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THERMAL BEHAVIOUR OF BLENDS OF HDPE WITH LONG-CHAIN BRANCHED HBPE

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Abstract

The thermal behaviour of new blends on the base of high-density polyethylene (HDPE) and of long-chain branched polyethylenes (HBPE) made by means of new metallocene catalysts has been studied by DSC in relation to the melting and crystallisation characteristics and discussed in the phase behaviour of the mixtures.

While HBPE's with 7.5 to 12 per cent by mass of octene as comonomer in the blends with HDPE are relevant for the formation of homogeneous composition regions. Especially, with higher HBPE contents, the phase separation and splitting of the melting and crystallisation peaks is observed. This behaviour has not been observed with 2 per cent by mass of octene in HBPE.

The dependence of the melting and crystallisation temperatures of HDPE/HBPE blends on the octene content of the HBPE's for constant composition of mixtures have been shown for both the homogeneous and heterogeneous mixing.

Blends of a high-molecular HDPE and a HBPE resulted in a reduction of the composition range not effected by phase separation.

Keywords: blends of HDPE with long-chain branched HBPE, differential scanning calorimetry, ethylene/octene copolymers, melting and crystallisation behaviour

Introduction

In recent years, the development of new catalysts on the base of specific metallocenes has led to new ethylene homopolymers and copolymers. Compared with the polymers prepared with common metallo-organic catalysts, these polymers have a rather narrow molecular weight distribution and a high uniformity of distribution of the comonomers both in the individual polymer chain and in the overall molecular weight range. Considerably higher contents of α-olefins can be incorporated into the polymer chain and long-chain α-olefins can be more efficiently be copolymerised [1–3].

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In this case, polyethylenes with long-chain branches are accessible by using bridged amidomonocyclopentadienyls as a catalyst which, in comparison to the low-density polyethylenes (LDPE), have a reduced number of long-chain branches which are nearly linear [3–6]. Blends of such long-chain branched polymers with high-density polyethylenes (HDPE) are expected to show new and interesting properties, in particular with relation to their thermal behaviour and the formation of different phases. Whereas, in general, blends of HDPE and LDPE form different and separate crystalline structures during the cooling of the melt and hence, these blends are not miscible, blends of HDPE and linear low-density polyethylenes (LLDPE) show cocrystallisation and a certain miscibility [7, 8]. The thermal behaviour of HDPE blends containing these new long-chain branched polyethylenes are expected to be in their phase behaviour between that of HDPE/LDPE blends and HDPE/LLDPE blends. These polymers shall be examined in detail in the following.

Since these new long-chain branched polyethylenes can imply the usual terms of HDPE, LLDPE and VLDPE because of the potential comonomer content, and polymers with densities considerably lower than 0.90 g cm^{-3}, the term HBPE for homogeneously branched polyethylene understood as a rather homogeneous comonomer distribution along the macromolecule (in difference to LLDPE) and the existing rather linear long chain branches seems to be helpful and will be used in this paper for these copolymers of ethylene with higher α-olefins.

Experimental

Materials

HDPE

The high-density polyethylene used was an ethylene copolymer prepared with the 1-butene comonomer through the vapour-phase process and a short-chain branching degree of 0.48 CH_3/100 CH_2 (HDPE 1) as well as an analogous high-molecular product (HDPE 2) with a short-chain branching degree of 0.06 CH_3/100 CH_2. The short-chain branching degree was determined by the FT-IR spectroscopy. The properties of these high-density polyethylenes and the molecular weight parameters determined by size-exclusion chromatography (SEC) at 135°C in 1,2,4-trichlorobenzene are given in Table 1.

HBPE

The polymers used as homogeneously branched polyethylenes are long chain branched ethylene copolymers with 1-octene as comonomer (AFFINITY polyolefin plastomers of the DOW Chemical Corporation) prepared through a high-

Table 1 Properties of the blend components

Property	Method	Unit	HDPE 1	HDPE 2	HBPE 1	HBPE 2	HBPE 3	HBPE 4
Octene content	ASTM- D-2238	wt%			9.5	2.0	7.5	12.0
MFI	190°C, 21,2N ASTM- D-1238	g 10 min^{-1}			1.05	2.5	1.01	1.05
MFI	190°C, 212 N ISO 1133	g 10 min^{-1}	14.0					
Viscosity number	ISO 1191	cm^3 g^{-1}	310	727				
Density	23°C ISO 1183	g cm^{-3}	0.943	0.948				
Density	ASTM-D-792	g cm^{-3}			0.909	0.935	0.914	0.902
$\overline{M}_w$	SEC	g mol^{-1}	206 000		96 700	82 500	97 800	111 000
$\overline{M}_w/\overline{M}_n$	SEC		18.7		2.86	2.52	2.60	2.69

temperature low-pressure solution process using single-site catalysts. The properties of these ethylene polymers and the molecular weight parameters are also presented in Table 1.

Methods

Sample preparation

The polymer blends of HDPE and HBPE were prepared by intensive homogenisation of the components in a Berstorff twin-screw extruder. The ratio between screw length and screw diameter L/D was 32 and the screw speed 400 rpm.

The mixtures prepared by homogenisation of HDPE and LLDPE in a twin-screw extruder were mixtures with the highest homogeneity compared to the mixing processes in solution and subsequent precipitation or the preparation in a roll mill [9].

For stabilisation, 0.299 per cent by mass of a mixture of equal percentage by mass of pentaerythrityl-tetrakis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] and tris-(2,4-di-tert-butyl phenyl) phosphite were added. The average melting temperature was 210°C, for the high-molecular HDPE 2 up to 236°C.

DSC

The temperatures typical of the melting and crystallisation behaviour of the polymer blends and the enthalpies were determined by the Perkin Elmer DSC-2C. The device was calibrated with indium (156.6°C) and tin (231.9°C) for the temperature and with indium (H=28.62 J g^{-1}) for the heat in accordance with the recommendation by the Gesellschaft für thermische Analyse e.V. (Thermal Analysis Association) 'Kalibrierung dynamischer Kalorimeter' (calibration of dynamic calorimeters).

The polymer blends were examined in the DSC-2C under the following conditions:

Weighed proportion	6–8 mg
Specimen pan	aluminium
Purge gas	20 ml of argon/min
Coolant	dry CO_2/ethanol mixture
Heating rate	10 K min^{-1}
Cooling rate	10 K min^{-1}

The typical temperatures and heat of the melting and crystallisation of polymer blends were determined by evaluating the peaks on the above mentioned basis.

The peak heights were determined in the DSC curves manually.

Results and discussion

The thermal behaviour of HDPE blends with long-chain branched HBPE polymers was studied at low and high octene concentration over the total composition range of the blends. For certain compositions, the studies were carried out as a function of the octene concentration as well as for a system containing a high-molecular HDPE and a HBPE of an average octene concentration.

Influence of HDPE/HBPE blend composition

HBPE blends with high octene content

The effect of the composition of blends of HDPE 1 and HBPE with 9.5 per cent by mass of octene (HBPE 1) on the melting behaviour of the mixtures is shown in the DSC curves of the second heat run cleared by the influence of the

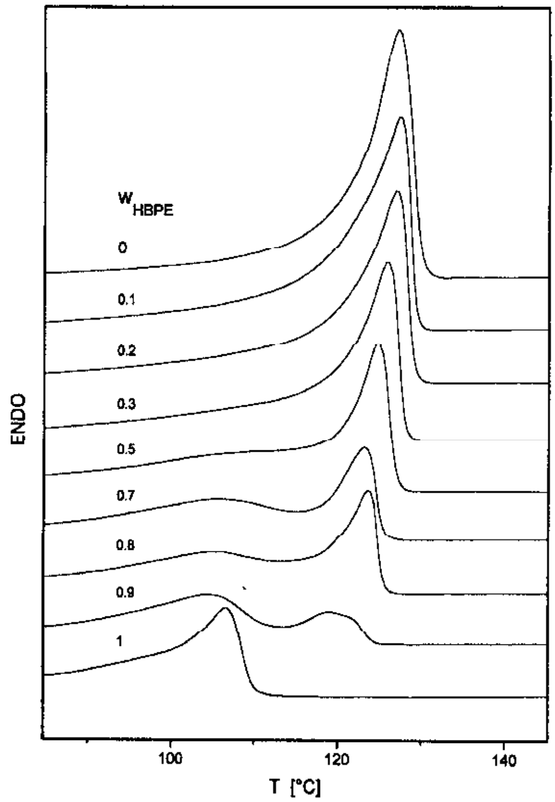

Fig. 1 Endothermal melting peaks of the blends of HDPE 1 and HBPE 1 (9.5 per cent by mass of octene) as a function of the mass fraction of HBPE (w_{HBPE}) in the mixtures (second heat run)

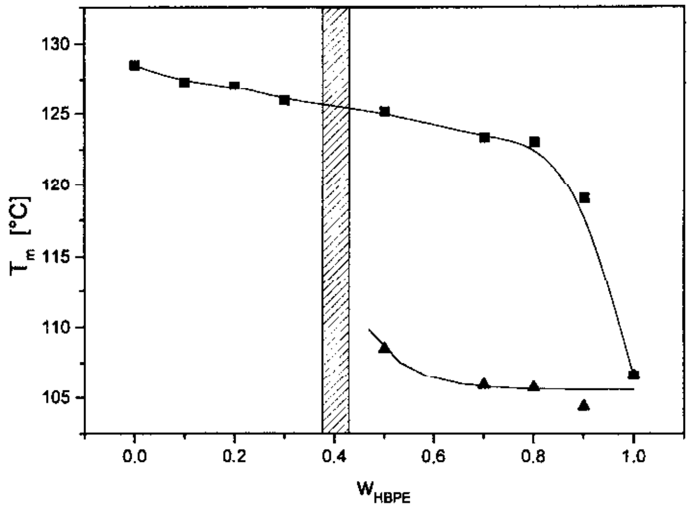

Fig. 2 Dependence of the melting temperature maxima (T_m) of the HDPE 1/HBPE 1 system (9.5 per cent by mass of octene) on the composition (w_{HBPE}: mass fraction of HBPE, second heat run)

thermal pretreatment during blend preparation, Fig. 1. From the curves with samples containing only a small HBPE content in the polymer blend only one endothermal melting peak in the temperature range relevant for the investigation of the blend characteristics can be found, another melting peak clearly appears starting with a composition of 50 per cent by mass of HBPE. The specific position of these maximum melting temperatures as a function of the blend composition can be seen in Fig. 2 for the second heat run. Whereas the joint melting peak of the blend components at a HBPE concentration below 50 per cent by mass decreases only underproportionally, the splitted melting peaks observed with a high HBPE content show quite a different shape. The upper melting peak is relatively constant with an increasing HBPE quantity at the previous temperature level and dramatically decreases only with more than 80 per cent by mass of HBPE towards the melting temperature of the pure HBPE. However, the lower melting peak steeply decreases and remains relatively constant at the pure HBPE level. A similar behaviour is found with the first heat run.

The peak heights of the endothermal melting peak as a function of blend composition are plotted in Fig. 3. Initially, the peak height of the pure HDPE component slightly increases by the addition of small HBPE quantities. With increasing HBPE content, however, it continuously decreases. The peak height of the reappearing endothermal melting peak at lower temperatures increases with an increasing HBPE content, in particular at high HBPE concentrations. The values of the higher melting peak are always above the values which are expected as a result of the additive capacity of the components and the values of the lower melting peak are always below those values expected.

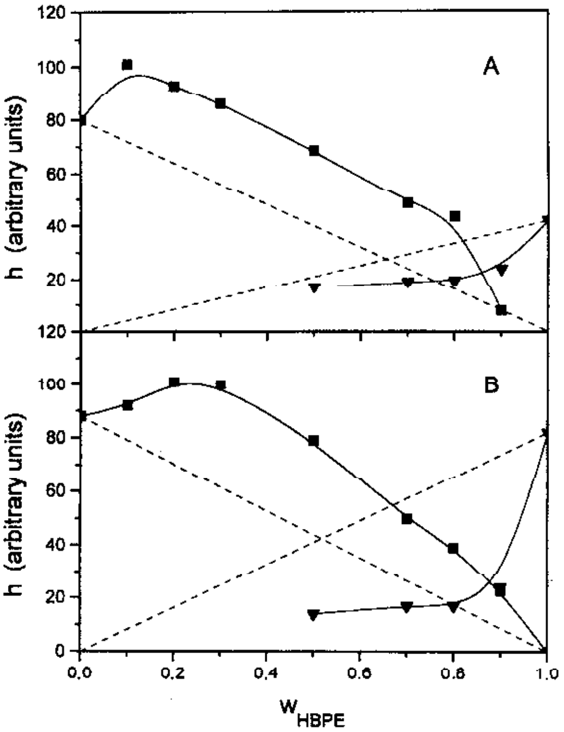

Fig. 3 Dependence of the peak heights (h) of the endothermal melting peaks (A) and the exothermal crystallisation peaks (B) of the blends of HDPE 1 and HBPE 1 (9.5 percent by mass of octene) on the mass fraction of HBPE (w_{HBPE})

The results of the melting behaviour of the HDPE/HBPE blends are confirmed by investigations on the crystallisation behaviour of these blends. Figure 4 presents the DSC curves of the cooling run for the blends from HDPE 1 and HBPE 1 with 9.5 per cent by mass of octene. Here too, after a single peak with a smaller HBPE content, a splitting into two exothermal crystallisation peaks occurs from a minimum of 50 per cent by mass of HBPE. As can be seen from the dependence of the temperatures of the crystallisation peaks on the blend composition in Fig. 5, the joint crystallisation peak only slightly decreases with a HDPE content of more than 50 per cent by mass with increasing HBPE quantities in the blend. In the case of two separate crystallisation peaks, the upper one remains relatively constant with increasing HBPE quantity and shows a significant decrease to the crystallisation temperature of the pure HBPE only with a HBPE content of more than 80 per cent by mass, whereas the lower crystallisation peak shows an immediate significant decrease and remains then constant at a low level.

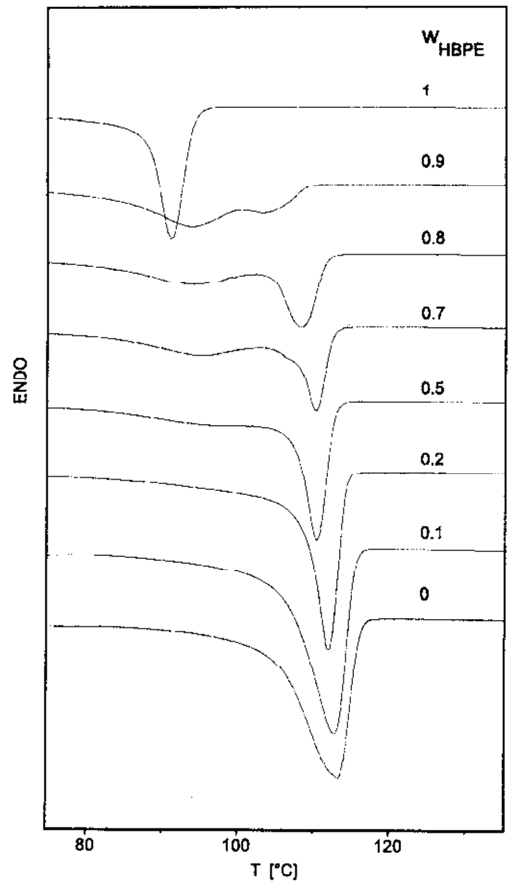

Fig. 4 Influence of the composition of the HDPE 1/HBPE 1 system (9.5 per cent by mass of octene) on the exothermal crystallisation peaks (T_c) of the blends (w_{HBPE}: mass fraction of HBPE)

The plotting of the peak heights of the exothermal crystallisation peaks of HDPE 1/HBPE 1 blends as a function of the mass fraction of the HBPE component in Fig. 3 supports the findings of the melting behaviour of these blends. For the crystallisation peak at higher temperatures, larger peak heights have been observed and for the lower crystallisation peak, lower peak heights than expected from the additive capacity of the components have been found. If the height of the exothermal crystallisation peak can approximately be considered as relative expression of the non-isothermal crystallisation speed [10], the conclusion drawn from the results in Fig. 3 is an increase in crystallisation speed of HDPE (or its cocrystallites) by the addition of HBPE, on the one hand, and a decrease of the crystallisation speed of HBPE (or its cocrystallites) by the addition of HDPE, on the other hand.

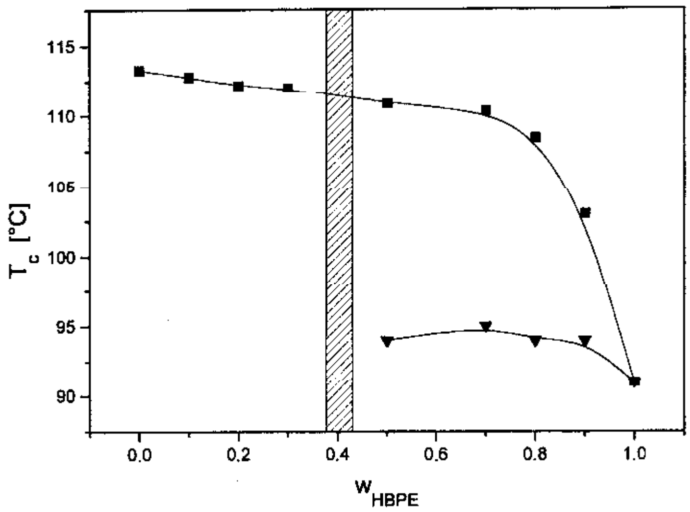

Fig. 5 Dependence of the maximum values of the crystallisation temperatures (T_c) of the blends of HDPE 1 and HBPE 1 (9.5 per cent by mass of octene) on the mass fraction of HBPE (w_{HBPE})

Thus, these blends of HDPE and a long-chain branched HBPE with an octene content of as high as 9.5 per cent by mass show completely different characteristics than the blends of HDPE and octene-containing LLDPE without long-chain branches with a similar density of 0.920 g cm^{-3} investigated by Hay and Zhou [9], where no splitting of the melting and crystallisation temperatures has been observed over the entire composition range of the blends. The same applies to the comparison of the investigations made by Haghighat and Birley [11] with the blends of HDPE and LLDPE with a chemical composition not specified in detail and the investigations of Hu, Kyu and Stein [12] on the basis of HDPE blends with LLDPE containing 1-butene. At the investigation of the isothermal crystallisation kinetics of HDPE and octene based LLDPE Rana [13] has shown a single crystallisation exotherm over the entire composition range too, characterising cocrystallinity between HDPE and LLDPE and confirmed by other experimental methods.

Similar characteristics in relation to the splitting of the melting and crystallisation temperature which depend on the blend composition were found for blends of two fractions of a short-chain branched LLDPE sample using octene as comonomer [14]. However, the polymer fractions used for the mixture are extreme values of the octene content and the molecular weight and are not comparable with the samples studied in this paper. Specially in blends of linear polyethylenes of not to low molecular weights with LDPE of much higher degrees of long chain branching extensive liquid-liquid phase separation in the melt and the existence of two melting peaks was observed particularly at higher

LDPE concentrations combined with cocrystallisation in all systems [15].These results suppose that the melting or crystallisation temperature found with a predominant HDPE content in the blend composition makes the composition range miscible for the blend components and indicates a cocrystallisation of HDPE 1 and HBPE 1. Here from a homogeneous single phase melt the HDPE and HBPE should undergo individual seeding of nuclei and merge together in the growth process to form cocrystallites according to Rana [13]. For concentrations from 50 per cent by mass of HBPE in the blend, the crystalline phase separates into two domains. In the domain with the higher melting or crystallisation temperature primarily for a higher HBPE content in the blend and in the domain with the lower melting or crystallisation temperature primarily for a lower HBPE content, a cocrystallisation with a varying composition cannot be excluded. In this range a liquid-liquid phase separation into a segregated two-phase polymer melt in

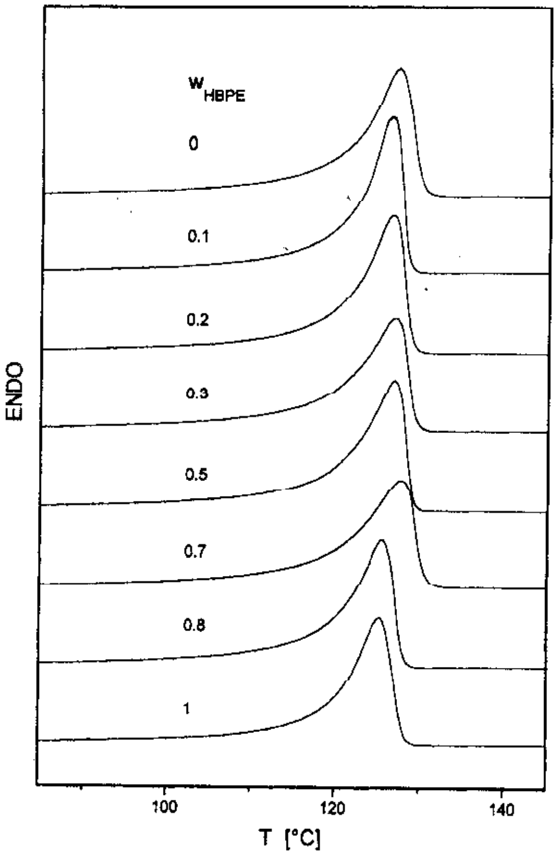

Fig. 6 Endothermal melting peaks of the blends of HDPE 1 and HBPE 2 (2 per cent by mass of octene) as a function of mass fraction of HBPE (w_{HBPE}) in the mixture (second heat run)

analogy to Hill *et al.* [15] has to be expected. Here the phase behaviour of the special blend of HDPE 1 and HBPE 1 of a relatively high octene content shows similarities with these of blends of linear polyethylenes with LDPE [15].

HBPE blends with low octene content

The DSC curves of the second heat run in Fig. 6 show the influence of the composition on the melting behaviour of the mixtures for blends of HDPE 1 and HBPE with an octene content of as low as 2 per cent by mass (HBPE 2). Any splitting of the melting peaks as for the blends of HDPE 1 and HBPE 1 with 9.5 per cent by mass of octene has not been observed in these mixtures. The dependence of the temperatures of the melting peaks (second heat run) on the percentage by mass of the HBPE component is presented in Fig. 7. As shown in this figure, the melting temperatures decrease more strongly when starting from the pure HDPE with the addition of HBPE than can be expected for an additive capacity according to their mass content. Initially, this decrease is constant, showing the homogeneity of the polymer mixtures. From a mass fraction of the HBPE

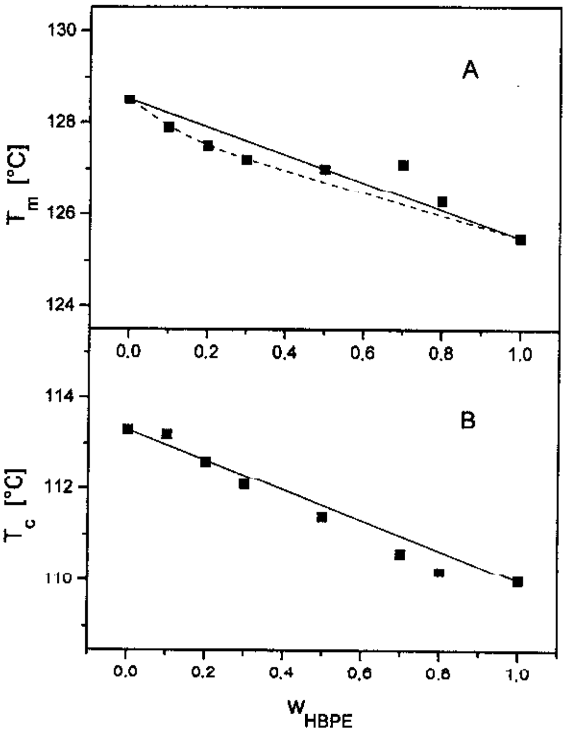

Fig. 7 Dependence of the melting temperature maxima (T_m, second heat run, A) and the crystallisation temperatures (T_c, B) of the HDPE 1/HBPE 2 system (2 per cent of mass of octene) on the composition (w_{HBPE}: mass fraction of HBPE; straight line: additive capacity)

component of approx. 0.5, the melting temperatures scatter more. Though there is no splitting of the melting peaks, this could be seen as an indication of possible inhomogeneities of the polymer mixture because of the small difference of the melting temperatures of the pure components of 3°C. The results from the first heat run confirm this relationship with regard to the thermal pretreatment of the samples. The results of the equally unimodal crystallisation peaks in terms of the crystallisation behaviour of the HDPE 1/HBPE 2 blends are also shown in Fig. 7. The maximum of the crystallisation temperatures shifts with increasing HBPE content in the blend towards low temperatures with a some larger decrease than expected from the additive capacity of the percentage by mass.

Figure 8 plots the peak heights of both the endothermal melting peaks and the exothermal crystallisation peaks of the HDPE 1/ HBPE 2 blends as a function of the composition.

While the peak heights of the melting peaks of the blends are relatively similar irrespective of the composition and above those of the individual components, the peak heights of the crystallisation peaks show an approximately additive behaviour as expected.

It can be seen from these results that the investigated blends of HDPE 1 and HBPE 2 with an octene content of only 2 per cent by mass can be generally characterised as miscible among the blend components and that they show a cocrystallisation, in particular since there is no splitting of the melting and crystal-

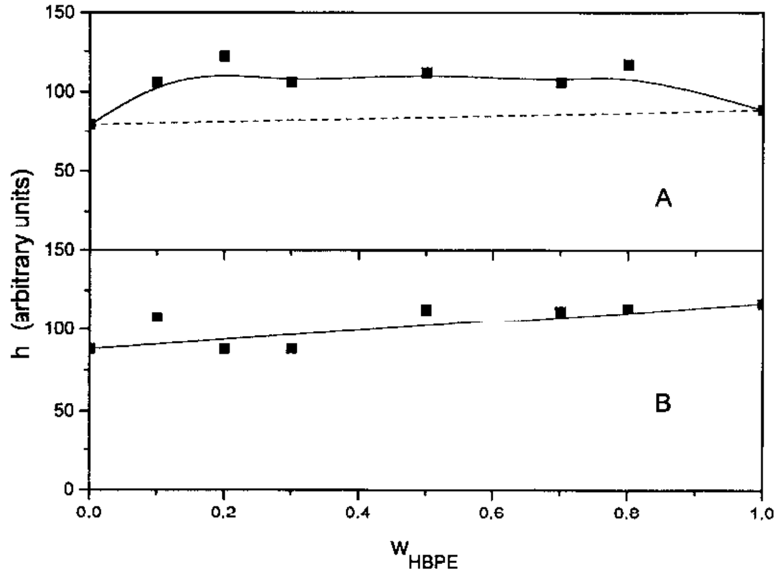

Fig. 8 Dependence of the peak height (h) of the endothermal melting peaks (A) and the exothermal crystallisation peaks (B) of the blends of HDPE 1 and HBPE 2 (2 per cent by mass of octene) on the mass fraction of HBPE (w_{HBPE})

lisation peaks. With regard to this the phase behaviour of this special blend of HDPE 1 with HBPE 2 of a low octene content and a relatively low concentration of long chain branches is comparable with this of HDPE/LLDPE blends investigated e.g. in [13].

Influence of octene concentration in HBPE

For the study of the influence of the octene concentration in HBPE on the thermal properties of blends with HDPE 1, HBPE's with octene concentrations as high as 7.5 to 12.0 per cent by mass were selected (HBPE 1, HBPE 3 and HBPE 4 in Table 1). For reference, all these HBPE's have the same melt index as a significant rheological parameter.

As the initial thermal investigations showed, the HDPE blends with HBPE 3 and HBPE 4 with 7.5 or 12.0 per cent by mass of octene provide similar properties as those with HBPE 1 and show single melting and crystallisation temperatures for high HDPE contents in the blend. With increasing HBPE content, each temperature splits into two peaks. For this reason, the influence of

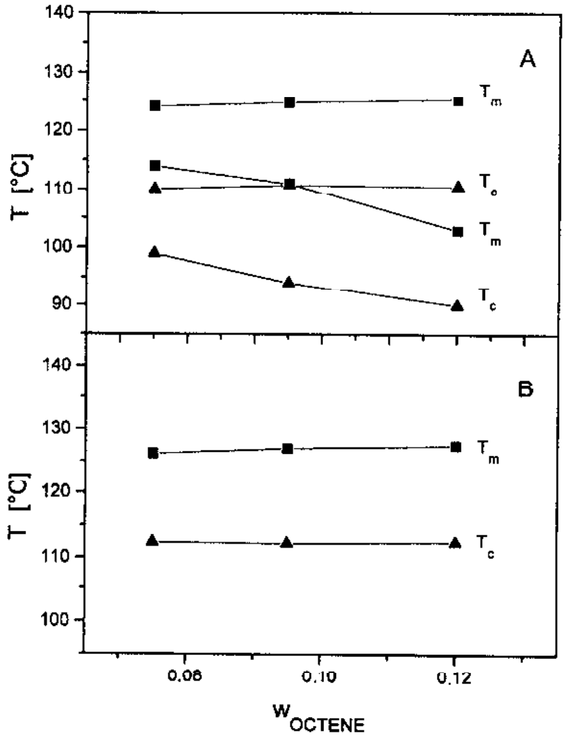

Fig. 9 Relationship between the melting temperature (T_m, second heat run) or the crystallisation temperature (T_c) and the mass fraction for octene (w_{octene}) in HBPE in HDPE 1/HBPE blends (A: HDPE/HBPE blends with 50 per cent by mass of HBPE; B: HDPE/HBPE blends with 20 per cent by mass of HBPE)

octene concentration was studied in both the homogeneous domain of the blends at a mass ratio of HDPE:HBPE=80:20 and the heterogeneous domain at a mass ratio of HDPE:HBPE=50:50.

Figure 9 shows the relationship between the melting temperatures of the second heat run and the crystallisation temperatures of the blends with 50 per cent by mass of HBPE as a function of the octene mass fraction, for the heterogeneous domain. It can be seen that with a constant composition of the polymer blends with regard to HDPE and HBPE the lower melting temperature and the lower crystallisation temperature which is to be assigned to a cocrystallisation of HBPE and HDPE, considerably decrease with the octene content increasing in HBPE. However, the upper crystallisation temperature and the upper melting temperature are relatively constant.

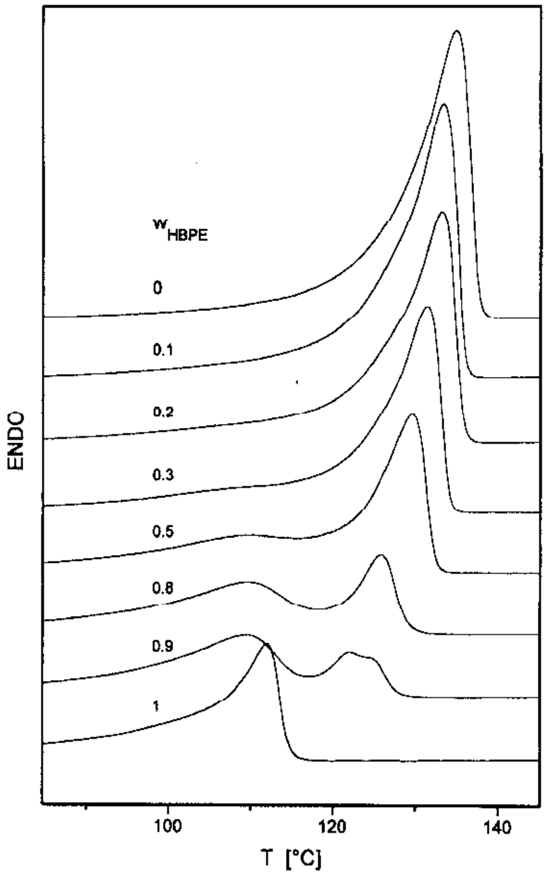

Fig. 10 Endothermal melting peaks of the blends of high-molecular HDPE 2 and HBPE 3 (7.5 per cent by mass of octene) in dependence of the mass fraction of HBPE (w_{HBPE}) in the mixture (second heat run)

For the homogeneous domain, the dependence of the melting temperatures (second heat run) and the crystallisation temperatures of the blends with 20 per cent by mass of HBPE on the mass fraction of octene is also plotted in Fig. 9. With equal HDPE/HBPE composition, the crystallisation temperature and the melting temperature are also rather constant with the rising octene content in HBPE – as for the upper temperatures in the heterogeneous domain. This relative constancy can be compared with the just slight decrease in the respective temperatures with the increasing HBPE content and hence, the overall octene content in the HDPE 1/HBPE 1 blends.

Blends with high-molecular HDPE

For the investigation of the thermal behaviour of blends of HBPE with a high-molecular HDPE, HDPE 2 with a considerably larger viscosity number (727 $cm^3 g^{-1}$) was used (cp. Table 1). HBPE 3 containing 7.5 per cent by mass of octene was employed as long-chain branched HBPE .

Similar to the HDPE 1/HBPE 1 system, the DSC curves show two ranges of the melting behaviour: one miscible range with only one melting temperature

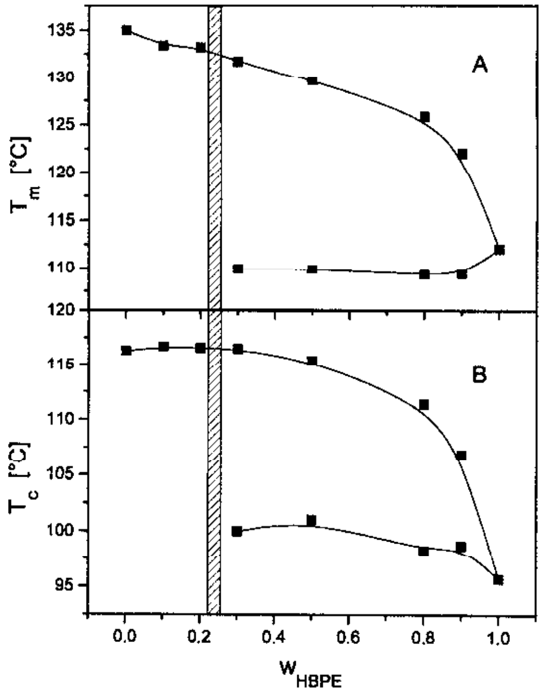

Fig. 11 Dependence of the maximum melting temperatures (T_m, second heat run, A) and the crystallisation temperatures (T_c, B) of the system from high-molecular HDPE 2 and HBPE 3 (7.5 per cent by mass of octene) on the composition (w_{HBPE}: mass fraction of HBPE)

and one non-miscible splitted in two melting temperatures (cp. Fig. 10). However, in contrary to the HDPE 1/HBPE 1 blends, the splitting of the melting peaks takes place with a clearly lower HBPE 3 content in the blend, i. e. a minimum of 30 per cent by mass. The dependence of the melting temperatures on the mass fraction of HDPE 3 in the HDPE 2/HBPE 3 blend system is plotted in the curve in Fig. 11. Apart from peak splitting, it can be seen that the melting temperature of the pure HDPE is considerably higher which is attributable to the far higher molecular weight, and that the melting temperature of the pure HBPE is considerably lower on account of the increased octene content. Compared to 5°C of the HDPE 1/HBPE 1 system, the decrease of the upper melting temperature up to approx. 80 per cent by mass of HBPE is much more clearly in the HDPE 2/HBPE 3 system with 9°C.

These findings are supported by the crystallisation behaviour of the HDPE 2/HBPE 3 blends. The dependence of the crystallisation temperatures on the blend composition in Fig. 11 also shows a splitting of peaks beginning at 30 per cent by mass of HBPE. However, the decrease in the upper crystallisation temperature up to

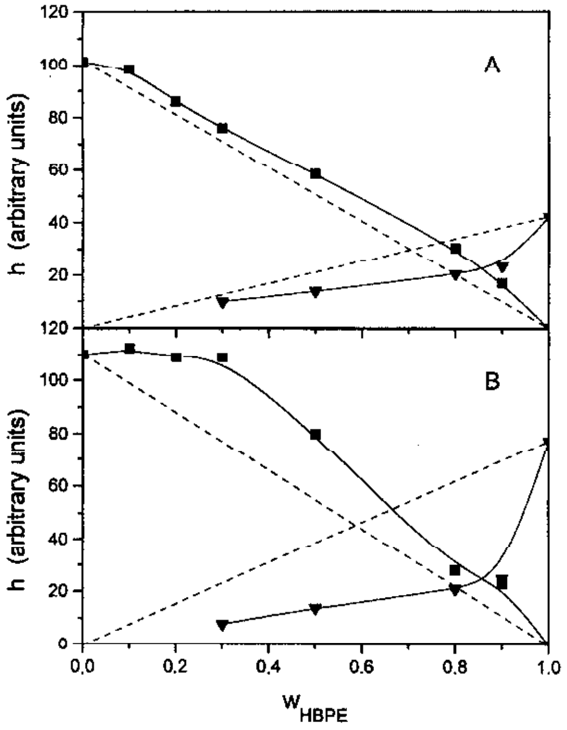

Fig. 12 Dependence of the peak heights (h) of the endothermal melting peaks (A) and the exothermal crystallisation peaks (B) of the blends of high-molecular HDPE 2 and HBPE 3 (7.5 per cent by mass of octene) on the mass fraction of HBPE (w_{HBPE})

a mass fraction of HBPE 3 of 0.5 is only about 1°C in this system as compared with the HDPE 1/HBPE 1 blends, where a difference of 2.5°C is observed.

Figure 12 evaluates the dependence of the peak heights of the melting temperatures (second heat run) and the crystallisation temperatures on the blend composition. The curve is similar to the HDPE 1/HBPE 1 system. However, the differences to the values expected from the additive capacity of the individual components, in particular for the melting temperatures, are remarkably smaller.

Hence, in the HDPE 2/HBPE 3 system too, a miscible composition range can be found with a high HDPE content which splits into two ranges starting from 30 per cent by mass of HBPE caused by the separation of the crystalline phase. In the range with the higher melting or crystallisation temperature to be assigned to HDPE and in the range with lower melting or crystallisation temperature to be assigned to HBPE, a cocrystallisation of the two mixing components is assumed to take place here. The behaviour of a more extensive phase separation area with a significant higher molecular weight of the linear polymer (HDPE) has been observed in blends of linear polyethylenes with LDPE's too [15].

Conclusions

In the polymer blends from high-density polyethylene (HDPE) and long-chain branched homogeneous polyethylenes (HBPE), a phase separation has been observed by the occurrence of several melting and/or crystallisation temperatures which are depending on the comparison of the blends. While blends of HDPE with HBPE of a low octene concentration (2 per cent by mass) are regarded to be miscible over the entire composition range, the blends with HBPE's of higher octene concentrations (7.5–12.0 per cent by mass) are not miscible over the entire composition range. Especially in the non-miscible range of such systems and with constant blend composition, a remarkable decrease in the lower melting temperature as well as a remarkable decrease in the lower crystallisation temperature which is assigned to the cocrystallisation of HBPE and HDPE has been observed with an increasing octene content in HBPE. The use of high-molecular HDPE components cause an extension of the non-miscible domain in HDPE/HBPE blends towards the composition with a higher HDPE content in the blends. So it has been found that the phase behaviour of blends of HDPE with homogeneously branched polyethylenes (HBPE) manufactured with new metallo cene catalysts is situated between these of HDPE/LLDPE and HDPE/LDPE blends.

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