polymer communications

Liquid–liquid phase separation in binary blends of a branched polyethylene with linear polyethylenes of differing molecular weight

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Four binary blends were studied, each containing the same lightly branched polyethylene with one of a series of linear polyethylenes (LPEs) of varying molecular weight. Liquid–liquid phase separation was observed in all blend systems but one. The liquid–liquid phase separated regions were in the form of closed loops, asymmetrically placed at low linear polyethylene content. The liquid–liquid phase separated regions were found to decrease in size as the molecular weight of the LPE decreased, very slowly where the molecular weight of the LPE was high but more rapidly by the time that the molecular weight of the LPE fell to 2×10^4. In the fourth system, where the molecular weight of the LPE was 2500, no liquid–liquid phase separation was seen. This system fills a logical position in the sequence: the liquid–liquid phase separated region has reduced to zero in size at this very low LPE molecular weight. This communication contains additional data on systems previously studied in part — the liquid–liquid phase separated regions had been recorded only for temperatures just above the melting point of the LPE. Now, as a result of improved experimental techniques, the full liquid–liquid phase separated loops, including upper critical temperatures, are reported.

(Keywords: phase separation; binary blends; polyethylenes)

Introduction

During the past few years, extensive studies concerning liquid–liquid phase separation (*LLPS*) in binary[1–6] and ternary[7] systems of linear with branched polyethylenes (LPEs with BPEs) have been carried out at the University of Bristol. We have examined nearly 40 systems to date, and in all cases but one we have found evidence for *LLPS*. Where the BPE is heavily branched we have found extensive *LLPS*[6], as have other authors[8–11]. However, our work is unusual in that it has been concerned mainly with blend systems in which the BPE is only lightly branched. In these systems the physical properties of the components are very similar, so that the usual direct methods for detecting *LLPS* cannot be used. As a result, we have had to develop special indirect methods to detect *LLPS*. Using these methods we have found phase separation of an unusual type in blends of LPEs with lightly branched BPEs: we always find a closed loop of *LLPS* at low LPE content.

In one of our early papers[3] we published partial phase diagrams showing the phase behaviour that occurred when one particular commercial BPE was blended with a series of commercial LPEs of differing molecular weights (*MWs*). At that time our techniques for examining phase behaviour at high temperatures had not been perfected. As a result, we published only the low temperature part of each phase diagram, indicating the liquid/solid phase separation and showing the width (in composition) of the *LLPS* region for each LPE/BPE pair just above the melting point.

Recently, some of our published results have been discussed from a theoretical standpoint by other authors[12]. These authors mention our partial phase diagrams[3] with interest, since *MW* is of importance in their predictive calculations; however it is clear that complete *LLPS* loops would be needed in order to carry out further modelling for these systems. It is with the authors of ref. 12, and many others who have shown interest in our work, in mind that this addendum to ref. 3 is published. The complete *LLPS* behaviour for blends of one commercial BPE with a series of LPEs of varying *MWs* is presented in this communication.

Experimental

Four of the polymers used in this work are commercial materials, and the fifth is a fraction of one of the other materials. Details of all polymers are given in *Table 1*.

The experimental methods have been described elsewhere (see, for instance, refs 2, 4, 5 and a discussion of the merits of the various techniques for detecting phase separation in ref. 13). Surface replicas of very fast quenched blends were used for the present work. Because the surface experiences the fastest cooling on quenching, we believe that it must be the part of the sample that is nearest in phase structure to the melt from which it came. We have shown that blends that were quenched from a phase-separated melt show two distinct crystal types, and that these crystals are found in groups separated on a scale of micrometres (e.g. ref. 2). We have measured diffusion rates in these blends and thus shown that it is not possible for the rather large-scale separation observed to take place during the short time of the quench[5]. We are confident that a study of surface replicas of quenched blends can give reliable information about the state of the melt prior to quenching, even when quenching from high temperatures[4,5].

Results and discussion

Figure 1 shows the phase behaviour of four blend systems. Only the *LLPS* part of the phase diagram is

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shown in each case; the liquid/solid separation observed on slow crystallization has been omitted (those data can be found in ref. 3, Figure 9). For each phase diagram shown in *Figure 1* the BPE is the same. The weight average *MW* of the LPEs decreases from about 2×10^6 for the Hizex (*Figure 1a*) to 2550 for the LPE fraction used in the blends shown in *Figure 1d*.

It is immediately clear that, in all cases but one, the phase behaviour is the same: a loop of *LLPS* is found at low LPE content. Where the *MW* of the LPE is higher and the *LLPS* loop larger, the bottom of the loop cannot be revealed because of crystallization effects. However, in each case we are able to see that the *LLPS* region is narrowing at low temperatures, implying that there is a lower critical temperature as well as the clearly visible upper critical temperature. For the system shown in *Figure 1c*, where the *MW* of the LPE is low and the *LLPS* loop small, we are able to detect regions of mixing at low temperatures and the whole loop is revealed.

The only system where we have not detected *LLPS* is shown in *Figure 1d*. However, it is clear that this system is not anomalous, but forms part of a pattern. Clearly the size of the *LLPS* region, particularly the width, decreases as the *MW* of the LPE decreases (compare *Figures 1a* to *c*). The change is small at high LPE *MW*, but becomes more rapid as the *MW* of the LPE drops. The Fraction 2155/BPE system fits into the sequence: the *MW* of Fraction 2155 is so low that no *LLPS* is observed. This decrease of *LLPS* with decreasing *MW* of the LPE in the blend has been discussed elsewhere in terms of a simple descriptive scheme[14] involving the consideration of free energies of mixing.

The BPE used in the present work was the first one with which we worked. It has a mixture of branch types (as well as a high polydispersity). We now know that the type of *LLPS* behaviour recorded here is also observed on blending LPEs with more uniform BPEs, for instance near random octene copolymers with lower polydispersity[6].

Table 1 Details of polymers used in this work

Polymer	M_w (daltons)	M_w/M_n	Long (branches/1000 C)	Short (branches/1000 C)
Hizex 240	2×10^6	12		
Rigidex 50	7×10^4	7		
Fraction 15000	15000	1.4		
Polymer Laboratory's Fraction 2155	2550	1.1		
BP PN220	2×10^5	8	16	10

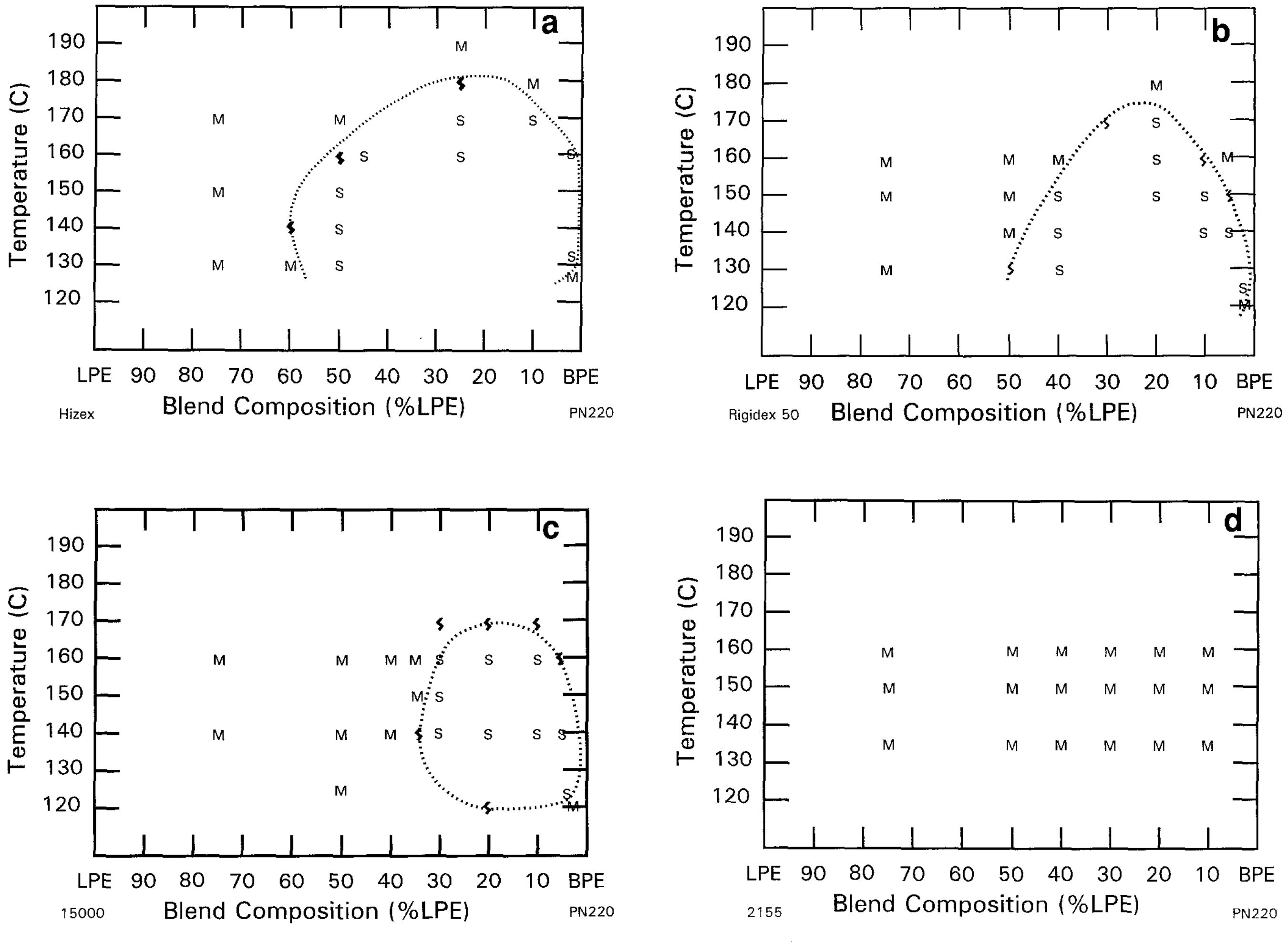

Figure 1 Experimental points obtained in the study of *LLPS* loops for LPE/BPE blend systems: M, experimental evidence for a mixed melt; S, a phase separated melt; ≤, a border-line case. In all blends the BPE was BP PN220 (details of *MW* and branching are given in *Table 1*). The LPEs were: (a) Hizex 240, $MW \approx 2 \times 10^6$; (b) Rigidex 50, $MW = 7 \times 10^4$; (c) a fraction of Rigidex 50 (Fraction 15000) $MW = 15000$; (d) Polymer Laboratory's Fraction 2155, $MW = 2550$

Summary

This communication is an extension to incomplete work published previously[3]. A lightly branched BPE was blended with a series of LPEs, of differing *MW*s. Data concerning the melt behaviour at high temperatures are added here, to complete the record of phase behaviour. The overall conclusions are the same as in the previous paper.

1. In three out of four cases, a closed loop of *LLPS* is found, asymmetrically placed at low LPE content.
2. The size of the loop of *LLPS* is rather insensitive to the *MW* of the LPE where the *MW* of the LPE is high.
3. However, *LLPS* region decreases in size as the *MW* of the LPE decreases, and more rapidly so by the time that the *MW* of the LPE has dropped to 1.5×10^4.
4. In the fourth system, where the *MW* of the LPE is 2550, no *LLPS* can be found. This system fills a logical position in the sequence: the *LLPS* region has reduced to zero in size at this very low LPE *MW*.

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