Interpretation of phase behaviour of blends containing linear low-density polyethylenes using a ternary phase diagram*

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When a linear polyethylene is blended with two homogeneous copolymers, of different comonomer content, the resulting ternary phase diagram shows three distinct regions of liquid–liquid phase separation. It is argued that we may usefully employ a ternary phase diagram to understand the degree of melt demixing occurring in some commercial polymers, such as linear low-density polyethylenes (LLDPEs), which are blends in themselves. Results obtained on blending LLDPEs with linear or randomly branched polyethylenes are presented, and it is shown that the observed phase behaviour may be interpreted as cloud point curves arising from sections through phase diagrams of ternary blend systems. The ternary phase diagram used in this work was originally determined experimentally for octene copolymers, but it is now shown to be equally applicable to butene copolymers.

(Keywords: polyethylene blends; phase separation; ternary phase diagrams)

INTRODUCTION

We have shown, in an extensive series of experiments using linear polyethylenes (LPE) and branched polyethylenes (BPE)[1–6], that liquid–liquid phase separation (*LLPS*) often occurs in melts of blends of LPE with BPE. In all but two of the binary blends (some 25 systems) that we have studied, we have found a region of phase separation asymmetrically placed at the low-linear-content side of the phase diagram; this phase-separated region appears to be of a closed loop nature. (The exceptions were: (a) when the molecular weight of the LPE was extremely low, in which case we found no *LLPS*[3]; and (b) when the BPE was extremely branched, in which case we found extensive *LLPS* that was symmetric[6].) A schematic phase diagram showing typical behaviour is sketched in *Figure 1*. Similar behaviour has been observed in other systems of blends of a linear homopolymer with a branched copolymer, in polypropylenes[7] and in polyesters[8]. Nesarikar *et al.* have recently shown that *LLPS* of a different type, showing symmetrical *LLPS* with upper critical behaviour, can occur within a commercial copolymer[9,10].

Most of the materials used in these studies were commercial polymers that are not homogeneous either in their molecular weights or in their branch content. Consequently, detailed modelling of the phase behaviour was not possible. However, recently an attempt has been made to model the behaviour of one of the systems that we have studied experimentally[11]. This work has taken note of the molecular weight distribution of each of the components. We have recently been able to study experimentally a series of specially polymerized ethylene/octene copolymers[6]. We found, to our surprise, that the width of the phase-separated region decreased as the octene content of the BPE was increased. This counter-intuitive observation, that more dissimilar polymers can be more compatible, led us to devise a simple scheme to aid the interpretation of our data[12]. In this scheme we ignore the distribution of molecular weight and branch content of the components and assume that they are basically compatible with very small free energies of mixing. However, we postulated that there is a further small, asymmetric, free energy of mixing for very low additions of linear to branched polymer. Such a scheme is able to describe phase behaviour of the type we have observed.

It has been suggested[13] that phase separation can lead to morphologies that may impart advantageous properties to the polymer. In particular it has been noted that certain very-low-density polyethylenes[14,15] and linear low-density polyethylenes (LLDPEs)[3] show thermal behaviour and internal morphologies which suggest that they may have undergone phase separation in the melt prior to crystallization; some of these polymers have been fractionated into components of varying branch content[16,17].

Rhee and Crist have investigated the effect of morphology on fracture toughness in a series of polyethylenes[18]. They noted that there can be extensive *LLPS* in systems that have high comonomer content (much higher than those used in our studies), and that this *LLPS* does not lead to any enhanced fracture toughness. In those polymers with similar branch content to the materials we have used, Crist often found that there was enhanced fracture toughness; however, in the

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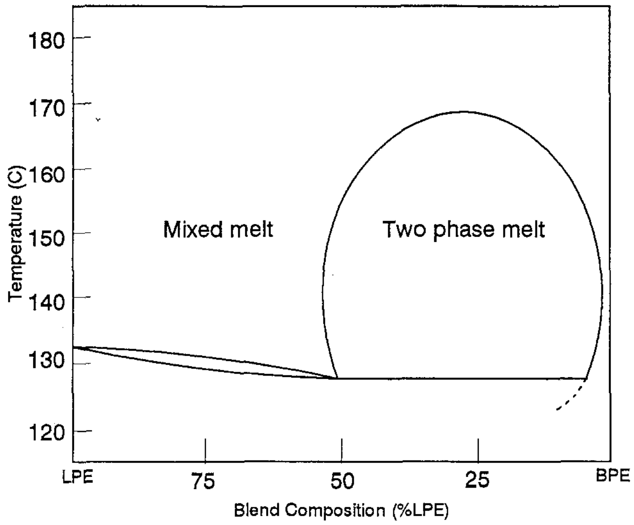

Figure 1 Sketch of the form of a typical 'phase diagram' for a binary blend of LPE with BPE

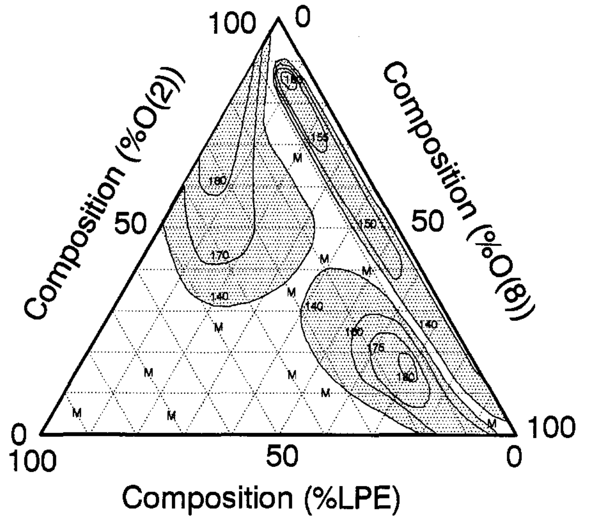

Figure 2 Sketch of the 'ternary phase diagram' for blends of LPE with two octene copolymers containing 2 and 8 mol% octene[6]. The contours show the extent of *LLPS* at the temperatures indicated

light of their calculations of the χ parameter, deduced from studies on the highly branched polymers, they did not expect any *LLPS*.

To begin to understand the phase behaviour of 'real' polymers, such as LLDPEs, we decided to blend three 'model' polyethylenes together to mimic the range of branch contents that may be found in commercial materials. The resulting ternary phase diagram was published recently[19] and is reproduced here as *Figure 2*. The notable features of this phase diagram are the three regions of *LLPS*, two large regions coming from the LPE–copolymer sides of the phase diagram and a long finger-like region extending just inside the copolymer–copolymer side of the diagram.

In our previous paper[19] we used the simple scheme originally derived for binary blends[12] to interpret this ternary phase diagram. Briefly, the free-energy curves of the binary case have to be generalized to become free-energy surfaces in the ternary case. The additional small free-energy term, which in the binary case is added to an otherwise negative and symmetric free-energy curve, now becomes a trough or ridge that runs parallel to the copolymer–copolymer side of the ternary free-energy surface, and is added to an otherwise smooth and negative surface. Such a logical extension of the binary model to a ternary system is able to predict, directly, the three regions of *LLPS* that we have found.

EXPERIMENTAL

In this work we have used a range of polymers — some specially prepared ethylene/octene copolymers, which were used in our previous work, and some commercial materials. They are: one LPE (Sclair 2907), three near-random, homogeneous ethylene/octene copolymers (which were made for us by DSM), two commercially available ethylene/butene LLDPEs, and an ethylene/octene LLDPE. The ethylene/octene copolymers contain 2, 5 and 8 mol% octene and are termed O(2), O(5) and O(8), respectively; details of their preparation are given elsewhere[6]. The two ethylene/butene LLDPEs (from Exxon) are said to contain 2 and 3 mol% butene and are termed B′(2) and B′(3), respectively. Both the ethylene/butene copolymers show morphological evidence of segregation when quenched from the melt at 145°C, suggesting a bimodal nature. The ethylene/octene LLDPE had an overall octene content of about 3 mol%. Temperature rising elution fractionation (TREF) experiments carried out at DSM indicated that it was bimodal in branching (*Figure 3*); this polymer is termed O′(3). We found that O′(3) itself shows clear morphological evidence of segregation if quenched from between 145 and 125°C, but appears mixed if quenched from above 145°C and if crystallized at 120°C. Details of all the materials are given in *Table 1*.

To investigate phase separation we have used the same experimental techniques as in all our recent work on LPE/BPE blends[1–7]. These techniques are, perforce, indirect because where the blend is biphasic the two blend components are too similar, as regards refractive index for example, to enable us to use direct techniques such as light scattering. To map out the phase diagram in very broad outline we made a selection of blends, quenched 2 mg samples very rapidly from 140°C and heated them at 10°C min^{-1} in a Perkin–Elmer DSC 7. We have previously shown (e.g. in references 1–3) that where a

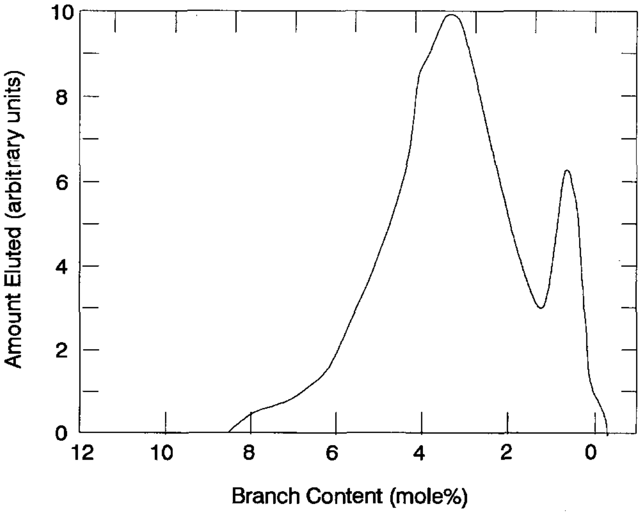

Figure 3 Temperature rising elution chromatogram from the LLDPE, O′(3). The data in this figure were kindly supplied by DSM

Table 1 Reference data for polymers used in this study

Polymer	M_w	M_w/M_n	Branch content (mol%)	Melting temperature of quenched polymer (°C)
B′(2)	3.1×10^4	4.2	2.1	123 plus small lower shoulder
B′(3)	5.27×10^4	4.8	3.2	121 plus shoulder at ~115
O(2)	5.1×10^4	2.2	2.1	117
O(5)	3.7×10^4	2	5.2	102
O(8)	4.3×10^4	2	8.0	88
Sclair 2907	10^5	3		131
O′(3)	4×10^4	4.2	3.1	103 and 119

blend is mixed in the melt, one endotherm is seen in a d.s.c. trace obtained by this method; however, two endotherms are recorded if the melt was separated into two phases prior to the quench. Having obtained an idea of the range of phase separation from d.s.c., we then made more blends and took surface replicas from samples quenched very rapidly from a number of temperatures. By examining the morphologies we were able to determine the temperatures where blends passed from separated (two clearly different crystal types) to mixed (only one crystal type); in particular we could pin-point the upper critical temperature. Details of the method are given in reference 6. Isothermal crystallization experiments were carried out to determine whether blends were mixed or separated at low temperatures (i.e. to look for lower critical temperature behaviour). Details of this technique are given in reference 5.

RESULTS AND DISCUSSION

Blends of LPE with O′(3)

We have already shown, in *Figure 2*, a projection of the ternary phase diagram for a blend of LPE with the two homogeneous ethylene/octene copolymers, O(2) and O(8). We have also shown, in *Figure 3*, the TREF curve for the LLDPE, O′(3). We note that O′(3) appears to consist of two distinct components, one linear-rich with a mean octene content of ~0.5 mol% (OL), and the other a branch-rich component with a mean octene content of ~4 mol% (OB). There is also evidence, from the small shoulder at ~100°C in the TREF curve, of a very small amount of linear material. We may argue that the ternary phase diagram for a blend of LPE with two homogeneous ethylene/octene copolymers, with octene contents of 0.5 and 4 mol%, should show similar features to the ternary phase diagram of *Figure 2*, and that we may consider the LLDPE, O′(3) to lie at a point close to a composition of 1% LPE, 25% of the 0.5 mol% copolymer and 74% of the 4 mol% copolymer. The phase behaviour of a blend of LPE with O′(3) may then be determined from consideration of such a ternary phase diagram.

We may use our experience with binary blends of ethylene/octene copolymers[6] to estimate how the experimentally determined phase diagram for the LPE/O(2)/O(8) system would be modified if the two copolymers were changed to a copolymer containing an average of 0.5 mol% octene, O′(0.5), and another with an average of 4 mol% octene, O′(4). We begin with the ternary phase diagram for the LPE/O(2)/O(8) system and consider how the extent of phase separation changes along each side of the ternary diagram when the components are changed. Our experience with the binary blends of ethylene/octene copolymers[6] leads us to expect that there should be greater *LLPS* in blends of more similar polymers. Thus we would expect wider regions of *LLPS* along each of the sides of the ternary phase diagram for an LPE/O′(0.5)/O′(4) system than for the original LPE/O(2)/O(8) system. Further, if the extent of *LLPS* is significantly increased, we may expect that two of the three distinct regions of *LLPS* seen in *Figure 2* may merge to form a single band of *LLPS*. Such a merging of these two regions of *LLPS* may, alternatively, be understood by applying the general considerations about free-energy diagrams, outlined previously in reference 12, to the specific case of the ternary phase diagram described in reference 19. If the curvature of the free-energy surface is small enough, then only a single region of *LLPS* will occur on the LPE-rich side of the ternary phase diagram[12,19].

We illustrate these arguments in *Figure 4*. A projection of the estimated ternary phase diagram with the maximum extent of the regions of *LLPS* for the LPE/O(2)/O(8) system is indicated by faint lines, and our expectation for the maximum extent of the regions of *LLPS* in the LPE/O′(0.5)/O′(4) system is indicated by the shaded areas. The composition of the LLDPE, O′(3), is shown on the diagram and a line from this point to the LPE apex of the phase diagram is marked. We may expect phase separation to be seen in blends of LPE with O′(3) for those compositions along this line which lie within the shaded regions. We have included, as an inset to *Figure 4*, a schematic cloud point curve for the LPE/O′(3) blend system which would be derived if successive sections of the ternary phase diagram were plotted out.

Clearly, the above approach, based on estimated changes in projected ternary phase diagrams as a result of changing the branch content of the components, can only yield general guidance to the form of *LLPS* that should be expected. We have determined the state of mixing, or demixing, in LPE/O′(3) blends by the usual techniques of d.s.c. and TEM. The results are shown in *Figure 5*. It is obvious that there is a strong resemblance between the predicted cloud point curve (inset to *Figure 4*) and the experimentally determined cloud point curve of *Figure 5*. This agreement gives us some confidence in our approach and leads us to test it further.

Blends of O′(3) with O(8)

To understand the phase behaviour of blends of O′(3) with O(8) we return to the ternary phase diagram for the LPE/O(2)/O(8) system. We now replace the LPE with the linear-rich component of O′(3), which we argued above has an average octene content of ~0.5 mol%, and the O(2) with the branch-rich component of O′(3), which we argued above has an average octene content of ~4 mol%. Once again, we take O′(3) to lie at a composition within this ternary phase diagram at a composition of ~1% of O(8), 25% of the 0.5 mol% copolymer and 74% of the 4 mol% copolymer.

We make similar qualitative arguments to those used above to estimate how the widths of the regions of *LLPS* change along the sides of the phase diagram. We expect

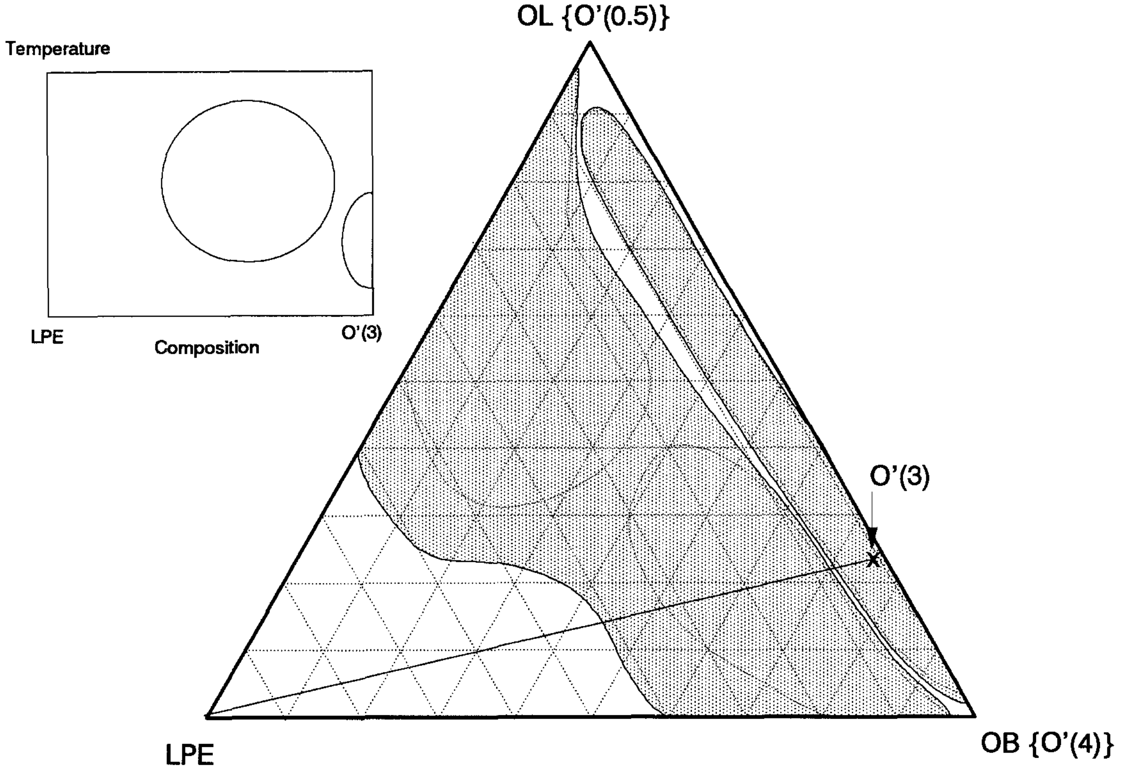

Figure 4 Sketch of the maximum region of *LLPS* expected for the projected ternary phase diagram for an LPE/O′(0.5)/O′(4) blend system. The inset shows the expected cloud point curve for blends of O′(3) with LPE

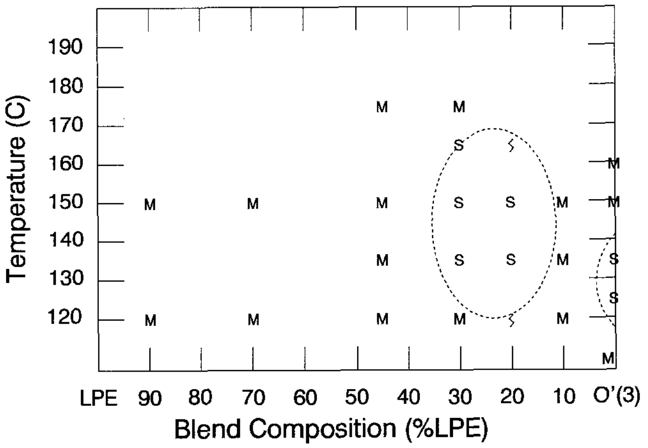

Figure 5 Experimentally determined cloud point curve for the LPE/O′(3) blend system

slightly more *LLPS* along the O′(0.5)–O(8) side than along the LPE–O(8) side in the original phase diagram, since the two polymers are slightly more similar. Conversely, we expect less *LLPS* along the O′(0.5)–O′(4) side as these two polymers are less similar than are LPE and O(2). However, the overall curvature of the free-energy surface should be lower in the O′(0.5)/O′(4)/O(8) system than in the LPE/O(2)/O(8) system, so we may anticipate the merging of the two regions of *LLPS* as before.

All the above arguments are illustrated in *Figure 6*; again we show the contours of the maximum extent of *LLPS* in the LPE/O(2)/O(8) system and our expectation of the regions of *LLPS* for a O′(0.5)/O′(4)/O(8) system. We show, in the inset, the cloud point curve which is therefore expected for blends of O′(3) with O(8).

Figure 7 displays the experimentally determined cloud point curve for the O′(3)/O(8) system. Again, there is good qualitative agreement between the experimental and predicted cloud point curves.

Blends of butene copolymers with octene copolymers

We do not have TREF data for the butene copolymers B′(2) and B′(3); however, both show two melting peaks when quenched from some temperatures, and show double morphologies in TEM. Thus we argue that these polymers should be considered as blends of a linear-rich component (BL) and a branch-rich component (BB). When these polymers are blended with homogeneous octene copolymers, we should expect to need a ternary phase diagram to be able to interpret the results.

Figure 8 shows the experimentally determined cloud point curve for the B′(2)/O(5) blend system. Tentatively applying the results obtained with octene copolymers to this octene/butene system, we find that it is possible to obtain such a cloud point curve from a projected ternary phase diagram of the type sketched in *Figure 9*. We have retained the three regions of *LLPS* found in the LPE/octene ternary system, and placed the components according to their branch content; we expect the most linear material present to be the BL component and the most heavily branched material to be O(5).

We can interpret the cloud point curves for other butene/octene blends in a similar way. *Figure 10* shows experimentally determined cloud point curves for: (a) B′(3) blended with O(5); (b) B′(3) blended with O(8); and (c) B′(2) blended with O(2). *Figure 11* shows the projections of ternary phase diagrams that could give rise to the observed cloud point curves of *Figure 10*. In *Figure 11a* we have drawn the regions of *LLPS* to be larger than those in *Figure 9*, since we argue that B′(3) is more similar

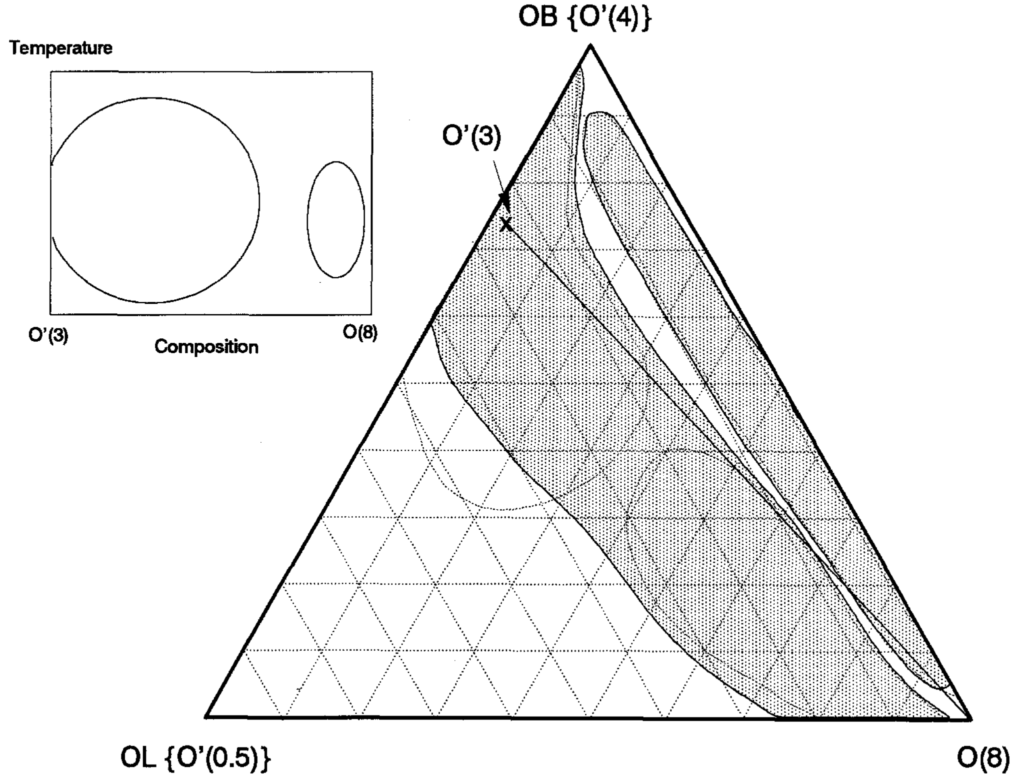

Figure 6 Sketch of the maximum region of *LLPS* expected for the projected ternary phase diagram for an O(8)/O'(0.5)/O'(4) blend system. The inset shows the expected cloud point curve for blends of O'(3) with O(8)

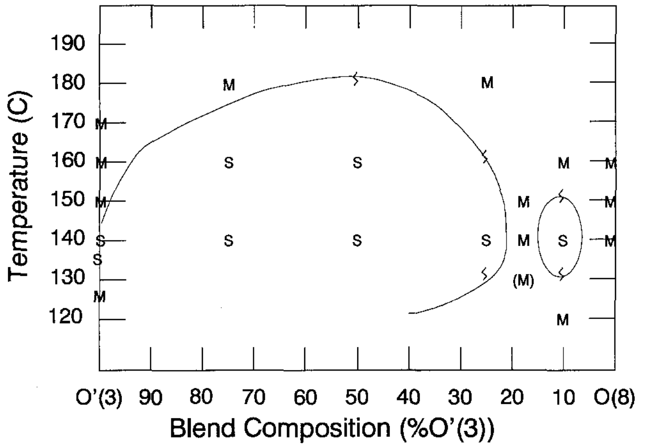

Figure 7 Experimentally determined cloud point curve for the O(8)/O'(3) blend system

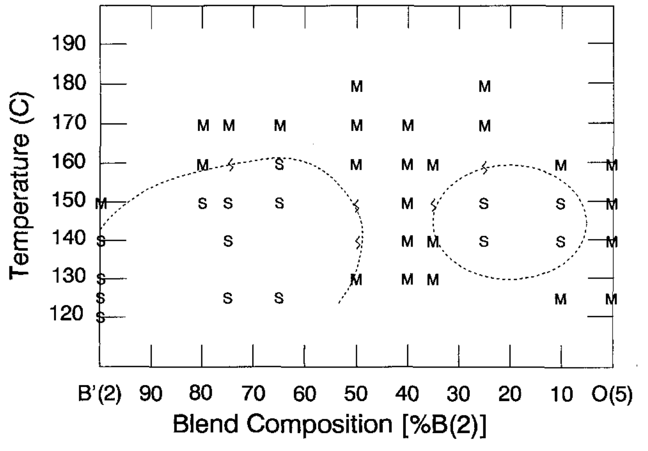

Figure 8 Experimentally determined cloud point curve for the B'(2)/O(5) blend system

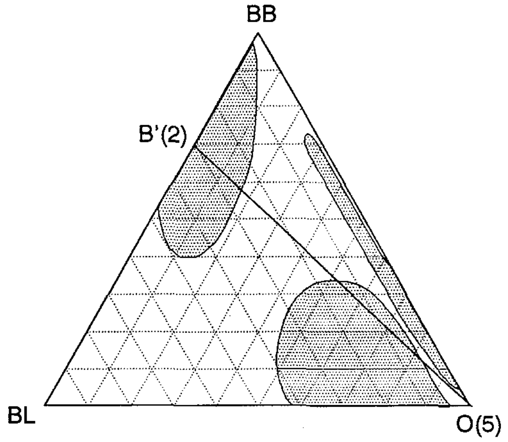

Figure 9 Sketch of the maximum region of *LLPS* for a projected ternary phase diagram that could produce a cloud point curve of the kind shown in *Figure 8*

to O(5) than B'(2) is to O(5). In *Figure 11b* we have reduced the size of the *LLPS* regions shown in *Figure 9* as O(8) is more dissimilar to B'(3) than is O(5). In *Figure 11c*, the diagram for the B'(2)/O(2) system, we have altered the positions of the three components; in this case the most branched component is the BB component, since it must have more than 2 mol% branching. Note that simply changing the positions of the components on the general phase diagram causes the change from two to one region of *LLPS*.

Generality of phase diagrams

The ternary phase diagram found for the LPE/O(2)/O(8) system appears to provide a general form for the type of phase behaviour that may be found in ternary blends of either butene or of octene BPEs. The simple arguments

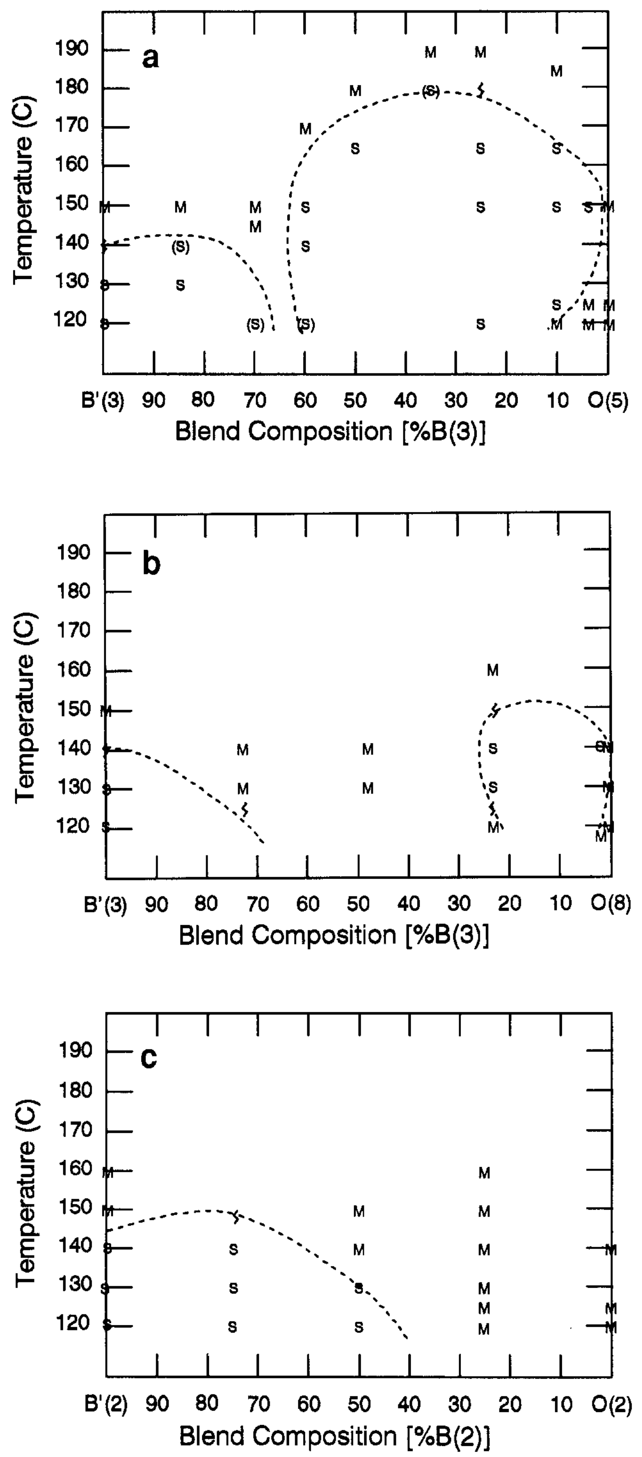

Figure 10 Experimentally determined cloud point curves for: (a) B'(3) blended with O(5); (b) B'(3) blended with O(8); and (c) B'(2) blended with O(2)

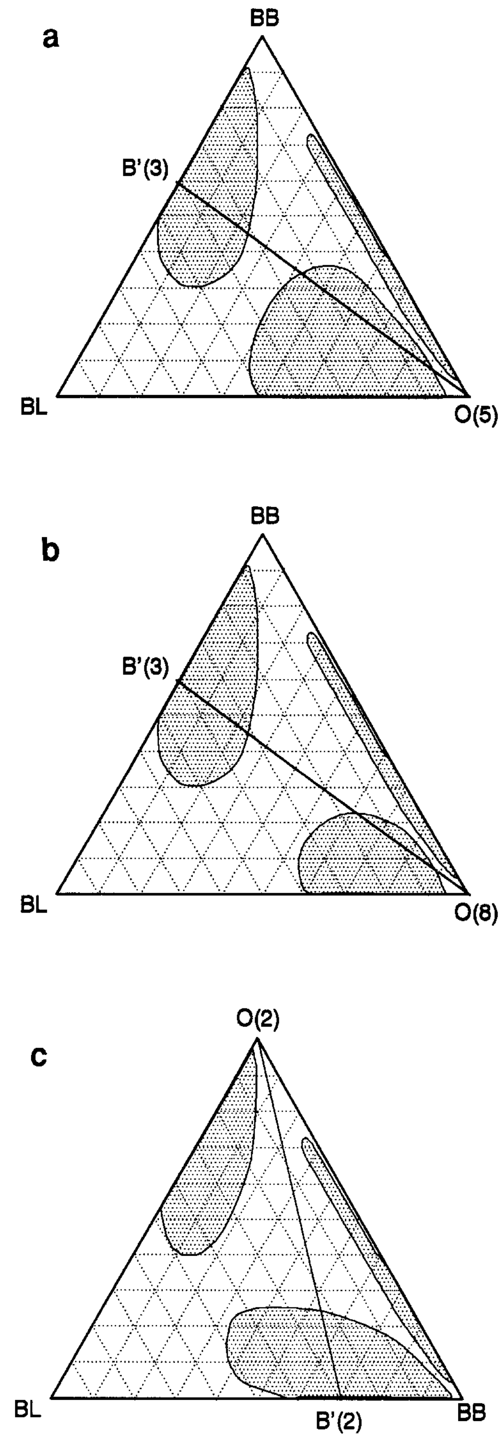

Figure 11 Maximum regions of *LLPS* for projected ternary phase diagrams that could give rise to the observed cloud point curves of *Figure 10*

based on previous experimental observations of the phase behaviour of binary blends of LPE with ethylene/octene copolymers can be readily extended to provide a generalized ternary phase diagram, and to predict how the sizes of the regions of *LLPS* will vary as the branch content of the copolymers changes. The projected phase diagrams (shown in *Figures 4, 6, 9* and *11*) are all equally successful in predicting the observed behaviour of our blends (*Figures 5, 7, 8* and *10*).

We recognize that the polymers we have used are themselves not pure single-component materials, but that they have distributions of both molecular weights and branch contents. We have previously noted and argued[3,12] that molecular weight and its distribution have little effect on binary 'phase diagrams' for blends of linear with branched polymers. All the polymers used in the work reported here have similar molecular weights and polydispersities. Thus we feel fully justified in ignoring molecular weight effects when considering phase behaviour, for the present purposes. However, any more detailed treatment, which applied quantitative rather than qualitative arguments, would certainly need to consider the molecular weights of each of the components, and may also need to take account of polydispersity.

The octene copolymers used were specially polymerized to ensure homogeneity of branch content[6], so that we may regard them as 'pure' single-component materials (if we ignore molecular weight distribution). The octene LLDPE, O′(3), clearly shows up as being bimodal in branch content by TREF and appears to be phase-separated in the melt at some temperatures, thus we are confident that it is sensible to consider this as a blend of two distinct components. The butene copolymers were not prepared to be homogeneous in branch content, so we consider it reasonable to suggest that they could be divided into two components with differing branch content, particularly as our standard experimental tests indicate that they are phase-separated in the melt at some temperatures.

The arguments in the previous paragraph force us to conclude that each of the blend systems studied in this work is really a ternary system, even though we can only investigate the phase behaviour along a single section of the ternary phase diagram. It is most notable that, once we take this view and interpret our results as coming from sections through ternary phase diagrams, the results are always consistent with ternary phase diagrams of similar general shape. This is the system that a simple extension of the scheme proposed for a binary mixture[12] would predict[19]. We therefore further suggest that this is a truly general diagram and should have widespread applicability.

CONCLUSIONS

We have shown that blends of a variety of LLDPEs with linear or randomly branched polyethylenes all show patterns of *LLPS* which are, at first sight, both complex and different from each other. However, for all the octene and butene LLDPEs we have studied, the regions of *LLPS* can be readily predicted in terms of ternary phase diagrams of the same type. This basic phase diagram was originally found for an octene copolymer system, but has now been shown to apply equally well to octene/butene systems. In addition, our simple model[12,19] allows us to estimate the differences in extent of *LLPS* in the various systems in a way that is consistent with the experimental results.

ACKNOWLEDGEMENTS

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