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Minimum branch content for detection of liquid–liquid phase separation, using indirect techniques, in blends of polyethylene with ethylene–octene and ethylene–butene copolymers

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The limits of detection of phase separation in linear/branched polyethylene systems have been investigated, using the very sensitive but indirect experimental methods developed at the University of Bristol. A linear polyethylene has been blended with a number of very lightly branched ethylene–octene and ethylene–butene copolymers (containing between 0.7 and 3.1 mol% of copolymer). Samples of blends and of mixtures of the components were examined by differential scanning calorimetry (d.s.c.) and by transmission electron microscopy (TEM). Results indicate that TEM is more sensitive than d.s.c. in detecting phase separation in quenched linear/lightly branched copolymer systems. TEM can detect phase separation in blends when the blended copolymer contains just below 1 mol% of either butene or octene comonomer. D.s.c. requires a higher comonomer content, just over 1.5 mol% of octene and somewhere between 1.3 and 3 mol% of butene comonomer. For both techniques, phase separation can be detected at similar levels of branching for blends containing linear polyethylene with ethylene/octene comonomer and for blends containing linear polyethylene with ethylene/butene comonomer. © 1997 Elsevier Science Ltd.

(Keywords: polyethylene blends; phase separation; limit of detection)

INTRODUCTION

The phase behaviour of blends of linear (LPE) with branched polyethylenes has attracted a good deal of attention recently[1–24]. A few studies have used neutron-scattering techniques to attempt to delineate the conditions under which phase separation in the melt will occur[16–21,23]. In general these studies indicate that phase separation only occurs when the copolymer is highly branched, typically with more than 60 branches per 1000 backbone carbon atoms. However, experiments using indirect techniques to examine rapidly quenched blend samples have suggested that phase separation, probably of a different type, can occur in blends where there is a much lower branch content in the copolymer—down to less than 10 branches per 1000 backbone carbon atoms[2–7,10,22,24].

We have developed a range of indirect techniques[6,11] and used them to show that in many blend systems, where the copolymer is lightly branched, there is a similar pattern of behaviour. All systems, when the molecular weight of the LPE is above 2500[2,3] (over 60 such systems have been studied), show an asymmetric region of phase separation in rapidly quenched samples. Only those blends rich in the branched component display phase separation. In each case the phase-separated region forms a closed loop, i.e. systems show both upper and lower critical behaviour. The phase behaviour, revealed by these indirect methods, is rather insensitive to the molecular weight of the linear component[2,3] and does not appear to depend strongly on the branch type[10,24]. The number of branch points along the copolymer chains is the most important factor influencing the extent of the liquid–liquid phase separation (LLPS)[6,9,10,24].

There must be a minimum level of branching for which this phase separation can be detected. Where there is separation of the blend melt, it will be into two components. The components will not be the pure materials which were blended, but intermediate blends, with closer melting points than those of the pure materials. The crystals obtained on quenching the two components (into which the blend separated in the melt) will become more and more similar as the level of branching reduces. The similarity will increase both as regards physical appearance (e.g. crystal thickness) and as regards melting point. Eventually, even if there is separation in reality, it will be into two components which, on crystallization, are so similar that they cannot be differentiated by our experimental techniques. We are interested to know the minimum level of branching for which our indirect methods, d.s.c. and transmission electron microscopy (TEM), can detect LLPS.

As regards d.s.c., the minimum level of detection will be when the melting peaks from the two quenched phase-separated blend components can just be distinguished.

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As regards TEM, the minimum level of detection will be when the two crystal populations can just be distinguished visually (probably by crystal thickness, but possibly by some other characteristic, e.g. spherulite banding). The two experimental tests (d.s.c. and TEM) may not have the same sensitivity.

We have already shown that LLPS can be detected in LPE/(near-random ethylene–octene (EO) copolymer) systems when the level of branching is as low as 2 mol% (10 branches/1000 backbone carbon atoms)[6]. We now have temperature-rising elution fractionation (TREF) fractions from an EO linear low-density polyethylene (LLDPE), with octene comonomer contents of 0.7, 1.5 and 2.0 mol%, and we use these to confirm the previous result and to see if LLPS can be detected where the octene content is below 2 mol%.

In the past we have not had access to any well-characterized, near-random copolymers other than EOs. However, from our work on blends of LPEs and EO copolymers with lightly branched (2 and 3 mol% overall) ethylene–butene (EB) LLDPEs we inferred that phase separation can still be detected when the butene content is as low as 2 mol%[10]. Recently, we have been fortunate to acquire lightly branched EB copolymers from two separate sources, and we have worked with these materials.

EXPERIMENTAL

Polymers

The linear polyethylene used throughout this work was Sclair 2907 from Dupont, Canada.

A group of three commercially available EB copolymers of low EB content were used, both as supplied and after fractionation by molecular weight. Details of this fractionation process are given by Hill and Barham[25], and details of the polymers and fractions used in the present work are given in *Table 1*. It was found that the narrower molecular weight fractions of these materials also had narrower branch distributions. To provide further materials, an EB LLDPE of overall butene comonomer content 3.6 mol% was fractionated, by preparative TREF, into nine narrow fractions at BP Chemicals, Grangemouth. The copolymers were characterized by gel permeation chromatography (g.p.c.) for molecular weight, and by *FT*i.r. for branch content; details of the former process are given by Hill and Barham[25] and of the latter by Morgan *et al.*[24].

Table 1 Polymers used in study

Polymer	M_w	M_w/M_n	Branch content (mol%)
LPE, Dupont Sclair 2907	10^5	3.5	0
TREF fractions of EO(3.1)			
EOF(0.7)	4×10^4	4	0.7
EOF(1.5)	4×10^4	4	1.5
EOF(2.0)	4×10^4	4	2.0
Commercial EB copolymers			
EB(0.1)	13×10^4	5	0.1
EB(0.5)	16×10^4	3.5	0.5
EB(0.9)	14×10^4	3.5	0.9
Fractions of EB(0.9) by *MW*			
EBF(0.5)	15×10^4	2	0.5
EBF(1.0)	1×10^4	2	1.0
TREF fractions of EB(3.6)			
EBF(1.3)	11×10^4	2	1.3
EBF(3.1)	10×10^4	3	3.1
EBF(4.4)	10×10^4	3	4.4

In our experiments we used three whole commercial EB copolymers (EB(0.1), EB(0.5) and EB(0.9)); two fractions from one of these EB copolymers (EBF(0.5) and EBF(1.0)); and three TREF fractions from EB(3.6), the 3.6 mol% LLDPE (EBF(1.3), EBF(3.1) and EBF(4.4)). Note that F indicates fraction, and the figures in parentheses indicate the comonomer content of the material in mol per cent. For example, EBF(3.1) is a fraction of an EB copolymer; this fraction was assessed by *FT*i.r., and contains 3.1 mol% of butene comonomer.

The EO copolymers were TREF fractions of a commercial EO LLDPE of overall octene comonomer content 3.1 mol%, EO(3.1). The whole polymer has been the focus of considerable research in the past[10]. TREF was performed at BP Chemicals, Grangemouth. The process was similar to that carried out for the EB LLDPE[24].

Blends, and methods of examination

All blends were made in solution, with xylene as the solvent. The blending method has been described elsewhere[1–3]. 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, others were held at 126°C for a further 4 days before quenching, so that any material rich in LPE could crystallize isothermally. The polymer was cleaned and dried and used to produce surface replicas, after permanganic etching[26–28]. We always take surface replicas because the surface experiences the fastest quench, and so is nearest in structure to the melt. Replicas were examined using a Philips 301 transmission electron microscope operating at 80 kV. Details of all our standard experimental methods can be found in the literature[1–5,11].

Choice of blends and mixtures for examination

We examined blends containing 10% LPE with 90% copolymer (termed 10% blends) of each LPE/copolymer pair. We know, from experience, that where phase separation can be detected it will be clearly seen in the 10% blend quenched from 140°C. We also studied the behaviour of some mixtures in the differential scanning calorimeter to see when we could distinguish the individual melting peaks of the two components. We first examined, by d.s.c., mixtures of the LPE with each copolymer, and of each 50% blend with the appropriate copolymer. We know that a blend does not phase separate into the two initial constituents, but into two phases, one rich in LPE and one poor in LPE. The LPE-rich phase usually contains between 60 and 30% LPE, and, where the copolymer has low branching (as for all blend systems examined here) the LLPS loop is wide[6].

Following this line of thought we chose to look at 50/50 mixtures of 50% blends with the copolymer. The two components of each mixture were held separately in the d.s.c. pan so that they were unable to mix during the melting and quenching process.

In summary, we have examined blends and mixtures of LPE with eight EB copolymers and three EO copolymers. For each system we have looked at five sample types, three by d.s.c. and two by TEM. Three types of sample were tested by d.s.c.—50/50 mixtures of LPE with copolymer, 50/50 mixtures of 50% blends with copolymer and 10% blends. Each blend or mixture was melted for 30 min at 150°C and then quenched into acetone at freezing point.

TEM tests were performed on surface replicas of 10% blends quenched from 140°C and on 10% blends isothermally crystallized at 126°C and then quenched.

RESULTS

D.s.c.

We are, or course, aware that double melting peaks can sometimes be seen where there is reorganization (annealing) during heating in the DSC[29–31]. We performed a series of experiments at varying heating rates to check whether such an explanation could be applied to the blend samples studied in this work. We are confident that whenever we report two melting endotherms here, they come from two distinct crystal populations and are not an artefact caused by internal rearrangements during heating.

In the 50/50 mixtures of the LPE with the copolymers we were able to resolve two melting endotherms on heating at 10°C min^{-1} in all cases except the mixture of LPE with the EB(0.1) copolymer. The melting temperatures of the LPE and the EB(0.1) are identical, within experimental error, so the failure to resolve two peaks in a 50/50 mixture is no surprise. We further found, not surprisingly, that all blends of these two materials showed a single melting endotherm at the same temperature. The results of all these experiments are summarized in *Table 2*.

The mixtures of 50% blends with the copolymers showed further systems where it was not possible to resolve two separate melting peaks on heating at 10°C^{-1}. This is illustrated by the series of d.s.c. traces in *Figure 1a*, showing the melting behaviour of mixtures of 50% PE/EO blends with the EO copolymers. In this figure it is apparent that there are two distinct melting peaks for the mixtures of 50% blends with the EOF(1.5) and EOF(2.0) copolymers while only a single peak is resolved in the mixture of 50% blends with the EOF(0.7). Full details of the systems in which we were able to resolve two peaks are given in *Table 2*.

Figures 1b and *1c* compare the melting behaviour of all specimen types (mixtures of LPE with the copolymer, mixtures of 50% blends with the copolymer and 10% blends) for two EB fraction systems. In *Figure 1b*, for the EBF(3.1) copolymer system, two peaks can readily be resolved in each of the mixtures, and the blend shows a very broad peak that clearly arises from the superposition of two separate peaks. In *Figure 1c*, for the EBF(1.0) copolymer, two peaks are clearly visible in the LPE/copolymer mixture, while in the 50% blend/copolymer system the peaks are barely resolved, and the blend shows a single melting peak.

The results shown in *Figure 1b* show that a 10% LPE/EBF(3.1) blend is phase separated prior to quenching from 150°C. On the other hand the data in *Figure 1c* are ambiguous. There are two possibilities. The 10% LPE/EBF(1.0) blend shows a single melting peak; this may be due to the blend being mixed, or it may be that it is separated into two components whose melting behaviour is too similar to distinguish (as is very nearly the case for the mixture of the 50% blend with the copolymer).

Overall, as the full results shown in *Table 2* indicate, we found that it became increasingly difficult to resolve two melting peaks in the blends as the comonomer content of the copolymer decreased. This places a practical limit on the level at which we can detect phase separation using our d.s.c. techniques. This limit is, for EB copolymers, between 3.1 and 1.0 mol% of butene content in the copolymer, and for the EO copolymers it is at about 1.5 mol% of octene content in the copolymer.

TEM

Results from quenched and isothermally crystallized materials were in agreement: where LLPS could be detected for one it could also be detected for the other.

Table 2 Experimental results

	D.s.c.			TEM 10% blend			
	Mixtures		Blends	Quenched	Isothermal	Separation	
	LPE/BPE	50%/BPE	10%	140°C	126°C	D.s.c.	TEM
EOF(0.7)	2 peaks	1 peak	1 peak	2 crystals?	2 crystals	No	?
EOF(1.5)	2 peaks	2 peaks	1 peak, + shoulder?	2 crystals	2 crystals	?	Yes
EOF(2.0)	2 peaks	2 peaks	2 peaks (overlap)	2 crystals	2 crystals	Yes	Yes
EB(0.1)	1 peak	1 peak	1 peak	1 crystal	1 crystal	No	No
EB(0.5)	2 peaks	1 peak	1 peak	1 crystal	1 crystal	No	No
EB(0.9)	2 peaks	2 peaks	1 peak	2 crystals	2 crystals	No	Yes
EBF(0.5)	2 peaks	1 peak	1 peak	1 crystal	1 crystal	No	No
EBF(1.0)	2 peaks	1 peak, + shoulder	1 peak	2 crystals	2 crystals	No	Yes
EBF(1.3)	2 peaks	2 peaks	1 peak	2 crystals	2 crystals	No	Yes
EBF(3.1)	2 peaks	2 peaks	2 peaks	2 crystals	2 crystals	Yes	Yes
EBF(4.4)	2 peaks	2 peaks	2 peaks	2 crystals	2 crystals	Yes	Yes

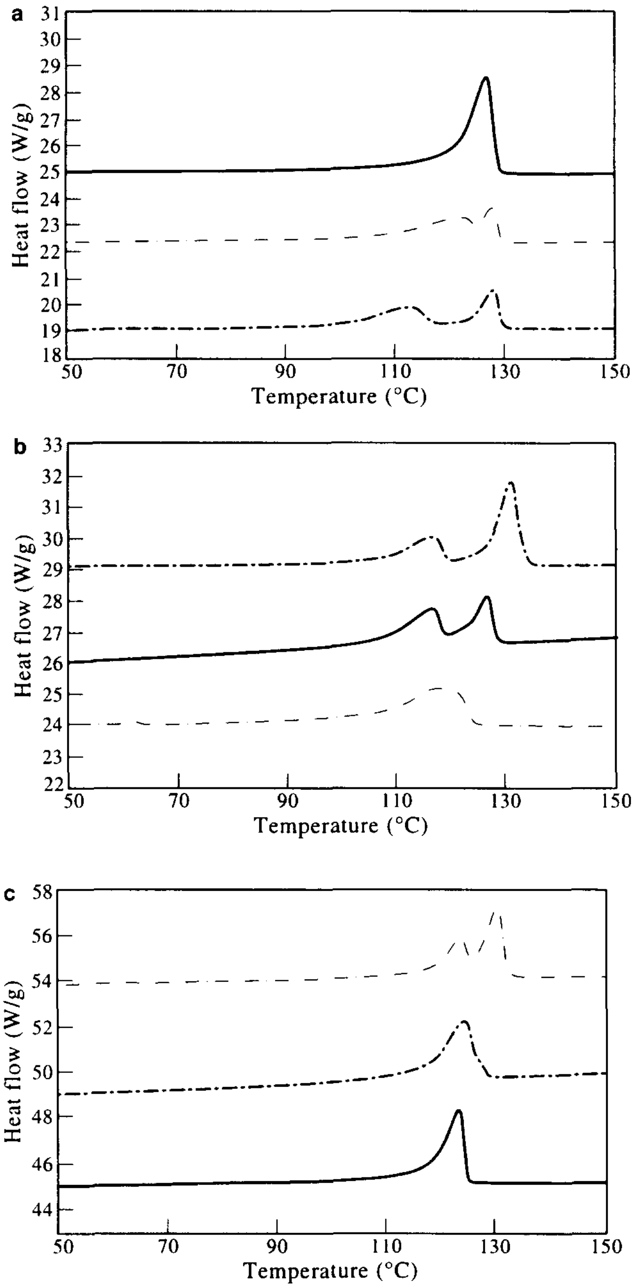

Figure 1 D.s.c. melting thermograms for various mixtures and blends after quenching from 150°C. All the thermograms were recorded at a heating rate of 10°C min^{-1}. The calorimeter was flushed with nitrogen. (a) 50/50 mixtures of LPE with EO copolymers. The top trace is from LPE mixed with EOF(0.7); the middle trace from LPE mixed with EOF(1.5); and the bottom trace is from LPE mixed with EOF(2.0). Two peaks can be resolved in the bottom two traces; if there are two peaks in the top trace they cannot be resolved. (b) Mixtures and blends of LPE with EBF(3.1). The top trace is from a 50/50 mixture of the two polymers; the middle trace is from a 50/50 mixture of a 50% blend with EBF(3.1); and the bottom trace from the quenched 10% blend. Two melting peaks are clearly resolvable in the top two traces. In the bottom trace two peaks cannot be separated, but the wide, flat melting peak looks like the superposition of two overlapping and roughly equal peaks. (c) Mixtures and blends of LPE with EBF(1.0). The top trace is from a 50/50 mixture of the two polymers; the middle trace is from a 50/50 mixture of a 50% blend with EBF(1.0); and the bottom trace from the quenched 10% blend. Two melting peaks are clearly resolvable in the top trace, just clearly resolvable in the middle trace. In the bottom trace only one peak is visible

(However, phase separation can be seen much more easily when the LPE-rich part of blend has been crystallized isothermally, because there is much more difference between LPE-rich polymer crystallized at 126°C and BPE-rich polymer crystallized on quenching than between the two materials when both have been quenched.) Again blends showed two distinct morphologies where the branching was heavier, but only one morphology where the branching was very light. The results are set out in *Table 2*, and examples of morphologies are shown in *Figure 2*.

Figure 2a illustrates a morphology typical of a blend crystallized isothermally from a mixed melt. In this micrograph, of a LPE/EBF(0.7) blend crystallized at 126°C, a region where three spherulites join can be seen. (The dark regions at the top and bottom, where no detail can be resolved, are caused by detached polymer blocking out the electron beam. In the spherulite at the bottom right, the lamellae are seen flat on, rather than edge on as in the other two spherulites.) In all three spherulites the large, dominant lamellar crystals can be seen to have the same thickness, and the three spherulites impinge on each other. We believe that these observations indicate crystallization took place from a mixed melt; if the melt had been separated we would expect to find regions of thinner (copolymer-rich) lamellae in between spherulites. However, where the lamellae are viewed edge on, we do see a few thin crystals between the thick lamellae within the spherulites. We believe that these crystallized on quenching and are made up of branched or possibly low molecular weight material which was separated, from within the homogeneous melt, on crystallization of the LPE-rich material.

Figure 2b illustrates a typical morphology of a blend crystallized isothermally from a phase-separated melt. In this case, a LPE/EBF(3.1) blend crystallized at 126°C, two distinct regions with different morphologies can be seen. In the lower-right diagonal half is a spherulite made up from thick lamellae that have crystallized isothermally at 126°C; these are seen in various orientations. At the top left of the figure much thinner lamellae are visible; these crystallized on quenching. The thin lamellae are formed from a region of the melt that contained so much branch rich material that it could not crystallize at a temperature as high as 126°C. We argue that this is strong evidence for phase separation, in the melt, into domains with sizes of several micrometres. In this micrograph thin lamellae can, again, be observed in between the thick lamellae of the spherulite that grew at 126°C. These thin lamellae grew, we believe, on quenching and were formed from a copolymer-rich melt segregated by crystallization within the LPE-rich domain as the spherulite grew. Thus we see segregation that can be assigned to crystallization effects on an interlamellar scale (as in *Figure 2a*) as well as much larger scale separation which, we believe, was present in the melt. (Both types of copolymer-rich, quenched material have the same melting point. This means that it is not possible to use d.s.c. to distinguish between the morphology of *Figure 2a*, believed to be the result of isothermal crystallization from a mixed melt, and that of *Figure 2b*, believed to be the result of isothermal crystallization from a separated melt. Both morphologies show two well-separated d.s.c. peaks on remelting, one from melting the isothermally crystallized LPE-rich material and one from melting the quenched copolymer-rich material.)

Figures 2c and *2d* illustrate mixed and separated morphologies in quenched blends. *Figure 2c*, the micro-

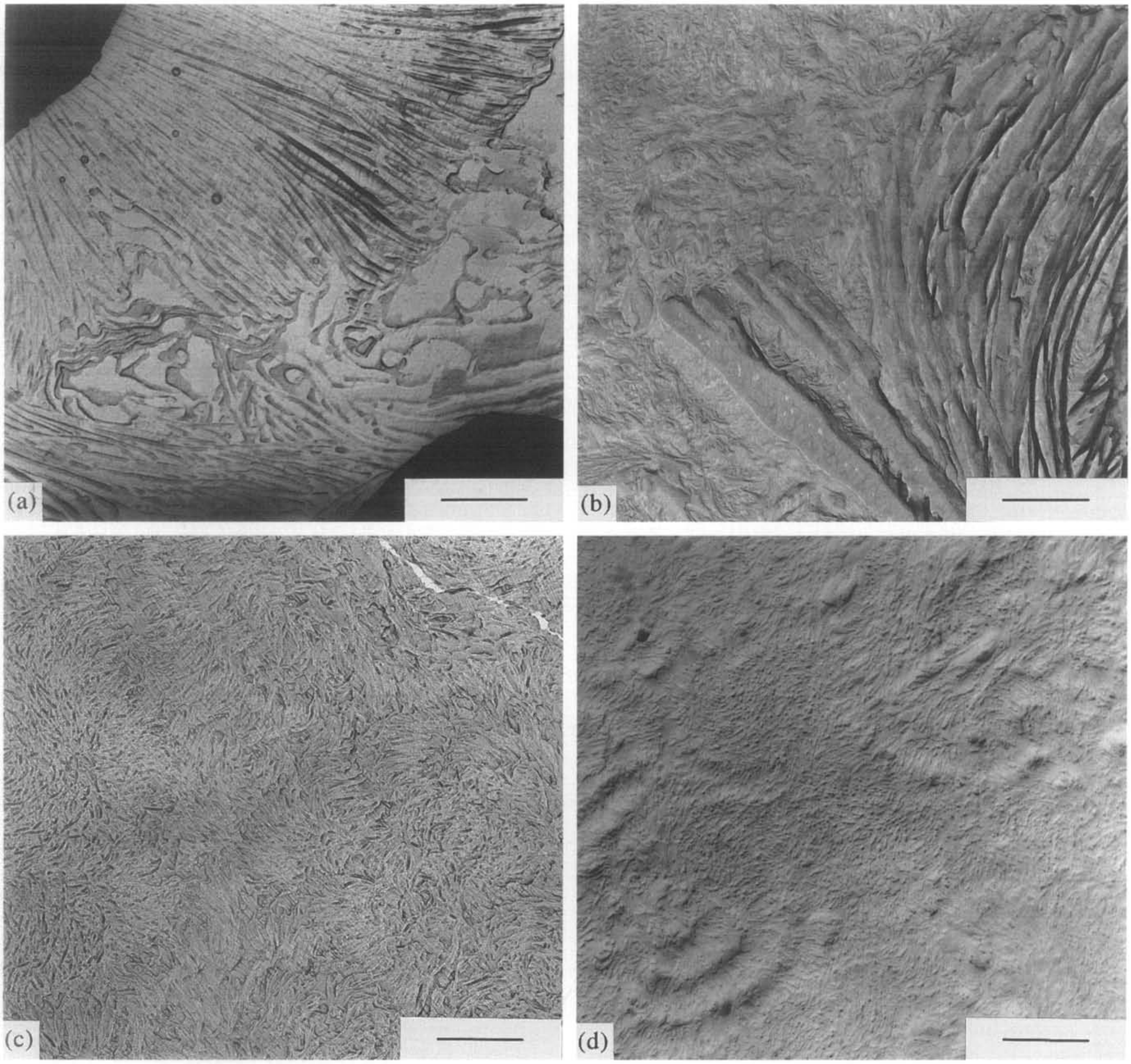

Figure 2 Electron micrographs of replicas of 10% blend samples. The scale bar represents 1 μm for all the micrographs. (a) A 10% LPE/EBF(0.7) blend crystallized isothermally at 126°C, showing a uniform morphology, indicating crystallization from a mixed melt. (b) A 10% LPE/EBF(3.1) blend crystallized isothermally at 126°C, showing two distinct morphologies, indicating crystallization from a phase-separated blend. (c) A 10% LPE/EBF(0.7) blend crystallized by rapid quenching from 140°C, showing a uniform morphology, indicating crystallization from a mixed melt. (d) A 10% LPE/EBF(1.3) blend crystallized by rapid quenching from 140°C, showing two distinct morphologies, indicating crystallization from a phase separated blend

graph of a LPE/EBF(0.7) blend that has been quenched from 140°C, shows a region where four spherulites impinge. The lamellae in all the spherulites look the same and all have the same thickness. In contrast, the morphology of the LPE/EBF(1.3) blend quenched from 140°C shown in *Figure 2d* reveals two distinctly different morphologies. There are regions, towards the top right and the bottom left, of the micrograph, where thicker lamellae are arranged in banded spherulites. The lamellae elsewhere in the micrograph are significantly thinner (and thinner than those in *Figure 2c*, as we would expect, because they have formed from a melt containing a more highly branched polymer).

For the LPE/EB blends, LLPS can be detected for EB(0.9), 0.9 mol%, and EBF(1.3), 1.3 mol%, and for blends containing more heavily branched EB copolymers. Thus we see that the minimum branching for detection of phase separation by TEM is just below 1 mol%. For the LPE/EO blends, phase separation is present and can be detected for a branch content of 1.5 mol%, and there are indications of it for a branch content of 0.7 mol%, i.e. again the minimum branching for detection of LLPS by TEM is just below 1 mol%.

Summary of results

The present results are summarized in *Table 3* with details given in *Table 2*; note, especially, the comparison between the results of the two techniques for quenched 10% blends (d.s.c. results in *Table 2*, column 4, and TEM

Table 3 Detection of LLPS by d.s.c. and by TEM

Comonomer	Minimum branching for detection by d.s.c.	Minimum branching for detection by TEM
Butene	Between 1.3 and 3 mol%	Just less than 1 mol%
Octene	Just over 1.5 mol%	Just less than 1 mol%

results in *Table 2*, column 5). We can see that for both branch types, TEM is a more sensitive technique than d.s.c. for detecting LLPS, and that the level of detection is similar for the two branch types, within the experimental errors imposed by the range of branch densities available. (We found TEM more sensitive than d.s.c. in detecting phase separation in a system reported in another recent study of LPE/EB blends[24].) The results for blends containing the whole EB copolymers agree with those for blends containing sharper fractions of one of these materials.

The results for LPE/EO copolymer blends are in agreement with the previous work, where EO copolymers of different molecular weights were used[6]. Phase separation was then observed by both TEM and d.s.c. for blends of LPE with both 2 mol% of EO copolymer and 3 mol% of EO copolymer; no materials of lower branch content were available at that time.

DISCUSSION

We will speculate, briefly, on the range of branch content for which LLPS can be expected. It is well known that LPE/BPE polymers are quite immiscible where the branch contents are high[14–17]. Polypropylene may be considered as an extremely branched polyethylene (one branch on every other backbone carbon), and many authors agree that polyethylene and polypropylene do not mix in the melt[12,13,32–37]. Thus, there is no doubt that LLPS can be found in LPE/BPE blends when the branching is high, but the lower limit for phase separation is yet to be established.

Assuming that our interpretation of the experimental data is correct, we have found the limit of branching, below which we cannot detect any evidence for phase separation for blends in the melt, to be about 1 mol% of branch content. However, we cannot be sure that no phase separation occurs at lower branch levels. We have used two techniques, TEM and d.s.c., and have shown that the limits of detection of the two are different. Thus, for d.s.c. at least, the fact that we are unable to detect phase separation is simply a reflection of the sensitivity of the technique employed.

As the branch content approaches zero, we could consider a blend of two LPEs with differing molecular weight distributions. Mumby and van Ruiten[38] have argued that the phase separation observed in one of the systems we have examined may arise from the breadth of the molecular weight distribution. However, in our experimental studies we have found the molecular weights to have little effect on the phase behaviour of LPE/BPE blends[2,3]. It is the branch content that appears to be the most important parameter in determining the amount of phase separation that is found[6,9,10,24]. Accordingly, we should assume that a blend of two LPEs would be fully miscible—and, indeed, we have been unable to see any morphological signs of phase separations[25] in blends of LPEs with molecular weights as different as 2×10^6 and 2.5×10^3. This implies that there must be some limit of branching below which phase separation no longer occurs. We have no way of estimating what this lower limit of branching for phase separation to occur should be. All we can say is that we can still detect phase separation in LPE/EB and LPE/EO systems where the copolymer contains just less than 1 mol% of copolymer (only 4 branches/1000 backbone carbon atoms), and we suspect that LLPS still takes place where the level of branching is lower.

There has been some argument in the literature as to the cause of the phase separation we observe. Some authors have suggested that the phase separation occurs on crystallization and does not reflect the state of the melt prior to quenching[18]. We have addressed this argument in detail elsewhere[4,22,23], where we show, for instance, that Ostwald ripening occurs in the separated phases[22] and respond[23] to the detailed arguments of Alamo *et al.*[18]. Although we are confident that our interpretation is correct, whatever the precise origin of the phase separation, we have in this work determined the limits of comonomer content for which it can be detected.

CONCLUSIONS

- TEM is more sensitive than d.s.c. in detecting phase separation in quenched LPE/lightly branched copolymer systems.
- TEM can detect LLPS when the blended copolymer contains just below 1 mol% of either butene or octene comonomer.
- D.s.c. requires a higher comonomer content than TEM for the detection of LLPS. D.s.c. requires just over 1.5 mol% of octene and somewhere between 1.3 and 3 mol% of butene comonomer.
- Using a given technique, LLPS can be detected at similar levels of branching for blends containing LPE with EO comonomer and for blends containing LPE with EB comonomer.
- As far as we can judge, from the limited selection of EB materials at our disposal, molecular weight distribution has little effect on detection of LLPS.
- It is remarkable that melt phase separation can be detected at such low branch contents. The most sensitive TEM test we have recorded (EO copolymer blends) has detected LLPS in a 10% blend where the copolymer contains only 4 branches/1000 backbone carbon atoms. The most sensitive d.s.c. test we have recorded (again EO copolymer blends) has detected LLPS in a 10% blend where the copolymer contained 8 branches/1000 backbone carbon atoms.

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