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A study of blends of isotactic polypropylene with high density polyethylene by transmission electron microscopy

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Isotactic polypropylene (iPP) was blended with a high-density polyethylene (HDPE) and the blends, quenched from the melt at temperatures between 170 and 200°C, were examined by looking at surface replicas in a transmission electron microscope. Widespread phase separation was evident and a range of morphologies recorded. Phase ripening takes place progressively with time as the blends are held in the melt. This ripening can be used to detect phase separation where the driving force is low (i.e. near to phase boundaries). The composition range where phase separation is observed decreases gradually with temperature between 200 and 170°C. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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Introduction

A preliminary study of phase separation in blends of isotactic polypropylene (iPP) with linear low-density polyethylene (LLDPE) using transmission electron microscopy (TEM) appeared in 1994[1]. TEM was shown to be a very effective tool for the study of phase separation in iPP/LLDPE blends.

Blends were melted, quenched from the melt, and used to make replicas for TEM. The replicas showed that phase separation is widespread in the system studied. To be specific, blends containing 99.9% iPP showed no sign of separated polyethylene (PE), but clear PE inclusions could already be seen in the 99.5% iPP blend. Various characteristic morphologies indicating phase separation were then seen for blends of iPP content down to and including 1%.

The 1994 work established the technique, and indicated widespread separation in one particular iPP/LLDPE system studied on quenching from 190°C only. However, LLDPEs are rather complex materials[2–7], for instance some have been observed to show morphologies indicating that they themselves phase separate in the melt[8,9]. Further, unusual morphology maps, indicating widespread phase separation, have been seen when LLDPEs have been blended with high-density PE (HDPE)[9], near-random ethyl-octene[9,10] and ethyl-butene copolymers[10] and an LDPE[11].

We have now followed up the initial work[1] with a study of a simpler system, iPP blended with an HDPE. Phase separation in the melt has been reported for iPP/HDPE blends[12–15]; experimental methods such as optical microscopy, scanning electron microscopy[12,13] and neutron scattering[14,15] have been used. In the light of these results we would expected to detect phase separation for our iPP/HDPE blend system by TEM. We wanted to confirm its presence, to discover if the phase separation was as widespread as in the iPP/LLDPE system studied previously and then to investigate how the phase behaviour depended on temperature

in the limited temperature range that we are able to study (i.e. 200–170 °C). We also hoped to look for phase ripening in the melt[16]; ripening has been recorded in other polyolefin blend systems[17–22].

Experimental

Materials. The iPP used was a commercial material, M_w 375 000, M_w/M_n 4.8, and the HDPE was BP HDPE 6070, M_w 72 000, M_w/M_n 6.

All the blends used for this study were prepared in solution where we know that very good mixing can be achieved[23]; details of the process are given in refs [23–27]. We label the blends by their iPP content; a 30% blend will have been made by dissolving 30% iPP with 70% PE (by weight) together and coprecipitating in excess non-solvent. Blends were dried, re-melted, and held in the melt for times between 20 min and 1.5 h before quenching into acetone at freezing point. We always use quenched blends because we believe that there is little time for diffusion during a fast quench, so the structure will be similar to that of the melt and there is strong evidence to support this. For instance, diffusion rates have been measured[26] in LPE/BPE blends and morphologies have been examined after cooling from the melt at increasingly slow rates[28]. Both sets of experiments confirm that the structure of a quenched blend is very close to that of the melt. In an unpublished study on iPP/PE blends, optical micrographs of melts of blends containing 50% iPP were correlated with TEM carried out on the same samples after quenching—it was clear that the phase boundaries did not change (within the errors of observation) on quenching[29].

We made replicas from the surfaces of quenched blends, using the Bristol variation[30] of the permanganic etching procedure that originated in Reading[31]. We always take surface replicas because the surface receives the fastest quench and so should be nearest in structure to the melt. Replicas were examined, some in our Philips 301 and others in our Philips 400T TEM.

The range of temperatures from which we quenched our specimens was limited by two factors: HDPE degrades significantly in 2 h if stored in the melt in the presence of
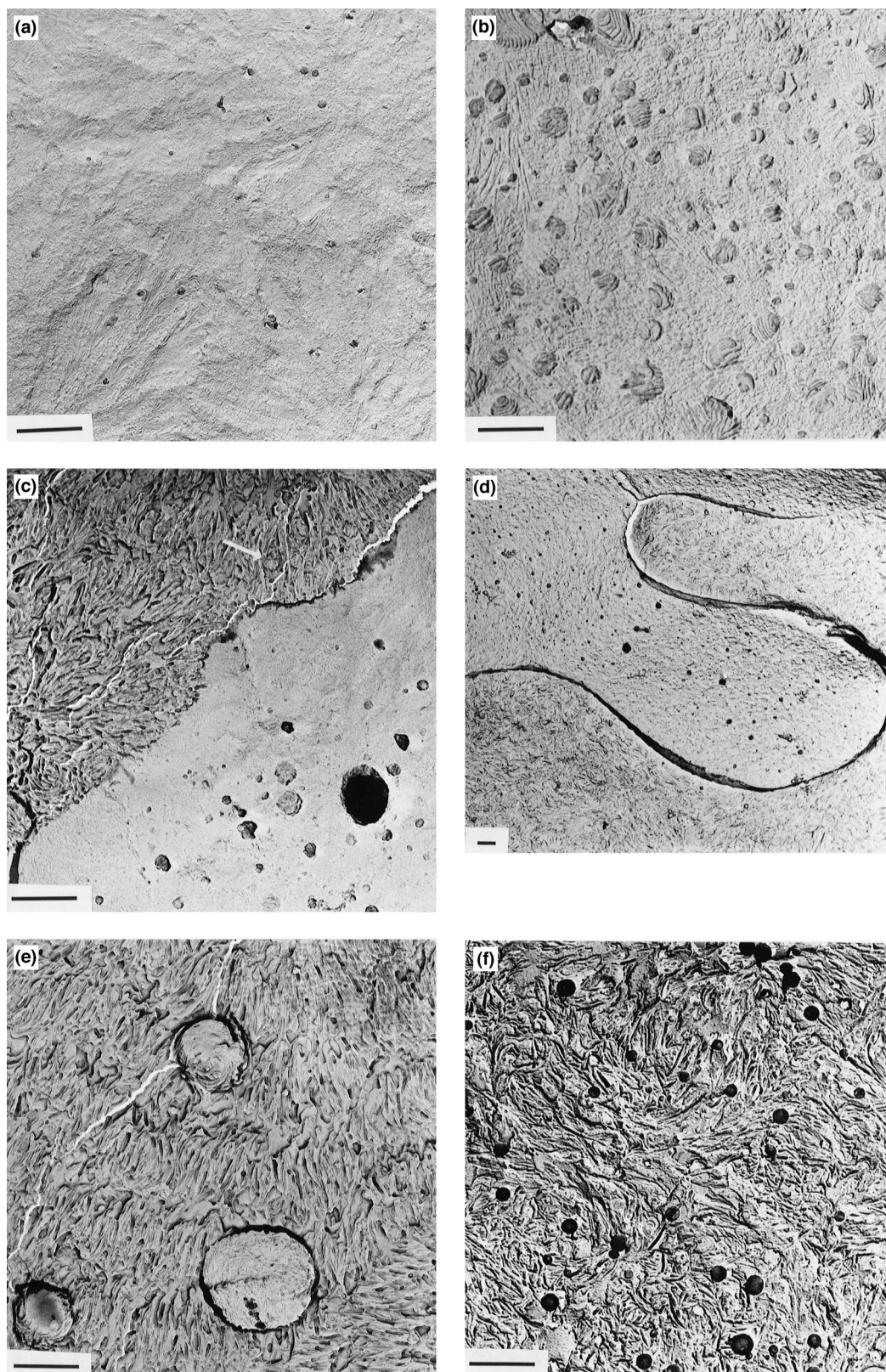

Figure 1 Morphologies found on quenching blends of the iPP/HDPE system. All micrographs are of replicas of quenched blends. The magnification is the same in all cases except for (d), which is at a lower magnification than the rest. Each scale bar represents 1 μm. (a) A 99.5% blend quenched from 200°C. The outlines of several iPP spherulites can be seen and there are small, scattered inclusions of PE. The lamellar structure is visible in some of these inclusions. The iPP lamellar structure is on a much finer scale than the PE lamellar structure. (b) A 90% blend quenched from 190°C. The outlines of the iPP spherulites are no longer clear. The regions of PE rich material are now unmistakable. (c) A 60% blend quenched from 190°C. There is a co-continuous structure, with an iPP rich region with PE inclusions (bottom right) and a PE rich region with some iPP rich inclusions. There are some very dark areas where polymer (PE) has detached from the blend sample and stuck to the replica. PE inclusions are much clearer in the iPP matrix than vice versa, but some iPP inclusions can be seen in the PE matrix, one is arrowed. (d) A lower magnification picture of a co-continuous structure showing the scale of the separation. This replica was obtained from a 40% blend quenched from 170°C. (e) A 30% blend quenched from 190°C. Here there is a PE rich matrix with iPP inclusions. The iPP crystals can be seen clearly in the biggest of these inclusions (there is some detached polymer adhering to the others). (f) A 2% blend quenched from 200°C. iPP inclusions again visible in a PE rich matrix. There is much detachment of iPP (dark regions, where the electrons were not able to penetrate) but iPP rich crystals are visible in some inclusions
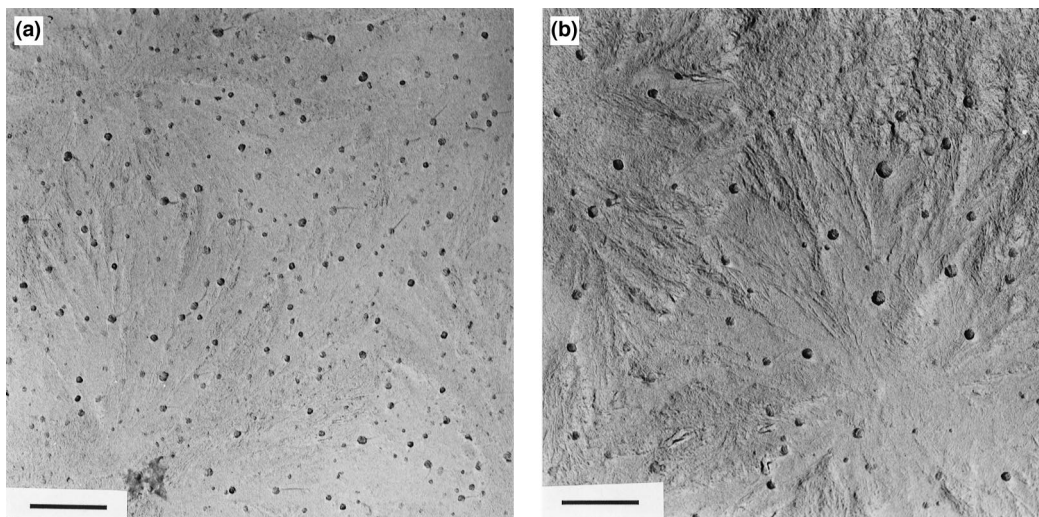
Figure 2 Phase ripening in the iPP/HDPE system. The magnification is the same in both pictures, and the same as that in *Figure 1a–c, e* and *f*. Each scale bar represents 1 μm. (a,b) Ripening at 190°C in a 98% blend. The material pictured in (a) was held in the melt for 20 min before quenching, and that in (b) for 1.5 h

Table 1 Phase behaviour as a function of blend composition (%iPP content) in the temperature range 200–170°C

Melt temp. (°C)	iPP	99.9	99.5	99	98	97%–3%	2	1	0.5	0.1	PE
200	M	S	S	S	S	S	S	S	T	M	M
190	M	M	S	S	S	S	S	S	T	M	M
180	M	M	S	S	S	S	S	S	M	M	M
170	M	M	T	S	S	S	S	T	M	M	M

oxygen at temperatures in excess of 200°C[25,32], and iPP begins to crystallize at about 165°C. Hence we worked between 170 and 200°C where both materials were in the melt and minimal degradation was expected over the time-scale of our experiments (up to 1.5 h).

Experiments on blends of differently branched polyethylenes[22], and with other polyolefin blend systems[17–21] have shown that phase ripening[16] can be observed where systems that are phase separated are held in the melt; significant ripening has been seen over minutes and hours. First, we wished to see if ripening could be observed in the iPP/HDPE system and, if it could, we hoped to use the phenomenon to identify phase separation where we believed that our blends were of a composition near to a phase boundary. In such blends the driving force for separation could be low; we argued that if we held such a blend in the melt for long times the minority phase might become visible on storage (as a result of increasing droplet size).

Results and discussion

Figure 1a–f shows some typical micrographs obtained from replicas of iPP/HDPE blends. As in the previous work[1] iPP crystals can be readily distinguished from HDPE crystals, and the TEM method is well able to detect phase separation. It is immediately clear that the morphologies are very similar to those that we saw in the iPP/LLDPE systems studied previously[1]. On quenching from the melt we see pure iPP structure over a very narrow composition range; then, as the HDPE content is increased, we see HDPE droplets in an iPP matrix (*Figure 1a,b*). The circular shape of the PE-rich regions implies that the inclusions are spherical. We would expect to find the circular regions in a range of sizes because we are, effectively, taking random sections through spheres. On further decrease of the iPP content (to about 65% iPP) we see a region with

interpenetrating and co-continuous iPP and HDPE phases (*Figure 1c,d*); then, at low iPP content (below about 35%), we see iPP droplets in an HDPE matrix (*Figure 1e,f*); finally, over a very narrow composition range, HDPE lamellae, with no visible iPP droplets.

Figure 2 shows that phase ripening is indeed observed in this system, as in other systems[17–22]. Comparing *Figure 2b* (1.5 h storage) with *Figure 2a* (20 min storage) we see the number of inclusions decreasing with storage time, but the average inclusion size increasing. The boundaries of the iPP-rich spherulites are much clearer in the replica of the ripened materials as are the iPP crystals; this is commonly observed after ripening in this system. We did not do quantitative studies of ripening to estimate diffusion rates; instead, we used it to confirm phase separation near to the phase boundary. For several temperatures and compositions clear droplets could be seen after storage in the melt for 1 or 1.5 h where none could be seen after storage for 20 min.

Using all the information from all micrographs of all blends we were able to construct a phase diagram for the temperature range 170–200°C. This is shown in *Table 1*. We indicate compositions and melt temperatures where the blends were clearly separated after storage in the melt for 20 min by 'S'. We mark compositions and melt temperatures where no separation could be seen after storage for 20 min, but where minority phase droplets became clear after storage for 1.5 h with 'T'; compositions and melt temperatures where no minority phase was seen even after long storage in the melt are marked 'M'.

Conclusions

We have shown that the TEM method works equally well for iPP/HDPE blends as for iPP/LLDPE blends, as we expected. The micrographs are very clear, and similar to

those shown in ref. 1; the same types of morphology are observed. Less data are available for the iPP/LLDPE system (that system was studied at 190°C only and ripening was not performed); however, there is no doubt that in both the iPP/LLDPE and iPP/HDPE systems phase separation is seen over a very wide range of compositions.

In the iPP/HDPE system of the present study we are unable to detect separation for compositions with less than 1% of the minority phase only. It is easier to detect the larger HDPE crystals in a matrix of fine iPP crystals than vice versa. For this reason there is more uncertainty in the phase boundary on the HDPE rich side of the phase diagram. The data recorded at the HDPE rich side of *Table 1* is an upper bound for iPP content in this respect.

Phase ripening has been observed, and it can be used to reveal phase separation when the driving force is low.

The phase separation is found for a wide range of compositions for temperatures in the range 200–170°C, but we see that the phase-separated region narrows slightly as the melt temperature is reduced within this range.

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