ELSEVIER

PII: S0032-3861(97)00108-0

Polymer Vol. 38 No. 22, pp. 5595–5601, 1997

0032-3861/97/$17.00 + 0.00

Liquid–liquid phase separation in blends containing copolymers produced using metallocene catalysts

M. J. Hill* and P. J. Barham
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK
(Received 2 August 1996; revised 1 January 1997)

Three commercial copolymers, two ethylene–butene and one ethylene–hexene, produced using metallocene catalysts, were each blended with a commercial linear polyethylene to form binary blends of various compositions. The three copolymers had quite similar molecular weights and molecular weight distributions. The blends were examined, using indirect experimental methods, to see if there was any phase separation in the melt. All three systems show phase separation in the melt at low linear polyethylene content at temperatures between about 125°C and 170°C. The behaviour of the linear/ethylene–hexene copolymer system was very similar to the behaviour of the two linear/ethylene–butene copolymer systems. Further, the behaviour of these blends is very similar to that which has been found for binary linear/lightly branched polyethylene blend systems where the copolymers were polymerized by other processes. © 1997 Elsevier Science Ltd.

(Keywords: polyethylene blends; metallocene catalysis copolymers; liquid–liquid phase separation)

INTRODUCTION

In the recent past we have published a number of papers on the phase behaviour of blends of linear polyethylene with lightly branched polyethylene (LPE/BPE)[1–16]. We have argued that the physical properties of the components are too similar to enable the detection of any phase separation directly in the melt. However, we have been able to observe biphasic structures in rapidly quenched samples, and we have interpreted these morphologies as clearly indicating liquid–liquid phase separation (LLPS), in the melts from which they were quenched.

We have studied 65 binary systems to date and produced 'phase diagrams' for all of them. These 'phase diagrams' are essentially morphology maps. We have called them 'phase diagrams' because the only explanation we have found for the observed behaviour is that the biphasic morphologies arise from LLPS in some polymer melts. These 'phase diagrams' indicate those melt temperatures and compositions which produce, after rapid quenching, a uniform, single morphology (indicative of a mixed melt), and those melt temperatures and compositions which produce two distinct crystal populations on quenching (indicative of a phase separated melt).

Our library of 'phase diagrams' include systems where the (weight average) molecular weight of the LPE has ranged between 2×10^3 and 2×10^6 [3,4]; where the branched materials are near random ethylene butene (EB) and ethylene octene (EO) copolymers[7,9,10,13,15,16]; and where the branched materials have been less well defined[1–6,12]. In all cases, except one (where the molecular weight of the LPE was very low indeed, 2×10^3 [3,4]) we have found LLPS of a characteristic type. The blends mix in the melt at high LPE content, but there is always a closed loop of LLPS at low LPE content.

The phase separation is on a large spatial scale; typically, phase separated regions are some microns in diameter and separated on a similar scale. The extent of the LLPS 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 phase behaviour very insensitive to the polydispersity of the LPE. However, the composition range over which phase separation reduces as the branch density increases[7,9,10,15] (e.g. the region of LLPS 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 LPE/EO systems the characteristic closed loop of LLPS is found for copolymer contents of up to 8 mol%, but when the octene content of the copolymer is 12 mol% a completely different type of phase behaviour is observed—the phase separation is then symmetric, wide-spread, but on a notably smaller spatial scale[7].

For lightly branched (up to 9 mol%) copolymers the extent of the phase separation 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, or EO or have mixed branching. We believe this important finding indicates that it is the number of branches that determines the phase behaviour, rather than the branch type[10,15,16]. We have also shown that when two near random lightly branched copolymers of different branch density are blended

---

* To whom correspondence should be addressed

Table 1 Details of the polymers used in this work

Polymer	Code	M_w	M_w/M_n	Branch content	Density (g ml^{-1})	MFI (dg min^{-1})
Sclair 2907	LPE	10^5	3.5	0	0.960	5
Exact 3028	EB(5.9)	1.32×10^5	1.95	5.9 mol%	0.900	1.2
Exact 3017	EB(6.3)	0.58×10^5	2.65	6.3 mol%	0.901	27
Exact 4044	EH(6.3)	0.79×10^5	2.5	6.3 mol%	0.895	16.5

together, the phase behaviour is similar to that observed on blending an LPE with one near random copolymer[9,10,13,15].

Most of our studies have used comparatively poorly defined materials, commercial LPEs with large polydispersities, LDPEs (some with more than one branch type) or LLDPEs with inhomogeneous branch densities. In some of our experiments we have used materials that are better defined, including EO copolymers with uniform branch content (produced using single site catalysis) and sharp fractions of LPEs. In this paper we report new work using EB and EH (ethylene–hexene) copolymers produced using metallocene catalysts; we have blended these with a commercially available LPE.

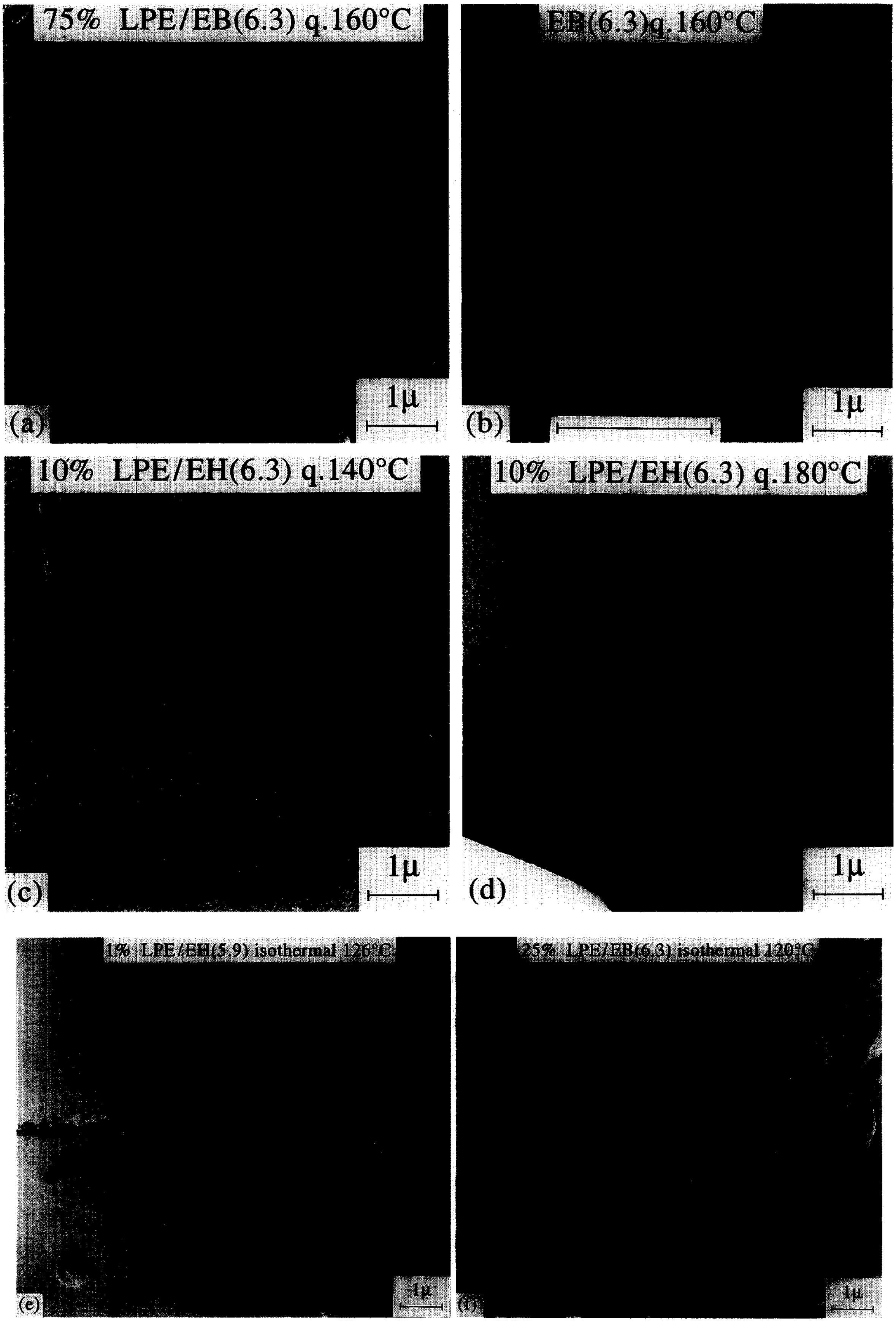
A good deal of work has been performed on the crystallization of EB and EH copolymers produced using metallocene catalysts (e.g. refs 17–21). Only a few studies have been performed on blend systems including EB and EH copolymers[17,21]; these have focused on either crystallization during slow cooling or on isothermal crystallization. The authors of these studies concluded that the blends they used were mixed at the time of crystallization, with any demixing that was observed occurring as a result of phase separation on crystallization. The present work is, as far as we know, the first study of the detailed morphology after quenching of blends containing copolymers made using metallocene catalysts with an LPE.

EXPERIMENTAL

We have blended three commercially available Exxon Exact copolymers with the LPE Sclair 2907 (from Dupont, Canada) in various proportions. Details of the materials used are given in *Table 1*. The copolymers used were 'lightly' branched, i.e. the level of branching was such that we would have expected, from our previous studies, asymmetric LLPS from blend systems where the level of branching of the copolymer was similar. The densities and melt flow indices of the materials are those quoted by Exxon. We assessed the comonomer contents using *FT*i.r. (details of our *FT*i.r. method are given in ref. 15) and the molecular weights using g.p.c. We label the materials by comonomer type and branch content; for instance an EB copolymer of 3.6 mol% butene comonomer content would be labelled EB(3.6). (The term 3.6 mol% means that of 1000 monomer units 36 are of the copolymer and the rest are ethylene. Both carbon atoms of each ethylene monomer are included in the chain backbone, as are two carbon atoms from each copolymer monomer. Thus, since each comonomer contributes two carbons, 1000 backbone carbon atoms contain two carbon atoms from each of 18 comonomers and there are 18 branches per 1000 backbone carbon atoms. An EB copolymer has two carbon atoms in each branch and an EH copolymer has branches of four carbon atoms.)

All blends were made in solution, with xylene as the solvent. We label blends by the LPE content, a 10% blend is one containing 10% LPE with 90% copolymer. The blending method has been described elsewhere[1,2]. Blends were dried and then small samples prepared. For d.s.c. 1–2 mg samples were sealed in d.s.c. pans, melted at 150°C for 20 min and then quenched by flicking into acetone at freezing point. The thermal analysis was performed at a heating rate of 10°C min^{-1}, using a Perkin–Elmer DSC 7 flushed with nitrogen. Our methods of thermal analysis have been discussed in detail elsewhere[11]. For TEM, flakes of blend, about 3 mm in diameter and 0.5 mm thick, were mounted between the thinnest possible cover slips and wrapped in metal foil. Samples were held in an oil bath at 140°C for 30 min. Some were then quenched directly into acetone at freezing point; other samples were held at 126°C or at 120°C for a further 4 days before quenching, so that any material rich in LPE could crystallize isothermally (the copolymers are unable to crystallize at these temperatures). The polymer was then cleaned, dried and used to produce surface replicas after permanganic etching[22–24]. We always take surface replicas because the surface experiences the most severe quench, and so is nearest in structure to the melt. We have previously shown that the morphology of the interior of these blends is similar to that of the surface[5]. Replicas were examined using either a Philips 301 TEM operating at 80 kV or a Philips 400T TEM operating at 100 kV. Details of all our

Figure 1 Transmission electron micrographs of replicas of blends of LPE (Sclair 2907) with copolymers made using the metallocene catalyst process. (a) A 75% blend of LPE/EB(6.3) after quenching from 160°C. The picture shows a typical banded spherulite. (The black spots, on this and other pictures, are etching debris.) (b) The exact copolymer EB(6.3) after quenching from 160°C. Very small crystals, showing no clear spherulitic arrangement, are typical of copolymers of this branch content quenched from above 130°C. The crystals are clearer in the magnified insert. (c) A 10% blend of LPE/EH(6.3) after quenching from 140°C. Groups of thick lamellae are particularly clear in the matrix of thinner lamellae. However, the actual size of the LPE rich (thick crystal) domains, is a little smaller than we typically find for blends of LPEs with conventional BPEs. (d) The 10% blend of LPE/EH(6.3) [as in (c)] after quenching from 180°C. Only one crystal type is visible. We believe that this indicates that although the melt was phase separated at 140°C it was mixed at 180°C—i.e. this system is upper critical. The crystals are much smaller than those obtained on quenching from the lower temperature. This is typical of LPE/BPE blends. We believe that it is because the material crystallizes at lower temperatures on quenching from higher temperatures. (e) A 1% blend of LPE/EB(5.9) after isothermal crystallization at 126°C (following complete melting at 150°C). The close grouping of the thick LPE rich crystals indicates that crystallization took place from a phase separated melt. (However, the morphology after crystallizing at 122°C indicates that the melt remixes at this lower temperature—the system is lower critical.) Note the small crystals in the quenched BPE rich phase, cf. (b). (f) A 25% blend of LPE/EB(6.3) after isothermal crystallization at 120°C (following complete melting at 150°C). These lamellae have not crystallized from phase separated droplets, but appear to have grown randomly. This indicates that they grew from a mixed melt[6]


75% LPE/EB(6.3) q.160°C
1μ
(a)
EB(6.3)q.160°C
1μ
(b)
10% LPE/EH(6.3) q.140°C
1μ
(c)
10% LPE/EH(6.3) q.180°C
1μ
(d)
1% LPE/EH(5.9) isothermal 126°C
1μ
(e)
25% LPE/EB(6.3) isothermal 120°C
1μ
(f)

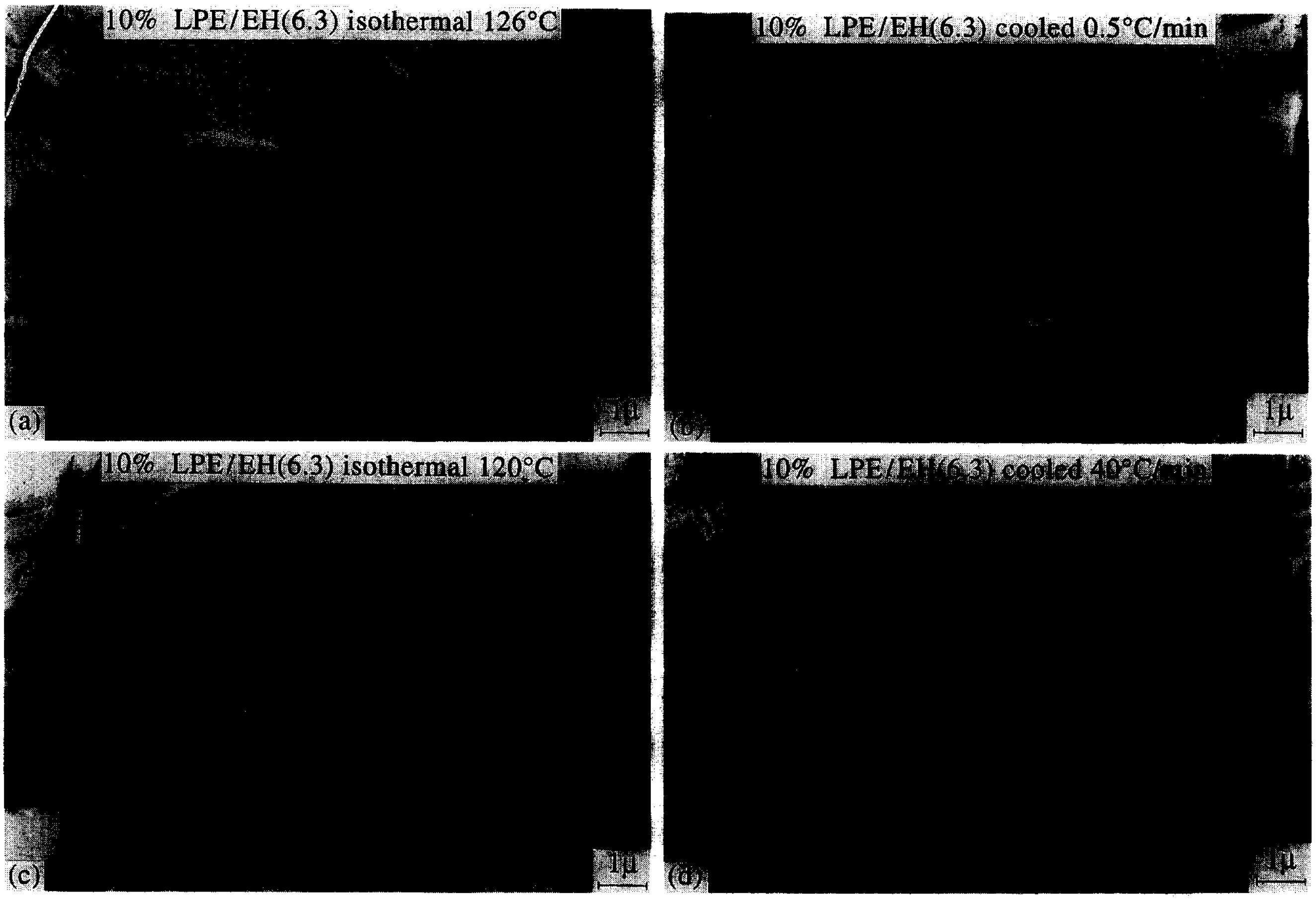


Figure 2 Transmission electron micrographs of replicas of 10% blends of the LPE Sclair 2907 with EH(6.3) [as are Fig. 1(c) and (d)]. All are printed to the same magnification; scale bars represent 1 μm. All pictures are of the same blend, 10% LPE/EH(6.3). (a) 10% LPE/EH(6.3) blend after isothermal crystallization 126°C. The LPE rich crystals are grouped, indicating crystallization from a separated melt. (b) 10% LPE/EH(6.3) blend after cooling at 0.5°C min^{-1} from 150°C. The morphology is like that seen in (a), but, overall in the specimen, the lamellae are a little less tightly grouped than those crystallized at 126°C. (c) 10% LPE/EH(6.3) blend after isothermal crystallization 120°C. The individual LPE rich crystals are scattered randomly, indicating crystallization from a mixed melt. (d) 10% LPE/EH(6.3) blend after cooling at 40°C min^{-1} from 150°C. The individual LPE rich crystals are much smaller than those in (d). They are scattered randomly, again indicating crystallization from a mixed melt. The LPE rich crystals are smaller than those in (c) because the temperature of crystallization was lower

standard experimental methods can be found in refs 1–6 and 11.

In order to obtain results comparable to those of other workers, we have, in addition, looked at blends after cooling from the melt both fast (40°C min^{-1}) and slowly (0.5°C min^{-1}). Samples prepared under these crystallization conditions were used to make surface replicas for examination in the TEM.

RESULTS

We experienced no problem in blending the copolymers made using metallocene catalysts with Sclair 2907. We found that the blends retained solvent to a greater extent than many of the blends that we have made previously. However, after holding the materials in a vacuum oven at room temperature for 2 days we were unable to detect any remaining solvent.

Transmission electron microscopy

Electron micrographs of quenched blends were particularly clear. *Figure 1* shows typical areas of replicas of quenched blends. We see only one crystal species (*Figure 1a*) if the LPE content is high. One crystal species is also seen on quenching the copolymers—the crystals are very small indeed for all three copolymers (*Figure 1b* shows one, the others are similar). On quenching blends, where the LPE content is low, from intermediate temperatures, we can clearly see two crystal species, groups of thicker crystals in a matrix of thinner crystals (*Figure 1c*). We have previously obtained similar micrographs on quenching blends of LPEs with copolymers made by other processes (see, for instance, refs 1–7 and 11–12, especially 2, 4, 6 and 7). Although the 10% blend gives two distinct crystal populations on quenching from 140°C (*Figure 1c*) only one crystal population is seen after quenching from temperatures above 170°C (*Figure 1d*). 126°C is above the maximum crystallization temperature for all three copolymers, but the LPE can crystallize isothermally. *Figure 1e* shows a group of LPE rich lamellae which have crystallized isothermally from a separated droplet of LPE rich melt in a 1% LPE/EB(5.9) blend. *Figure 1f* shows a 25% LPE/EB(6.3) blend after crystallization at 120°C; no clear segregation is visible—these LPE rich lamellae appear to have crystallized isothermally from a mixed melt. These morphologies are, again, typical of those found on isothermal crystallization of blends containing conventional copolymers[1–5].

A range of morphologies can be obtained by altering the cooling rates. The morphologies obtained on quenching 10% blends of LPE/EH(6.3) are shown in

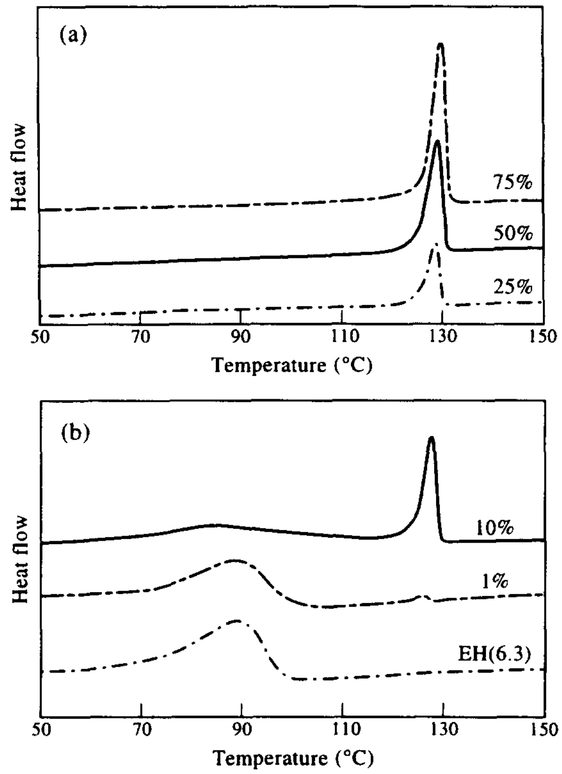


Figure 3 D.s.c. traces obtained on reheating quenched blends selected from LPE/EH(6.3) system. Note the clear higher peak in the trace from the 1% quenched blend. Note, also, that the 25% blend does show two melting peaks, but this is not very obvious unless the vertical scale is expanded. All traces obtained by heating at 10°C min^{-1} under nitrogen

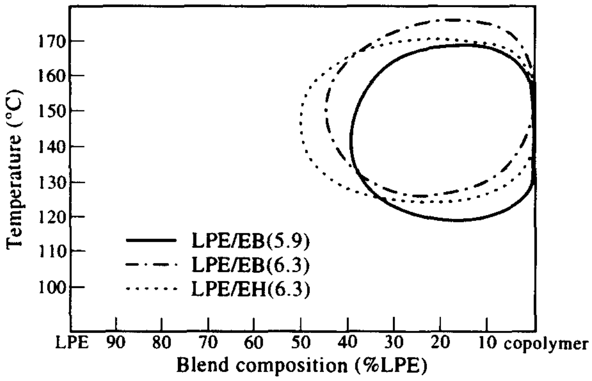


Figure 4 The phase behaviour, deduced by our indirect methods, for the three blend systems, LPE/EB(5.9), LPE/EB(6.3) and LPE/EH(6.3). All systems show a closed loop of phase separation. The remixing temperatures are rather higher than those usually found for systems where the copolymers are of greater polydispersity

Figure 1c (two crystal types on quenching from 140°C) and *Figure 1d* (one crystal type, on quenching from 180°C). *Figure 2* shows further morphologies obtained from this blend. On isothermal crystallization at 126°C (*Figure 2a*) the LPE rich lamellae are found in groups, indicating crystallization from a phase separated melt (cf. the 1% LPE/EB(5.9) blend of *Figure 1e*). A similar morphology is obtained on slow cooling (0.5°C min^{-1}), *Figure 2b*. However, on isothermal crystallization at 120°C the LPE rich lamellae are large and found individually, as shown in *Figure 2c*. On fairly rapid cooling (40°C min^{-1}) the lamellae are individual, not grouped (*Figure 2d*), but these lamellae are much smaller than those obtained on isothermal crystallization.

Thermal analysis

The d.s.c. results are also similar to those from blends of LPEs with copolymers synthesized by other methods. *Figure 3* shows some typical results. Where the LPE content is high, 75% and 50%, we see only one melting peak (again indicating one crystal species). Where the LPE content is low, 25%–1%, we can see two melting peaks (indicating two crystal species). All blends showing one d.s.c. melting peak after quenching from 150°C also show a single morphology in the TEM after quenching from 150°C. All blends showing two d.s.c. melting peaks after quenching from 150°C show two morphologies in the TEM. The TEM and d.s.c. results are in agreement.

Phase behaviour

The results, outlined above, indicate that for all three LPE/copolymer systems blends are always mixed at high LPE content (single morphology, single d.s.c. peak), but there are three temperature bands for low LPE content. On quenching from high temperatures (~180°C and above for the 10% blends) low LPE content blends show one lamella type; on quenching from medium temperatures (~170–125°C for 10% blends) the blends show two lamellar types and double d.s.c. peaks; and on quenching from the lowest temperatures obtainable, ~120°C and below, the blends show morphologies indicative of crystallization from mixed melts. We believe that these results indicate that the melts are mixed in the high temperature range, phase separated in the medium temperature range and, once again mixed in the low temperature range.

The complete morphology maps, or 'phase diagrams', for the three blend systems, as deduced by our indirect methods, are shown in *Figure 4*. It is immediately clear that they are all very similar to each other—and similar to 'phase diagrams' obtained for blends containing conventional copolymers of similar molecular weights and branch contents.

DISCUSSION

We first note that, as judged by our experimental techniques, the phase behaviour of melts of the LPE Sclair 2907 with each of the three metallocene copolymers studied is comparable with the phase behaviour of blends of Sclair 2907 (and other LPEs) with other copolymers of similar branch content. We would judge that there is asymmetric LLPS, at low LPE content, for all three systems. The difference between the behaviour of these and other systems is a second order one; the lowest temperatures at which any LLPS is seen are rather higher than those of many of the systems previously studied[1-6].

Secondly, we note that the phase behaviour of melts of the LPE Sclair 2907 with the EH metallocene copolymer is similar to that found in binary blends of LPEs with EB or EO copolymers[7,9,10,15,16]. This is the first EH copolymer that we have used. As we had expected[10,15,16], blends containing an EH material are no different from others with copolymers of different branch lengths.

The widths of the phase separated regions in all three 'phase diagrams' are similar and much as we would have expected from our previous work using copolymers polymerized by the older processes. The branch contents of the three materials used in this work are very similar, and we have shown that branch content is the most important parameter in determining the width of the LLPS region[7–10,15]. Unfortunately, the molecular weights of the two EB copolymers differ, as do the branch contents. As a result we cannot make any detailed deductions as to the effect of either molecular weight or branch content alone on the phase behaviour. However, we are rather surprised that the LLPS region in the LPE/EB(6.3) system is marginally wider than the LLPS region in the LPE/EB(5.9) system. EB(6.3) has both higher branch content and lower molecular weight than EB(5.9) (*Table 1*) so we would have expected any difference in width of the LLPS region to be the other way round. The differences between the highest temperatures for LLPS and between the lowest temperatures for LLPS for these two LPE/EB systems are more striking than the difference in width of the LLPS region. We believe that such detailed changes, as functions of molecular weight and molecular weight distribution, in systems containing well defined materials, will lead us to a fuller understanding of the details of phase behaviour. Note also that EH(6.3) is very similar to EB(6.3) both as regards branching and molecular weight (*Table 1*) but the LLPS loop is distinctly wider, in concentration, in the LPE/EH(6.3) system. This points to a further detailed change in phase behaviour, this time as a function of branch length.

The results obtained on isothermal crystallization and on cooling at different rates are similar for all three systems, as are the results obtained on quenching. From the morphologies observed after isothermal crystallization, we see that the lower remixing temperatures (T_R) are quite high for these blend systems. Mixed morphologies can be found for all blend compositions crystallized at 120°C in the LPE/EB(6.3) and LPE/EH(6.3) systems, this was not the case in most of the systems that we have studied previously[1–7]. When blends are slow cooled, from temperatures where they are phase separated, to some temperature below T_R, they will remix before crystallization if there is enough time to do so. From *Figure 2a* (isothermal crystallization at 126°C) we see that 126°C is still within the LLPS region for the 10% blend of the LPE/EH(6.3) system but *Figure 2c* (isothermal crystallization at 120°C) shows that 120°C is below T_R; thus, for the 10% blend, T_R lies between 126 and 120°C. The morphology of the 10% blend cooled at $0.5°C\,min^{-1}$ from 150°C (*Figure 2b*) indicates crystallization from a separated melt, but possibly not as well separated as the melt at 126°C. Crystallization took place before the sample remixed fully. D.s.c. results indicate that crystallization takes place at 123°C on cooling at $0.5°C\,min^{-1}$; thus T_R is probably in the range 125–124°C. However, *Figure 2d* shows that, on cooling from 150°C at $40°C\,min^{-1}$, the 10% blend of the LPE/EH(6.3) system did have time to remix before it crystallized. The small crystals in *Figure 2d* indicate that the crystallization took place well below 120°C. Even so, it is clear that the remixing must have taken place quite rapidly as the temperature dropped between T_R (125–124°C) and the crystallization temperature. D.s.c. indicates that the crystallization temperature for this blend, cooled at $40°C\,min^{-1}$, is 102°C.

Our methods, involving the examination of fast quenched blends in the solid state, show that blends containing metallocene catalyst copolymers behave no differently from blends containing materials polymerized in other ways. However, we must compare these results with those obtained by other workers. No one would deny the fact that two crystal types are seen in micrographs such as *Figure 1c*, or that two melting points are visible on some d.s.c. traces. However, there are two views as to the origin of these effects. We believe that these two crystal types reflect the existence of a phase separated melt before quenching. However, other workers[17,21] believe that blends of LPE with lightly branched copolymers made by metallocene catalysts are always mixed in the melt, and, if more than one crystal type is apparent after quenching, it is the result of separation on crystallization. It should be noted that those authors who claim that blends of LPE with lightly branched copolymers made by metallocene catalysts are always mixed in the melt, have not studied rapidly quenched blends. The phase diagrams shown in *Figure 4* indicate that the remixing temperatures (T_R) are high for these blends. Further, the morphologies obtained on cooling (rather than quenching), *Figures 2c* and *d*, show that either mixed or demixed morphologies can be obtained, depending on the cooling rate. The LPE/copolymer blends studied by other workers, after cooling (not quenching) from the melt, could well have crystallized from mixed melts, as did our $40°C\,min^{-1}$ sample. Thus, depending on cooling rates and T_R of the system used, there may be no conflict between our experimental results and those of other workers who have studied similar systems; it is probable that the only differences are of interpretation of the data.

Our ideas of LLPS are based on our considerable experimental background[1–16], and particularly on three observations. We have measured diffusion rates[6] and have shown that it is not possible for separation, on the spatial scale that we observe, to take place during the (very short) time of the quench[6]. Secondly, we have shown that the average size of the inclusions of the minority phase in blends increases with time in the melt. This Ostwald ripening in LPE/BPE blends[13] is very difficult to explain if the observed separation occurs only on crystallization. A further important observation is that those blends containing lightly branched copolymers that are found to contain two crystal types on quenching from lower temperatures (e.g. 140°C), show only one crystal type on quenching from higher temperatures (e.g. 180°C and above); as illustrated by *Figures 1c* and *d* of this paper and other examples in ref. 5. This is not the effect of degradation, because a double morphology is again obtained if the blend is reheated to 140°C and quenched following storage at the higher temperature[5,13].

The results of the present experiments, with blend systems including copolymers made by the metallocene catalyst process, are in agreement with our previous data from other systems (where the copolymers were made by other processes). It is quite possible that our results are also in agreement with those of other workers who have used similar systems, but cooled the blend melts at $40°C\,min^{-1}$ or less (we cannot be sure without knowing the remixing temperatures and cooling rates for their systems). In our view, it is still the case that the only explanation for all the morphological evidence taken together, is that, at some temperatures, there is liquid–liquid phase separation in melts of blends LPE with lightly branched copolymers where the LPE content of the blend is low.

CONCLUSION

Using indirect methods we have looked at binary blends of an LPE with each of three lightly branched copolymers made by using metallocene catalysts. We have found that

(a) Binary blend systems of an LPE with each of the three copolymers studied show the same phase behaviour as blends of the same LPE with copolymers of similar molecular weight and branching made by other processes.

(b) The EH copolymer (made by the metallocene catalyst process) behaves in a similar way to EB copolymers (made by a range of processes) and to EO copolymers (made by single site catalysis) in binary blends with an LPE.

(c) For the low copolymer content (5.9–6.3 mol%) copolymers (produced using metallocene catalysts) used here, the widths of the phase separated regions in all three 'phase diagrams' are very much as we would have expected from our work using copolymers made by other processes.

(d) Blends that have been cooled, rather than quenched, from separated melts can show morphologies indicative of crystallization from mixed melts. This indicates that these blends remix relatively fast when cooled below their lower critical temperatures.

ACKNOWLEDGEMENTS

We would like to thank Mr R. L. Morgan and Mrs Anna Halter for characterization of the materials for branch content (by *FT*i.r) and molecular weight (by g.p.c.) respectively. We would also like to thank BP Chemicals, DSM and Solvay for a grant to support this work.

REFERENCES

1. Barham, P. J., Hill, M. J., Keller, A. and Rosney, C. C. A., *J. Mats. Sci. Letters*, 1988, **7**, 1271.
2. Hill, M. J., Barham, P. J., Keller, A. and Rosney, C. C. A., *Polymer*, 1991, **32**, 1384.
3. Hill, M. J., Barham, P. J. and Keller, A., *Polymer*, 1992, **33**, 2530.
4. Hill, M. J., *Polymer*, 1991, **35**, 1994.
5. Hill, M. J. and Barham, P. J., *Polymer*, 1992, **33**, 4099.
6. Hill, M. J. and Barham, P. J., *Polymer*, 1992, **33**, 4891.
7. Hill, M. J., Barham, P. J. and van Ruiten, J., *Polymer*, 1993, **34**, 2975.
8. Barham, P. J., Hill, M. J., Goldbeck Wood, E. G. and van Ruiten, J., *Polymer*, 1993, **34**, 2981.
9. Thomas, D., Williamson, J., Hill, M. J. and Barham, P. J., *Polymer*, 1993, **34**, 4919.
10. Hill, M. J. and Barham, P. J., *Polymer*, 1994, **35**, 1802.
11. Hill, M. J., Organ, S. J. and Barham, P. J., *Thermochimica Acta*, 1994, **238**, 17.
12. Puig, C. C., Odell, J. A., Hill, M. J., Barham, P. J. and Folkes, M. J., *Polymer*, 1994, **35**, 2452.
13. Hill, M. J. and Barham, P. J., *Polymer*, 1995, **36**, 3369.
14. Schipp, C., Hill, M. J., Barham, P. J., Cloke, V., Higgins, J. S. and Oiarabal, L., *Polymer*, 1997, **37**, 2291.
15. Morgan, R., Hill, M. J., Barham, P. J. and Frye, C., *Polymer*, 1997, **38**, 1903.
16. Hill, M. J., Barham, P. J. and Morgan, R., *Polymer*, 1997, **38**, 3003.
17. Stein, R. S. and Zachmann, H. G., *PMSE Abstracts*, 1995, **209**, 48.
18. Alamo, R. G., Viers, B. D. and Mandelkern, L., *Macromolecules*, 1993, **26**, 5747.
19. Alamo, R. G. and Mandelkern, L., *Thermochimica Acta*, 1994, **238**, 155.
20. Lu, L., Alamo, R. G. and Mandelkern, L., *Macromolecules*, 1994, **27**, 6571.
21. Galante, M. J., Alamo, R. G. and Mandelkern, L., *Polymer Preprints*, 1995, **209**, 272.
22. Olley, R,. Hodge, A. M. and Bassett, D. C., *J. Polym. Sci., Polym. Phys.*, 1979, **17**, 627.
23. Bassett, D. C. and Hodge, A. M., *Proc. Roy. Soc. A*, 1978, **359**, 121.
24. Patrick, M., Bennett, V. and Hill, M. J., *Polymer*, 1996, **37**, 5335.