Liquid liquid phase separation in polypropylene homopolymer/polypropylene copolymer melts

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Polypropylene was blended with a terpolymer (containing ethylene and butylene as well as propylene). Melts of some blends showed liquid liquid phase separation at certain temperatures. The separated region was in the form of a closed loop and was found at low homopolymer content. This is the type of liquid liquid phase separation which has previously been observed for blends of polyethylene homopolymers with copolymers (linear with branched polyethylenes).

(Keywords: liquid liquid phase separation; polypropylene; blends)

Introduction

In recent years we have established conditions under which blends of linear with branched polyethylene (LPEs with BPEs) undergo liquid liquid phase separation (LLPS) in the melt[1-7]. We have studied more than 20 PE blend systems and have found, for some conditions of temperature and composition, LLPS in melts of all blends except one. LLPS was not found when the LPE was of very low molecular weight (2155); this was not unexpected since LLPS is found to decrease with decreasing molecular weight of the LPE. Further, provided the branch content was less than about 50 branches per 1000 carbon atoms, we found that the separated region was always in the shape of a closed loop, placed asymmetrically at low homopolymer (LPE) content; *Figure 1* shows typical behaviour.

We have developed a simple scheme, based on free energy diagrams, to explain such novel behaviour[8]. We are therefore very interested to investigate the generality of the model. We wish to know whether the phase behaviour that we have shown to be generally present in LPE and BPE systems, i.e. a closed loop of LLPS placed asymmetrically at the low homopolymer side of the phase diagram, is specific to the LPE/BPE system or if it is more general and also found in other homopolymer/copolymer melts.

In this communication we present results from a study of blends of polypropylene (PP) with a terpolymer of propylene with ethylene and butylene (TP). Using methods similar to those that we developed for the examination of PE blend melts, we have been able to establish that the PP/TP system behaves like the LPE/BPE systems that we have studied, i.e. (i) there is LLPS in melts of PP/TP blends; (ii) the LLPS region is asymmetrically placed at low homopolymer content; (iii) the LLPS region is a closed loop.

Experimental

The polymers used were the PP homopolymer, Atochem P3400 MNI, and the TP, Himont Moplen EP3 C37F; the latter contains 95% propylene, 4% ethylene and 1% butylene. Both the polymers have weight average molecular weights of about 50000.

The polymers were blended by dissolving in xylene and precipitating rapidly by pouring the solution into acetone (a non-solvent) at its freezing point; this technique is known to produce well mixed blends[1-3].

We are unable to examine the melt directly for phase separation, since the physical properties of the two components are so similar. As in our previous work on LPE/BPE blends, we have used indirect techniques, examining very rapidly quenched samples and assuming that any large scale phase separation observed in the quenched samples could not have taken place in the time available before crystallization occurred during quenching. We have demonstrated from diffusion studies[5], in the case of LPE/BPE blends, that it is not possible for the molecules to move sufficiently far apart during quenching to explain observations of two different morphologies, well separated on the scale observed, unless the samples were phase separated in the melt. The principal techniques used to examine quenched blends were differential scanning calorimetry (d.s.c.) and transmission electron microscopy (TEM) of surface replicas. Surface replicas are used because the surface experiences the most rapid quenching and is therefore closest to the melt in phase structure. A Perkin-Elmer DSC 7 was used for all d.s.c., with a heating rate of 10°C $\min^{-1}$. Surface replicas were made by a single stage process following light permanganic etching[9]; they were examined using a Philips 301 transmission electron microscope.

Working with PP/TP blends proved a little more difficult than working with PE blends. We have shown[4] that our PE blends do not degrade to an extent that noticeably affects the mixing and segregation, until they have been held in the melt at 200°C for well over 1 h. We have also shown[1-5] that PE blends can reach what appears to be an equilibrium state in 20–30 min, i.e. a blend segregated on a (typical) scale of a few micrometres will remix, if held at a suitable temperature for 20–30 min. Thus, for the temperatures at which we were

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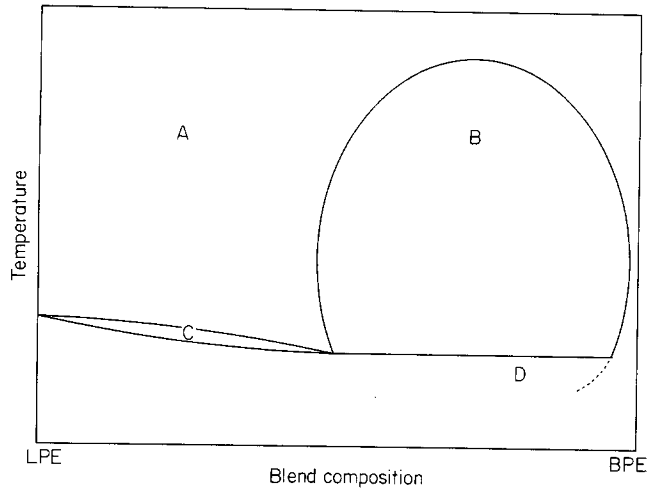

Figure 1 Sketch of a 'phase diagram' illustrating typical phase behaviour of LPE/BPE blends. A, mixed melt; B, biphasic melt; C, crystallization from mixed melt; D, crystallization from metastable, supercooled, biphasic melt

examining PE blends (usually well below 200°C), remixing could be followed to completion without fear of any problems due to degradation. However, the PP/TP blends were, of necessity, held at temperatures above 170°C and often above 200°C. At temperatures above 200°C degradation effects can be observed after holding in the melt for 10–15 min. Accordingly, it was not always possible to hold the blends in the melt for sufficiently long to be sure that mixing (or demixing) had proceeded to completion; the PP/TP blends were usually held in the melt for about 10 min rather than the 30 min we would have preferred. Thus, although we know that our results are qualitatively correct, we cannot place as much reliance on the actual temperatures of phase transition as we could when investigating PE blends.

Results

Figure 2 shows a typical set of d.s.c. thermograms, obtained on reheating a set of blends quenched from 180°C into acetone at its freezing point. It is clear that the PP, TP and blends of 75 and 50% PP content show single peaks on remelting; however, blends of 25, 10 and 5% PP content show double peaks on remelting. We have argued previously[1,2] that where there is one melting peak there is one crystal species only, but where there are two peaks there are two crystal species. Note that where there are two peaks, although they are of different heights for the different blend compositions, the two melting temperatures are the same. This is consistent with the supposition that whenever two crystal species are obtained on quenching from 180°C, the two species have the same composition, irrespective of the composition of the whole blend. This is indicative of LLPS (as has been argued in more detail in references 1 and 2).

In our previous studies we found, for PE blends, that where d.s.c. indicated one crystal species TEM showed crystals of one thickness only, but where d.s.c. indicated two crystal types a double morphology, with thicker and thinner crystals, was revealed by TEM[1–7]. In our current work we found that quenched PP/TP blends etched well and gave good replicas. When the replicas were examined some cases were found where only one morphology was present, and in others two well separated morphologies could be seen. *Figure 3* shows examples of replicas of mixed and segregated blends. As in the previous work with PE blends, d.s.c. and TEM results were in good agreement. The blends were quenched from a range of temperatures to see whether they were mixed or segregated.

Discussion

The results are collected in *Figure 4* which is presented as a 'phase diagram'. Of course our results cannot properly represent the equilibrium phase behaviour of such a complex system, but merely give an indication of the observed state of mixing, or demixing, in typical melts. From *Figure 4* it is immediately clear that LLPS can occur in melts of PP/TP blends and that the LLPS region is asymmetrically placed at low homopolymer compositions. Note that the width of the region of LLPS decreases as the temperature is raised from 220 to 250°C, which is indicative of upper critical temperature behaviour (with a critical temperature above 250°C, a temperature we cannot reach without severe degradation). Also note that when the temperature is reduced to 150°C the width of the region of LLPS again decreases, indicating lower critical temperature behaviour (with a critical temperature around 150–160°C, a temperature region that is difficult to investigate due to the onset of crystallization). We may therefore conclude that the region of LLPS is in fact of a closed loop nature, as we have seen in LPE/BPE blend systems.

To summarize our results for the PP/TP blend system: (i) there is LLPS; (ii) the LLPS region is asymmetric at low homopolymer content; and (iii) the LLPS region is a closed loop. However, although it is certain that there is LLPS, the extent of the LLPS region may be rather less than that indicated since, as explained above, the

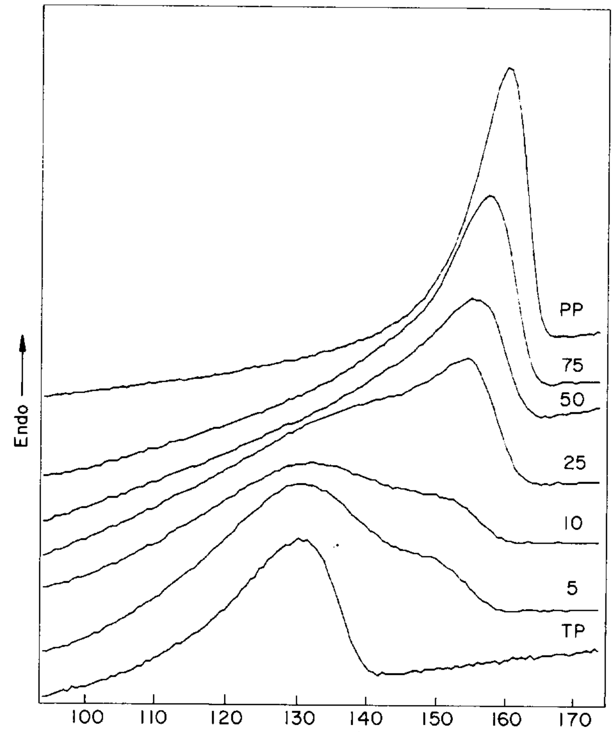

Figure 2 D.s.c. melting endotherms of PP/TP blends with compositions as marked in the figure, quenched from the melt at 180°C; data recorded at 10°C min^{-1}

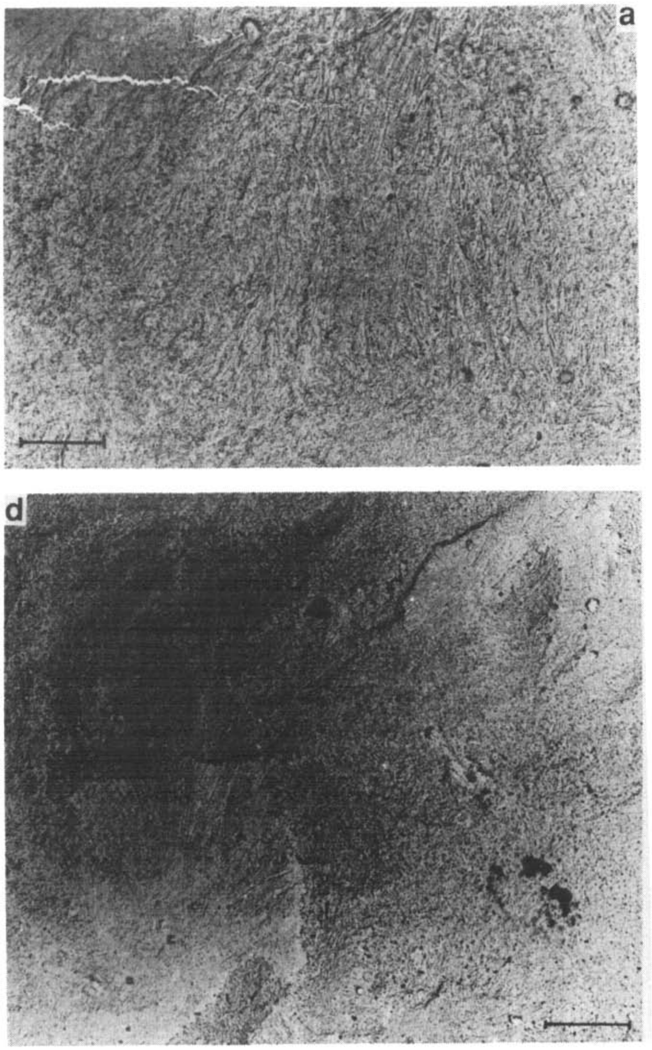

Figure 3 Transmission electron micrographs of surface replicas of quenched PP/TP blends: (a) 75% blend quenched from 180°C, illustrating a 'mixed' morphology; (b) 25% blend quenched from 180°C illustrating a 'segregated' morphology – note the different appearance of the 'spherulites' at the top left and bottom right of the micrograph, which have a texture typical of polypropylene. The scale bar is 1 μm

blend was left in the melt for rather short times due to the tendency of the material to degrade, therefore we have not drawn any phase boundaries in *Figure 4*.

The situation with this PP homopolymer and copolymer system is similar to that found for blends of LPE with BPE, i.e. PE homopolymer and copolymer. Thus we have shown that this phase behaviour does not only apply to PE systems, but to at least one other polyolefin. We also know, from other recent studies[10,11], that the behaviour is not confined to polyolefins. There is evidence that similar conditional LLPS also takes place in blends of the bacterial homopolymer polyhydroxybutyrate (PHB) with copolymers of hydroxybutyrate and hydroxyvalerate (PHB/HV). In these systems, too, it appears that LLPS is of a closed loop nature and is found in blends of low homopolymer content.

When we first found LLPS in one LPE/BPE blend we were surprised that it occurred at all, and thought that it might be restricted to one or two special polymer pairs. However, we now find that the phenomenon is quite widespread and are eagerly seeking the cause for this common, but unexpected, behaviour. We have made a start in this endeavour with our simple model[8], which suggests that there must be an additional, asymmetric, free energy of mixing term which is not included in the usual models for phase separation. As yet we have not been able to identify the physical origin of this term.

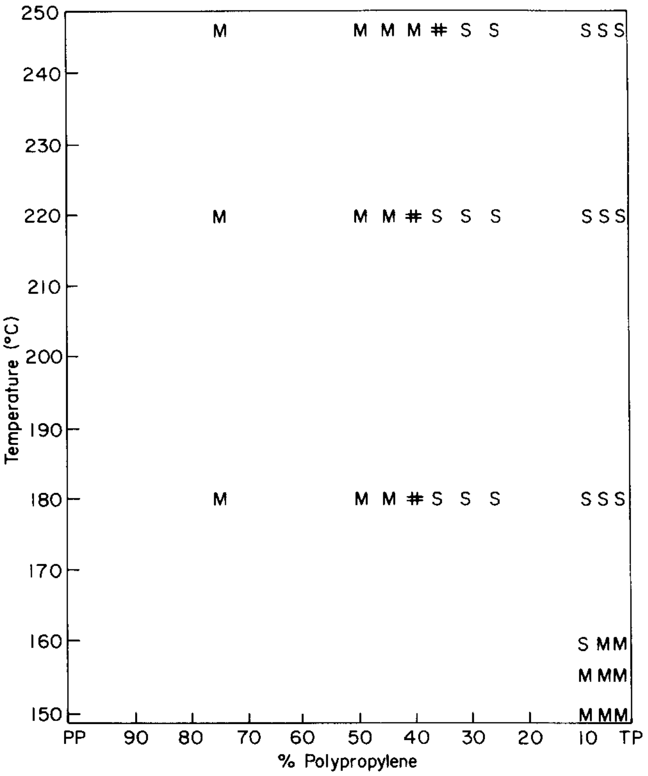

Figure 4 'Phase diagram' as determined by the techniques described in the text for the PP/TP blend system. M, a mixed melt; S, a phase separated melt; #, borderline cases

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