Mixing and demixing of heterogeneous ethylene–octene copolymers: evidence for binodal melt demixing*

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Morphology, fractionation and differential scanning calorimetry (d.s.c.) studies point to very-low-density polyethylene (VLDPE) being a heterogeneous blend of molecules with widely different comonomer contents. The morphology of VLDPE shows distinct regions of highly different crystallinity. This highly crystalline dispersed phase occurs in smooth, spherical compact semicrystalline domains, which are believed to be due to demixing in the melt. The mixing and demixing of a heterogeneous ethylene–octene copolymer as a function of time and temperature and the influence of crystallization on this behaviour is studied with d.s.c. and transmission electron microscopy. The results show clearly that mixing occurs at higher temperatures, that demixing occurs in the melt and that under certain conditions this demixing is binodal in character.

(Keywords: very-low-density polyethylene; octene; copolymers; demixing; upper critical solution temperature; binodal; differential scanning calorimetry; transmission electron microscopy)

INTRODUCTION

Mathot and Pijpers[1] showed by using a kind of temperature rising elution fractionation (t.r.e.f.) that very-low-density polyethylenes (VLDPEs) consist of chains widely differing in comonomer content. This broad distribution of comonomer content results in crystals having a broad distribution of melting temperatures. The morphology of VLDPE shows distinct regions of highly different crystallinity, as observed by Deblieck and Mathot[2]. They recognized that it was possibly caused by melt demixing. The highly crystalline dispersed phase in the investigated material occurred in smooth, spherical compact semicrystalline domains (c.s.d.).

Studies on phase-separation behaviour in blends of branched and almost linear polyethylenes at the University of Bristol[3,4] also point to liquid–liquid phase separation. The idea is that polyethylene molecules which differ mainly in branch content will show partial thermodynamic demixing.

The aim of the present study is to investigate whether the phase-separation behaviour of a heterogeneous ethylene–octene copolymer in the melt may cause the dispersed morphology and the observed thermal behaviour.

MATERIAL

The sample originated from synthesis using a Ziegler–Natta catalyst and a mixture of ethylene and 1-octene. This procedure was shown to produce a heterogeneous copolymer, meaning that different copolymer chains may differ widely in amounts of comonomer[1]. The characteristics of the ethylene–octene copolymer studied here are:

Density (23°C) = 896 kg m^{-3}
Melt flow index = 3.5 dg min^{-1}
CH_3/1000C = 28.8
C_8 fraction = 6.6 mol% (22.1 wt%)

The heterogeneity of the sample is reflected in its very broad and bimodal range of melting, extending from −50 to 128°C, as can be seen in *Figures 1* and *2*.

EXPERIMENTAL DETAILS AND RESULTS

Morphology

Transmission electron micrographs were obtained from ultrathin sections of VLDPE material that had been bulk-fixed and stained by means of chlorosulphonation in the vapour phase[5]. The time–temperature program applied to the sample prior to taking micrographs is shown schematically in *Figure 3*. Each sample was thermally pretreated by holding at 220°C for 30 min and subsequent cooling at a rate of 10°C min^{-1} (position I in *Figure 3*). During cycling through the crystallization–melting transition, the holding time at 150°C and 40°C is 5 min. Thus the micrographs in *Figure 4* were obtained at position I in *Figure 3*, and the micrograph in *Figure 5* was obtained at position II. Both show a dispersed phase consisting of linear-rich material, but in *Figure 5* the number of

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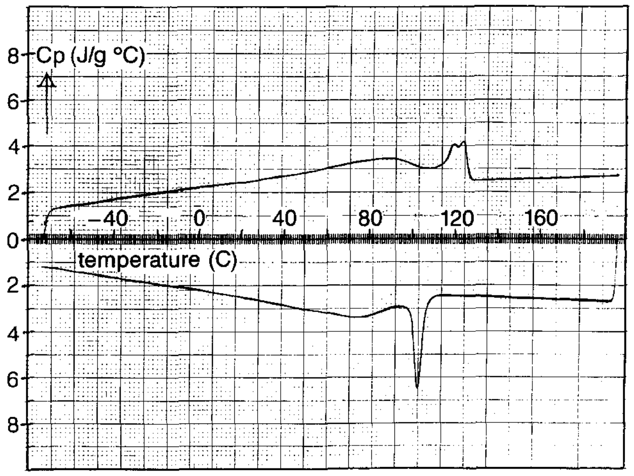

Figure 1 DSC-2 continuous specific heat capacity curves for cooling and subsequent heating at a rate of 10°C min^{-1}

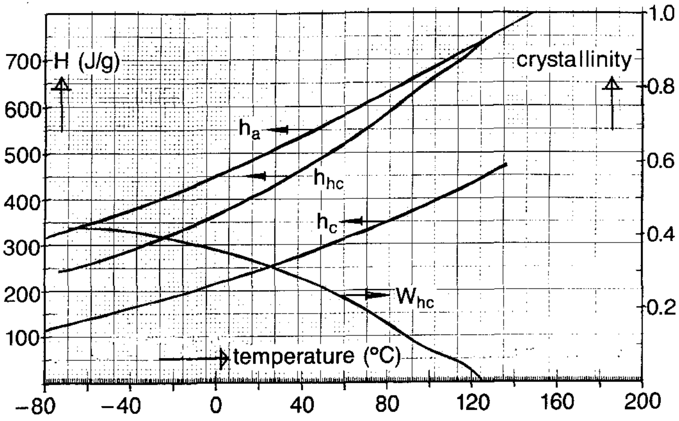

Figure 2 Specific enthalpy heating curve (h_{hc}), the reference curves (ref. 1) for purely amorphous polyethylene (h_a) and purely crystalline polyethylene (h_c), and the enthalpy-based crystallinity heating curve (W_{hc})

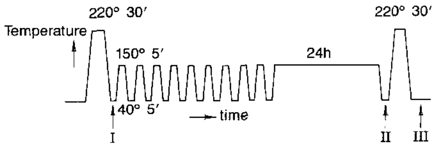

Figure 3 Diagram showing the thermal pretreatment of the sample. Heating and cooling rates were 10°C min^{-1} throughout. Micrographs were taken at positions I and II

regions has decreased while their size has increased. These regions were termed compact semicrystalline domains (c.s.d.) by Deblieck and Mathot[2].

Thermal analysis

D.s.c. measurements were performed on a Perkin–Elmer DSC-2 using sample weights of typically 5 mg. The block surrounding the d.s.c. unit was thermostatted at −120°C by a Cryoson TRL5 unit using liquid nitrogen. All thermal pretreatments were carried out at a rate of 10°C min^{-1}, starting at 220°C for 30 min and cooling down to 150°C. From this point on the procedures were different, as schematically shown with the d.s.c. curves.

A continuous c_p measurement was performed between −70 and 200°C on cooling and subsequent heating

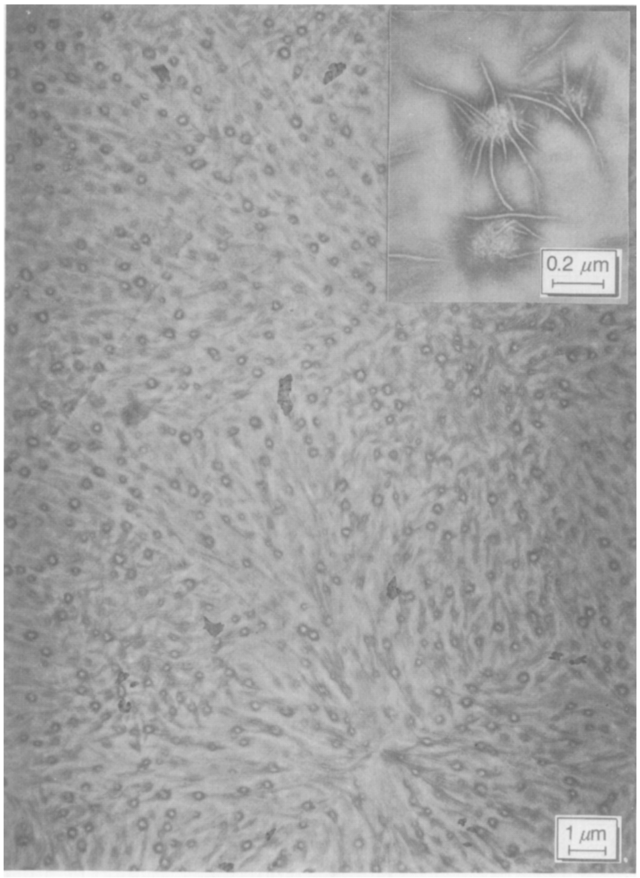

Figure 4 TEM micrographs obtained at position I, showing very small c.s.d.

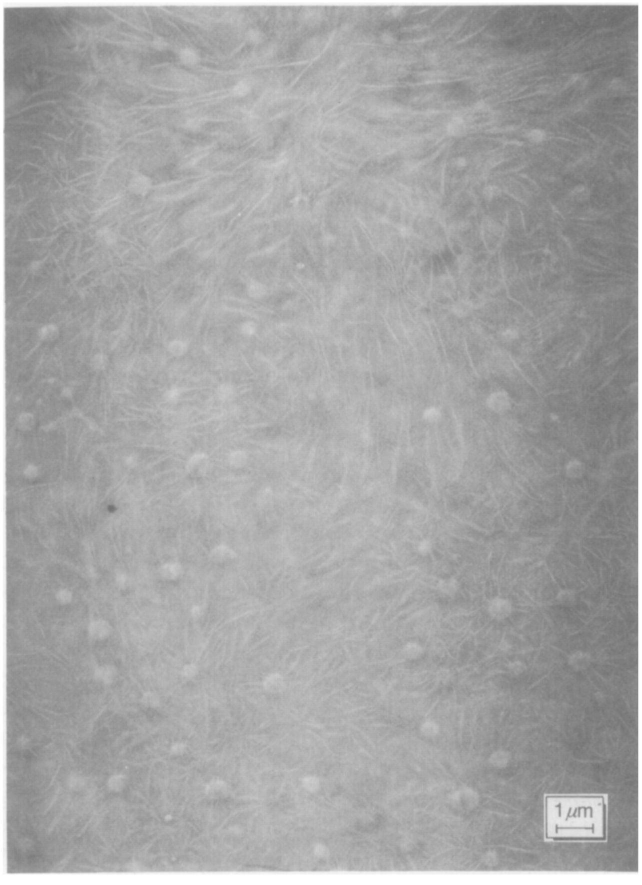

Figure 5 TEM micrograph obtained at position II, showing very coarsened spherical c.s.d.

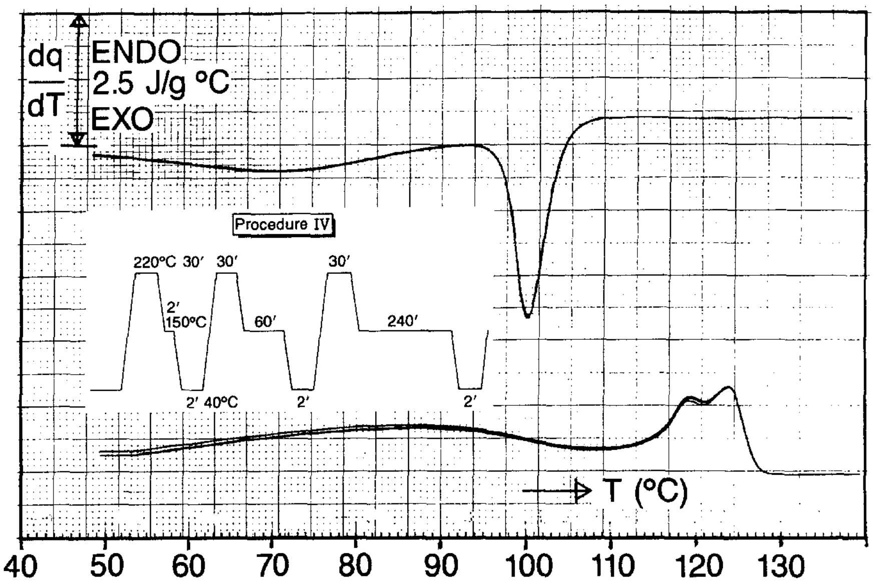

Figure 6 Cooling curves and heating curves after holding the sample isothermally at 150°C for 2, 60 and 240 min (procedure IV), showing that variation in holding time at 150°C does not have an effect on the crystallization and subsequent melting behaviour

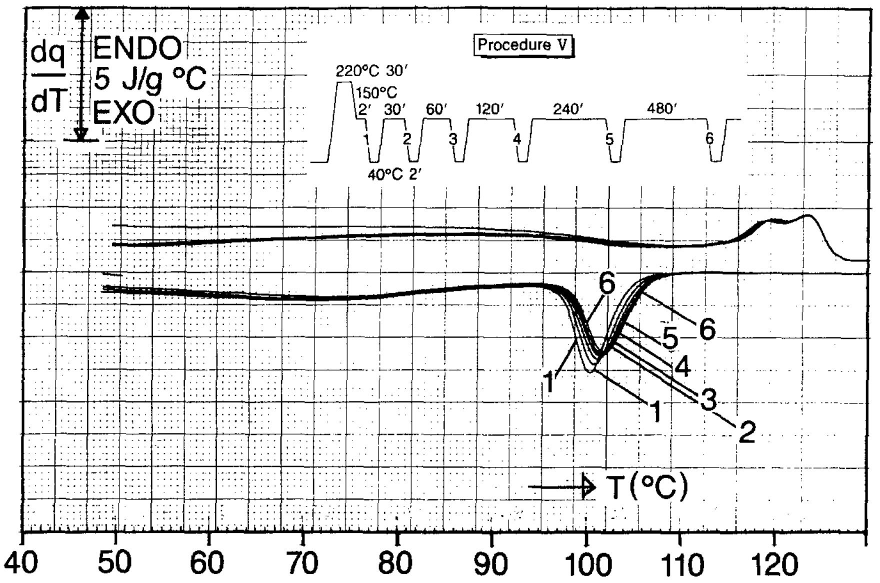

Figure 7 Cooling and heating curves, showing an increase in both crystallization and melting temperature with cycling between 150 and 40°C and increasing holding times at 150°C (2, 30, 60, 120, 240 and 480 min, procedure V)

(*Figure 1*). The heating curve was integrated with respect to temperature to give a specific enthalpy heating curve. From this the crystallinity as a function of temperature was calculated[1] using the reference specific enthalpy curves for purely amorphous and purely crystalline polyethylene (*Figure 2*).

Mixing and demixing was studied by varying the annealing time at 150°C. If the annealing temperature was reached coming from 220°C, no effect whatsoever was observed on the position of the crystallization peak (*Figure 6*). If, on the other hand, the annealing temperature was reached coming from 40°C, the crystallization peak shifted to higher temperature every time the annealing time was increased and the sample was cooled to 40°C and reheated to 150°C (*Figure 7*). Finally also an increase in crystallization temperature was observed if the sample was first annealed at 220°C for 30 min and then cycled through the crystallization and melting transition between 40 and 150°C (*Figure 8*).

DISCUSSION

Figure 1 shows a very broad and actually bimodal distribution of melting temperatures, with the high-temperature melting peak split up because of recrystallization during heating. Starting at the glass transition around −50°C, the crystallinity continuously decreases with increasing temperature as shown in *Figure 2*.

The morphology, as seen in *Figure 4*, not only shows spherulitic superstructures of typically 15 μm but also clearly shows that the sample is phase-separated into small c.s.d. during cooling down from what was a mixed

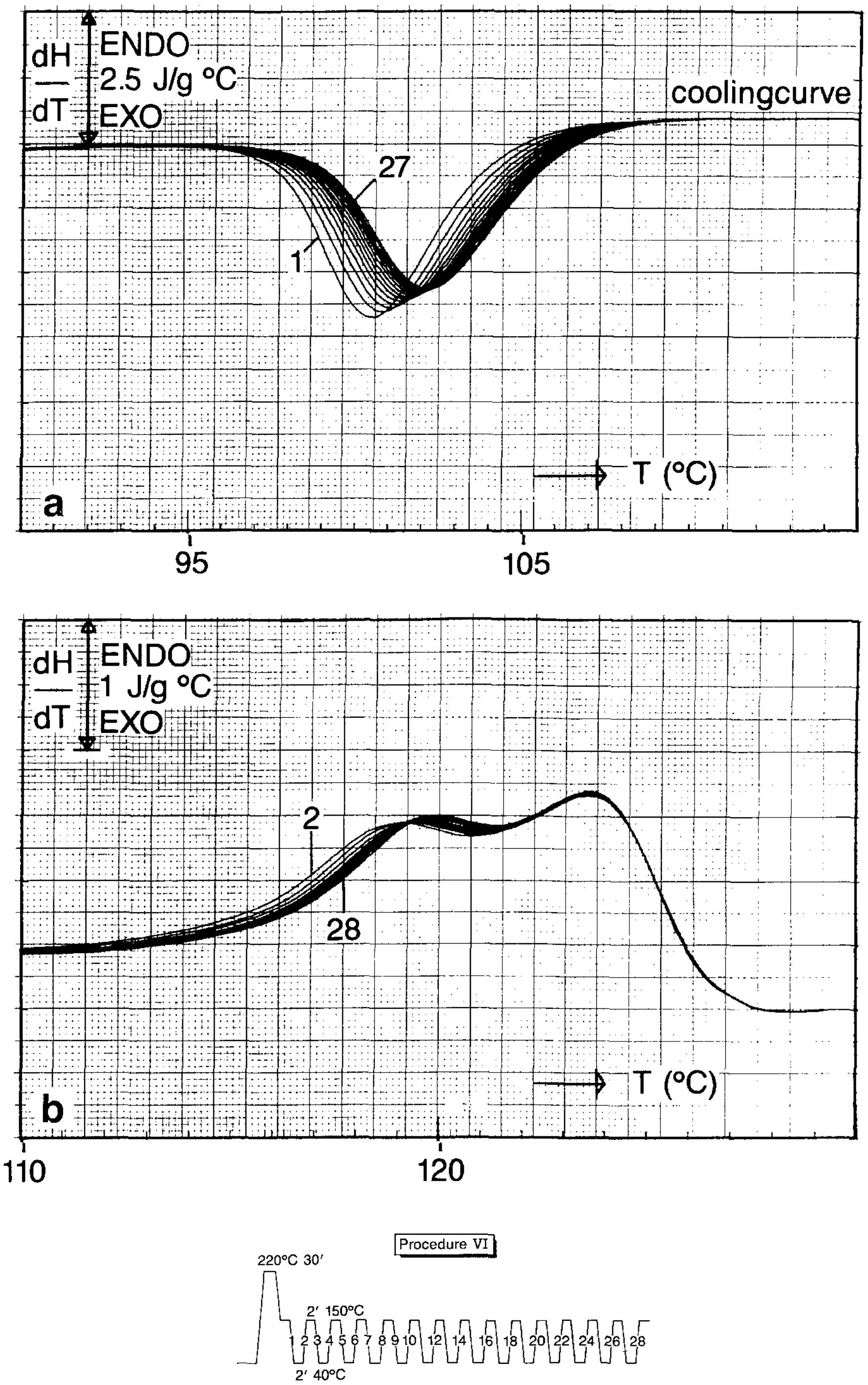

Figure 8 (a) Cooling and (b) heating curves after repeated cycling between 150 and 40°C with a constant holding time of 2 min at both temperatures (procedure VI), showing a steady increase in both crystallization and melting temperature with cycling

melt according to d.s.c. results (discussed later). The fact that the morphology as seen in *Figure 4* is not that of a homogeneous (mixed) melt is due to changes in the melt structure during cooling[4].

There are two possible mechanisms that might have resulted in the observed morphology. The first is that the crystallizing lamellae of linear material in a homogeneous melt nucleated the phase separation, the kinetics of the latter being fast enough to develop small, linear-rich droplets along the growing lamellae. The other possibility is that at lower temperatures the spinodal region is entered on cooling, leading to spontaneous phase separation. The spherulitic superstructure might then have developed from occasional heterogeneous crystallization nuclei from which lamellae emanate, which in their turn nucleated crystallization in the supercooled linear-rich dispersed phase.

Figure 5 shows fewer but larger c.s.d. than *Figure 4*, indicating that the annealing temperature (150°C) lies within the two-phase region of the phase diagram and that annealing has led to coalescence of small phase domains. Note also the spherical form of the c.s.d. Both the larger diameter and the shape indicate that the linear-rich domains *must* have been present in the melt at 150°C.

It must be borne in mind that a higher crystallization temperature of the linear-rich material must be interpreted as due to a lower local concentration of branched material. This branched material hinders crystallization of the linear-rich chains. Therefore, the lowest crystallization temperature is always obtained when the sample is cooled after annealing for 30 min at 220°C, indicating that it was homogeneously mixed. Recognizing that annealing in the melt may destroy crystallization nuclei and that this would cause a shift of the crystallization peak to lower temperature, the higher crystallization temperatures on annealing at 150°C can only be explained by demixing. The linear-rich chains will concentrate in domains, thereby locally lowering the branch concentration and thus increasing their crystallization temperature. On cooling these domains may form the c.s.d. Any influence of degradation was ruled out since d.s.c. results were only accepted if, after an annealing experiment, the cooling curve after annealing for 30 min at 220°C coincided with the curve recorded at the beginning of the experiment.

Figure 6 shows that when the sample is annealed for various times at 150°C and when this temperature is reached coming from a homogeneous (mixed) melt, there is no change in crystallization and subsequent melting temperature. All three cooling and heating curves are plotted in *Figure 6* and they are seen to coincide. When, on the other hand, the annealing temperature is reached coming from 40°C (*Figure 7*), the crystallization and melting peaks shift to higher temperatures on crossing the crystallization–melting transition and with prolonged annealing time at 150°C (procedure V). The kinetics of mixing appeared to be remarkably fast. The increase of the crystallization temperature as a result of cycling (such as in *Figure 8*) can be nullified by just scanning up to 165°C and holding it at that temperature for 2 min. In this case the crystallization peak on cooling down from 165°C coincides with the peak on cooling down from 220°C. The combined results presented in *Figures 6* and *7* therefore show that at 150°C the system is inside the two-phase region in the phase diagram although the system is not able to demix spontaneously if it is cooled to that temperature from a mixed melt (binodal demixing). This means that for the sample studied, 150°C is in between the binodal and spinodal curves in the phase diagram. Clearly the spatial fluctuation in concentration of branched material remaining after lamellae of the more linear material have melted (octene cannot be incorporated into the crystal lattice) is enough to nucleate the phase separation.

A question one might ask is whether the shift observed in *Figure 7* is due to the fact that the crystallization–melting transition is crossed several times or due to the increased annealing time at 150°C. *Figure 8* demonstrates that repeated cycling through the crystallization–melting transition results in a steady but decreasing shift to higher temperature and accounts largely for the effect seen in *Figure 7*. This implies that the relatively long annealing times add very little to the shift of the crystallization peak to higher temperatures and thus to the composition. This is in accordance with the observed fast kinetics of mixing. Apparently the composition that emerges after crystallization separation remains on annealing. Repetitive crystallization separation in subsequent cycles through the crystallization–melting transition then causes the linear-rich phase to become richer with every cycle. This explains the observed shift of the crystallization peak to higher temperature in both *Figures 7* and *8*. Annealing after subsequent cycles in *Figure 7* clearly does not lead to the same crystallization temperature as would have been expected from a simple two-component phase diagram. This indicates that the multicomponent system under investigation cannot be described in every detail with a simple two-component phase diagram.

As expected, there is only an effect on the position of the lowest part of the high-temperature peak since the dip is due to recrystallization during heating and the highest part of the high-temperature peak results from subsequent melting. Therefore, only the lowest part of the high-temperature peak represents melting of crystals formed during the previous cooling run.

CONCLUSIONS

The VLDPE material studied in this investigation behaves as a reactor blend showing liquid–liquid phase separation in the melt with upper critical solution temperature (*UCST*) behaviour.

Mixing occurs at high enough temperatures.

The dispersed phase (c.s.d.) in all TEM micrographs occurs as smooth, spherical domains. This symmetry argument points clearly to melt demixing as opposed to crystallization segregation. Melt demixing is supported by d.s.c. results showing that the crystallization temperature is raised on annealing above the melting temperature.

The demixing process of this material at 150°C is shown to be binodal in character. The spatial fluctuation in octene comonomer originating from crystallization segregation may nucleate the demixing.

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