

Polymer Communication

Morphology maps of binary blends of copolymers produced using the metallocene catalyst process

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Abstract

Three lightly branched commercial polyethylene copolymers, produced using the metallocene catalyst process, were blended together in binary pairs. Two of the materials were ethylene–butene copolymers of differing butene content, the third was an ethylene–hexene copolymer with the same branch content as the more lightly branched ethylene–butene material. Note that the components of one system differ in both branch type and branch content; those of another, in branch content but not branch type; and those of the third in branch type only. Morphology maps were produced for all three systems. Where the two components had the same branch content, only one crystal type was seen on quenching melts of all compositions from all temperatures. Where the branch contents varied, two crystal types were seen when blends of some compositions were quenched from some temperatures, and the morphology maps resembled those found when copolymers produced by traditional methods are blended—or when a linear polyethylene is blended with a lightly branched copolymer. These findings confirm the view that it is the branch content of the copolymers that effects the morphology most strongly, the branch type is of secondary importance. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the recent past we have published a series of papers on the behaviour of blends of linear polyethylenes (LPE) with lightly branched polyethylenes (BPE) [1–21]. We were originally interested in phase separation, but argued that the physical properties of the components are too similar to enable the detection of any such separation directly in the melt and so indirect methods were adopted. We observed biphasic structures in blend samples of some compositions rapidly quenched from some melt temperatures. We have studied nearly 70 binary systems to date and produced “morphology maps” for all of them. The maps indicate those melt temperatures and compositions that produce two distinct crystal populations on quenching and those that produce only one. We have, in the past, interpreted double morphologies as being the result of quenching from a phase separated melt, and single morphologies as the result of quenching from a single phase melt. Recent work [21] has cast some doubt on this interpretation but the morphological observations remain clear.

Our library of “morphology maps” includes systems

where the (weight average) molecular weights of the LPEs have ranged between 2×10^3 and 2×10^6 [3,4]. In some cases the branched materials were well-defined, e.g. near random ethylene butene (EB), ethylene hexene (EH) or ethylene octene (EO) copolymers [7,9,10,13,15,16,18]. In other cases the branched materials were less well defined, e.g. low density or linear low density polyethylenes [1–6,10,12,17,20,21]. In all the blend systems that we have studied where the branch content of the BPE has been above 1 mol% (except one, where the molecular weight of the LPE was very low indeed, 2×10^3 [3,4]) we have found morphology maps of a characteristic type. The quenched blends of high LPE content show a single uniform morphology. However, there is always a closed loop of double morphology (with domains of thicker lamellae in a matrix of randomly oriented, thin lamellae) for low LPE content blends quenched from lower temperatures. We have not been able to find any double morphologies, of similar appearance, in quenched blends of two LPEs with widely differing molecular weights [22].

In the regions of double morphology (in the LPE/BPE blends) the separation between groups of crystals of the dispersed phase is on a large spatial scale; typically, the minority domains are some microns in diameter and separated on a similar scale. The extent of the double

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Table 1
Details of the polymers used in this work

Copolymer	Branch content (mol%)	M_w	M_w/M_n
EB(6.3)	6.3	58k	2.65
EB(9.4)	9.4	91k	2.00
EH(6.3)	6.3	79k	2.5

morphology region is dependent on the molecular weight of the LPE, but only changes slowly for molecular weights of above about 5×10^4 [3,4]. We have looked at LPEs with polydispersity between 1.1 and 7, and found the morphology maps very insensitive to the polydispersity of the LPE. However, the composition range over which double morphology is found reduces as the branch density increases [7,9,10,15]. For example, the region of double morphology is wider, in composition, when an LPE is blended with a 2 mol% EO copolymer than it is when the same LPE is blended with an 8 mol% EO copolymer [7].

For lightly branched (up to 9 mol%) copolymers, made by conventional processes, the extent of the region of double morphology observed for binary blends is the same, within the experimental errors, where the molecular weights of the two components and the branch density of the copolymers are similar, whether the copolymers are EB, EH, EO or have mixed branching. We believe this important finding indicates that it is the number of branches that determines the behaviour, rather than the branch type [7,10,15,16]. We have also shown that when two near random lightly branched copolymers of different branch density are blended together, the behaviour is similar to that observed on blending an LPE with one near random copolymer [9,10,13,15].

We have one publication describing experiments showing that when a commercially available LPE is blended with EB or EH copolymers produced using metallocene catalysts, the resulting morphology maps are very similar to those produced when the copolymer was made by more conventional processes [18]. We have not, however, previously blended two metallocene catalysed materials, and in this paper we examine the morphology maps produced when pairs of such copolymers are blended. We are interested to see if the copolymers made by the metallocene catalysis process behave in the usual way when blended together. Also, since we have materials of the same branch content, but different branch types (and, sadly, somewhat different molecular weights) we investigate further the effect of differing branch types.

2. Experimental

2.1. Materials

The materials used in this work were commercial ethylene/butene and ethylene/hexene copolymers obtained from

Exxon. The molecular weights and polydispersities were assessed by GPC [22] and the branch contents by FTIR [15]; the materials are listed in Table 1. As above, we use EB to indicate an ethylene/butene copolymer and EH to indicate an ethylene/hexene copolymer; the number in brackets indicates the branching in mol%.

Binary blends were made using the three commercial Exxon Exact materials listed in Table 1. Three systems were studied:

EH(6.3)/EB(9.4),

EB(6.3)/EB(9.4),

EB(6.3)/EH(6.3)

Note that the components of the first system differ in both branch type and branch content; those of the second in branch content but not branch type; and those of the third in branch type only. Unfortunately, the molecular weights differ somewhat. We label each blend by the content of the less branched material, e.g. a 10% EB(6.3)/EB(9.4) blend contains 10% EB(6.3) and 90% EB(9.4).

2.2. Methods

The materials were blended in solution using methods which we have described previously, e.g. [1,2,11]. These particular materials tend to retain solvent, so they were held in a vacuum oven (overnight minimum) after blending and before further experimentation.

The blends were studied by TEM and by DSC, again using the methods that we have often employed before. We look at quenched blends so as to avoid morphological changes (related to diffusion rates and liquid/solid separation [6,18,20]) introduced when crystallisation takes place during slow cooling from the melt. The blends were held in the melt for 30 min before quenching into acetone at freezing point.

Preliminary DSC experiments indicated that quenched blends containing EB(9.4) continued to crystallise slowly (over some days) when held at room temperature, so each DSC run was made as soon as the blend had been quenched. The exact experimental procedure was to heat a blend sample to 120°C in the DSC and then hold it at that temperature for 20 min. The sample was then cooled to 20°C as rapidly as possible in the DSC (with cooler operating). On reaching 20°C the sample was immediately raised to 120°C at 10°C/min whilst the data was recorded.

3. Results

3.1. TEM

Micrographs of replicas of quenched blends are shown in Fig. 1. All of the micrographs are of 10% blends, Fig. 1(a)–(c) show one example from each blend system, all quenched

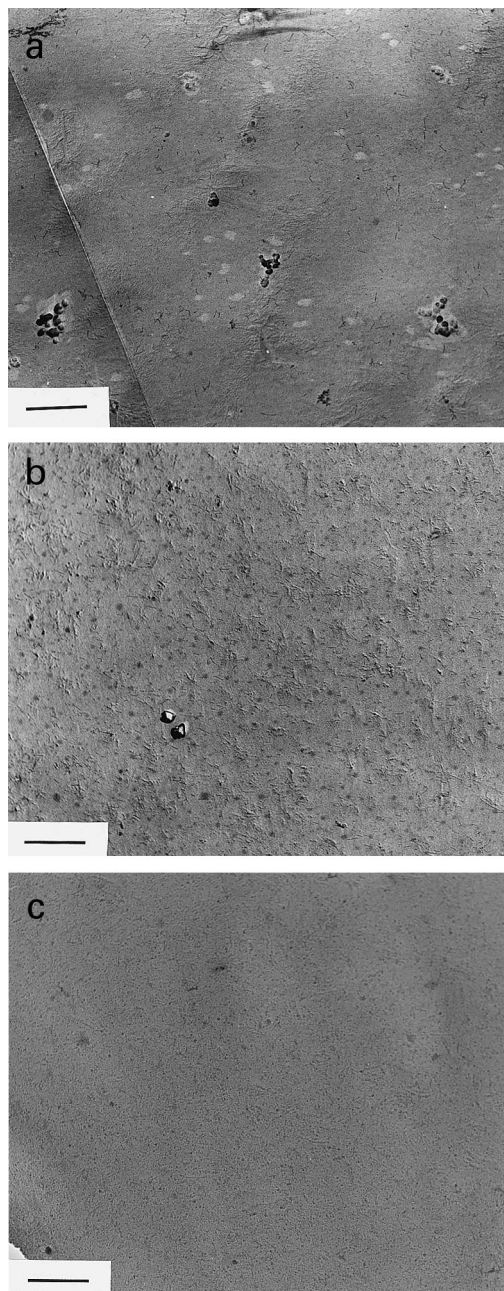


Fig. 1. Electron micrographs of replicas of 10% blends, from all the blend systems studied, all after quenching from 80°. All figures are at the same magnification, and in each case the scale bar represents one micron. (a) EH(6.3)/EB(9.4) 10% blend. Here we see well-spaced groups of thicker crystals in a matrix of thinner crystals (the details of these are not very clear at this magnification), there is a group of thick crystals top right and another at the top, just left of centre. There is some detached polymer adhering to this latter group (looking like a dark streak). The dark, round objects, seen towards the bottom of the picture, are etching debris. (b) EB(6.3)/EB(9.4) 10% blend. The groups of thicker crystals are clearly visible, but much smaller and spaced more closely. (c) EB(6.3)/EH(6.3) 10% blend. Only one crystal type is visible.

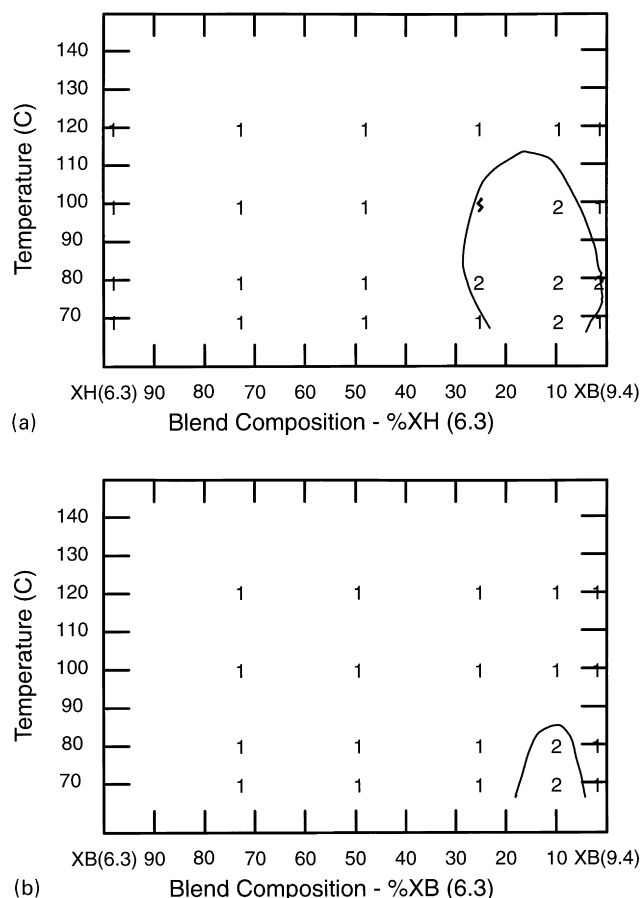


Fig. 2. Morphology maps for the EH(6.3)/EB(9.4) (a) and EB(6.3)/EB(9.4) (b) systems. (1) Indicates a single crystal type observed; and (2) that two crystal types were observed (as in Fig. 1(a) and (b)). Note that the region of double morphology is larger, and found at higher temperatures, for the EH(6.3)/EB(9.4) blend system. There is no region of double morphology observed for the EB(6.3)/EH(6.3) blend system.

from the melt at 80°. ¹ It is clear (from Fig. 1(a)) that the 10% EH(6.3)/EB(9.4) blend shows a double morphology with domains of thicker crystals in a matrix of thinner crystals (although it is hard to make out the details of the thinner crystals at this magnification); the 10% EB(6.3)/EB(9.4) blend (Fig. 1(b)) also shows a double morphology, but on a notably smaller scale and the 10% EB(6.3)/EH(6.3) blend (Fig. 1(c)) shows a single morphology with one crystal type only. All blends from the EB(6.3)/EH(6.3) system quenched from all temperatures, showed only one crystal type. Blends of a relatively small range of compositions (with high EB(9.4) content) from both the other systems showed double morphologies (as Fig. 1(a) and (b)) when quenched from low temperatures, but single morphologies (like that of

¹ Note that these branched materials do not crystallise when held in the melt at 80°C for several days. After crystallisation, at lower temperatures, they have correspondingly low melting points—whereas a typical LPE can crystallise over days at 129°C, can crystallize rapidly at 115°C and melts at about 127°C after quenching, EH(6.3) will not crystallise at all at 80°C and melts at about 90°C after quenching.

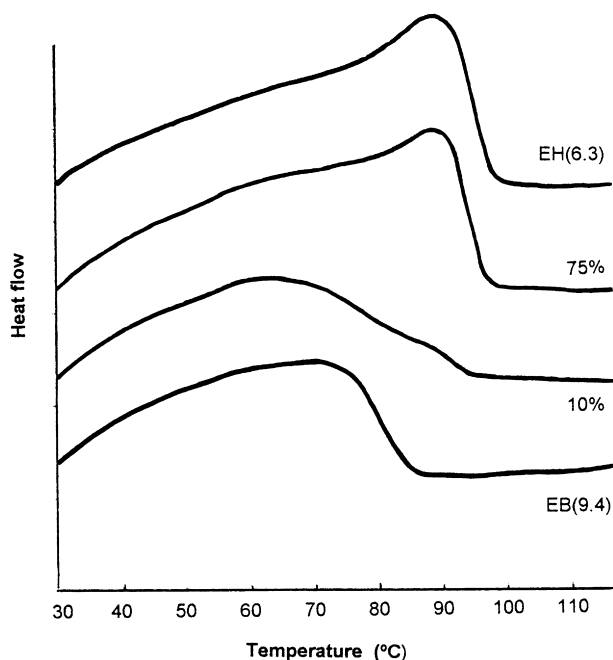


Fig. 3. Examples of DSC traces obtained on heating quenched materials from the EH(6.3)/EB(9.4) system from 20 to 120°C at 10°C/min. The figure shows traces of EH(6.3) and EB(9.4) (broad, single peaks), the 75% blend (again a broad, single peak) and from the 10% blend (two broad peaks, one corresponding in temperature to the EH(6.3) peak and the other to the EB(9.4) peak).

Fig. 1(c)) when the blends of high EB(9.4) content were quenched from higher temperatures and when blends of low EB(9.4) content were quenched from all temperatures. The results are set out in detail in Fig. 2, where the symbol 2 indicates a double morphology, two types of crystal on quenching, and the symbol 1 only one crystal type observed on quenching. Note that the region of double morphology is largest for the EH(6.3)/EB(9.4) system.

3.2. DSC

In this study we found that the DSC results were less clear than they have been in many previously studied systems because the peaks were low and quite broad (note that the branching is quite high in all cases). However, it was possible to detect single melting peaks after quenching for some blends and double melting peaks in other cases; examples are shown in Fig. 3. The single melting peaks were found when blends of low EB(9.4) content, from the EH(6.3)/EB(9.4) and EB(6.3)/EB(9.4) blend systems, were re-heated after quenching and when all blends from the EB(6.3)/EH(6.3) system were re-heated after quenching. Blends with two clear DSC melting peaks were recorded when blends of high EB(9.4) content, from the EH(6.3)/EB(9.4) and EB(6.3)/EB(9.4) blend systems, were re-heated after quenching. The results from the EH(6.3)/EB(9.4) and EB(6.3)/EB(9.4) blend systems are in agreement with the TEM results presented earlier.

We have not, previously, recorded single DSC peaks for all compositions except where either the molecular weight of the LPE was exceptionally low (2155 [3,4]) or where the branch content of the copolymer was very low (e.g. LPE/EB(0.5) and LPE/EO(0.7) blends [16]).

3.3. Summary of results

The results obtained from DSC and from TEM were in agreement although the TEM results were clearer than the DSC results—largely because the DSC peaks were rather broad. The morphology maps, deduced from the TEM and DSC experiments, can be seen in Fig. 2.

For the EH(6.3)/EB(9.4) and EB(6.3)/EB(9.4) systems we found morphology maps of “the usual sort”, (i.e. closed loops of double morphology on quenching from low melt temperatures and where the content of the more branched material was high). The double morphology region was wider in the EH/EB system than in the EB/EB system. Our methods are unable to detect any sign of a second morphology on quenching any blend of EB(6.3)/EH(6.3) from any temperature.

4. Discussion

We have previously found that blend systems of two lightly branched copolymers, e.g. [7,13,15] give morphology maps of the same sort as do systems blends of LPE with one lightly branched copolymer, e.g. [4,18]. In this respect the results from the EH(6.3)/EB(9.4) and EB(6.3)/EB(9.4) blend systems are in agreement with our previous work using copolymers made by conventional processes.

For LPE/BPE blends we find smaller regions of double morphology for the systems containing the LPE with lower molecular weights [3,4]. The fact that the double morphology region of the EB(6.3)/EB(9.4) system is smaller than that of the EH(6.3)/EB(9.4) system is, therefore, not unexpected since the molecular weight of EB(6.3) copolymer is lower than that of EB(9.4). It is interesting that we see larger regions of thicker crystals in the 10% EH(6.3)/EB(9.4) micrographs (Fig. 1(a)) than in the EB(6.3)/EB(9.4) system (Fig. 1(b)). The larger size scale of Fig. 1(a) is more typical of the other systems that we have studied after holding in the melt for 30 min—smaller structures (which later ripened) have been seen after holding in the melt for shorter periods [13].

The fact that we can see rather similar behaviour in the EB(6.3)/EB(9.4) and EH(6.3)/EB(9.4) systems, and no double morphologies in the EB(6.3)/EH(6.3) system, once again indicates that the most important factor leading to morphology maps of the type seen in the EH(6.3)/EB(9.4) and EB(6.3)/EB(9.4) systems is the degree of branching. However, the differences observed between these two systems show that molecular weight and/or branch type do have some influence on the morphologies of quenched blends.

5. Conclusions

Morphology maps with loops of double morphology (found on quenching blends with low content of the less branched component) were obtained on testing blends of these metallocene catalyst copolymers where the branch content differed between the components.

For the same branch contents the region of two morphologies was wider where the branch types concerned were different (but note that there are also differences in molecular weight and polydispersity between the constituents).

Where the branch types were different (ethylene/butene and ethylene/hexene copolymers) but the branch content was the same, single morphologies were seen for all compositions, quenched from all temperatures investigated.

It appears that blends of lightly branched metallocene produced copolymers behave similarly to blends of copolymers produced by other means when blended together. We have previously found that the morphology maps of binary blends of these materials with LPEs are also similar to those of LPEs with copolymers prepared by more conventional methods.

Once again, branch content is seen to be the key variable in determining the morphologies of quenched blends.

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