ELSEVIER

Polymer 40 (1999) 337–348

polymer

Morphology, melting behaviour and co-crystallization in polyethylene blends: the effect of cooling rate on two homogeneously mixed blends

R. L. Morgan[1], M. J. Hill*, P. J. Barham

H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

Received 23 May 1997; revised 11 February 1998; accepted 18 February 1998

Abstract

The crystalline textures of a blend of linear polyethylene with low density polyethylene and a blend of deuterated linear polyethylene with low density polyethylene have been investigated as a function of rate of cooling from the melt. Differential scanning calorimetry, transmission electron microscopy and Fourier transform infrared spectroscopy have been used to study co-crystallization and phase segregation. On the basis of previous studies, the blend compositions were chosen so that the melt contained a single phase. Segregation between components was found to occur, as a result of crystallization, during cooling at all rates other than rapid quenching. The degree of segregation was found to increase with decreasing cooling rate. The morphologies resulting from this phase segregation during crystallization, have been compared with morphologies, previously determined, of blends of other compositions rapidly quenched from what was believed to be a phase separated melt. The scale of phase segregation is found to differ by more than an order of magnitude between the two types of morphology. The results support the argument that those rapidly quenched samples, which contain two crystal types, do so because of phase separation in the melt and not because of phase separation on crystallization. A comparison is made between two methods of sample preparation for transmission electron microscopy: permanganic etching/replication and chlorosulfonic fixation/sectioning. We have found the latter method better for revealing detailed morphological features between large lamellae.

Keywords: Morphology; Melting behaviour; Polyethylene blends

1. Introduction

The crystallization behaviour of blends of linear polyethylene (LPE) with branched polyethylene (BPE) has been a topic of debate for over 30 years. Recently the phase behaviour of these blends in the melt has also attracted interest. The chemical similarity of the components makes it difficult to study this behaviour directly. Neutron scattering studies have been made on the melts of polyethylene blends [1–8], but these have required the use of deuterated polyethylene. Neutron scattering techniques have detected phase separation only in blends containing a highly branched component, with typically more than 60 branches per 1000 backbone carbons. Experiments performed at this laboratory, using indirect techniques, have suggested that phase separation can occur in melts of blends where the branch content of the BPE is less than the lower limit determined from neutron scattering [9–21]. The phase separation detected indirectly, in blends containing lightly branched polyethylenes, is on a larger scale than that determined from neutron scattering in blends containing more heavily branched polyethylenes [2,4]: microns rather than hundreds of nanometers. The indirect techniques involve the study of the crystalline texture of blends after rapidly quenching from the melt at a cooling rate which is thought to be sufficient to preserve its phase structure. In such studies the effects of the crystallization behaviour of polyethylene blends must also be considered. Here we attempt to separate the effects of liquid–liquid phase separation and liquid–solid phase separation using two relatively simple blends.

In all systems studied by the indirect techniques, when the molecular weight of the LPE is above 2500 and the branch content of the BPE is below ≈60 branches per 1000 backbone carbon atoms, the region of phase separation has been found to lie in a loop placed asymmetrically on the BPE rich side of the phase diagram [3]. Fig. 1 gives an example of such a phase diagram. It has been shown that the phase behaviour does not depend strongly on the molecular weight of the LPE [11,12] or on the branch type of the BPE [20,21],

---

* Corresponding author.

[1] Present address: Smith and Nephew Group Research Centre, York Science Park, Heslington, York YO10 5DF, UK.

PII: S0032-3861(98)00193-1

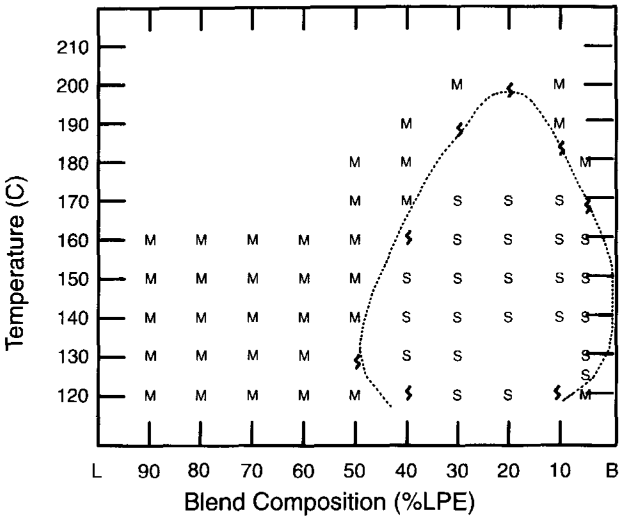

Fig. 1. Phase diagram of the blend system of the LPE, Sclair2907, with the LDPE, PN220. "M" indicates that the melt was found to consist of single phase, and "S" that it was found to be separated into two phases. The phase behaviour was determined by the indirect means described in the text

but that the branch content of the BPE is of primary importance [15].

The crystalline textures of rapidly quenched blends have been determined using differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Blends quenched from the single phase region of the phase diagram in Fig. 1 exhibit a single melting peak and a uniform morphology indicating one crystal population (banded throughout for some compositions and blend systems, unbanded throughout for others). Blends quenched from the two phase region of the phase diagram exhibit two melting peaks and a double morphology, indicating two crystal types. An example of such a double morphology is shown in Fig. 2. Two types of crystal can be seen, a thicker crystal population which exhibits banding and a thinner population which is unbanded. Each crystal type is isolated into domains with dimensions on the scale of microns.

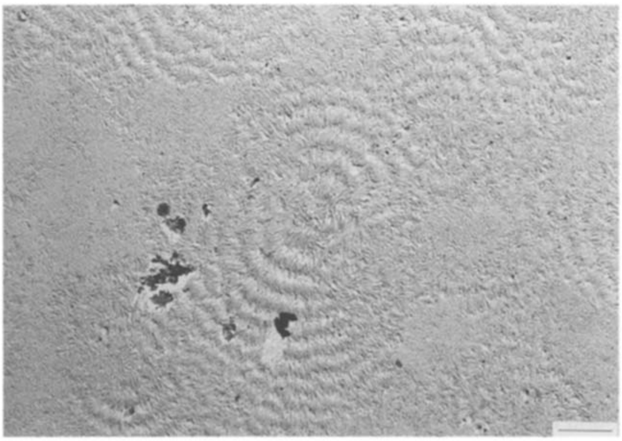

Fig. 2. TEM micrograph of a surface replica of a 20% LPE/LDPE blend. Two crystal types are present, located in separate micron scale domains. The domains of the thicker crystals exhibit banding, whilst the domains of the thinner crystals are unbanded. The scale bar is 1 pm

Some authors have argued against the study of the crystalline texture to determine the melt phase behaviour [3]. They suggest that the effects attributed to liquid–liquid phase separation are in fact caused by a separation between components during crystallization and that the crystallization took place from a mixed melt. We have reasoned against such arguments, citing diffusion measurements [14] and the ripening of the observed phase domains with time [19]. In this paper we address, in detail, the effect of phase separation during crystallization.

The degree of co-crystallization in polyethylene blends was first studied in the 1960s, using differential thermal analysis techniques [22–25]. More recent studies have employed further techniques: electron microscopy, both small and wide angle X-ray scattering, small angle light scattering, infrared spectroscopy and neutron scattering [26–45]. In general LPE and BPE have been found to separate on crystallization, to varying degrees. It is expected that some segregation will occur in all systems at slow enough cooling rates. The more similar the temperature ranges over which the pure components in the blend crystallize, the slower the cooling rate required to observe any segregation in a blend. In some cases, where the crystallization ranges of the blend components are very similar, segregation has not been detected even after cooling at the slowest rate used (typically 1°C/min). Such crystallization behaviour can be achieved when a low molecular weight LPE is blended with a BPE of particular branch content [34,35] or when a medium–high molecular weight LPE is blended with a BPE of very low branch content [36–42]. In some cases complete co-crystallization has been reported in blends of LPE with linear low density polyethylene (LLDPE) [29,36–42], but it should be noted that LLDPEs are very broad in intermolecular branch distribution and so they will contain both material prone to co-crystallization with the LPE and material prone to segregation. When studying the co-crystallization of a LLDPE with a LPE the LLDPE cannot be treated as a single component. In other systems, for example blends of medium–high molecular weight LPE with low density polyethylene (LDPE) or with hydrogenated polybutadienes, varying degrees of segregation have been reported, depending on the experimental techniques, the materials used and the cooling rate [26–28,31–33,36–45]. In the latter systems some authors have found that very fast quenching can prevent crystallization induced segregation [26,44].

Little systematic work has been performed on the variation of segregation and co-crystallization in a particular blend as a function of cooling rate. Here, we report how separation between components on crystallization varies with cooling rate. We aim to determine whether such segregation can occur at the very fast quenching rates which, it has been argued, preserve the phase structure of the melt. We have chosen to study blends of an LPE with an LDPE, because LDPEs are known from studies using such techniques as temperature rising elution fractionation, to be narrower in their intermolecular branch content distribution than LLDPEs.

Knowledge of the crystalline texture of these commercial materials, following different crystallization conditions, is of industrial importance as different processing methods impose different crystallization conditions.

We report here on the crystalline texture of a blend of chosen composition after cooling from the melt at different rates. To concentrate on the phase separation that occurs during crystallization, a blend composition was chosen which was believed to have a single phase melt at all temperatures previously studied [9–11]. DSC was used to monitor the crystallization behaviour during cooling and the melting behaviour on reheating. TEM was used to study morphology; two TEM sample preparation techniques were employed: permanganic etching followed by replication and chlorosulfonic fixation followed by sectioning and staining. Co-crystallization has been further studied on a molecular level using Fourier transorm infrared spectroscopy (FTIR). The FTIR method involved the study of band splitting in the spectrum of blends of a deuterated LPE with a LDPE, following the methods of Tashiro *et al.* [36–42].

2. Experimental

2.1. Materials

The polymers used in this study are listed in Table 1. Blends composed of 60% LPE/40% LDPE were studied by DSC and TEM. Blends of 50% DLPE/50% LDPE were studied by FTIR and DSC. The blend compositions were chosen so that the blends could be cooled from a melt known to be composed of a single phase. In the LPE/LDE system the phase separated region has a maximum width of 50% (this is the system shown in Fig. 1 [9–11]). The width of the phase separated region in the DLPE/LDPE system is much less, no phase separation is ever seen at DLPE contents above 30% [7]. The blends were made in a 0.4% solution with xylene and were precipitated using acetone as the non-solvent. This solution blending method has been discussed elsewhere in detail [9–11].

2.2. Sample preparation

All samples were held in the melt at 150°C for 20 min, to eliminate any effects of thermal history, before cooling to room temperature. A range of methods were used to cool the samples at predetermined rates from the melt. The fastest cooling rate imposed was achieved by flicking the sample from a Kofler hot-bench into acetone at its freezing point. Visual observation suggests that crystallization occurs in less than a second using this method. On this basis, the cooling rate during rapid quenching can be calculated to be in excess of 1000°C/min. However, at such cooling rates there will be a considerable temperature gradient through the thickness of a polymer sample, with the surface experiencing the fastest quench. In addition, during the rapid crystallization that occurs the heat of fusion liberated will limit the actual rate of cooling during crystallization. It is therefore difficult to quantify the cooling rate on rapid quenching. The samples for DSC were held in aluminium DSC pans on the hot-bench and the samples for TEM and FTIR were held between thin glass cover slips. The slowest cooling rate used was achieved by holding the samples in an oil bath, switching the oil bath off and allowing the samples to cool with the oil. Measurements of temperature against time showed that the cooling rate was approximately 1°C/min in the range of temperature over which crystallization took place. Samples for DSC, in pans, and samples for TEM, between cover slips, were wrapped in a thin layer of aluminium foil for this preparation method. An intermediate rate was achieved by lifting samples out of the oil and allowing them to cool in air, whilst still covered in aluminium foil. It was established, through studies of the melting behaviour of samples cooled at known rates, that the method of cooling in air gave a cooling rate of 60°C/min. Other cooling rates were provided by preparing the sample in a Perkin Elmer DSC7 with a refrigeration unit attached. This allowed cooling at controlled rates, of up to 80°C/min, over the temperature range of crystallization. Samples for FTIR were prepared in the DSC rather than in an oil bath, to avoid contamination by oil; these samples were held between slivers of mica in the DSC pan to aid the removal of thin films without deformation.

2.3. Differential scanning calorimetry

A Perkin Elmer DSC7, flushed with nitrogen, was used to record crystallization exotherms and melting endotherms. A heating rate of 10°C/min was used throughout. The instrument was calibrated with indium. Thermal lag effects were accounted for, where necessary, by using indium melting data recorded at different heating rates.

Table 1
Properties of polymers used in this study

Polymer type	Name	M_w	M_w/M_n	Branches per 1000 backbone carbons
LPE	Dupont Sclair 2907®	10^5	3	None
DLPE	MSD MD-775	2×10^5	2.2	None
LDPE	BP PN220	2×10^5	8	16 short, 10 long

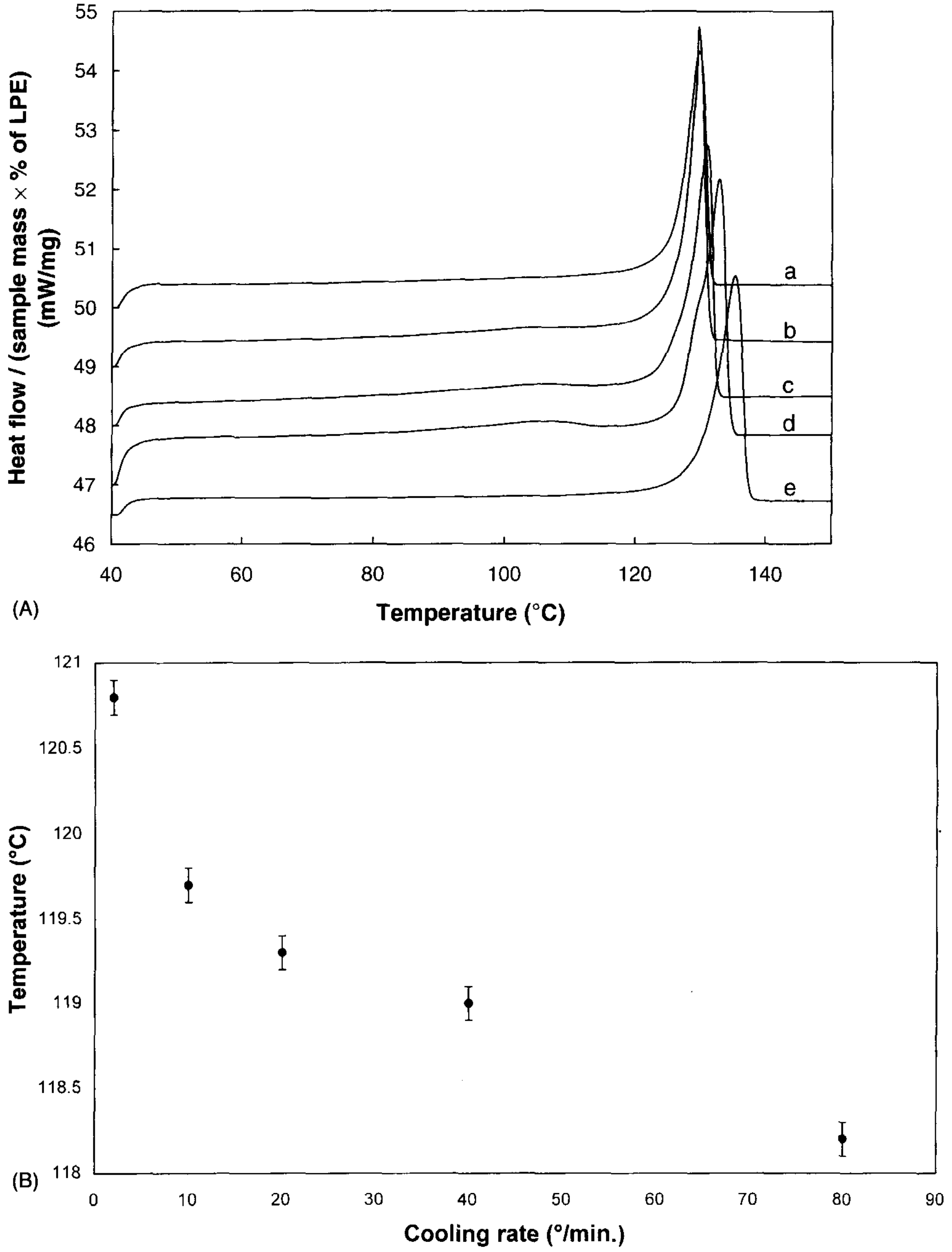

Fig. 3. (A) DSC melting traces of 60% LPE/LDPE blends, cooled from the melt at the rates of: (a) rapid quenching; (b) 60°C/min; (c) 10°C/min; (d) 1°C/min; and (e) LPE, cooled from the melt at 1°C/min. In each case the heating rate was 10°C/min. (B) Graph of crystallization exotherm peak temperature, for LPE rich material in 60% LPE/LDPE blends, plotted as a function of cooling rates. Corrections has been made for the effects of thermal lag. (C) Enlarged section of the DSC melting traces of 60% blends shown in (A) (curves a–d). The low melting temperature peak at 108°C/min is shown in more detail and the melting trace of PN220, cooled from the melt at 1°C/min, is included (curve e). It should be noted that no such peak is present in the trace of the sample that had been rapidly quenched (curve a)

2.4. Transmission electron microscopy

Samples were studied in a Philips 400T transmission electron microscope operating at 100 keV. The samples were prepared by two methods. Surface replicas were obtained using the Bristol version of the permanganic etching and replication method originated by Bassett and Hodge [46]; the experimental details of our method are described in Patrick *et al.* [47]. The etched polymer surface was shadowed with platinum/palladium at a 30° angle and with carbon at 90°. Polyacrylic glue was used to remove the replica. Stained sections were obtained following the procedure of Kanig [48]. Samples were treated with chlorosulfonic acid for long enough times to avoid crystal shrinkage during microscopy [49] and short enough times to avoid lamellar degradation [50,51]. Blend samples were treated

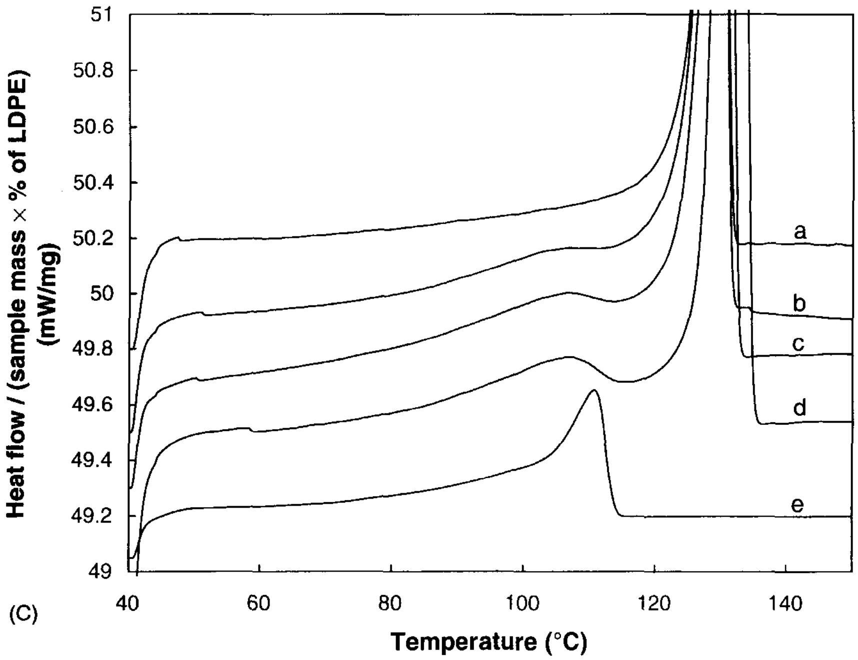

Fig. 3. (*continued*).

at 25°C for times between 6 and 10 days and LPE samples were treated at 37°C for 3–4 days. The exact times are not given because the fixing time needed depends on the speed of penetration of the acid into the sample which, in turn, depends on the sample morphology. Sections of between 40 and 80 nm thickness were cut at room temperature using a LKB ultramicratome. The sections were subsequently stained for 2 h in a 1% aqueous solution of uranyl acetate.

2.5. Fourier transform infrared spectroscopy

A Nicolet 510P spectrometer was used to record spectra using a spectral resolution of 2 cm^{-1}. Thin film samples were prepared by melt pressing prior to the thermal treatments described.

3. Results and discussion

3.1. Melting and crystallization behaviour

Differential scanning calorimetry was used to study the melting behaviour of 60% Scair 2907/PN220 blends and the two pure components, cooled from the melt at different rates. The melting behaviour provides global information on crystal populations for comparison with the morphologies detected by TEM. Fig. 3*A* shows the melting traces of material that had been cooled at the following rates: rapid quenching, 60°, 10° and 1°C/min. The main melting range peaks at temperatures between 128° and 132°C. The melting trace of pure LPE, cooled from the melt at 1°C/min, is included for comparison. After cooling at a particular rate the melting peak temperatures of the blend are approximately 2°C lower than those for pure LPE. The major melting peak shifts to higher temperatures for lower cooling rates. The crystallization exotherms recorded were used to plot the graph, shown in Fig. 3*B*, of the temperature of the exotherm peak *versus* cooling rate. The data in Fig. 3*B* have been corrected for thermal lag, which is also a function of cooling rate. The exotherm peak temperature can be seen to rise with decreasing cooling rate.

In Fig. 3*A* an additional melting peak can be seen at ~108°C in some of the traces. Fig. 3*C* displays this section of the melting trace in more detail, together with a melting trace of the LDPE for comparison. The melting trace of the pure LDPE has been scaled so that it corresponds to the mass of LDPE material in the blend. After cooling at the slower three rates a melting peak can be clearly seen, with a constant peak temperature of 108°C, a similar peak temperature to that of pure PN220. After rapidly quenching the blend from the melt no such melting peak is detected; the major melting peak rises continuously from low temperature without a maximum at 108°C. After cooling at slower rates, the area under the low temperature melting peak increases with decreasing cooling rate, although peak overlap makes this hard to quantify. After cooling at the slowest rate used, 1°C/min, the area under the low temperature peak in the blend is lower than the area under the peak of the pure LDPE and there is a 2°C temperature difference between the peaks.

The melting behaviour can be interpreted as follows. On rapid quenching a single crystal population develops, but at all slower cooling rates two crystal populations are formed. The main endotherm is due to the melting of a crystal population which is rich in LPE. However, because this crystal population has a lower melting range than pure LPE, we believe that it contains some LDPE. It has been shown previously that the diluant effect of the molten LDPE is not sufficient to suppress the melting point of pure LPE by the amount observed [52]. We suggest that the rise in main melting peak temperature with decreasing cooling rate results, at least partly, from the rise in crystallization temperature. The lower melting peak corresponds to a second crystal population which melts at a slightly lower temperature than pure LDPE. The melting temperature range suggests that the second population consists entirely of LDPE, with a higher average branch content than in pure LDPE. The number of crystals in the LDPE rich crystal population increases with decreasing cooling rate.

The variation in crystal populations can be explained in two ways. Firstly, we could argue that at lower cooling rates the first crystallized material, rich in LPE, excludes an increasing amount of LDPE. On cooling to lower temperatures the excluded LDPE crystallizes to form a separate population. Thus, at the fastest cooling rate it is thought that all the LDPE that crystallizes does so in co-crystals, rich in LPE. Secondly, we could argue that the composition of the first crystallized population does not vary with cooling rate, but the presence of these lamellae inhibits the separate crystallization of LDPE material. This inhibition would be required to lessen with cooling rate. In the literature both explanations have been suggested [43,44].

3.2. Morphology studied by TEM

The morphology of 60% LPE/LDPE blends and the pure components, after cooling from the melt at different rates, have been studied by TEM. Two sample preparation techniques have been used: permanganic etching followed by replication and chlorosulfonic fixation followed by sectioning. In previous papers from this laboratory dealing with polyethylene blends the former technique has been used to study morphology, so the results of this technique will be discussed first.

Fig. 4 shows replicas of 60% LPE/LDPE blends, cooled from the melt at three different rates: rapid quenching, 60° and 1°C/min. The rapidly quenched sample has a non-banded spherulitic morphology, shown in Fig. 4*a*. One crystal population is present, composed of short, tightly packed lamellae. After cooling from the melt at 60°/min the morphology is more complex. In the replicas studied, both banded regions (where the lamellae are radiating out from the spherulite core) and disordered central regions were present. More lamellar detail could be seen in the latter regions and Fig. 4*b* shows such an area. The crystals present have a narrow range of thickness, allowing them to be classed as a single crystal population. The crystal thickness appears greater than that of the crystals in the rapidly quenched sample. Long, "dominant lamellae" are present and shorter, "subsidiary lamellae" cross between them approximately at right angles. Fig. 4*c* shows the morphology of a blend cooled at the slower rate of 1°C/min. The presence of dominant and subsidiary lamellae is more

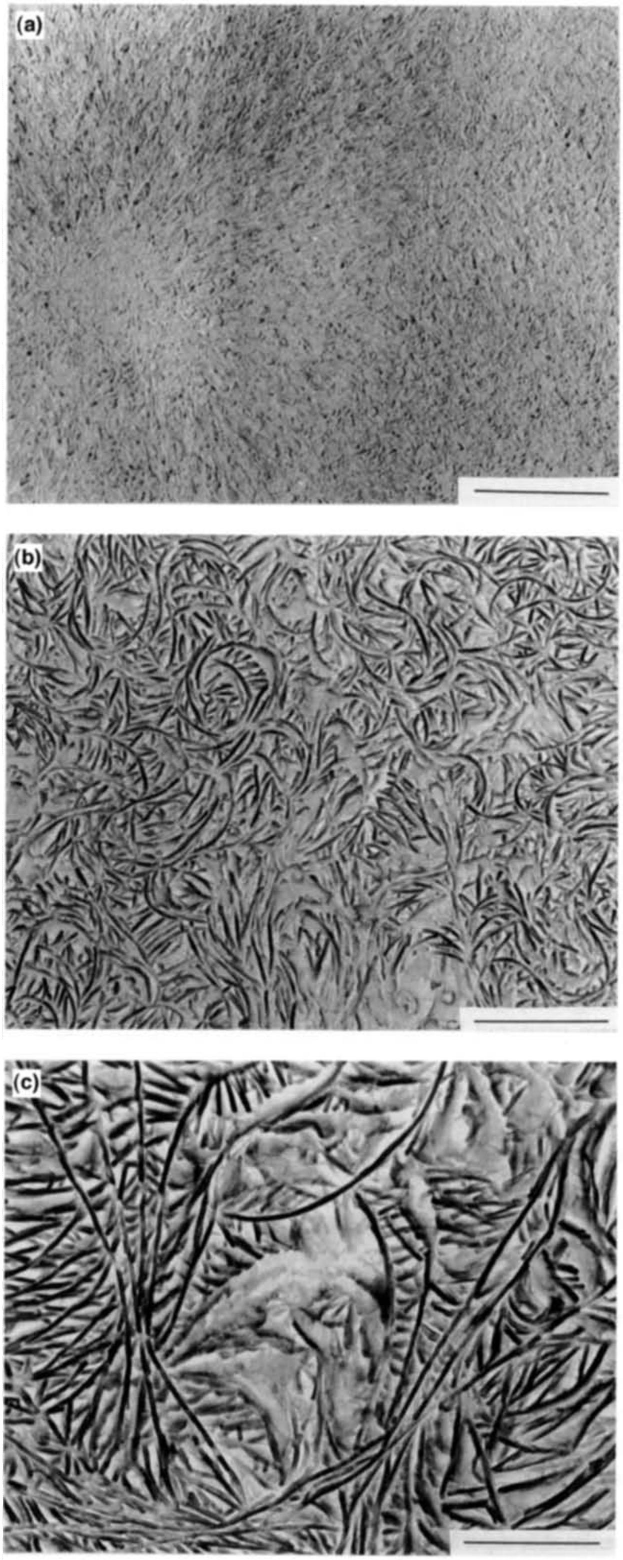

Fig. 4. TEM micrographs of surface replicas of 60% LPE/LDPE blends, cooled from the melt at different rates. The scale bars are 1 μm. (a) Rapidly quenched; (b) cooled at 60°C/min; (c) cooled at 1°C/min

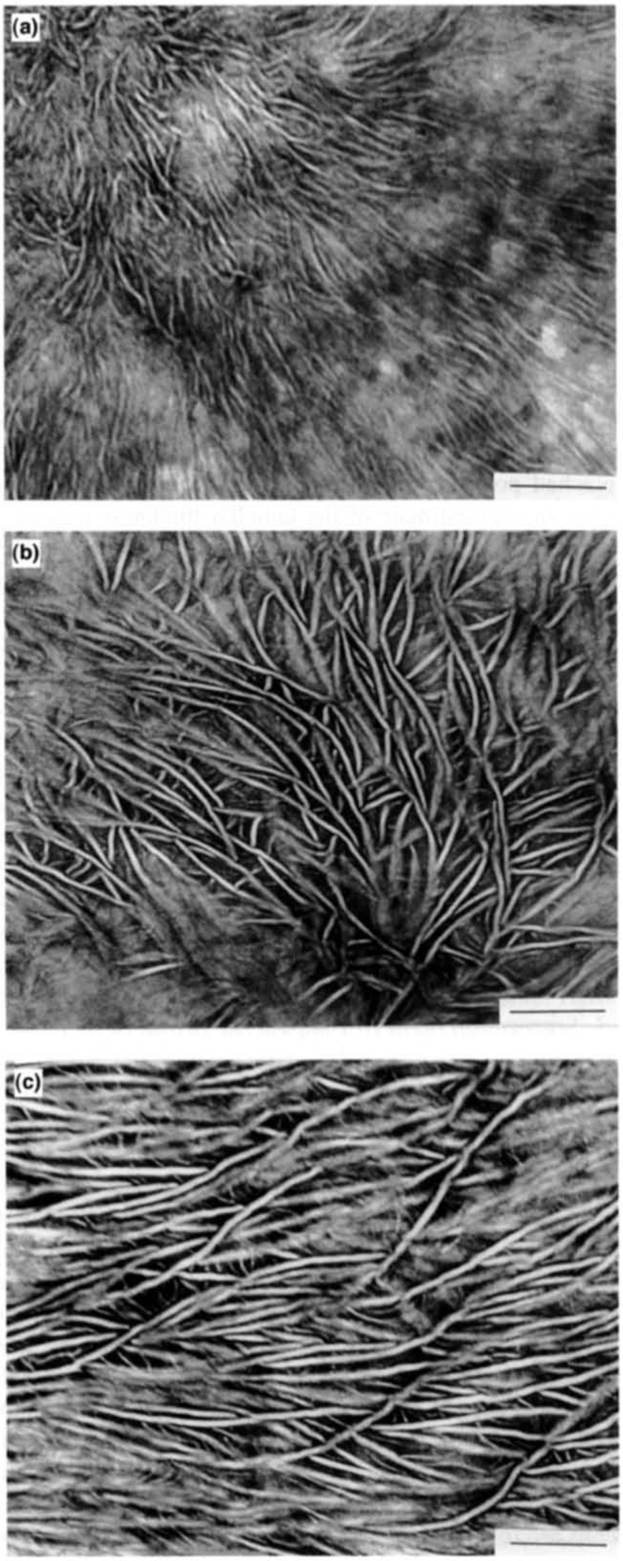

Fig. 5. TEM micrographs of stained sections, cut from material fixed with chlorosulfonic acid. The 60% LPE/LDPE blends were cooled at different rates from the melt. The scale bars are 200 nm. (a) Rapidly quenched; (b) cooled at 60°C/min; (c) cooled at 1°C/min, fixed for 6 days at 25°C

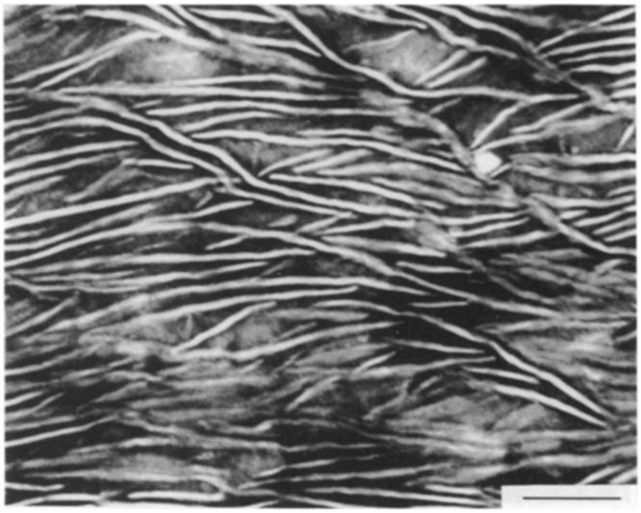

Fig. 6. TEM micrographs of a stained section, cut from a 60% LPE/LDPE blend cooled at 1°C/min from the melt. The material had been fixed in chlorosulfonic acid for 10 days at 25°C. The scale bar is 200 nm

obvious here than in Fig. 4*b* and the thicknesses are greater than after cooling at the faster rates. Comparison of these morphologies with the melting behaviour highlights an anomaly. The melting behaviour suggests that two crystal populations, with different thicknesses, should be visible in Fig. 4*b* and *c*. In each figure, however, only one crystal population can be seen.

In order to investigate this anomaly a second preparation technique for TEM was used to study samples prepared under the same conditions as those shown in Fig. 4. The results of the second technique are shown in Fig. 5 and it should be noted that these micrographs are of higher magnification than those in Fig. 4. The stained section of a quenched blend, shown in Fig. 5*a*, displays the same morphology as the replica: non-banded spherulites composed of short, tightly packed lamellae that form a single population. The sections of the samples cooled at slower rates show a more complex morphology, as do the replicas. Dominant and subsidiary lamellae are present in both, but, in contrast to the morphology revealed by the replicas, a second crystal population of thinner lamellae can be seen. These thin lamellae are most obvious in the sample cooled at the slowest rate, Fig. 5*c*. The short, thin lamellae are located between the thicker lamellae and are not found to congregate at spherulite boundaries. The existence of this second crystal population is further confirmed by varying the time for which the samples were fixed in chlorosulfonic acid. The sample cooled at 1°C/min, shown in Fig. 5*c* was fixed for 6 days at 25°C. This can be compared with a section from a sample which had been fixed for 10 days at 25°C, shown in Fig. 6. After the longer fixing time the thin crystals are no longer visible. This is because thinner polyethylene lamellae are more susceptible to degradation than thicker lamellae [50,51]. It is therefore evident that, when studying morphologies such as these, it is important to determine a fixing time which allows the observation of as wide a range

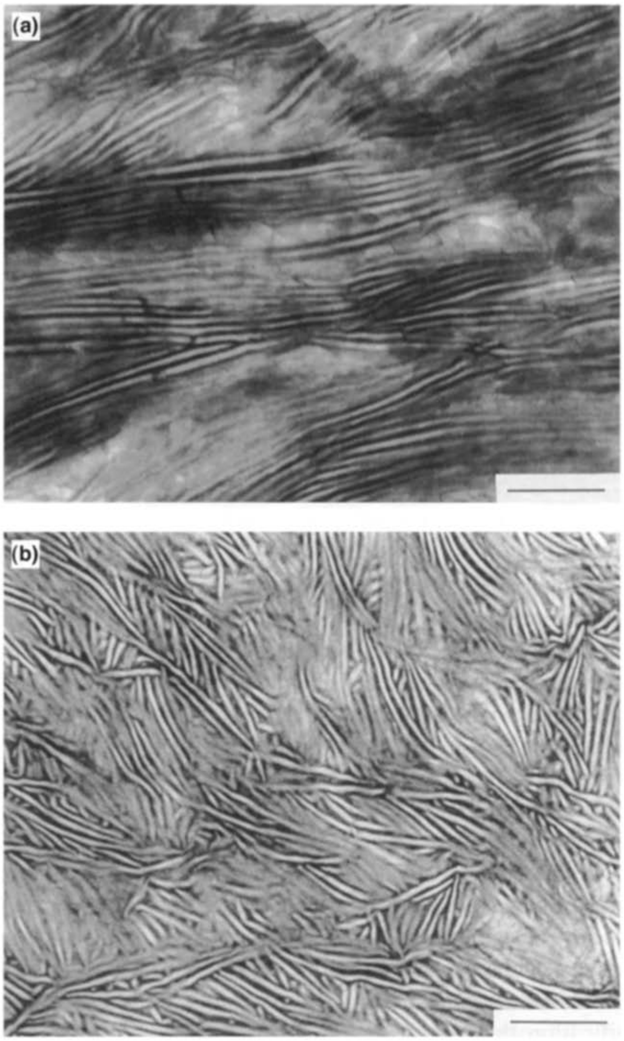

Fig. 7. TEM micrographs of stained sections, cut from LPE blend material fixed with chlorosulfonic acid. The samples had been cooled at two different rates from the melt. The scale bars are 200 nm. (a) Cooled at 60°C/min; (b) cooled at 1°C/min

of crystal thickness as is achievable. The micrographs, showing two crystal types, can be further compared with the micrographs of stained sections of pure LPE, cooled at 60° and 1°C/min, shown in Fig. 7. The thick lamellae are less widely spaced in the LPE micrographs than in the blend, reflecting the lower concentration of LPE in the blend. For the LPE, the inter-lamellar regions are featureless, containing only amorphous material and none of the thin crystals present in the blend. This confirms our interpretation of the blend morphology.

The morphologies revealed by fixing and sectioning compare favourably with the DSC data; the latter revealed the presence of two crystal populations in 60% blends cooled at 60° and 1°C/min. Comparison with DSC suggests that the thicker lamellae in the micrographs are co-crystals, rich in LPE, whilst the thin crystals, confined to the inter-lamellar regions, are composed almost entirely of the LDPE. LDPE, rejected from the first crystallizing material to inter-lamellar regions, crystallizes on further cooling to form the second, thinner crystal population.

The failure of the permanganic etching and replication technique to detect the thin crystal population in the blends requires some discussion. The thin crystal population was detected using chlorosulfonic fixation/sectioning, when a short enough fixing time was used. However, variation of the permanganic etching time, from 2 h to 10 min, produced little change in replicas. It has been established that in polyethylene thinner lamellae are etched more rapidly by permanganic reagents than thicker lamellae [53]. Thus, in the blends, the thick, LPE rich lamellae, will protrude from the surface to a greater extent than either the amorphous material or the thin crystals in the inter-lamellar regions. It has been shown that highly protruding lamellae obscure inter-lamellar features by shielding them from the evaporation metal during shadowing so that they do not contribute to the relief of the replica [47]. It has also been noted that detached polymer is left on the replica and that this can cause an over-estimate of the lamellar thickness measured from replicas [47]; comparison of Figs 4 and 5 supports this. It follows that when the replica is removed from the etched polymer surface, lamellae protruding furthest from the surface are likely to detach to the greatest extent. Thus, the LPE rich lamellae may be expected to cause a large amount of material to become detached from the polymer surface and this detached material may obscure inter-lamellar features. It is likely that it is a combination of these two factors that makes the permanganic etching/replication technique fail to detect the thin crystal population. Such problems are not apparent in the replicas of quenched samples, where the lamellae are more tightly packed and similar in crystal thickness, resulting in an etched surface of more uniform height.

3.3. Segregation between components measured by FTIR

For an FTIR analysis of co-crystallization to be possible, one of the blend components must be deuterated. Accordingly, FTIR measurements were made on a different blend system from that used in the work reported so far in this paper. A direct comparison cannot, therefore, be made with the morphologies and thermal behaviour of the hydrogenous system. However, a direct comparison can be made between FTIR measurements and the melting behaviour of the DLPE/LDPE system. Fig. 8 shows that similar melting behaviour is found for this system as for the LPE/LDPE blends, although the lower crystallization temperature range of the LDPE than the LPE could be expected to favour co-crystallization in the DLPE/LDPE system. A single melting trace is found after rapid quenching, whilst two melting peaks are found under other crystallization conditions. The size of the low temperature melting peak appears to increase with decreasing cooling rate, although overlap of the two melting ranges makes this difficult to quantify. Fig. 9*A*, *B* show CD_2 rocking and CH_2 rocking infrared adsorption

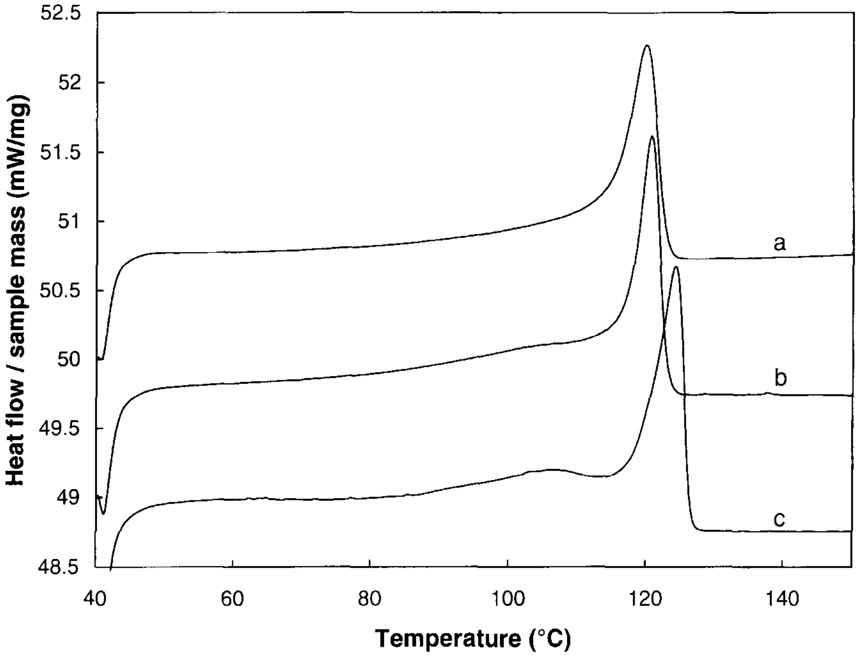

Fig. 8. DSC melting traces of 50% DLPE/LDPE blends, cooled from the melt at the rates of (a) rapid quenching; (b) 60°C/min; and (c) 1°C/min. In each case the heating rate was 10°C/min

bands, respectively, after subtraction of the contribution from amorphous material. Bands are shown for 50% DLPE/LDPE blends, crystallized under different conditions, along with the band for the pure components. Spectra of the blend and of the pure components, recorded in the melt at 140°C, were used to represent the contribution of amorphous material to the CD_2 and CH_2 rocking bands at room temperature. It is realized that when using melt spectra in this way an assumption is made that the temperature dependence of the amorphous band profile is negligible. Before entering into further discussion it is necessary to comment on the formation of such band-shapes.

A single mixed crystal of deuterated polyethylene with hydrogenous polyethylene will contribute two types of band to the crystalline component: a singlet and a doublet [54,55]. A single component arises either from a CH_2 (or CD_2) stem isolated from like stems, surrounded by stems of the other type or, alternatively, from like stems arrayed in a regular manner along the (200) or (020) plane. The doublet arises from interactions between pairs of like groups in adjacent like stems. The splitting width of the doublet (the spectral difference between the two peaks positions) depends on the deuterated to hydrogenous stem content of the crystal. Thus both the relative intensities of the two band types and the width of the doublet depend on the composition of the crystal. Since both of these factors affect the band shape, the co-crystallization in a blend sample can be assessed via the profile of the crystalline component of particular infrared bands. A quantitative analysis can be made by decomposing a band into the three peaks arising from the doublet and singlet. Alternatively a qualitative assessment can be made of the degree of co-crystallization based on the band shape. We are only interested in the overall trend of co-crystallization with cooling rate so a qualitative assessment was performed.

In Fig. 9*A* the variation with cooling rate of the CD_2 rocking band shape can be seen. The crystalline component shown is composed of both a singlet and a doublet. As the cooling rate is lowered the band becomes more split in appearance, resulting from a lower singlet contribution and a more widely split doublet. This is indicative of decreasing co-crystallization with decreasing cooling rate. Analysis of the CH_2 rocking band is made more complicated by the inclusion of a significant amount of LDPE material in both crystal populations, each with a different composition and so each contributing a doublet of different width and intensity. However, the same trend of increased splitting with decreasing cooling rate is apparent in the CH_2 rocking band, shown in Fig. 9*B*, as in the CD_2 rocking band.

In this paper two explanations have been proposed to explain the variation of morphology and thermal behaviour with cooling rate. A single crystal population forms on rapid quenching but two crystal populations form on slower cooling. Either the degree of segregation between components increases with decreasing cooling rate or, alternatively, the formation of the second population is suppressed, to a degree dependent on cooling rate, by the first formed crystal population. The *FT*i.r. results clearly support the former explanation: less LDPE material is included in the first formed crystal population for lower cooling rates. It should be noted that even after cooling slowly, at 1°C/min, the CD_2 band of the blend is less split than for the pure material,

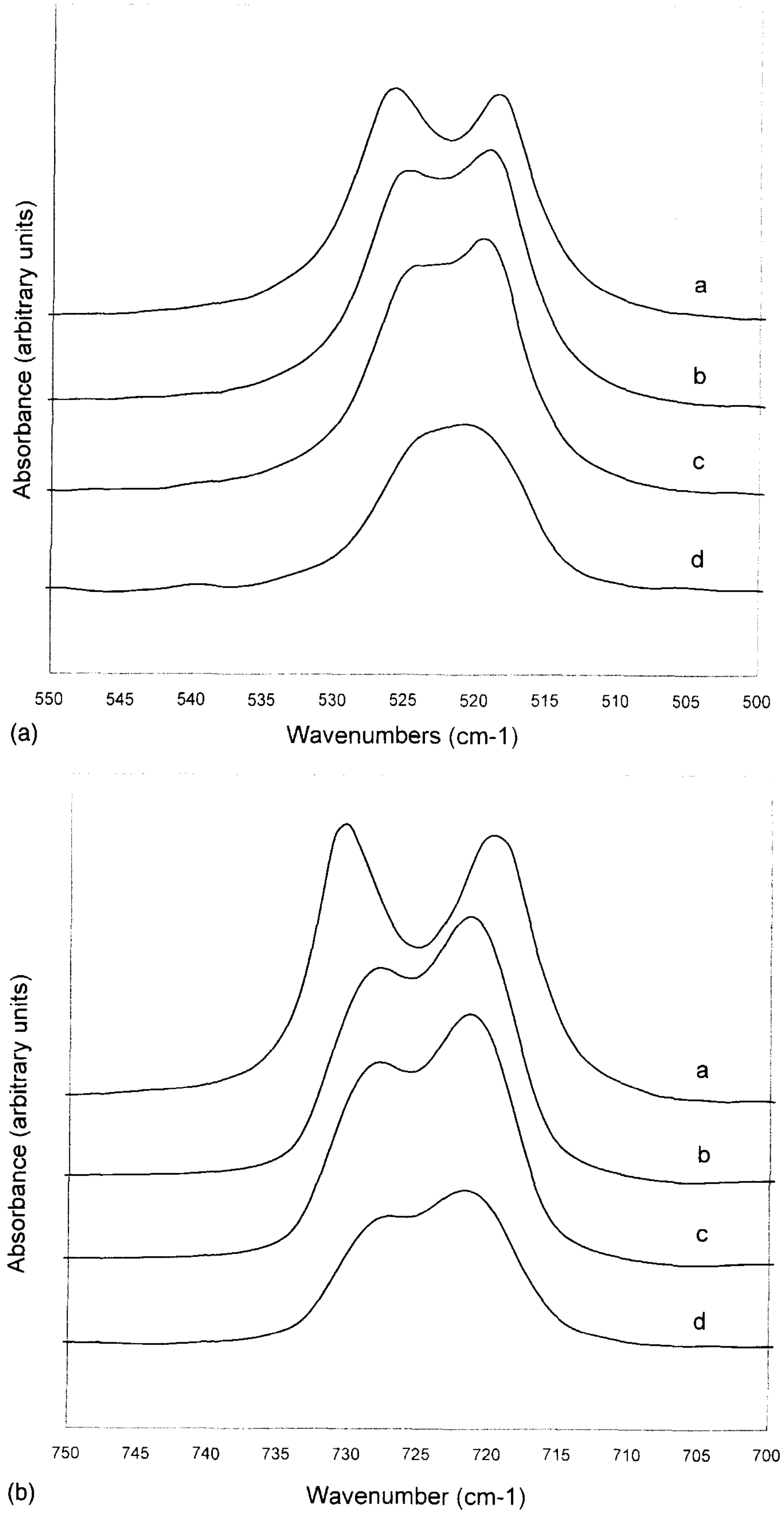

Fig. 9. (A)CD_2 rocking infrared absorption bands of (a) DLPE, rapidly quenched from the melt and of 50% DLPE/LDPE blends cooled from the melt at the rates of (b) 1°C/min; (c) 60°C/min; and (d) rapid quenching. (B) CH_2 rocking infrared absorption bands of (a) LDPE, rapidly quenched from the melt; and of 50% DLPE/LDPE blends cooled from the melt at the rates of (b) 1°C/min; (c) 60°C/min; and (d) rapid quenching

because of co-crystallization of the two components. This evidence for co-crystallization confirms that the lower melting point of linear polyethylene rich crystals in the blend, compared with those in the pure linear polyethylene, is a result of inclusion of LDPE material rather than a dilution effect.

3.4. Implications of the co-crystallization studies

We have shown that, of the crystallization conditions imposed, only rapid quenching prevents the formation of two crystal populations, each rich in one of the blend components. The degree of segregation increases with decreasing cooling rate, as shown most clearly in the present work by the *FT*i.r. results. The absence of LDPE rich crystals in rapidly quenched material is the result of inclusion of this material in the same crystals as the LPE; it is not because of suppression of crystallization of the LDPE by LPE crystals. Clearly, the cooling rate has a significant effect on the degree of co-crystallization and segregation between the LPE and LDPE blend systems studied. The factors that affect co-crystallization, changing with cooling rate are likely to be the relative crystallization rates of the two components, the time available for transport of material and the crystal thickness of the LPE rich crystals.

In Fig. 2 we showed an example of a double morphology, formed in a LDPE rich blend during rapid quenching. The morphology is composed of two types of tightly packed lamellae, thicker lamellae, showing a banded texture, and thinner lamellae, showing no banding. The two textures are separated into domains with dimensions on the scale of microns. It has been argued that this type of morphology results from the melt being separated into two phases [9–21]. The rapidly quenched 60% blend shows only one crystal texture (Fig. 4A). It has previously been argued that blends showing single crystal textures, including this 60% blend, come from single phase melts [9,10]. The different lamellar types formed in 60% blends on slower cooling are separated on a much smaller scale than those in Fig. 2. The thin lamellae are located between individual thick lamellae; the two lamellar types are not separated into domains like those in Fig. 2 and the length scale of segregation is of the order of 20 times lower. We argue that the work presented here is sufficient to refute the suggestion that the double morphologies in some rapidly quenched material are the result of phase separation on crystallization [3]. The morphologies generated by phase segregation during crystallization are clearly different from those formed during rapid quenching. The occurence of liquid–liquid phase separation remains the best explanation for the spatially well separated double morphologies found in some rapidly quenched material. In subsequent papers we will address the combined effects of liquid–liquid phase separation and liquid–solid phase separation in blends of differing composition.

4. Conclusions

After rapid quenching the 60% LPE/LDPE blend contains a single crystal population, indicating the melt itself is quite homogeneous. On cooling at rates of 80°C/min, or slower, segregation occurs between the blend components during crystallization as seen both by the FTIR data and in the electron micrographs. The electron micrographs further show that these slowly cooled, 60% LPE/LDPE blends, contain two crystal populations, with different thicknesses and compositions. The thinner crystals being located in between individual thicker crystals, on a length scale of approximately 50 nm.

Previous work has shown that many LDPE rich blends, rapidly quenched from some temperatures in the melt, can contain two crystal populations separated into domains with dimensions on the scale of microns. The scale of separation between the two crystal types observed in rapidly quenched, LDPE rich, blends is different from the scale of separation observed in blends cooled slowly from homogeneous melts. The difference in scale suggests that the reasons for the formation of the two types of morphology are also different. The double morphologies found in some rapidly quenched blends are best explained in terms of liquid–liquid phase separation, rather than crystallization induced phase segregation.

Acknowledgements

The authors wish to thank Mrs Anna Halter for help with FTIR studies and BP Chemicals, DSM and Solvay for a grant to support this work.

References

[1] Bates FS, Wignall GD, Koehier WC. Phys Rev Lett 1985;55:2425.
[2] Krishnamoorti R, Graesley WW, Balsara NP, Lohse DJ, Butera R-J, Fetters LJ, Schulz DN, Sissano JA. Macromolecules 1994;27:2574.
[3] Alamo RG, Londono JD, Mandelkern L, Steffling FC, Wignall GD. Macromolecules 1994;27:411.
[4] Londono JD, Narsten AH, Honnell KG, Hsieh ET, Johnson TW, Bates FS. Macromolecules 1994;27:2864.
[5] Nicholson JC, Finerman TM, Crist B. Polymer 1990;31:2287.
[6] Tashiro K, Imanishi K, Izuchi M, Kobayashi M, ltoh Y, Imai M, Yamaguchi Y, Ohashi M, Stein RS. Macromolecules 1995;28:8484.
[7] Schipp C, Hill MJ, Barham PJ, Cloke VM, Higgins JS. Polymer 1996;37:2291.
[8] Wignall GD, Alanio RG, Londono JD, Mandelkern L, Stehling FC. Macromolecules 1996;29:5332.
[9] Barham PJ, Hill MJ, Keller A, Rosney CCA. J Mater Sci Lett 1988;7:1271.
[10] Hill MJ, Barham PJ, Keller A, Rosney CCA. Polymer 1991;32:1384.
[11] Hill MJ, Barham PJ, Keller A. Polymer 1992;33:2530.
[12] Hill MJ. Polymer 1994;35:1991.
[13] Hill MJ, Barham PJ. Polymer 1992;33:4099.

[14] Hill MJ, Barham PJ. Polymer 1992;33:4891.

[15] Hill MJ, Barham PJ, van Ruiten J. Polymer 1994;34:2975.

[16] Barham PJ, Hill MJ, Goldbeck Wood EG, van Ruiten J. Polymer 1994;34:2981.

[17] Thomas D, Williamson J, Hill MJ, Barnham PJ. Polymer 1993;34:4919.

[18] Hill MJ, Barham PJ. Polymer 1994;35:1802.

[19] Hill MJ, Barham PJ. Polymer 1995;36:3369.

[20] Morgan RL, Hill MJ, Barnham PJ, Frye CJ. Polymer 1903;1997:38.

[21] Hill MJ, Barham PJ. Polymer 1997;38:5595.

[22] Clampitt BH. Anal Chem 1963;35:1834.

[23] Gray AP, Casey K. Polym Lett 1964;2:381.

[24] Clampitt BH. J Polymer Sci A 1965;3:671.

[25] Sato T, Takahashi M. J Appl Polym Sci 1969;13:2665.

[26] Norton D, Keller A. J Mater Sci 1984;19:447.

[27] Reckinger C, Larbi FC, Rault J. J Macromol Sci Phys 1985;B23:511.

[28] Vadhar P, Kyu T. Polym Engng Sci 1987;27:202.

[29] Hu SR, Kyu T, Stein RS. J Polym Sci, Polym Phys Edn 1987;25:71.

[30] Kyu T, Hu SR, Stein RS. J Polym Sci, Polym Phys Edn 1987;25:89.

[31] Song HH, Stein RS, Wu DQ, Ree M, Chu B, Phillips JC, LeGrand A, Chu B. Macromolecules 1988;1988:21.

[32] Song HH, Wu DQ, Chu B, Satkowski M, Ree M, Stein RS, Phillips JC. Macromolecules 1990;23:2380.

[33] Alanio RG, Glaser RH, Mandelkern L. J Polym Sci, Polym Phys Edn 1988;26:2169.

[34] Conde Brafla MT, Iragorri Sainz JI, Terselius B, Gedde UW. Polymer 1989;30:410.

[35] Conde Braña MT, Gedde UW. Polymer 1992;33:3123.

[36] Tashiro K, Stein RS, Hsu SL. Macromolecules 1992;25:1801.

[37] Tashiro K, Satkowski MM, Stein RS, Li Y, Chu B, Hsu SL. Macromolecules 1992;25:1809.

[38] Tashiro K, Izuchi M, Kobayashi M, Stein RS. Macromolecules 1994;27:1221.

[39] Tashiro K, Izuchi M, Kobayashi M, Stein RS. Macromolecules 1994;27:1228.

[40] Tashiro K, Izuchi M, Kobayashi M, Stein RS. Macromolecules 1994;27:1234.

[41] Tashiro K, Izuchi M, Kaneuchi F, Jin C, Kobayashi M, Stein RS. Macromolecules 1994;27:1240.

[42] Tashiro K, Imanishi K, Izumi Y, Kobayashi M, Satoh M, Stein RS. Macromolecules 1995;28:8477.

[43] Minick J, Moet A, Baer E. Polymer 1995;36:1923.

[44] Wignall GD, Londono JD, Lin JS, Alamo RG, Galante MJ, Mandelkern L. Macromolecules 1995;28:3156.

[45] Ueda M, Register RA. J Macromol Sci Phys 1996;B35:23.

[46] Bassett DC, Hodge AM. Proc Roy Soc A 1978;359:121.

[47] Patrick M, Bennet V, Hill MJ. Polymer 1997;37:5335.

[48] Kanig G. Prog Colloid Polym Sci 1975;57:176.

[49] Hill MJ, Bradshaw DG, Chevili RJ. Polymer 1992;33:874.

[50] Martinez-Salazar J, Keffer A, Cagiao ME, Rueda DR, Baltá Calleja FJ. Coll Polym Sci 1983;261:412.

[51] Martinez-Salazar J, López Cabarcos E, Rueda DR, Cagiao ME, Baltá Calleja FJ. Polym Bull 1984;12:269.

[52] Puig CC, Hill MJ, Odell JA. Polymer 1993;34:3402.

[53] Freedman AM, Bassett DC, Olley RH. J Macromol Sci Phys 1988;B27:319.

[54] Tasumi M, Krimm SJ. J Polym Sci, Polym Phys Edn 1968;6:995.

[55] Bank MI, Krimm SJ. J Polym Sci, Polym Phys Edn 1969;7:423.