polymer communications

Preliminary studies of polypropylene/linear low density polyethylene blends by transmission electron microscopy

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Binary blends of polypropylene with a linear low density polyethylene were prepared in solution, dried and studied by transmission electron microscopy using surface replicas of samples prepared by remelting and quenching. Very clear micrographs were obtained with a wealth of morphological detail. Phase separation was observed over a wide composition range for blends quenched from 190°C. A few samples were prepared by melt mixing in a twin-screw extruder; others, containing deuterated polypropylene, were prepared by solution blending. These special blends showed the same morphologies as normal blends prepared in solution to the same composition.

(Keywords: polypropylene; polyethylene; blends)

Introduction

This paper describes a preliminary survey of blends of polypropylene (PP) with a linear low density polyethylene (LLDPE) using transmission electron microscopy (TEM). We are interested in polyolefin systems in the melt, and especially in the extent of melt mixing and of phase separation. Where there is phase separation we wish to know the sizes and shapes of the phases. The present work forms part of a wider study of PP/LLDPE blends, including neutron scattering and d.s.c. experiments; these will be published elsewhere[1].

A number of studies have been carried out on liquid–liquid phase separation (*LLPS*) in polyolefin blends, in particular on blends of linear with lightly branched polyethylenes (LPEs with BPEs)[2–10]. In these systems the melt was found to be mixed at some compositions and temperatures but phase separated under other conditions. Blends of PP with a lightly branched terpolymer of PP have also been studied and similar results obtained[11]. The PP/LLDPE system forms a natural extension to this work.

In the past, PP has been blended with high density PE (HDPE). Phase separation has been detected in PP/HDPE melts using light microscopy, scanning electron microscopy[12,13] and neutron scattering[14,15]; ref. 12 contains two electron micrographs of phase separated PP/HDPE blends. Noel and Carley[13] reported phase separation for blends of between 90 and 10% PP content. Wignall *et al.*[14] looked at a 50/50 blend at 200°C and observed two phases. Lohse[15] reported that blends of PP with ethylene/propylene copolymers are immiscible in the melt, even when the ethylene content of the copolymer is as low as 8%.

The brittleness of PP is much reduced when it is blended with LLDPE of broad molecular weight. Utracki and co-workers studied a PP/LLDPE system in detail[16–19]. They studied the morphology[16] (by scanning electron microscopy) and reported two dispersed phases for all blend compositions, except between 25 and 50% PP where they found phase cocontinuity. (Phase cocontinuity was also found in PP/HDPE blends of 50:50 composition[12].) Utracki and co-workers studied PP/LLDPE blends in the solid state, using d.s.c. and d.m.t.a. and looked at the mechanical properties[17,18] as well as at melt rheology[18]. The results led them to believe that blends containing a small percentage of LLDPE (5% and less) may be miscible.

TEM, using replicas, has been shown to be a very effective method to study *LLPS* in LPE/BPE blends where direct methods are difficult because of the physical similarity of the blend components[2–10]. In the present study we show that TEM is an equally effective tool for the study of PP/LLDPE blends. We found that the PP/LLDPE blends investigated were generally separated in the melt, although mixing was observed for very low concentrations both of PP in LLDPE and of LLDPE in PP. We found a wide range of morphologies, which we describe here in outline only. We present preliminary information on the sizes and shapes of the phases. Most of the blends studied contained normal hydrogen containing PP (HPP) and were prepared by solution blending. In addition, a few blends (containing HPP) were prepared by melt mixing and a few others, containing deuterated PP, were prepared by solution blending. The behaviour of these blends is compared with that of the solution blended HPP/LLDPE blends of the same composition.

We believe that this brief exploration indicates an alternative method for investigation of PP/LLDPE phase diagrams and opens up a wide field for morphological study.

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Experimental

Three polymers were used in this study, two PPs and the LLDPE. Details of these materials are given in *Table 1*. One PP was deuterated (DPP) and this material was also used for neutron scattering studies, to be reported separately[1]. We label blends by the PP content, e.g. an 80% blend contains 80% PP and 20% LLDPE.

Most of the blends were made in the laboratory by solution blending. This involved dissolving the materials together in xylene and coprecipitating in methanol, a non-solvent, at room temperature (details of this method are given in refs 2 and 3). These blends are termed solution blended (SB). We caution that when solution blending, a small proportion of one or other of the components may stick to the side of the flask and remain partially undissolved. In the present case we suspect that PP dissolves less easily than LLDPE, and so the actual content of PP in an SB sample can be slightly less than would be expected, unless great care is taken in solution blending.

A few blends were melt mixed at BP Chemicals, Grangemouth[20]. Each blend was premixed to the required proportions by hand, prior to extrusion compounding in a Leistritz LS 30 34 counter-rotating twin-screw extruder (34 mm diameter parallel screws, length-to-diameter ratio 19:1) fitted with a two-hole strand die. The screw speed was 100 rev min^{-1}, the barrel and die temperatures both 210°C and the throughput was approximately 5 kg h^{-1}. The strands were cooled in a water bath and pelletized. These blends are termed melt mixed (MM).

The blends were examined by TEM using replicas of fast quenched (rather than as-made) samples. For LPE/BPE blends it has been shown that complete mixing is possible by solution blending[2,3]. However, some blends do not mix in the melt for thermodynamic reasons and the presence, on quenching from the melt, of two well separated crystal populations with different crystal thicknesses is one clear indication of *LLPS*[2–5]. The distance over which the separation occurs can be assessed from micrographs, and for LPE/BPE blends it is in the range of micrometres. Measurement of diffusion rates in LPE/BPE blends has shown that phase separation on the scale observed cannot have occurred as a result of diffusion during quenching[6] and is, therefore, characteristic of the melt itself. We do not believe that diffusion in an LLDPE/PP melt is significantly faster than diffusion in an LPE/BPE blend melt.

For TEM, small blend samples (roughly 5 mm × 3 mm and 0.5 mm thick) were mounted between the thinnest possible glass cover slips, wrapped in one layer of aluminium foil and held in an oil bath at 190°C for 30 min before quenching into acetone at its freezing point. Surface replicas were taken. The surface was used for replication because it is the most rapidly cooled part of the sample and hence the closest in phase structure to the melt. The surfaces were subjected to permanganic etching for 30 min using the polyethylene recipe[2,3,21]. Replicas were then made by a one-stage process[22] and subsequently examined in a Philips 301 TEM.

Table 1 Characteristics of the polymers used

Polymer	Name	M_w	M_w/M_n
HPP	Himont Moplen 5305	3.8×10^5	4.84
DPP	Synthesized[a]	2.8×10^5	4.22
LLDPE	BP Innovex LL 0209AA	1.2×10^5	4.4
(ethylene–butene copolymer 7.8 wt% butene)			

[a] Synthesized in the Department of Chemistry at the University of East Anglia

Results

Typical morphologies are displayed in *Figures 1* and *2*. *Figure 1* shows the five basic morphologies that we have found for HPP/LLDPE blends prepared by solution blending. These can be summarized as follows:

(i) PP spherulites (*Figures 1a, b*);
(ii) LLDPE inclusions in PP (*Figures 1c, d*);
(iii) phase inversion (*Figure 1e*)
(iv) PP inclusions in LLDPE (*Figures 1f, g*);
(v) typical quenched LLDPE (*Figure 1h*).

When blends of 99.9 and 99.5% PP were quenched from 190°C there was no sign of phase separation, and the morphology looked like that of quenched PP — compare *Figures 1a* (PP) and *1b* (the quenched 99.5% PP blend). In contrast, the quenched 99.0% blend showed clear PE-like inclusions (as *Figure 1c*). It might be thought that a 99.5% blend contains so little PE that any phase separated inclusions could be missed. However, it is our experience that for a phase separated blend containing only 0.2% of LPE in BPE, separated LPE-rich regions can be seen in all micrographs[2–4]; building on this experience we are confident that 0.5% of phase separated PE in PP would be easy to detect from surface replicas (particularly as the difference in appearance between PP and PE is much greater than that between LPE and BPE).

It is clear from the micrographs in *Figures 1c–g* that on quenching from 190°C all HPP/LLDPE blends in the composition range 95 to 2% are biphasic, showing two clear morphologies (PP-like and LLDPE-like). The separation is on a scale of micrometres. It is not possible for the materials to diffuse this distance during the time of the quench (a small fraction of a second) so we may safely conclude that the quenched solid is separated on the same scale as the melt. Hence it appears that there is very little melt mixing in this system at 190°C. A more detailed examination reveals that inclusions of the minority polymer can be seen at both 99.0 and 1.0% PP content, and two clear morphologies can be seen at all compositions examined within these limits (see details in *Table 2*).

A few melt mixed HPP/LLDPE blends were available and a small number of DPP/LLDPE blends (solution blended only). Some representative pictures for melt mixed HPP/LLDPE and solution blended DPP/LLDPE samples are shown in *Figure 2*. It is obvious from a comparison of MM 80% HPP/LLDPE (*Figure 2a*) with SB 80% HPP/LLDPE (*Figure 1d*) that the phase morphologies are very similar for the two methods of mixing. Similarly, we see that the DPP/LLDPE blends are very similar to the HPP/LLDPE blends of the same composition (cf. the 20% blends, *Figures 2b* and *1f*).

Discussion

The existence of *LLPS* in PP/PE blends is already well established (refs 12–19 and further references therein). In this communication we are drawing attention not so much to the *LLPS* itself as to the clear way in which it can be revealed by TEM. Hence the first point to stress is that *LLPS* in PP/LLDPE blends can be studied very successfully by TEM using surface replicas.

Secondly, TEM reveals good, homogeneous mixing. Looking at different parts of a large replica, or looking at different replicas of samples of the same composition and prepared in the same way, we find that all areas are of similar appearance. MM samples look very like SB samples; this is also the case for LPE, lightly branched BPE blends, prepared by solution and melt mixing[23]. (Note that in the PP/PE blends MM samples may, in general, be better characterized as to concentration, because of the problem (noted above) of imperfect dissolution of PP, unless great care is taken in solution blending.)

Thirdly, we would like to highlight certain details of the morphologies.

(a) The morphology of LLDPE always resembles normal quenched LLDPE, but we find a range of PP morphologies. Very large spherulites, extending over several grid squares, are observed for the highest PP concentrations (*Figures 1a, b*), but the spherulites reduce in size as the PP concentration drops. At 95% they extend over a few micrometres only (*Figure 1c*). At lower concentrations it is not easy to identify the outline of spherulites (*Figures 1d, e*). Much further study is required here; electron diffraction would show whether different PP crystal phases, as well as different PP morphologies and spherulite sizes, are found. Noel and Carley[13], who

Table 2 Blends studied

Solution-blended (SB) HPP/LLDPE (% PP listed)

100	99.9	99.5	99.0	95	90	80	75	65	59	55	52	50	48	45	20	10	5	3	1	0
PP spherulites			PP spherulites with PE inclusions					[a]	Phase inversion					PE spherulites with PP inclusions						PE

Solution-blended (SB) DPP/LLDPE

99.0	20	10	1
PP spherulites with PE inclusions	PE spherulites with PP inclusions		some PP inclusions

Melt-mixed (MM) HPP/LLDPE

80	50
PP spherulites with PE inclusions	Phase inversion

[a] The 65% HPP sample was on the border between two morphologies, parts of the sample showing PP spherulites with PE inclusions but most of the sample showing the phase-inversion morphology

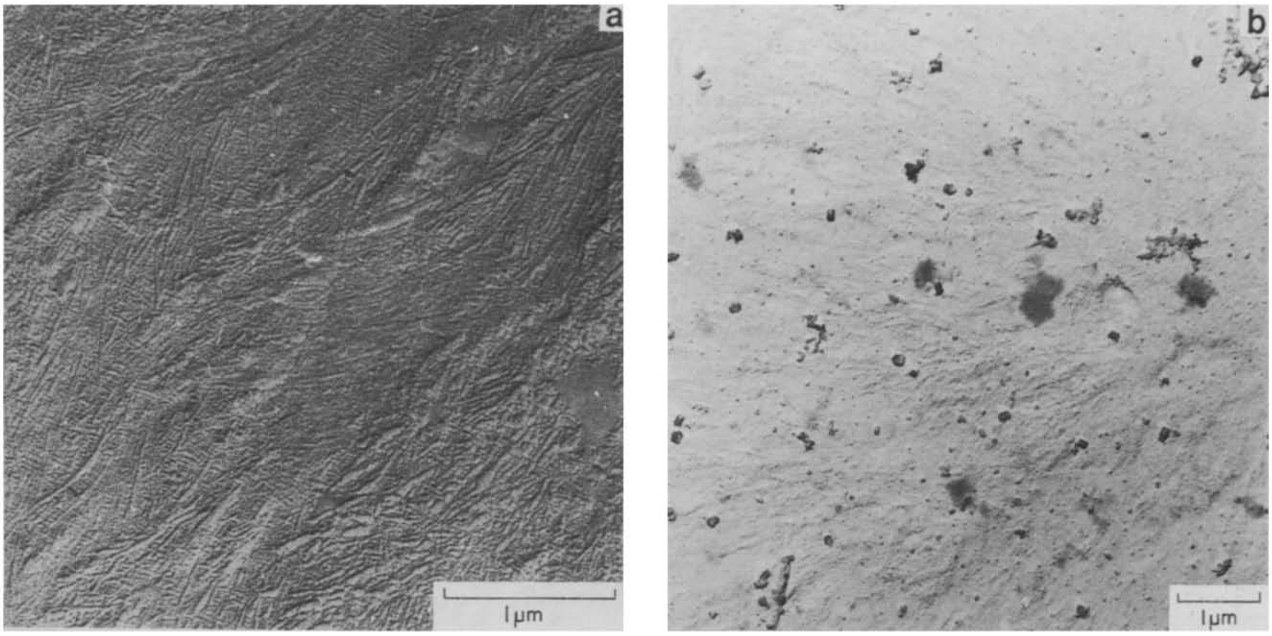
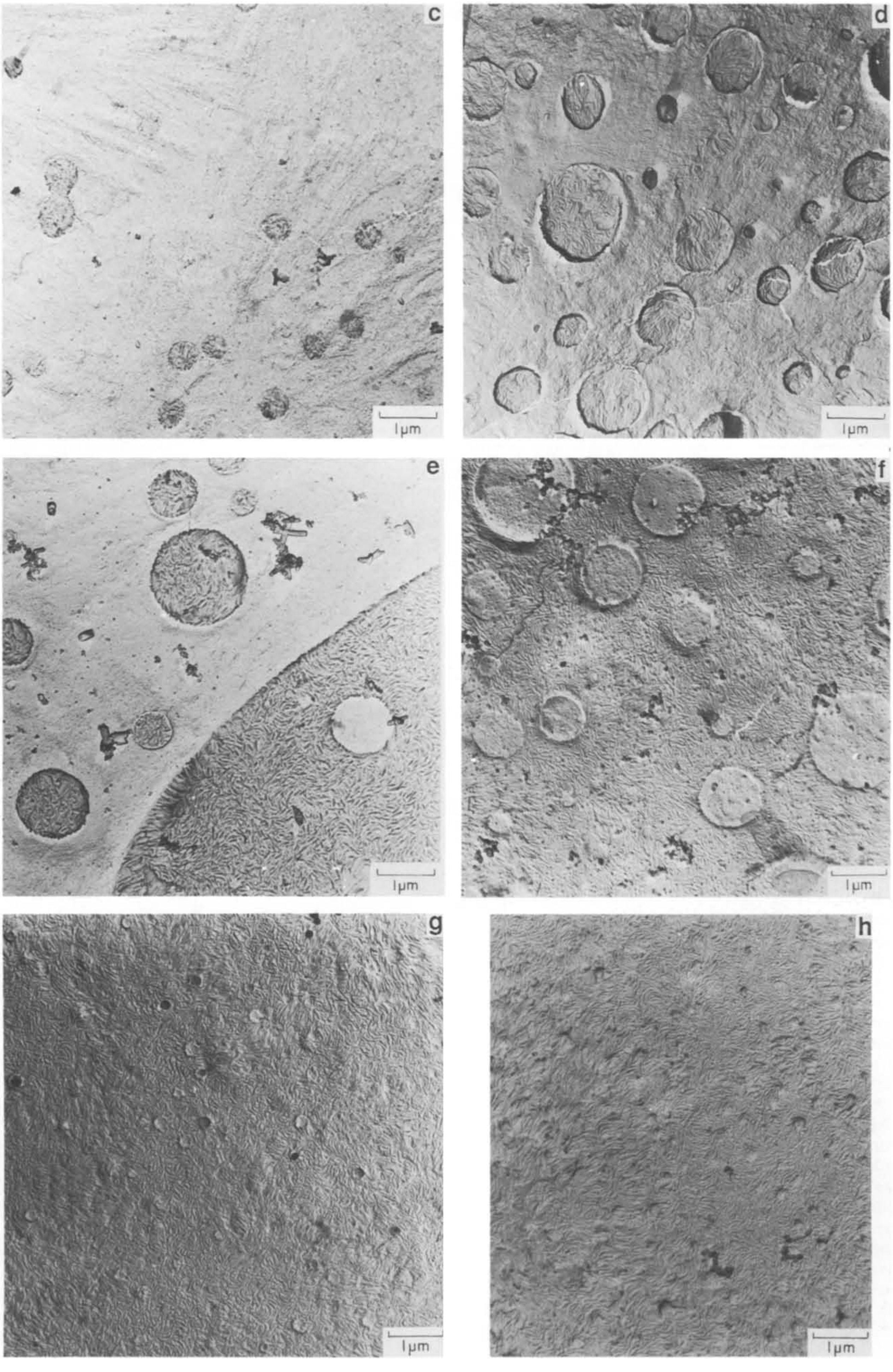


Figure 1 Morphologies seen in solution blended HPP/LLDPE blends; micrographs of surface replicas taken from blends quenched from 190°C. (a) Part of a spherulite of HPP; this picture is at a higher magnification than the others because the PP morphology is on a finer scale than that of the LLDPE and the phase separation of blends. (b) Part of a spherulite of a 99.5% blend; no LLDPE inclusions are visible — the dark spots are debris from the etchant, not PE. (c) A quenched 95% blend, showing clear inclusions of lamellar LLDPE in parts of three different PP spherulites. (d) A quenched 80% blend, showing larger LLDPE inclusions. (e) A quenched 50% blend, showing the phase inverted morphology; note the inclusions of PP in the LLDPE-rich region and vice versa. (f) A quenched 20% blend, showing large PP inclusions in an LLDPE matrix. (g) A quenched nominally 2% blend showing small PP inclusions in an LLDPE matrix. Where the inclusions appear dark, polymer has been detached and adheres to the replica. (h) Quenched LLDPE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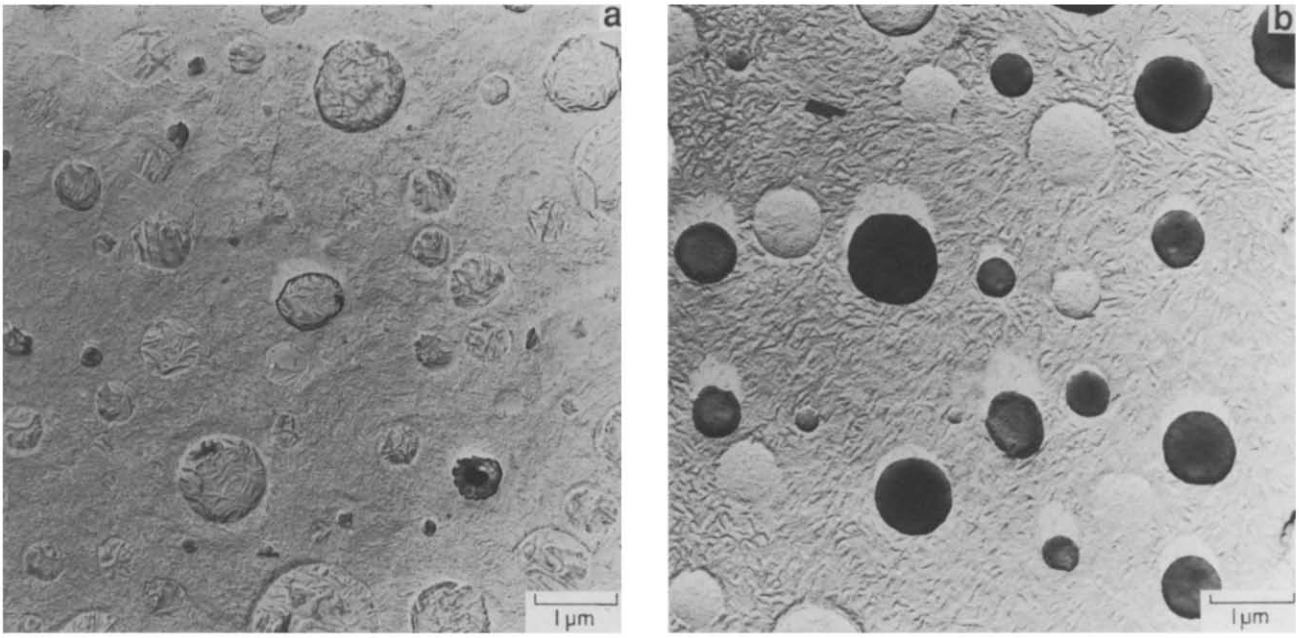

Figure 2 Micrographs of surface replicas taken from blends quenched from 190°C. (a) A quenched MM 80% blend of HPP/LLDPE. (b) A quenched SB 20% DPP/LLDPE blend; there is a good deal of detached DPP (dark material) in this region

used light microscopy, reported changes in size of HPP spherulites on blending with increasing amounts of HDPE.

(b) The inclusions appear as circles, even when they are within phase inverted regions. The observation of circles in two dimensions implies that the inclusions are spheres in three dimensions. Spheres would be expected for *LLPS*.

(c) The phase inversion morphology appears to stretch from approximately 46 to 65% HPP in our system, a different range from that reported for the LLDPE and PP used by Utracki[16]. There are indications that in this morphological region the PP is found preferentially, but not always, on the sample surface, i.e. when the samples were melted between glass cover slips the PP was preferentially next to the glass. There is considerable scope for further study here, in particular as to the implications for surface energy values.

(d) A fourth point concerns the phase diagram for HPP/LLDPE melts. From the present TEM data we can say that there is a very wide region of *LLPS* for this blend system in the melt at 190°C. All compositions between (and including) 99.0 and 1% PP content were found to be phase separated. There appeared to be very narrow regions of mixing at extremely low PP content and at extremely low PE content. The TEM results, for those DPP/LLDPE blends that we have, agree with the TEM results for HPP/LLDPE blends of the same composition and with the neutron scattering data[1]. We would like to quench from other temperatures to see, from the morphologies, whether the region of *LLPS* becomes wider or narrower. This method of plotting phase diagrams has been used to good effect for LPE/BPE blends[3–5,7,9,10]. PP could be regarded as the ultimate in heavily branched PEs. If we take this view, the result here is in line with results obtained on blending LPEs with BPEs; very branched BPEs show phase separation over a very wide concentration range when blended with LPEs[7,24–26].

Conclusions

We have found TEM to be a very valuable tool with which to look at PP/LLDPE blends. Solution blending gives good, well mixed samples. We have obtained a wealth of morphological information; the material presented here is only an initial survey and there is a great deal more to learn.

The extent of *LLPS* at 190°C has been determined for our particular HPP/LLDPE system. More of the phase diagram could easily be revealed. The few melt-mixed samples that we have, appear well mixed and are morphologically very like the corresponding solution blended materials. The limited range of solution-blended DPP/LLDPE samples that we have examined are morphologically indistiguishable from the corresponding HPP/LLDPE blends.

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