewing part of the fold surface as well as the *c*-axis crystallization direction. The lamellae are long (> 10 $\mu$m) and primarily straight although some curving or kinking is seen in the lower left-hand and far right-hand corners of the micrograph. The LDPE morphology (*Figure 13e*) is radically different from that of the HDPE and shows a greater range of thicknesses but a lower density of assemblies. The crystallite dimensions measured via WAXD provided average values. In the case of the (200)

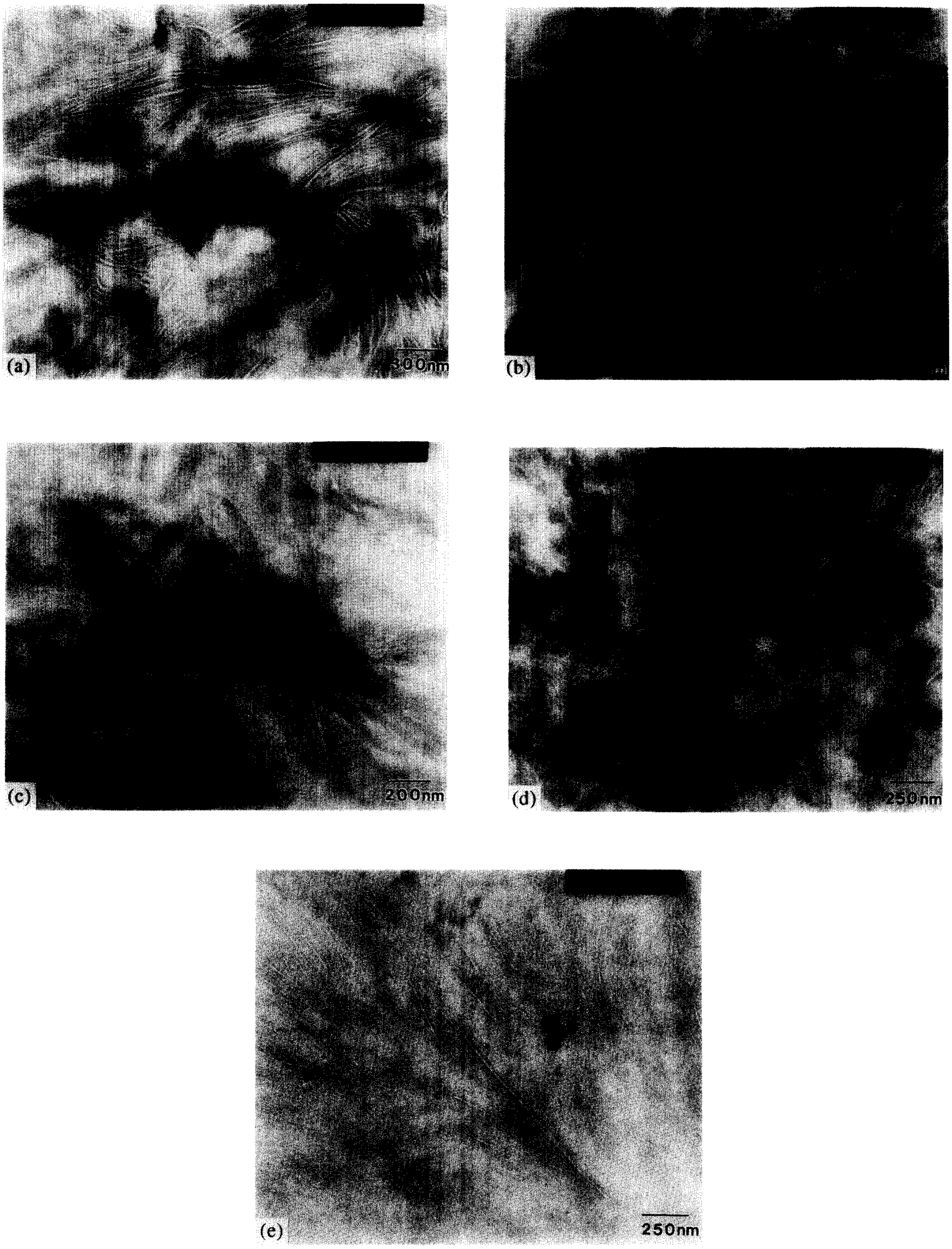

**Figure 13** Transmission electron micrographs of thin sample sections. (a) Slowly cooled HDPE plaque; the lamellar thicknesses are between 250 and 300 Å and little kinking is observed. (b) Slowly cooled 75 wt% HDPE blend; the lamellar thicknesses are between 150 (lower right-hand corner of micrograph) and 200 Å. More curvature is seen in the lamellae than found for the HDPE homopolymer. (c) Slowly cooled 50 wt% HDPE blend; the lamellar thicknesses are less than 150 Å. However, there does appear to be a distribution of thicker lamellae as well. (d) Slowly cooled 25 wt% HDPE blend; the lamellar thicknesses are around 125 Å and the density of lamellae is much less than that found for the 50 wt% blend. (e) Slowly cooled LDPE plaque; the lamellar thicknesses are around 125 Å and appear to be much less curved than found in the blends

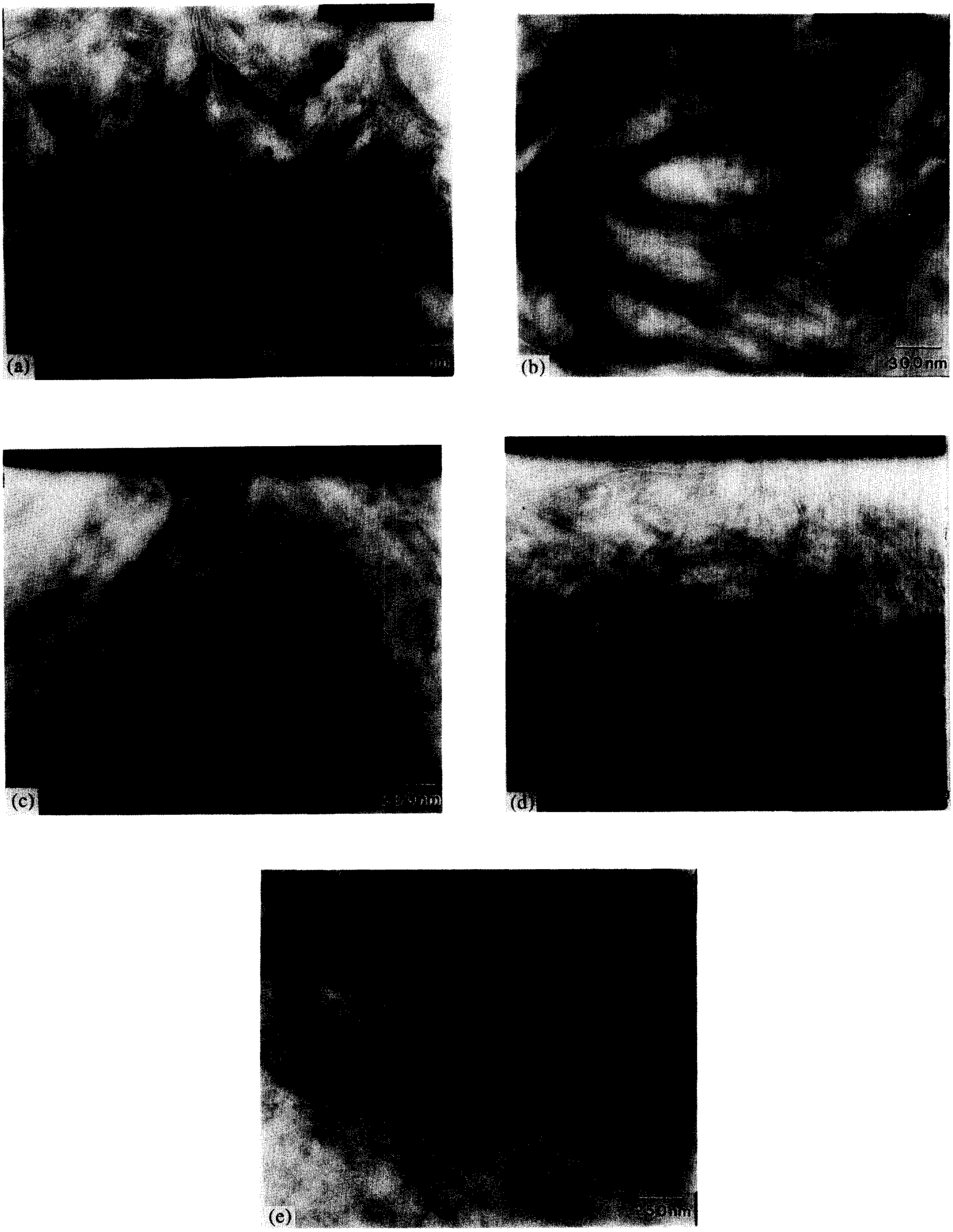

**Figure 14** Transmission electron micrographs of thin sample sections. (a) Rapidly cooled HDPE plaque; the lamellar thicknesses are between 200 and 250 Å. In comparison to the slowly cooled homopolymer, the lamellae are not as straight or as long. (b) Rapidly cooled 75 wt% HDPE blend plaque; the lamellar thicknesses are between 175 and 200 Å. The thicker lamellae are probably the high-density phase. (c) Rapidly cooled 50 wt% HDPE blend plaque; the lamellar thicknesses are between 150 and 175 Å. (d) Rapidly cooled 25 wt% HDPE blend plaque; the lamellar thicknesses are between 125 and 150 Å. There are apparently two lamellae populations though, one less than 150 Å and one around 200 Å. Thinner lamellae are dispersed within the thicker ones. (e) Rapidly cooled LDPE homopolymer plaque; the lamellar thicknesses are around 125 Å and have a great deal of short-range curvature

dimension, this would correspond to the lengths seen in the micrographs. However, the values in the micrographs are three orders of magnitude larger. Therefore, the WAXD data provide more of a qualitative measurement of the phase separation and change in average crystallite dimensions, while the microscopy is a quantitative measurement of these changes. The lamellar directionality is more obvious from top to bottom rather than the variety of orientations seen in the HDPE. The lamellae are approximately 120 Å in thickness, half of that seen in the HDPE micrograph. When considering the slowly cooled blends alone, the most notable features are the change in density of the lamellae as well as an increase in coarseness away from the fine, regular texture of the HDPE lamellae. As might be suspected from the d.s.c. endotherms, a decrease of 25 wt% HDPE leads to a coarsening of the lamellae and a subsequent decrease in melting temperature (*Figure 13b*). Here, the lamellae are approximately 170–225 Å in thickness and the degree of curvature is significantly higher than that of the homopolymer. The thickness of the lamellae in both the 75 and 50 wt% HDPE blends (*Figure 13c*) differ by only 10% although the absolute number decreases. Moreover, the lamellae appear to be straighter than those observed in the HDPE. Although no statement will be made here about which lamellae constitute which phase, it is obvious that the blends reflect both the high-density and low-density components. This is seen dramatically in the 25 wt% HDPE blend which has long, straight, thin lamellae visible in the LDPE (*Figure 13e*) but kinked lamellae are also markedly present in the 75 and 50 wt% blends (*Figures 13b* and *13c*).

When comparing heat treatments there are a number of statements to be made (*Figures 13a–e, 14a–e*). First, the differences in crystallinity between the slowly cooled and rapidly cooled 75 and 50 wt% HDPE blends are not reflected in the morphology. The number, orientation and curvature of the lamellae are not differentiable. However, there is a difference in thickness, most dramatic in the HDPE homopolymer. The lamellar thicknesses measured from both the slowly cooled and rapidly cooled materials are presented in *Table 3*. One point which has been reiterated in this discussion is the idea that the rapidly cooled 25 wt% HPDE blend and LDPE have similar morphologies. In comparing *Figures 14d* and *e*, the same morphology is observed, in which the lamellae are long and not kinked as seen in the slowly cooled 25 wt% blend (*Figure 13d*). Some evidence of the HDPE phase exists in the tighter grouping of lamellae in the upper left-hand corner of *Figure 14d* but none of the lamellae exhibit the curvature seen in the other blends. Also of note is the apparent nucleation of one lamella on the side of another. It may be argued that these are two different planes of lamellae but no evidence of defocusing is present. Whether these are lamellae of one phase, perhaps minor, nucleating on the second is not distinguishable although it is likely with a large number of nucleation sites that randomness may prevail.

**Table 3** Lamellar thicknesses measured from transmission electron micrographs of thin sections taken from both the slowly cooled (SC) and rapidly cooled (RC) plaques

| Material | Heat treatment | Lamellar thickness (Å) |
|---|---|---|
| HDPE | SC | 225–250 |
| | RC | 190 |
| 75/25 | SC | 170–225 |
| | RC | 170–225 |
| 50/50 | SC | 150–200 |
| | RC | 150–200 |
| 25/75 | SC | 70–125 |
| | RC | 70–125 |
| LDPE | SC | 125 |
| | RC | 125 |

## DISCUSSION

The miscibility of two semicrystalline polymers is based upon both thermodynamic and kinetic factors. In the case of PE/PE blends, it is assumed that the ability to form a co-crystalline phase in the solid state depends on microstructural factors. For both HDPE/LDPE and ultra-high molecular weight PE/LDPE blends the phase separation which occurs is postulated to be due to the non-linearity of the LDPE[7,9]. Therefore, it is relevant to consider the changes in morphology on various structural levels in order to gain insight into the scale at which the segregation is evident.

The results on this HDPE/LDPE blend system have shown that little distortion of the unit cell dimensions is visible. With respect to scale, this corresponds to approximately two C–C linkages, a dimension which is probably only distorted by polar interactions not present in these materials. However, at the crystallite level, the ability of the LDPE to act as a diluent[9] and therefore disrupt the higher order of the HDPE is apparent. Branch inclusion into the crystallite has been postulated to exist for methyl branches and may serve to explain the difference in *d*-spacings[10–12]. The heterogeneity of the branching distribution as well as molecular weight makes it difficult to separate the effects of the structure when discussing the primary reason for phase segregation. It is still possible to make some general statements concerning the features of the blends.

The crystallite dimension reflects the regularity of the molecular order on scales upwards of 100 Å. Although it is an average measure, since the peaks of the HDPE and LDPE cannot be distinguished, the values indicate that longer-range crystalline domains have been unable to form as the LDPE weight content increases. This change in dimensions leads to clues about larger entities such as lamellae and spherulites. Most interesting is that the average lamellar thicknesses of the 25 wt% HDPE blend and LDPE rapidly cooled materials are identical, indicating that the LDPE probably dictates the lamellar distribution.

Another qualitative method to examine the interaction of the two phases was to compare the area ratios from the d.s.c. endotherms (*Table 2*). Since no co-crystallization is immediately apparent due to the formation of separate melting peaks, then each component must crystallize separately and the ratio of each blend component peak to the pure material peak should be equal to the respective weight fractions. It is seen that the LDPE ratios are less than the weight fraction in all blends. The mechanistic reason for this seems quite straightforward. As the HDPE crystallizes, the LDPE is still in the melt. The HDPE then hinders the crystallization of the LDPE chains further. The LDPE cannot then assume its optimum crystalline form and smaller crystallites are obtained. It has been suggested that the increase in free volume caused by the presence of branches facilitates the crystallization of the linear component[19]. An increase in crystallinity may then be expected at low branch levels. This is not the case for this system since the high concentration of short branches and the limited diffusion of the polymer chain compensate for any increase in free volume.

An additional comment which needs to be made with respect to the observed lamellar morphologies is the similarity between the blends and the HDPE for the slowly cooled materials. Although the total percentage crystallinity decreases with increasing LDPE, the crystalline entities seem to be the same. In contrast to this observation is the stark difference in the morphologies of the rapidly cooled blends. It can be said then, that the crystallinity is not an accurate indication of the morphological transitions found as a function of thermal treatment and LDPE content.

## CONCLUSIONS

The unit cell of HDPE/LDPE blends which have been melt-extruded is not distorted by the addition of LDPE. At larger scales, that is, between 100 and 300 Å, the disorder created by blending is apparent. The crystallites become less regular along the (110) and (200) directions which suggests that the presence of the LDPE hinders crystallization of the HDPE. When the content of HDPE is greater than 50 wt% the crystallite dimension is determined by the HDPE for both heat treatments. The fact that the crystallite dimension of the rapidly cooled 25 wt% HDPE blend is the same as that of the LDPE indicates that longer-range dimensions may be dictated by the LDPE.

The decrease in crystallite dimensions and subsequent peak broadening leads to the conclusion that co-crystallization is not found in the HDPE/LDPE blend system. Additionally, examination of the d.s.c. endotherms shows two peaks, reflecting two crystalline phases. It is suggested that the shift of the peaks towards one another with increasing LDPE content is an intermediate density phase composed of the less branched LDPE chains and the long chain branches of the HDPE.

The crystalline phases are not composed of spherulitic structures but rather lamellae which decrease in size and population with LDPE composition. The random nature of these lamellae and their characteristic groupings are also dependent upon the weight fraction of LDPE and the thermal treatment.

The work presented so far has shown the structural levels associated with two thermal heat treatments. The morphology presented in this paper will provide a basis for the deformation model which will be presented in future work[13]. In this work[13], the mechanical properties will be presented and the morphological deformation model developed, which will aid in explaining the processes associated with each blend, specifically, the rapidly cooled materials.

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