A comparison of blends of linear with branched polyethylenes prepared by melt mixing and by solution blending*

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(Received 23 September 1993; revised 26 November 1993)

Blends of a linear and a lightly branched polyethylene were prepared by solution blending and in the melt, by mixing in a screw extruder, and the phase morphologies were compared. First, the melt phase behaviour of the solution-blended system was studied by differential scanning calorimetry and transmission electron microscopy. A loop of liquid–liquid phase separation was found at low linear-polyethylene content. Three melt-mixed blends were then prepared and characterized, again by differential scanning calorimetry and transmission electron microscopy. The general pattern of phase behaviour of these melt-mixed blends was similar to that obtained by solution blending the same pair of polymers (i.e. a region of phase separation was again found at low linear-polyethylene content). Where the phase behaviour allowed mixing, the screw extruder produced blends with uniform composition throughout the sample. The morphologies of the melt-mixed materials showed enhanced nucleation, compared with the solution-blended materials, and orientation effects, particularly at low linear-polyethylene content.

(Keywords: polyethylene blends; liquid–liquid phase separation; melt mixing)

INTRODUCTION

In the recent past we have published a number of papers reporting experimental evidence for liquid–liquid phase separation (*LLPS*) in melts of blends of linear with branched polyethylenes (LPEs with BPEs)[1–8]. We have shown that *LLPS* is observed in melts of such blends except where the molecular weight (*MW*) of the LPE is extremely low[3]. For branch contents of less than about 50 branches per 1000 backbone carbon atoms, the separated region is always in the shape of a closed loop, placed asymmetrically at low BPE content; *Figure 1* shows typical behaviour for a binary system. We have collected data from about 30 LPE/BPE systems. We have used LPEs of differing *MW* and BPEs of differing *MW*, differing branch type, branch content and branch distribution. We believe that this work has now firmly established that *LLPS* of the type shown in *Figure 1* is generally found in binary blends of LPEs with lightly branched BPEs.

Clearly it is of great significance to see how the phase separation, which we so commonly observe, affects the bulk properties of blends. It has, for instance, been suggested that fracture toughness is increased where blends are phase separated[3,9]. In order to investigate this we need large quantities of material for mechanical testing. All our phase diagrams were deduced using polymers which were solution blended. Solution blending is quite satisfactory for the small quantities of material needed to test for phase separation, but it is impractical as a method of preparation for the much larger quantities needed for mechanical testing. Melt mixing is an obvious way to obtain large quantities of material.

We are also interested in investigating the process and effects of melt mixing. In this paper we report the results of our initial melt mixing experiments. We wanted to know how blends obtained by melt mixing compare with those obtained on solution blending the same polymers. In particular, we were concerned to see whether the material was uniformly blended; whether complete mixing could be achieved; whether a meaningful phase diagram could be obtained and, if so, if it was similar to that obtained on solution blending the same pair of polymers.

Another area of interest is to assess the effects of the applied strong shear and extensional flow-fields upon the phase diagram of the LPE/BPE blend. Phase behaviour in flow has recently been a very active research area, but there is little understanding of the effects upon the mixing and demixing of polymer blends. Some reports suggest that even modest strain rates (less than $1\ s^{-1}$) can significantly affect the phase behaviour[10–14]. Shear flows have been variously reported as favouring

* Presented at 'Physical Aspects of Polymer Science — Polymer Physics Group 16th Biennial Meeting', 15–17 September 1993, University of Reading, UK

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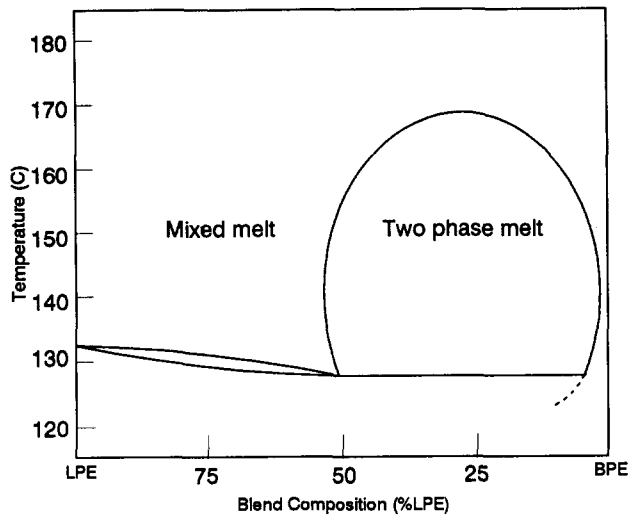

Figure 1 Typical phase diagram for a binary LPE/lightly branched BPE system

mixing or demixing, even though the interpretation of the experimental results (mostly based upon light scattering) is open to considerable uncertainty[10]. Most investigations at low shear rates have found that flow favours mixing, whilst at higher shear rates demixing is most commonly reported. It is clear that the relative viscosities of the two phases play an important role. There is little understanding of the effects of flow-induced molecular orientation, which are likely to be of great significance in melt processing. We might, therefore, expect differences in the phase behaviour of our LPE/BPE blends prepared by solution blending and melt mixing. In melt mixing, the blends are subjected to considerable shear and extensional flow-fields in the extruder.

A key result of this study is that uniform mixing of an LPE with a BPE can be obtained by melt extrusion. The phase behaviour of blends made in this way is broadly similar to that of the same materials when solution blended. There are some morphological differences between blends prepared by melt mixing and solution blending with regard to both orientation and nucleation effects.

EXPERIMENTAL

Two polymers were used for this study, both produced by BP Chemicals: the LPE was Rigidex HD6070, density 960 kg m^{-3}, which was blended with PN 220, density 918 kg m^{-3}. The melting points of the quenched LPE and BPE are 131 and 110°C, respectively. The homopolymers were characterized by gel permeation chromatography (g.p.c.) before and after melt mixing.

Melt mixing was carried out in a co-rotating twin screw extruder fitted with a capillary of length-to-diameter ratio 17, operating at a wall shear rate of 10^2 s^{-1} and working at 100 rev min^{-1}. The wall temperature in the die was 170°C; the actual temperature would have been somewhat higher (we estimate some 10°C higher), owing to work dissipated, with the highest temperatures occurring in the most viscous samples. The extrudate was quenched into water at 20°C within 5 s, and then pelletized. Samples of pure LPE, pure BPE, and mixtures containing 75, 40 and 10% LPE were passed through the extruder (the resulting melt mixed blends are termed 75%, 40% and 10%, respectively).

Small quantities of LPE and BPE were blended in solution and precipitated into acetone, a non-solvent, at freezing point[1,2]. The phase behaviour of the unsheared, solution-blended materials was then established. We wished to identify the region over which *LLPS* occurred.

The phase diagram for the solution-blended (SB) material was determined using the indirect methods used previously[1-8]; differential scanning calorimetry (d.s.c.) and transmission electron microscopy (TEM) were employed to characterize rapidly quenched blends. It was necessary to use these indirect techniques because the usual methods for direct detection of phase separation (e.g. light scattering) cannot be used here since LPEs are too similar to lightly branched BPEs with regard to many physical properties (for instance, refractive index). However, we have found that d.s.c. and TEM give very reliable results when rapidly quenched blends are examined. Such samples are of two types. In some cases a single phase morphology is seen with a unimodal distribution of lamellar thickness; these materials give a single d.s.c. peak on melting and we believe that they crystallized on quenching from a mixed melt. Other blend compositions show a two-phase morphology with well-separated regions composed of lamellae of distinctly different thicknesses. Such materials always give two distinct d.s.c. peaks on heating after quenching from the melt. We have also shown that it is not possible for the large-scale phase separation that we observe (on a scale of micrometres) to take place during rapid quenching[5]. Hence we associate these biphasic samples with a two-phase melt.

The melt mixed (MM) samples were characterized by the same methods used to study SB materials.

RESULTS AND DISCUSSION

Polymer molecular weights

The molecular weights of the LPE and the BPE were determined by g.p.c. both before and after melt extrusion. We found that the weight average molecular weights (M_w) were 72 000 ± 3000 and 112 000 ± 5000 for the LPE and the BPE, respectively. After melt processing, the molecular weights were redetermined and no significant degradation was found. This is consistent with recent work[15] on the stability of BPE during screw extrusion. The polydispersities of the polymers were 6 and 14 for the LPE and BPE, respectively. (Note that the M_w quoted for the BPE is the value measured by g.p.c. and is uncorrected for branching. We have not determined the correction factor, but we believe that it would be in the region of 2, which would bring the g.p.c. value to about 200 000, the value previously quoted for this material[1,2].) The manufacturers quote the melt flow indices for these two materials as 7.6 and 0.6 g/10 min, respectively (ISO test).

Phase diagrams

Our studies of the SB materials confirmed that these two polymers showed *LLPS* of the usual binary type on solution blending; the *LLPS* region for this system is shown in *Figure 2*. The choice of blends to mix in the extruder was made on the basis of this *LLPS* loop. The 75% blend was chosen as being well into the mixed region

at all temperatures, the 10% blend as being clearly in the separated region (except at very high temperatures) and the 40% blend because it was near to the phase boundary and might show up any small changes in width of the *LLPS* loop which could occur as a result of flow in the extruder.

Both the surface and the interior of MM samples were examined by d.s.c. and TEM. Several samples were cut from each SB and MM blend and used for d.s.c. Typical d.s.c. results are shown in *Figure 3*. The d.s.c. traces from quenched samples are of two main types, showing either a single peak or two well-separated peaks. In some MM samples an additional small shoulder can be seen at intermediate temperatures (e.g. the 10% and 40% 'surface' traces in *Figure 3b*). Samples containing 75% LPE, of all types, were found to be of single phase; 10% samples were found to be biphasic; and 40% samples were found to be mixed in most, but not all, cases.

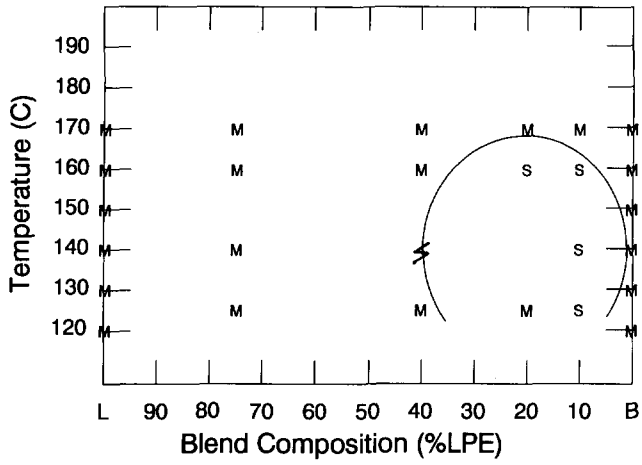

Figure 2 *LLPS* loop for Rigidex HD6070 and PN 220 when solution blended. M, melt was mixed at the temperature and composition indicated; S, melt was separated into two phases; ≤, borderline case, showing some signs of separation

We may draw several conclusions from the d.s.c. studies. As expected, it is apparent that melt mixing gives uniformly blended samples to the first approximation. However, there can be slight differences between the surface and the core of MM pellets: 40% samples appear to be slightly separated at the surface, but mixed in the core (we believe this to be the result of the formation of 'row structures' at the capillary wall during flow; this is discussed later). It is also readily apparent that complete mixing is possible. Single-phase samples can be obtained from pellets by melt mixing (e.g. all 75% MM samples display a single melting peak, indicating that they were crystallized from a homogeneous mixed melt).

The phase behaviour of MM samples is very similar to that of SB samples, in that the region of *LLPS* is asymmetrically placed at high BPE contents. The data for the MM samples were only obtained at a single set temperature, nominally 170°C (although the actual temperature would have been somewhat higher as we have already mentioned). We should expect from the SB

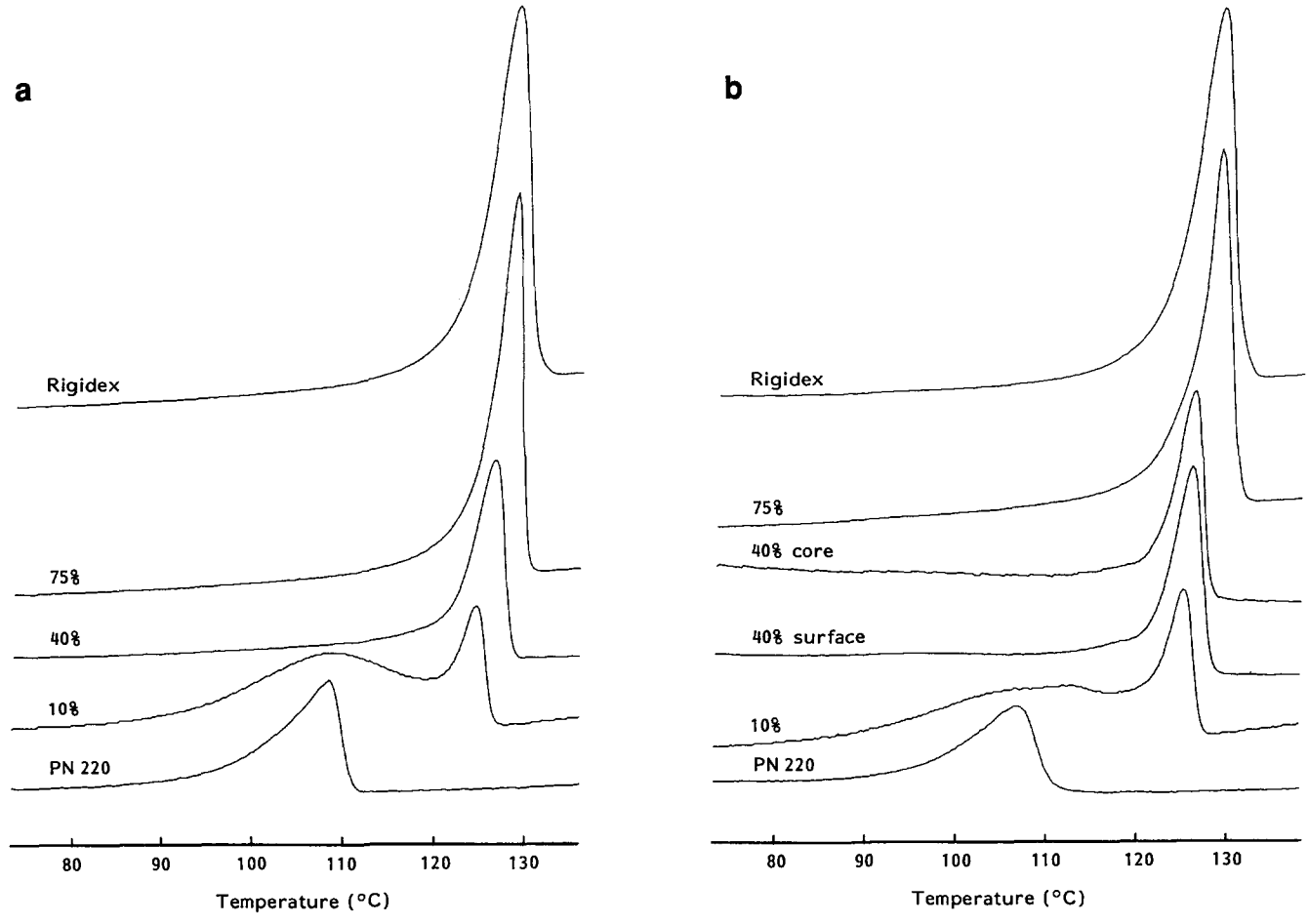

Figure 3 Typical d.s.c. traces obtained at a heating rate of 10°C min^{-1}. (a) SB blends of the compositions indicated after quenching from 140°C; (b) MM blends; the samples were water quenched after the extrusion and had no further thermal treatment

phase diagram, shown in *Figure 2*, that the melts would all be mixed at these high temperatures. Since, as shown above, complete mixing in the melt is possible, the observation of clear demixing in the 10% MM samples suggests that they could well have been phase separated in the melt; if this was the case then we would have to further argue that the upper critical temperature was raised by the influence of the flow. However, it is also possible that the separation took place on quenching. The MM samples were quenched into water at room temperature and the pellets were considerably thicker than the SB samples used to determine the phase diagram (furthermore, these latter were quenched into acetone at freezing point).

A further experiment was carried out to distinguish between the two possible reasons for separation in the 10% MM samples. A 10% SB blend sample, similar in size and shape to a MM pellet, was held at 180°C for 30 min and then dropped into water at room temperature. This sample was examined by d.s.c. and TEM. D.s.c. showed two clear peaks and TEM showed slight phase separation, even on the surface. This indicates that the separation which occurred in the 10% MM sample, quenched from 180°C, well above the upper critical temperature, could have taken place during the quench through the phase-separated region. Thus there is no clear evidence that the upper critical temperature is raised as a result of flow in the extruder. Very recent work has shown that the 10% blend in this system is quenched directly into the spinodal region and separates very rapidly[16].

Further information on the phase behaviour can be obtained from TEM. *Figures 4–6* show some typical electron micrographs. The TEM and d.s.c. results are in agreement in all respects, confirming our first three conclusions. However, TEM can sometimes tell us more than d.s.c.; for instance TEM can indicate the scale on which phases are separated whilst d.s.c. can only indicate that phase separation exists.

Nucleation effects

There seem to be more nucleation sites in MM samples of all types than in the equivalent SB materials (compare *Figures 4a* and *5a*). However, when MM material has been redissolved and precipitated, the number of nuclei drops close to that observed in material which was initially solution blended (compare *Figures 4a–c* with *6a–c*). The morphology of the 40% and 10% SB blends and MM blends that have been redissolved are essentially identical (see *Figures 4b, c* and *6b, c*). Although there is clearly mixing for the 75% blends of both types, the morphology is different. The SB blends give banded spherulites while the redissolved MM blends do not. Optical microscopy shows similar sized spherulites in these two preparations and confirms the absence of banding in the redissolved MM blends.

We believe that there may be heterogeneous nucleating materials present in the original homopolymer pellets which are washed out in the solution process, reducing the nucleation density in both types of SB samples (i.e. those prepared by dissolving the original homopolymer pellets and those prepared by dissolving melt-mixed blends). The polymer is not dissolved during melt mixing, so that no loss of heterogeneous nuclei would be expected. Thus we believe that the nucleation density is reduced by the preparation method of the SB blends, but not in MM blends, and this is a fundamental and permanent difference between the two types of material.

Orientation effects

Orientation effects, in the form of row structures, are clearly visible in MM samples of low LPE content (*Figure 5b* and, especially, *Figures 5c* and *d*, where the orientation completely changes the morphology). When the MM blends were held in the melt, these orientation effects persisted over quite long times. TEM showed that orientation effects were much reduced, but still visible after a 10% MM blend had been stored for 17 h at 160°C. We believe that as the melt flows in the extruder, molecular orientation and extension occur, particularly in the higher *MW* BPE. On cooling, extended chain crystals are formed, which will act as nuclei for the familiar row-nucleated structures[17], which are clearly visible in many of the micrographs (e.g. *Figures 5c* and *d*).

The effect of shear on the phase behaviour

It is well known[11,12] that shear can affect the phase behaviour of blends; in general, the greater the difference in the viscosity of the two blend components, the larger

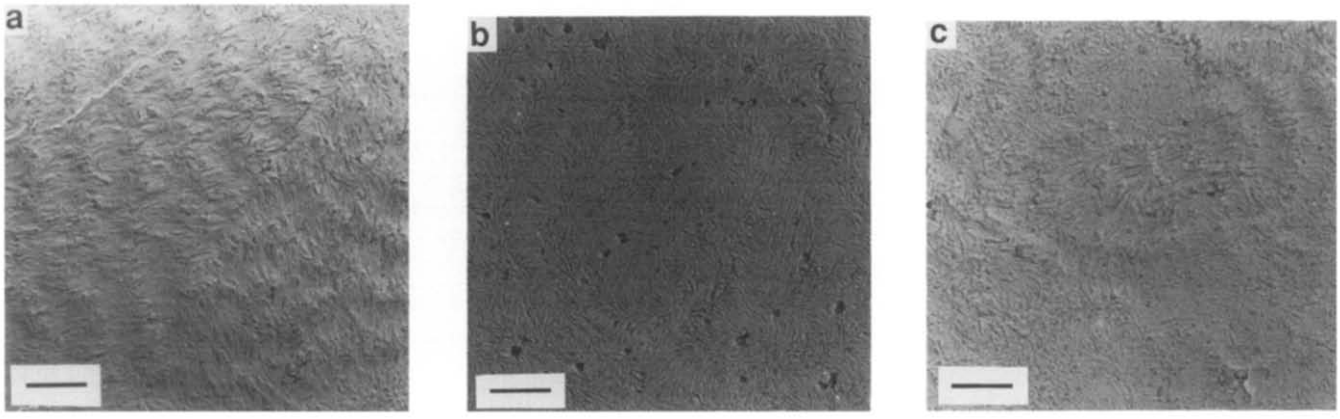

Figure 4 Transmission electron micrographs of surface replicas of SB materials. The scale bars represent 1 μm. (a) The 75% blend quenched from 140°C. The micrograph shows the junction between two large banded spherulites. The lamellae are all of equal thickness, indicating a mixed melt before quenching. (b) The 40% blend quenched from 140°C. Most of the lamellae are of equal thickness, but there are occasional groups of slightly thicker lamellae (e.g. top right), indicating that this composition is near to the phase boundary at this temperature. (c) The 10% blend quenched from 140°C. Note the group of thick lamellae (top right) in a matrix of thinner lamellae. This morphology is typical of a phase-separated blend

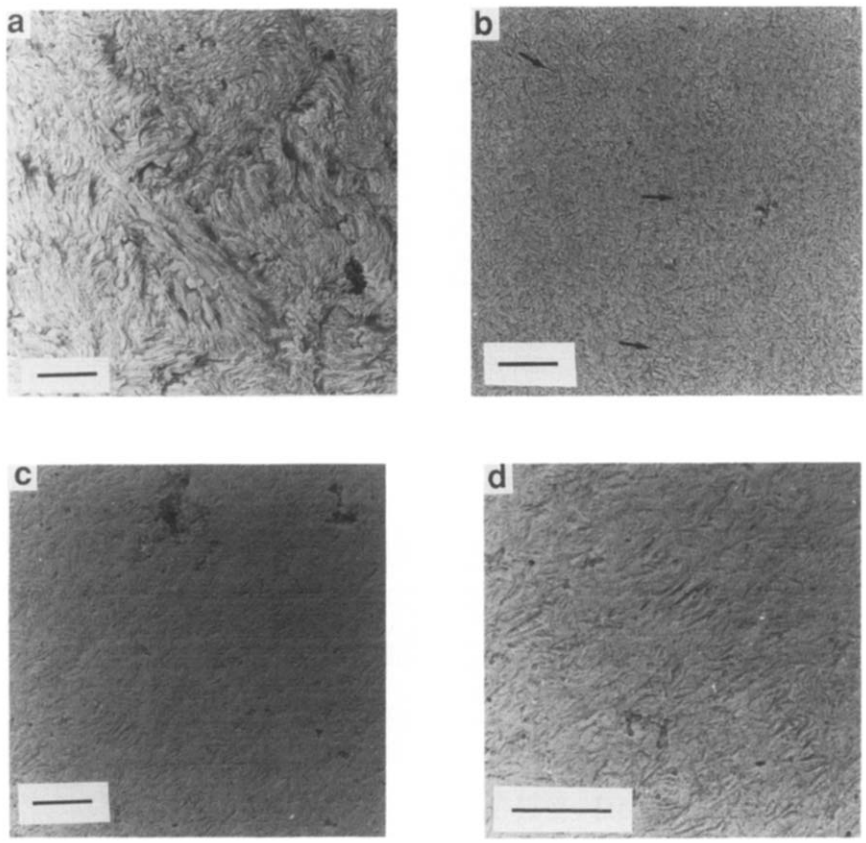

Figure 5 Transmission electron micrographs of blends obtained from melt mixing without further heat treatment. The micrographs are of surface replicas. The scale bars represent 1 μm. (a) The 75% blend. Note that the spherulites are much smaller than in the SB material (*Figure 4a*), but all the lamellae are of equal thickness, indicating a mixed melt before quenching. There is some detached polymer adhering to this replica, appearing as dark patches. (b) The 40% blend. The lamellae are surprisingly small. There are a few row structures; examples are arrowed. (c) The 10% blend. Here row structures are numerous and the character of the morphology is quite different from that of the quenched 10% SB blend. It is difficult to pick out regions of thinner lamellae at this magnification. (d) Part of *Figure 5c* at higher magnification. Regions of thinner lamellae can be seen between the thicker crystals forming the row structures

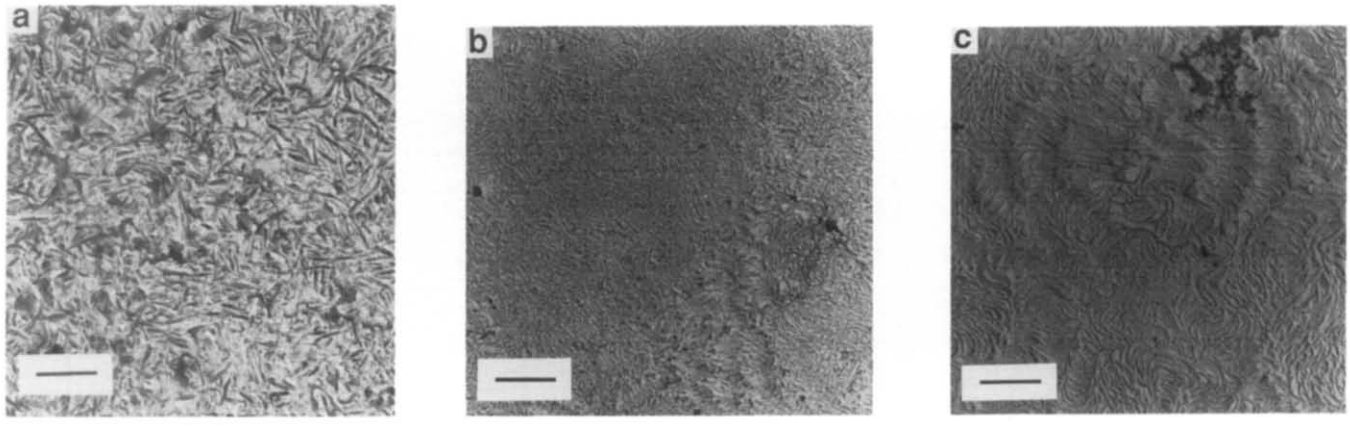

Figure 6 Transmission electron micrographs of surface replicas of melt mixed blends after they had been redissolved, precipitated, dried and then quenched from 140°C. The micrographs are of surface replicas. The scale bars represent 1 μm. (a) The 75% blend quenched from 140°C. There are no obvious spherulitic structures. All the lamellae are of equal thickness, indicating a mixed melt before quenching. There is some detached polymer adhering to this replica, appearing as dark patches on the print. (b) The 40% blend quenched from 140°C. This micrograph looks very like *Figure 4b*, the original 40% SB blend. Most of the lamellae are of equal thickness, but there are occasional groups of slightly thicker lamellae (towards the bottom right), indicating that this composition is near to the phase boundary at this temperature. (c) The 10% blend quenched from 140°C. This micrograph looks very like *Figure 4c*, the original 10% SB blend. The morphology is typical of a phase-separated blend, with a group of thick lamellae towards the top of the figure, in a matrix of thinner lamellae

is the effect of flow on the phase behaviour. The two polymers used in this study have quite dissimilar viscosities, as revealed by their melt flow indices. Furthermore, at the high shear rates used in our work we found that the BPE had the lower viscosity, as assessed by a measurement of the torque on the screw extruder. Accordingly we might reasonably expect to find some comparatively large effect on the phase behaviour[10]. In fact, owing to rapid phase separation during the relatively slow 'quenching' of MM samples, we have not been able

to see any change. A further complication is that under these high shear rate conditions we observe a significant degree of orientation in the demixed samples. Orientation is clearly of great importance in the understanding of melt-processed phase behaviour; it might favour either mixing or demixing, and there appears to be little theoretical understanding of its effects.

CONCLUSIONS

Melt mixing has been shown to be very successful in preparing uniformly blended samples from pellets of the two constituent homopolymers. MM blend samples can be prepared in a completely mixed state, with full cocrystallization; on the other hand, where the phase separation is more stable, two crystal types are found. The phase behaviour of the MM system is similar to that found on solution blending the same polymers.

There are two other differences between SB and MM blends, which can be broadly summarized as nucleation and orientation effects. The nucleation density is higher in the MM materials; we suspect that heterogeneous nuclei are depleted in the solution process. We see clear orientation effects in MM materials of 40% LPE content and less. They are particularly evident in the 10% MM blends, where they dominate the morphology. We believe these orientation effects to be a result of the extension of the higher MW material during flow, and subsequent row-nucleated crystallization. The orientation can be reduced, and eventually eliminated, by holding MM blends in the melt for rather long periods.

Clearly, detailed work needs to be done, but we have found that, for this blend system at least, complete mixing can be achieved, giving material of uniform composition where the phase behaviour allows mixing. Although we have looked at only three MM blends, there is every indication that in this system the general pattern of phase behaviour is similar to that obtained on solution blending the same pair of polymers. We are now in a good position to produce large, uniform, well-characterized samples with which we can begin to measure mechanical properties.

ACKNOWLEDGEMENTS

The authors thank Dr Chris Frye, of BP Chemicals Grangemouth, for arranging the supply of polymers for this work. C. C. P. thanks Universidad Simón Bolívar and Fundación Grand Mariscal de Ayacucho, Venezuela, for financial support, and M. J. H. thanks DSM for financial support for parts of this work.

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