Thermal analysis of single-site polymers in binary blends of low-molecular-weight linear polyethylene and high-molecular-weight branched polyethylene

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Abstract

The cocrystallization phenomenon has been studied by blending a low-molecular-weight linear polyethylene (LPE) with a high-molecular-weight lightly branched ethylene–hexene copolymer, as a function of blend composition and cooling rate. The materials are based on single-site catalysts. Differential scanning calorimetry indicates that the upper limit on the degree of branches for cocrystallization with LPE is lower than observed in blends with Ziegler–Natta based materials, in accordance with results obtained by other authors on different single-site blend systems. The effect of the cooling rate on blends with low LPE content is probed, and the observed behaviour is discussed in light of earlier observations on similar blends. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polyethylene blends; Single-site materials; DSC; Ethylene-hexene copolymers; Cocrystallization

1. Introduction

The occurrence of cocrystallization in blends of linear polyethylene (LPE) and linear low density polyethylene (LLDPE) has attracted great interest during the last two decades [1–24], mainly because of a growing commercial interest due to the enhanced mechanical properties observed in such blends, and the need to obtain a more fundamental understanding of the morphological aspects that govern the phenomenon of cocrystallization. Much of the work has been

focused on blends where the molecular weight of the components is similar and the LLDPE is a lightly branched ethylene-butene copolymer [1–12], but work with other copolymers or varying molecular weights have also been reported [13–19]. Even though there are some discrepancies in the results reported by these authors, it seems to be possible to draw some conclusions regarding the phenomenon of cocrystallization. The molecular weight of the components in the blends seems only to be of secondary importance in determining the occurrence or extent of cocrystallization [20,21], which also seems to be the case for the type of short chain branches (SCB) [21,22]. However, there are no systematic studies that finally puts an end to this discussion, and the possibility of effects due to molecular weight and type of branching will probably

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be debated further. On the other hand, the amount of SCB seems to be an important factor [1–9,21,22]. This factor, together with the crystallization conditions, more or less determines whether or not and to what extent cocrystallization occurs. Tashiro et al. [1–9] report cocrystallization for all blend compositions in blends of LPE with a commercial LLDPE, containing 3.4 mol% ethyl SCB. By increasing the content of SCB to 8.2 mol%, separate crystallization of the two components is found to be the dominant mechanism. Also work by Alamo et al. [21] supports the importance of the branching content. However, most of the work performed by the aforementioned authors has included highly polydisperse materials, and it is well known that conventional Ziegler–Natta (Z–N) LLDPE shows a considerable compositional heterogeneity. A few workers have utilized model LLDPE samples, the hydrogenated polybutadienes [21,23], which have a narrow molecular weight distribution (MWD), but still the use of these blends as models suffers from the heterogeneity in the short chain branching distribution (SCBD). It has in fact been argued [23] that blends of LPE with a Z–N LLDPE should be viewed upon as containing a continuum of components, with branching content from zero (LPE) and upward, and it is therefore very difficult to determine which component of LLDPE takes part in the cocrystallization. The possibility of segregation in LLDPE is also present. It is therefore reasonable to expect that a LLDPE with narrow MWD and uniform short chain branching distribution (SCBD) will behave differently upon crystallization than Z–N LLDPE. The introduction of single-site catalysts have made it possible to synthesise LLDPE with a narrow MWD and almost uniform SCBD. Blends containing single-site materials should therefore be well-suited to omit the problems occurring in blends with Z–N materials, as mentioned above. In recent work, Zhao et al. [24] report cocrystallization for all blend compositions in blends of LPE with a single-site ethylene-octene copolymer containing 0.72 mol% SCB. By increasing the content of SCB to 1.4 mol%, cocrystallization is found to occur when the content of LPE is higher than 50%, and by further increasing the content of SCB to 4.8 mol%, no cocrystallization is observed. Therefore, Zhao et al. conclude that the upper branching limit still allowing cocrystallization to occur probably is much lower in blends with single-site materials, than in blends with Z–N

based materials. Zhao et al. argue that in conventional Z–N LLDPE there exists long segments between branches that can easily cocrystallize with LPE, but the more uniform SCBD in single-site LLDPE makes cocrystallization more difficult. As a continuation of the work reported on blends of single-site based materials, studies on samples prepared by blending a single-site low-molecular-weight LPE with different single-site high-molecular-weight LLDPEs, with hexene as comonomer, is presented. Differential scanning calorimetry is used to examine the blends, and the interpretation of a single melting point is discussed. The conclusions reached by Zhao et al. [24] on octene-based systems are found to be valid also for hexene based systems. Furthermore, the effect of cooling rate is studied on blends with low LPE content, and the observed phenomenon are discussed and compared to observations and comments made by others. The authors of this paper wish to emphasise that the results obtained on the blend systems reported here only should be taken as first indications of the behaviour of the systems, and merely work as an introduction to the blend systems. The DSC results reported here will be supported by TEM, AFM and optical microscopy measurements which will be reported in separate papers.

2. Experimental

A low-molecular-weight LPE has been blended with three different high-molecular-weight ethylene–hexene copolymers, denoted LLDPE(1), LLDPE(2) and LLDPE(3). The samples are based on the single-site technology, and kindly supplied from Borealis, Finland as experimental quality materials. Relevant characteristics of the samples are presented in Table 1. Blends with varying LPE content were made by dissolving both components (total amount of 1 g in 50 ml boiling xylene) under constant stirring for at least 30 min followed by precipitation in an excess amount (300 ml) of methanol, a non-solvent. After filtering and repeated washing sequences in methanol, the fluffy material was ground into small pieces. In this way, the total surface of the material is increased, making diffusion of remaining xylene out of the material easier. The material was then dried overnight in an oven at 60°C and thereafter 48 h in a

Table 1
Characteristic data for the single-site materials used in the study

	LPE	LLDPE(1)	LLDPE(2)	LLDPE(3)
Mw (g/mol)	22 650	121 500	132 000	77 000
Density (g/cm^3)	0.9728	0.9295	0.9267	0.9159
Mw/Mn	4.2	3.0	3.1	2.0
Type SCB	–	Butyl	Butyl	Butyl
SCB content (mol%)	–	1.2	1.6	3.6

vacuum oven at 60°C. Films for DSC. were made in a Schwabenthan polystat 200T press at 160°C, by allowing the fluffy polymeric material to melt in the press, followed by a pressure sequence of a few seconds and thereafter allowing the film to cool in air. Identical disks of 1–2 mg were encapsulated in DSC aluminium pans. Thermal behaviour was performed using a Perkin-Elmer DSC-7 flushed with nitrogen The aluminium pans were equipped with holes allowing any remaining xylene to be effectively transported away by the inert nitrogen atmosphere during the first heating scan in DSC. The second run was recorded, in order to eliminate any effect of the thermal history. The results obtained by allowing more than two runs did not deviate from the second run. Calibration was regularly checked against the onset melting temperature of a pure indium sample. The melting temperature of the samples were identified with the maximum in the endothermic peak.

3. Results and discussion

The DSC melting curves for the pure components as well as 25/50, 50/50 and 75/25 blends of LPE with LLDPE(1) are shown in Fig. 1. The heating- and cooling rates applied were 10°C/min, and the second run is recorded. The measured curves indicate that cocrystallization takes place to some extent in the blends. This is seen by noting that the original melting peaks of the components in the blends disappear and are replaced with a single peak with a melting point in between those of the two original peaks. However, even though the 25/75 blend only shows one single melting peak, it is clear from Fig. 1 that the peak is rather broad and extends far into the low-temperature region. It is therefore suggested that this broad peak consists of two separate melting peaks. The low-

temperature peak will represent the LLDPE(1) component while the high-temperature peak will represent an LPE-rich component. Several authors [20,22] have pointed out that the observation of a single peak in the DSC is a necessary, but not sufficient argument for cocrystallization. The possibility of overlapping peaks is always present in DSC traces, especially when the separation between the melting points of the original components is small, as is the situation for LPE and LLDPE(1) reported here. By applying DSC samples of small mass (1–2 mg) being equal in size, any effects of thermal lag among the samples will most probably be eliminated. Furthermore, the use of sample pans equipped with holes will probably eliminate any effects of remaining xylene. These two factors will make the DSC results easier to interpret. It is therefore believed that the extent of cocrystallization is limited
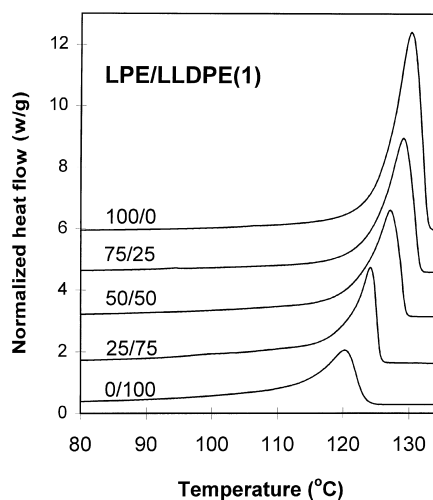

Fig. 1. DSC melting curves showing blends of LPE/LLDPE(1) for the following compositions; 0/100, 25/75, 50/50, 75/25 and 100/0. The heating and cooling rates applied were 10°C/min.
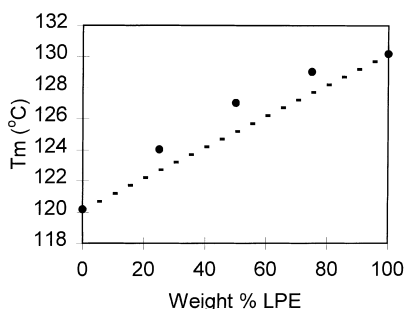
Fig. 2. Melting point Tm (●) plotted versus wt.% LPE in the LPE/ LLDPE(1) blend The straight line segments (-) represent the expected behaviour if perfect cocrystallization was the dominate crystallization mechanism.

Fig. 3. DSC melting curves showing blends of LPE/LLDPE(2) for the following compositions; 0/100, 25/75, 50/50, 75/25 and 100/0. The heating and cooling rates applied were 10°C/min.

in the 25/75 and 50/50 blends of LPE and LLDPE(1). The broad tails of these blends are most probably due to the existence of two crystal populations having almost the same melting point. Some degree of cocrystallization is however present due to the depression of the apparent single melting peak compared to the pure LPE peak. For higher LPE content, as shown in 75/25, there are no indications of a second component, which means that cocrystallization most probably is the dominant crystallization mechanism. Furthermore, by plotting the melting point versus LPE content a deviation from a straight line is found, where the straight line illustrates the expected behaviour if perfect cocrystallization was the dominate crystallization mechanism in these blends. The observed deviation therefore illustrates that the extent of cocrystallization is limited in these blends. This is shown in Fig. 2.

Similar behaviour is found in the LPE/LLDPE(2) blend system, as shown in Figs. 3 and 4. In these blends it is more obvious that cocrystallization only occurs to a limited degree which is expected since LLDPE(2) has a higher content of SCB than LLDPE(1). DSC melting curves for the pure components as well as the blends containing 25%, 50% and 75% LPE in blends of LPE/LLDPE(3) are shown in Fig. 5. The pure LLDPE(3) in 0/100 shows a melting peak at 116°C and a second broad peak ranging from about 30°C with a maximum at 101°C. Based on this observation it is suggested that LLDPE(3) consists of a fraction with a relatively low content of comonomer, responsible for the highest melting peak, and a fraction with higher comonomer content melting at a much broader temperature range. The actual content
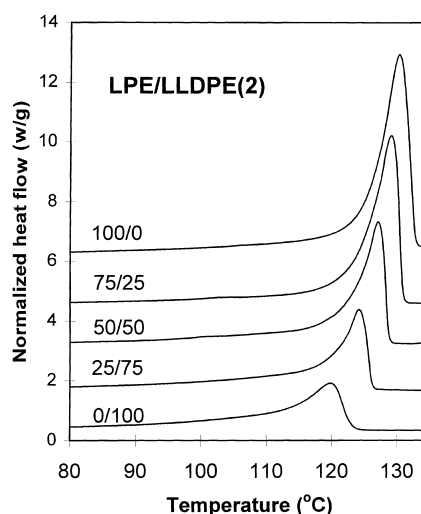
and distribution of short chain branches of LLDPE(3) will be determined later using a fractionation technique followed by examination by nuclear magnetic resonance (NMR). Even though an NMR characterisation of the two fractions in LLDPE(3) is not performed, the average content of SCB in LLDPE(3) is known to be 3.6 mol%. Judged from the partial areas of the two fractions in LLDPE(3) as shown in 0/100 in Fig. 5, and the observed melting points of the fractions as compared to the melting points of LLDPE(1) and LLDPE(2), the comonomer content in the fraction of
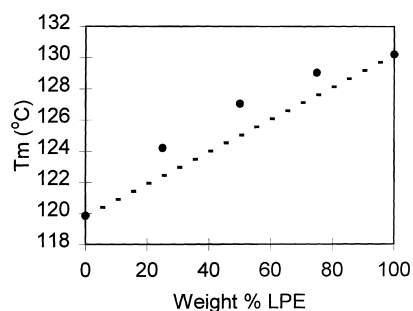

Fig. 4. Melting point Tm (●) plotted versus wt.% LPE in the LPE/ LLDPE(2) blend. The straight line segments (-) represent the expected behaviour if perfect cocrystallization was the dominant crystallization mechanism.
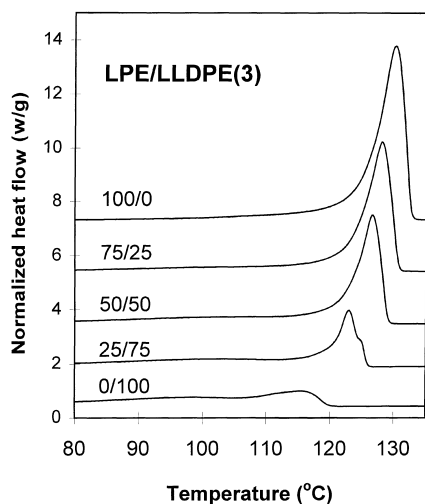
Fig. 5. DSC melting curves showing blends of LPE/LLDPE(3) for the following compositions; 0/100, 25/75, 50/50, 75/25 and 100/0. The heating and cooling rates applied were 10°C/min.

behaviour is shown better in Fig. 6. A 50/50 blend of LPE/LLDPE(3) is obtained by precipitation from a xylene solution, and a simple 50/50 mixture of LPE and LLDPE(3) is obtained by packing film of the two species in the same DSC sample pan. As seen in Fig. 6, the mixing reveals the two separate components in the blend, LPE and LLDPE(3). The blend, however, shows one sharp melting peak in between the original LPE and the component of LLDPE(3) with the highest melting point. Fig. 6 also indicates that the component of LLDPE(3) with the lowest melting point is rather undisturbed by the blending. Furthermore, due to a lower melting point than LLDPE(1) and LLDPE(2), the fraction of LLDPE(3) with the highest melting point probably has a higher content of SCB than LLDPE(1) and LLDPE(2). It is therefore expected that the extent of cocrystallization is further reduced for low LPE content in the LPE/LLDPE(3) blend system. This is in fact observed in Fig. 5, where the blend with 25% LPE shows a shoulder on the high melting peak, indicating that separation among the components exists to some extent. By further reducing the amount of LPE in the blends, the separation of the peaks becomes more obvious, as seen in Fig. 7. Again a cooling/heating rate of 10°C/min was applied. Some degree of cocrystallization is, however, also present in these blends due to the observed depression of the melting point of the LPE component.

LLDPE(3) with the lowest melting point is estimated to be 4–5 mol%. The melting curves in Fig. 5 further suggest that the component of LLDPE(3) with the highest melting peak is able to cocrystallize with LPE to some extent, when the content of LPE is 50% and higher. However, the component of LLDPE(3) which has the highest comonomer content (lowest melting point) is almost undisturbed by the blending. This
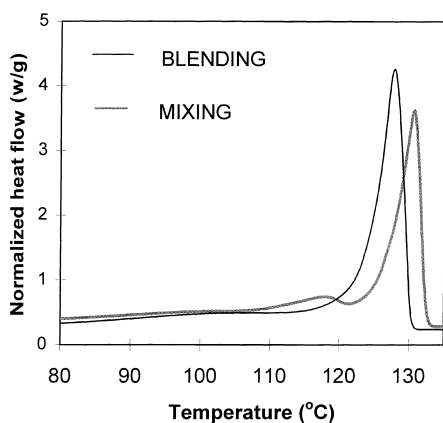

Fig. 6. Comparison of DSC melting curves between a 50/50 blend of LPE/LLDPE(3) and a 50/50 mixing of LPE/LLDPE(3). The blend is made in a common solution while the mixing is obtained by packing film from the two components in the same DSC sample pan. The heating and cooling rates applies were 10°C/min.
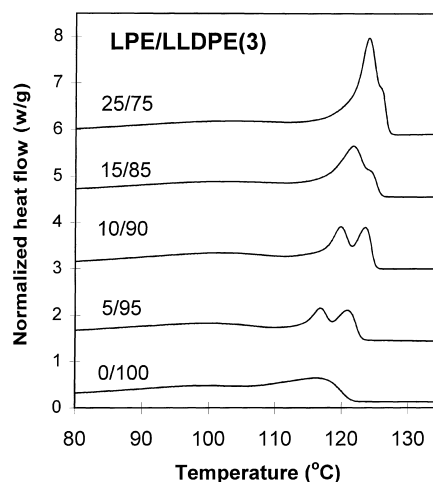

Fig. 7. DSC melting curves showing blends of LPE/LLDPE(3) for the following compositions; 25/75, 15/85, 10/90, 5/95 and 0/100. The heating and cooling rates applied were 10°C/min.

In summary, the results from DSC indicate that when the amount of SCB in blends of LPE and ethylene–hexene copolymers is 1.2 mol%, cocrystallization is only possible to some extent, and is more limited for low LPE content than for high LPE content. By increasing the amount of branching to 1.6 mol%, this behaviour becomes more obvious, i.e. the extent of cocrystallization is further reduced. If the branching content is increased to 4–5 mol%, the extent of cocrystallization seems to be very limited, if present at all, for all blend compositions. In the introduction, results by Zhao et al. [24] were reported, indicating that the branching limit still allowing cocrystallization probably was lower for single-site materials than for Z–N materials. The results on low-molecular-weight LPE/high-molecular-weight ethylene–hexene copolymer blends reported in this paper seem to be in agreement with this.

The remaining part of this paper will be considered with the behaviour observed when the cooling rate in the LPE/LLDPE(3) blend system is varied. As is seen in Fig. 7, the blends with low LPE content show two sharp melting peaks in addition to one broad melting peak at lower temperature. This behaviour is shown to be unaltered upon several cooling- and heating scans at 10°C/min. However, by reducing the cooling rate, the separation of the two sharp peaks is found to be reduced and disappears completely when a low enough cooling rate is applied, which seems to be 1°C/min in this case. This is seen in Fig. 8 for the 10/90 LPE/LLDPE(3) blend and Fig. 9 for the 5/95 LPE/LLDPE(3) blend. A further reduction of the cooling rate to 0.5°C/min or using higher cooling rates than indicated in Figs. 8 and 9 will not alter the behaviour any further. The results are rather surprising, since it is expected that some separation eventually will occur if the cooling rates are low enough. Morgan et al. [25] have commented on the dependence of cooling rate for blends of low-molecular-weight LPE with high-molecular-weight branched PE, where the temperature range for crystallization is very similar for the two components. It is expected that such blends will not separate even when a very low cooling rate is applied (usually 1°C/min). This is, however, not compatible with the behaviour observed here, since a separation at higher cooling rates (e.g. at 10°C/min in Fig. 8) is observed which disappears when the cooling rate is lowered.
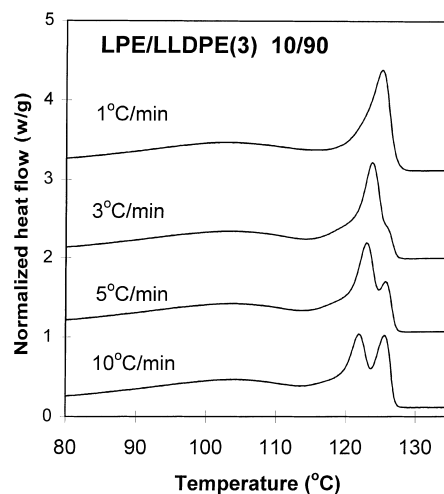

Fig. 8. DSC melting curves showing a 10/90 blend of LPE/LLDPE(3) after applying the following cooling rates: 1°C/min, 3°C/min, 5°C/min and 10°C/min. The heating rate applied was 10°C/min.

In what follows, some other possible qualitative explanations for the observed peak multiplicity and their dependency on the cooling rate will be given, based on comments and observations made by others. Behrstein and Egorov [26] have entered several reasons which can explain the presence of two or more
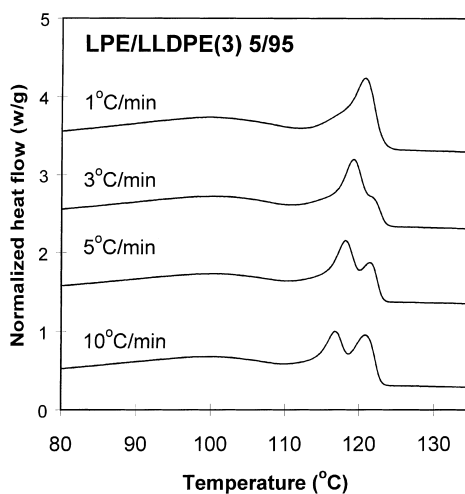

Fig. 9. DSC melting curves showing a 5/95 blend of LPE/LLDPE(3) after applying the following cooling rates: 1°C/min, 3°C/min, 5°C/min and 10°C/min. The heating rate applied was 10°C/min.

endothermal peaks in DSC, and they state that reorganisation and recrystallization are the most common reasons for the observed multiplicity. However, recrystallization, which means a partial or complete melting of the initial lamellae followed by recrystallization, creating larger lamellae melting at higher temperatures, is unrealistic since the temperature difference between the two peaks (e.g. at 10°C/min in Fig. 8) is very small. The presence of secondary crystals formed by low-temperature annealing is for the same reason unrealistic On the other hand, structural reorganisation which means a thickening of the thinner lamellae in the solid state prior to melting, becomes more important when approaching the melting point. By applying a lower cooling rate the system becomes closer to its equilibrium state and less reorganisation is present in the following heating scan. Reorganisation during melting could therefore be able to explain the observed phenomenon in Fig. 8. The observation of two melting peaks can furthermore be explained by the presence of crystals of varying structure and/or size [26]. However, the multiplicity is then expected to be enhanced instead of disappearing upon lowering the cooling rate. Therefore any structural- or thickness distribution of a cocrystal formed from LPE and the fraction of LLDPE(3) with the highest melting point, cannot explain the observed dependency of the cooling rate. Another explanation could be given from the LLDPE(3) component alone, i.e. a cocrystal made partly from the component with the highest amount of comonomer in LLDPE(3) and partly from the component with the lowest amount of copolymer in LLDPE(3). This was suggested in an early work of Datta and Birley [13], who observed a cooling rate dependency in an octene-based LLDPE similar to the observations presented in Figs. 8 and 9, and explained the behaviour by the limited diffusion time when the cooling rate applied was 10°C/min. However, LLDPE(3) alone does not show a cooling rate dependency as the LPE/LLDPE(3) blends do for low LPE content, and therefore the blends need to be considered. A related explanation could then be given by arguing that one of the two sharp peaks (for 10°C/min in Fig. 8) is the result of cocrystallization between a fraction of LPE and the fraction with the lowest amount of comonomer in LLDPE(3), and the second peak is the result of cocrystallization between LPE and the fraction of LLDPE(3) with the highest amount of

comonomer, where the latter peak came into being as a consequence of the limited diffusion time when the applied cooling rate was 10°C/min. By reducing the cooling rate, the two components have got time enough to separate, and one of the peaks disappear, as seen in Fig. 8 or Fig. 9. However, since the fraction of LLDPE(3) with the highest amount of comonomer probably contains as much as 4–5 mol% SCB, the possibility of cocrystallization of this fraction with LPE seems rather unrealistic, in light of the results given above and results presented by others [24].

Hill and Barham [27] have studied blends of LPE/ethylene–hexene copolymer for low LPE content (10% LPE), and based on observations by DSC and TEM upon quenching from the melt, Hill and Barham suggest that there exists three temperature bands in the melt. Upon quenching from 180°C and higher, their results support that the morphology is indicative of crystallization from a mixed melt, upon quenching from 170–125°C, the results indicate crystallisation from a separated melt, and from 120°C and below, the results are again indicative of crystallization from a mixed melt. Furthermore, they claim that the results obtained by others, when applying various cooling rates, can be explained in view of such a temperature-band scheme. In this way, Hill and Barham explain an observed segregation on slow cooling (0.5°C/min), in a 10% LPE/ethylene–hexene copolymer blend, from 150°C by the high crystallization temperature when such a low cooling rate was applied. As a consequence, the melt did not reach the remixing temperature before it crystallized.

The observed behaviour in the LPE/LLDPE(3) blend system reported in this paper, could in fact be explained by allowing the melt to be divided into several temperature zones, following the ideas presented in [27]. The single peak observed for low LPE content in LPE/LLDPE(3) blends, when a low cooling rate is applied (Fig. 8) could then be explained by crystallization from a mixed melt. The crystallization took place at 115°C, a temperature thought to be higher than the lower remixing temperature where the melt turns from a mixed state to a separated state. The observed segregation when a higher cooling rate is applied (10°C/min) could be explained by crystallization from a separated melt, since the crystallization now took place at 104.3°C, a temperature thought to be lower than the lower remixing temperature (the

crystallization temperatures stated above are collected from the crystallization traces not shown in this paper). However, the authors of this paper wish to emphasise that the observed separation presented here could as well be the result of a crystallization-induced separation, due to differences in crystallization kinetics of the two components in the blend. Therefore, the observed separation could also be the result of crystallization from a mixed melt at different crystallization temperatures. As a consequence, both the observed cocrystallization for 1°C/min in Fig. 8, and the separation shown for 10°C/min in Fig. 8, could be the result of crystallization from a mixed melt at different crystallization temperatures.

4. Conclusions

Based on the previous discussion it is concluded that the lower limit on the branching content still allowing for cocrystallization in blends of single-site LPE and single-site lightly branched ethylene–hexene copolymers probably is lower than observed from corresponding blends with Z–N materials, in accordance with results obtained by others [24] on single-site LPE/ethylene–octene comonomer blends.The observed dependency of the cooling rate for the LPE/LLDPE(3) system for low LPE content is not readily explained from earlier observations. A study of the crystallization kinetics of the two components in the blends could probably explain the observed phenomenon, even though an explanation from a division of the melt into several temperature bands according to whether the melt is mixed or separated seems to be possible and deserve more attention. Also, possible effects due to reorganisation during the heating scan could be important.

Acknowledgements

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