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Phase separation in melt blends of single-site linear and branched polyethylene

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Abstract

The phase behaviour in the melt in blends of a single-site linear polyethylene and several single-site branched ethylene-1-alkene copolymers is examined, using an indirect technique based on examination of rapidly quenched melts in the solid state using differential scanning calorimetry, transmission electron microscope and atomic force microscopy. The extent of phase separation is found to have increased if the amount of comonomer in the branched blend component is increased. This result is observed for ethyl and butyl type short chain branches and found to be valid as long the amount of comonomer is less than approximately 5.0 mol%. For higher amounts of comonomer incorporation, the extent of phase separation is found to have approximately fixed. These observations might be partly predicted from theory if an extra repulsive potential is added to the ordinary Flory–Huggins equation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene blends; Single-site catalysts; Phase separation

1. Introduction

The phase behaviour in the melt in blends of linear polyethylene and lightly branched polyethylene has been studied extensively for the last two decades. In a recent work, the phase behaviour in the melt was investigated in several blends of a single-site linear polyethylene (LPE) and different single-site based ethylene copolymers, where the type of short chain branches (SCB) involved ethyl, butyl and hexyl branches [1]. The phase behaviour in the melt was studied using a technique that involves examination of rapidly quenched melts in the solid state using differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The extent of phase separation in the melt (i.e. how widespread in temperature and compositions the phase separation was found to be) was found to depend on the molecular weight of the blend components and the amount of SCB in the branched blend component. In particular, the extent of phase separation was found to be increased when the amount of comonomer in the branched blend component was increased (for fixed molecular weight, linear blend component and type of comonomer), in blends containing ethylene–hexene copolymers.

The effect of the amount of comonomer in the branched blend component on the extent of phase separation is further examined in this work. The observation in the ethylene–hexene blend system reported in Ref. [1] and briefly described above, is further studied and more data is added. In addition, results from blends containing ethylene–butene copolymers and ethylene–octene copolymers are included. These results are discussed in view of predictions from the Flory–Huggins equation.

2. Experimental

A low-molecular weight single-site LPE is employed in this work. This sample will be denoted LPE(26k) where 26k indicates that the molecular weight of the sample LPE(26k) is 26 000 g/mol. LPE(26k) is supplied from Borealis AS. Furthermore, three different single-site ethylene–butene copolymers are used. These copolymers are denoted EB, EB(5.3) and EB(7.7). The letters indicate that butene is used as comonomer, while the number in the parentheses

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gives the amount of comonomer (in mol%) in the copolymers (the amount of comonomer in EB was not determined due to a bimodal appearance of this sample). EB is a copolymer supplied from Borealis AS. EB(5.3) and EB(7.7) are EXACT copolymers from Exxon Chemicals, used as received. In addition, four different single-site ethylene–hexene copolymers are used in this work. These are denoted EH(1.8), EH(3.1), EH(4.0) and EH(4.9), where the letters and numbers in the parentheses are given for the same reason as the ethylene–butene copolymers. EH(4.9) is a commercial EXACT copolymer supplied from Exxon Chemicals, while EH(1.8) and EH(4.0) are copolymers made in the lab at NTNU in Norway. EH(3.1) is a copolymer supplied by Borealis AS. Finally, two different single-site ethylene–octene EXACT copolymer grades from Exxon Chemicals, denoted EO(4.8) and EO(7.4) are employed as received. The samples together with relevant information are listed in Table 1.

The weight-average molecular weight as well as the polydispersity were determined from GPC [1], while the amount of comonomer was determined from FTIR [1]. As already mentioned, one of the samples (EB) showed two separate melting peaks, a rather sharp 'linear' peak at 115.2°C and in addition, a broad melting peak at 100°C. The result from FTIR of this sample is somewhat meaningless, since the result represents an average of the comonomer content in each of the fractions that constitute the sample. The amount of comonomer in the 'linear' fraction in EB was instead judged to be 2.5 mol%.

All blends were made in solution in boiling xylene in various compositions from the LPE component and each of the copolymers.

A blend containing *x* wt% of LPE(26k) and *y* wt% of e.g. EB(5.3) will be denoted *x*/*y* LPE(26k)/EB(5.3). After precipitation in cold methanol, filtration, drying and vacuum treatment, a film, 50 μm in thickness was made in an IR film press.

Table 1
Characterisation of the single-site materials used in this work

	M_{w} (g/mol)[a]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[b]	T_{m} (°C)[c]	SCB (mol%)[d]
LPE(26k)	26 000	5	126.6	–
EB	110 000	4.2	115.2/100	
EB(5.3)	95 000	2.3	94.0	5.3
EB(7.7)	95 000	2.4	88.0	7.7
EH(1.8)	115 000	2.5	116.2	1.8
EH(3.1)	185 000	3.0	109.0	3.1
EH(4.0)	105 000	3.1	105.5	4.0
EH(4.9)	110 000	3.6	95.0	4.9
EO(4.8)	100 000	2.4	90.7	4.8
EO(7.4)	109 000	2.7	71.6	7.4

[a] Weight-average molecular weight determined from GPC.

[b] Polydispersity determined from GPC.

[c] Melting point determined from DSC after the samples were quenched from 170°C. The heating rate was 10°C/min.

[d] Amount of short chain branches (SCB) in mol% determined from FTIR.

Films for DSC were encapsulated into DSC sample pans, packed into one thin layer of aluminium foil and immersed in a silicone oil bath at a predetermined temperature. After 30 min the samples were quenched in methanol at its freezing point (−98°C). Films for AFM and TEM were put between thin glass cover, immersed into the oil bath and thereafter quenched. The films for TEM were thereafter treated in chlorsulfonic acid following the method by Kanig [2,3], while the films for AFM were treated in a mixture of potassium permanganate, sulphuric acid and orthophosphoric acid and thereafter washed according to published procedure [4]. A complete description of sample preparation and instrumentation is found in Ref. [1].

Based on observations from DSC, AFM and TEM, several morphology maps are created. The morphology map is simply a coordinate system, where the *x*-axis gives the amount (in wt%) of the linear component in the blend. The *y*-axis gives the temperature from which the melt was quenched. A particular blend, quenched from a particular temperature determines a coordinate (*x*,*y*) in the morphology map. The coordinate (*x*,*y*) will be written as an 'M' (mixed) in the morphology map if DSC, AFM and TEM results indicate that the particular blend is homogeneous in the melt prior to quenching. The letter 'S' will be used if the blend is believed to be separated in the melt prior to quenching.

3. Results

Morphology maps of the LPE/EB(5.3) and LPE/EB(7.7) blend systems are shown in Fig. 1. The only main difference between these blend systems is the amount of comonomer in the branched blend component. The molecular weight, type of comonomer and the linear blend component are fixed, and are therefore not believed to influence the results, shown

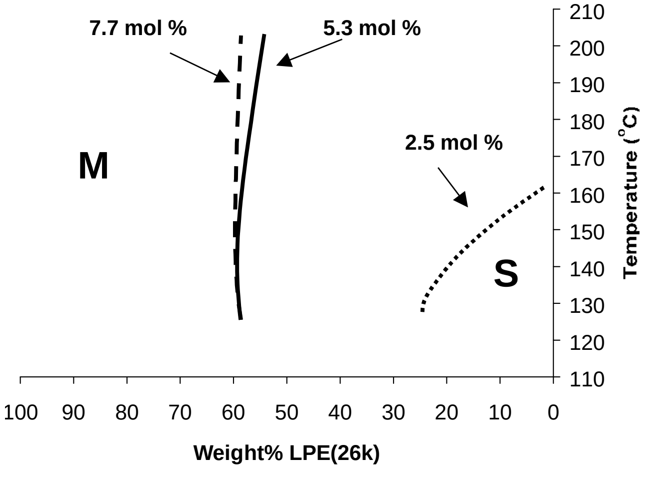

Fig. 1. Morphology maps of the blend systems LPE/EB(5.3) and LPE/EB(7.7). In addition, the extent of phase separation in the blend system LPE/EB is shown, when only the "linear" component in EB is considered.

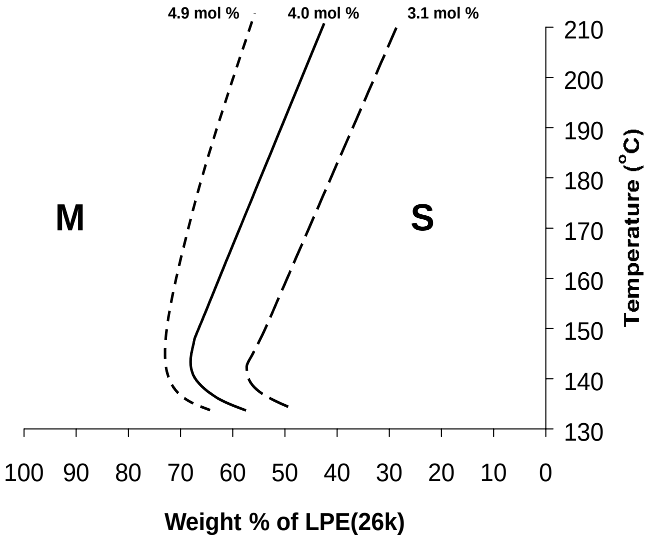

Fig. 2. Morphology maps of the blend systems LPE/EH(3.1), LPE/EH(4.0) and LPE/EH(4.9).

in Fig. 1, significantly. The morphology maps of these blend systems are believed to be equal within experimental errors. The extent of phase separation in the LPE/EB blend is very similar to the behaviour shown in Fig. 1. This is due to the presence of the fraction responsible for the broad melting peak at 100°C in the EB fraction. However, if only the 'linear' component in EB is examined, the amount of phase separation is found to be very limited (from DSC results), as shown in Fig. 1.

The extent of phase separation in the blends LPE/EB(5.3) and LPE/EB(7.7) is found to be wide in both composition and temperature, in agreement to results reported earlier [1].

An almost similar behaviour is observed in the blends containing ethylene–hexene copolymers. This is shown in Fig. 2. The main difference among the blends is the amount of comonomer in the branched blend component, however, the molecular weight of the EH(3.1) blend component is higher than the other two copolymers (see Table 1). However, since the molecular weights of these ethylene–hexene copolymers are above 100 000 g/mol, a difference in molecular weights among the copolymers is not expected to influence the extent of phase separation significantly [1]. As shown in Fig. 2, the extent of phase separation isobserved to be systematically reduced as the amount of comonomer in the branched blend component is reduced. In addition to the blend systems shown in Fig. 2, a morphology map of the LPE/EH(1.8) blend system was constructed. This blend showed no evidence of phase separation, i.e. the melt was found to be homogeneous.

The behaviour of the blends containing ethylene–octene copolymers are shown in Fig. 3. The extent of phase separation in the LPE/EO(7.4) blend system is found to be approximately equal to the phase separation observed in the LPE/EO(4.8) blend system.

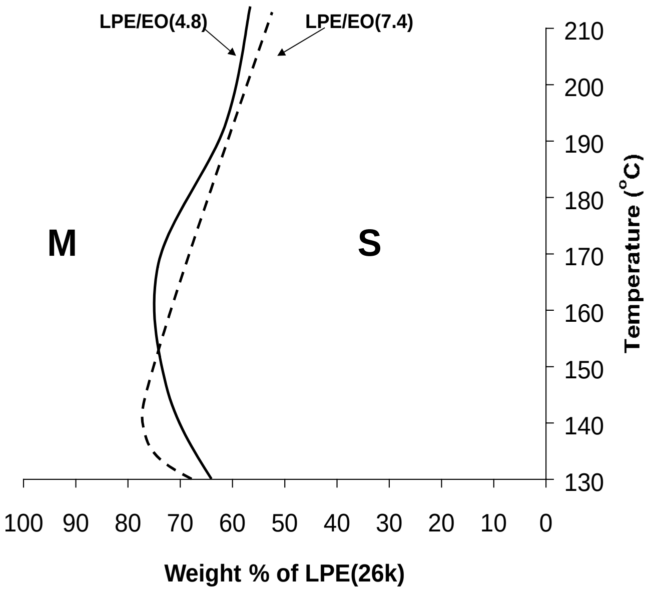

Fig. 3. Morphology maps of the blend systems LPE/EO(4.8) and LPE/EO(7.4).

4. Discussion

The results obtained in this work, presented above, and results presented elsewhere [1] are found to be quite different from results presented by others in three different aspects. Each of these aspects will be discussed briefly below. First, the extent of phase separation in most of the blends studied in this work is found to be significantly wider in both temperature and composition than reported by others (see e.g. Hill et al. [5]), on similar blend samples. This is in agreement with earlier work [1], where several moments were considered, to explain the discrepancy between the results reported there [1] and results reported by others [5].

Secondly, the extent of phase separation is found to be reduced when the amount of comonomer in the branched blend component is reduced, in ethylene–butene blend systems and in ethylene–hexene blend systems studied here. Quite a different conclusion has been reached by others on similar blend systems [6–9]. In those works, the extent of phase separation was found to have reduced when the amount of comonomer was increased in blends containing ethyl branches and in blends containing hexyl branches. It is claimed that such behaviour can be understood if an extra asymmetric free energy term is added to the Flory–Huggins equation [10]. However, the results from those works [6–9] are not based on blend samples manufactured by single-site technology, which is used solely by the authors of this paper. The behaviour observed in this work and elsewhere [1], furthermore suggests that the melt is homogeneous when the amount of comonomer is low enough, i.e. the linear blend component is found to be compatible with the branched blend component in the melt when the amount of branching is reduced below a certain value. A blend of two LPE will represent the extreme limit in this aspect, where the amount of comonomer is reduced to zero in the branched blend component. No indications of phase separation is observed in such blends, even for a significant difference in molecular weight among the blend components [1]. These results are in agreement with observations made by others [11], and are believed to support the results obtained here.

The third observation made in this work that differs from previously obtained results, is evident from the results shown in Figs. 1 and 3. In the ethylene–butene blend systems shown in Fig. 1 it is observed that an increase in the amount of comonomer beyond 5.3 mol% will only introduce a slight extension of the region of phase separation. Due to possible experimental errors, the extent of phase separation in these blends is believed to be equal. A similar behaviour is observed in the ethylene–octene blend system shown in Fig. 3. These results indicate that the extent of phase separation is more or less saturated when the amount of comonomer is approximately 5.0 mol% and will not increase significantly when the amount of comonomer is further increased. This result seems to be general, i.e. the effect appears in blends containing ethylene–butene copolymers, ethylene–hexene copolymers (not shown in Fig. 3, but observed in two blend systems containing hexene as the comonomer) and ethylene–octene copolymers.

In order to find out whether this effect was the result of non-equilibrium conditions in the melt, the samples were kept in the melt significantly longer than 30 min, which was the normal retention period. However, the results shown in Figs. 1–3 remained unchanged even when the samples experienced retention times of 2 h in the melt, prior to quenching.

A similar principal observation was made when effects of molecular weight on the extent of phase behaviour were explored [1]. It was then observed that the extent of phase behaviour in the melt increased significantly when the molecular weight of the branched blend component increased, for molecular weights below 100 000 g/mol. If the molecular weight of the branched blend component was increased beyond this value, the extent of phase separation was found to increase only slightly. The authors of this paper have no knowledge of similar results presented elsewhere.

4.1. A theoretical approach

In the previous discussion it was shown that the results obtained in this work and elsewhere [1] differ from results obtained elsewhere in three different ways. The influence of the amount of comonomer in the branched blend component to the extent of phase behaviour in the melt, for relatively low amounts of comonomer, represents one of these major differences. The extent of phase behaviour in the melt is found to be reduced as the amount of comonomer is reduced, as shown in Fig. 2. In what follows, this observation will be discussed in the light of predictions from theory. The behaviour shown in Figs. 1 and 3, referred to as saturation of the melt, will not be further discussed in this work.

The results shown in Fig. 2 are not expected from the free energy of mixing ΔG given by the Flory–Huggins expression [10]

$$\Delta G/kT = \chi\phi_1\phi_2 + (\alpha\phi_1/n_1)\ln(\phi_1) + (\beta\phi_2/n_2)\ln(\phi_2), \quad (1)$$

where χ is the interaction parameter, $\phi_1(\phi_2)$ is the concentration of the linear (branched) component and $n_1(n_2)$ is the degree of polymerisation of the linear (branched) component. α and β are constants (>1) introduced to account for entropy contributions from branches. k is the Boltzman constant, while T is the temperature. When the amount of comonomer is increased, by increasing the parameters α and β in Eq. (1), the free energy of mixing, determined from Eq. (1) shows a dependency of the composition of the blend as shown in Fig. 4. The curves are concave and slightly asymmetric placed towards the copolymer rich part of the blends. The latter observation is due to the difference in molecular weight of the blend components. No inflection points are present, and the blend components are therefore expected to be completely miscible in the blend [12].

The value of the interaction parameter was chosen to $\chi = 0.0002$, based on results obtained by others [13–23]. It is therefore clear that the results shown in Fig. 2 and indicated elsewhere [1] cannot be predicted from Eq. (1), with the chosen value of the interaction parameter (for any value of α and β (>1)).

In order to incorporate the results shown in Fig. 2, a different scheme will be suggested, in close analogy to a method described by Barham et al. [10].

An extra term is added to the Flory–Huggins Eq. (1) that is thought to be repulsive and asymmetrically placed towards the copolymer-rich side of the blends. However,

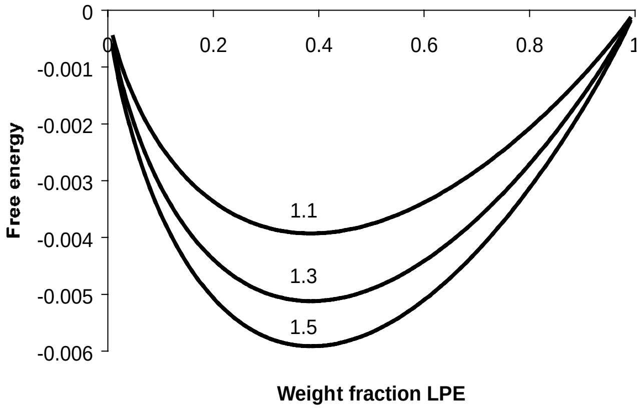

Fig. 4. The free energy of mixing determined in Eq. (1), given as a function of the amount of the linear component in the blend, for increasing comonomer content in the branched blend component. For simplicity, the α and $-\beta$ parameters were chosen to be equal and took values of 1.1, 1.3 and 1.5, as indicated on the curves. The interaction parameter was chosen to have a small positive value $\chi = 0.0002$. The degree of polymerisation for the linear (n_1) and branched (n_2) components were $n_1 = 100$ and $n_2 = 1000$.

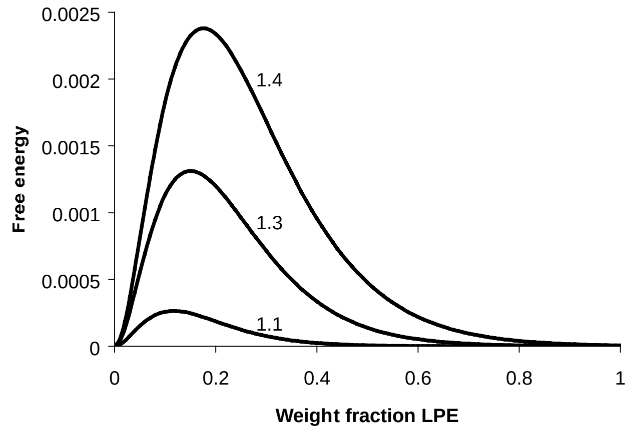

Fig. 5. The repulsive potential determined in Eq. (2), given as a function of the amount of linear component in the blend, for increasing amount of comonomer in the branched blend component. The constants c_1 and c_2 that appear in the expression of the potential are 10/7 and −19, respectively, while the α and $-\beta$ parameters were chosen to be equal and took values of 1.1, 1.3 and 1.4, as indicated on the curves.

in contrast to the work in Ref. [10], the potential is thought to be a function of both the composition of the blend and the amount of comonomer in the branched blend component.

It is furthermore assumed that the extra potential increases in strength and in 'range' (composition) as the amount of branches in the branched blend component increases. The behaviour of such an excess energy term is shown in Fig. 5, as a function of the composition in the blend for different amounts of branches in the branched blend component. The extra repulsive potential, denoted $\Delta G_{\mathrm{extra}}$ could be represented by the expression

$$\Delta G_{\mathrm{extra}} = c_1(\alpha - 1)\phi_1^2 \exp[c_2(2 - \alpha)\phi_1], \tag{2}$$

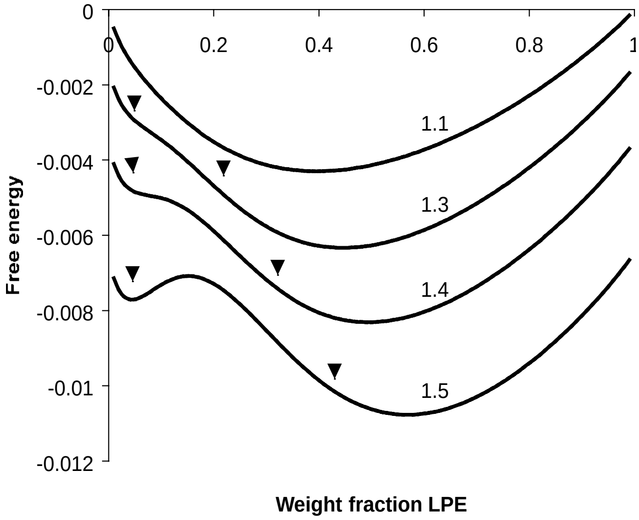

Fig. 6. The total free energy of mixing ΔG_{Tot} determined in Eq. (3), given as a function of the amount of the linear component in the blend, for increasing comonomer content in the branched blend component. The α and $-\beta$ parameters were chosen to be equal and took values of 1.1, 1.3, 1.4 and 1.5, as indicated on the curves.

where c_1 and c_2 are constants. The total free energy of mixing ΔG_{Tot} is thought to represent the sum of the contributions from each of the terms in Eqs. (1) and (2), i.e.

$$\Delta G_{\mathrm{Tot}} = \Delta G + \Delta G_{\mathrm{extra.}} \tag{3}$$

In Fig. 6, the total free energy of mixing, ΔG_{Tot} is shown as a function of the composition of the blend, for different amounts of branches in the branched blend component. When only small amounts of branches are present in the blend components ($\alpha = 1.1$ shown in Fig. 6), the curve is concave and the melt is thought to be homogeneous, in agreement to the behaviour observed in this work. However, when higher amounts of branches are present in one of the blend components, spinodal points are present. The melt is believed to be separated in the regions (indicated by arrows as shown in Fig. 6) between the spinodal points [12]. It is furthermore observed that the 'distance' (in terms of the amount of the linear blend component) between the spinodal points increases as the amount of branches in the branched blend component increases. The interpretation of this result is that the extent of phase separation is increased (in composition) as the amount of branches in the branched blend component is increased. This is in agreement to the experimental observations shown in Fig. 2.

5. Conclusions

In this work, quenched blends of a single-site based LPE with several different single-site ethylene-1-alkene copolymers are studied by DSC, TEM and AFM. The aim of this work has been to clarify how the amount of comonomer in the branched blend components affects the extent of phase separation in the melt in these blends. Based on the materials employed and the experimental procedures that are followed, the following conclusions are reached:

- The extent of phase separation is found to be increased if the amount of comonomer in the branched blend component is increased. This result is observed for ethyl and butyl type SCB and is found to be valid as long the amount of comonomer is less than approximately 5.0 mol%. For higher amounts of comonomer incorporation, the extent of phase separation is found to be approximately fixed.
- The extent of phase separation in the melt is found to be wider in both temperature and compositions than reported by others.
- These observations might be partly predicted from theory if an extra repulsive potential is added to the ordinary Flory–Huggins equation.

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