

## Thermal Analyses of Blends of Hyperbranched Linear Low-density Polyethylene (LLDPE) with High-density Polyethylene and LLDPE Prepared by Dissolving Method

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Blends of high-density polyethylene (HDPE), moderate and hyper-branched LLDPEs (LLDPE and HbPE, respectively) have attained widespread commercial applications, though the understanding of the mechanical and melt-flow properties of such blends has been handicapped by the absence of a consensus concerning the degrees of mixing of the components. Moreover, usually the blends are obtained by melt blending, which may not ensure the initial homogeneity of the components. In our work the mixtures were prepared by dissolving the conventional LLDPE having branching content 7.2 wt% with HbPE with comonomer content 17.8 wt% in xylene at 130 °C and stirring for 2 hours. The same procedure was applied for the blending of HDPE with HbPE. After dissolving the mixtures were cooled in liquid nitrogen and after that freeze dried in vacuum line. The ratio of components in the blends was varied. Differential scanning calorimetry has been used to investigate the miscibility and thermal behavior of the blends. For this purpose isothermal and non-isothermal treatment of prepared blends were conducted. By preliminary study the double melting peaks in non-isothermal endotherms have been observed in all the studied blends. The presence of two peaks in DSC scan can be attributed to the formation of separated crystals from both the high density/linear low density and highly branched components. However, certain limited degree of co-crystallization is detected in all the LLDPE/HbPE blends and HDPE/HbPE blend rich in HbPE component

*Keywords:* blends, hyper-branched linear low density PE, thermal behaviour, differential scanning calorimetry.

### 1. INTRODUCTION

Blends of linear low density polyethylene (LLDPE) with different types of polyethylenes have been widely investigated from scientific as well as industrial interests and attained widespread commercial applications.

One of the most important problems that have to be solved is the phase segregation between the components of the blends. For example as it is known from the literature the blend of high density polyethylene (HDPE) with low density polyethylene (LDPE) shows segregation between these two components when cooled slowly from the melt [1–3]. Only quenching of the melts showed a uniformly mixed crystalline sample, or a co-crystallized sample. But the phenomenon is limited to the sample with high HDPE content or to those with a low degree of branching in branched PE [4, 5]. For the blend of LDPE with LLDPE a formation of separated crystals of phase segregation was suggested [6]. For the blend between HDPE and slightly branched LLDPE the co-crystallization was reported even under the condition of slow cooling [7–10]. Therefore the crystal segregation and co-crystallization are dependent in a complicated manner upon the couples of the selected PEs, the crystallization conditions, etc.

The molecular weight of the components in the blends, as it has been suggested elsewhere [8, 11], is of secondary importance in determining the occurrence or extent of co-crystallization. At the same time the amount of short chain branching (SCB) and type of catalyst seems to be impor-

tant factors [12–14]. The higher the branching content, the lower is the possibility of co-crystallization between the components. Zhao et al. [15] conclude that the upper branching limit still allowing co-crystallization to occur probably is much lower in blends with single-site materials than in blends with Ziegler-Natta based materials. Zhao et al. argue that in Z-N LLDPE there exists long segments between branches that can easily co-crystallize with HDPE or LPE, but the more uniform SCB distribution in single site LLDPE makes co-crystallization more difficult.

Much of the works present in literature has been focused on blends between LPE or HDPE and the LLDPE, which is a lightly branched ethylene-butene copolymer, obtained by single site catalyst [7–11, 16, 17]. Moreover, in performed works the mixtures are generally prepared by melt-blending, which may not ensure the initial homogeneity of the components, because it is not certain that sufficient time was allowed for the molecules to inter-diffuse to the homogeneous state.

In present work we prepared the blends of hyper-branched LLDPE with HDPE and moderate branched LLDPE. These blends were prepared with mixing of components in solution and keeping them for several hours in that state before drying. Although HDPE, LLDPE and hyper-branched LLDPE differ in the amount and distribution of the comonomer, chemically they should be miscible. To our knowledge this is the first study of thermal behavior of hyper-branched LLDPE blends. Blends were analyzed with a view to determine the extent to which the polymers either co-crystallize or crystallize independently.

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## 2. EXPERIMENTAL PART

### 2.1. Materials

All materials used in this study are commercial materials kindly supplied from Borealis, Finland. Single site catalyzed hyper-branched LLDPE (HbPE) is used as common component for all the blends. HbPE is a copolymer of ethylene with 1-butene. The Ziegler-Natta catalyzed polyethylene samples with different degrees of branching, i.e., fractionated high-density polyethylene (HDPE) having presumably low amount of branches and linear low density polyethylene moderately branched (marked in text as just LLDPE) were used as the second component in the blends. LLDPE is a copolymer of ethylene with 1-hexene. HDPE sample was fractionated by molar mass (MM) according to Holtrup technique which is a solvent/non-solvent extraction [18]. In the present study the first fraction of fractionated HDPE was used in order to have the high-density sample with a few branches. The molecular parameters of pure components are listed in Table 1.

**Table 1.** Molecular characteristics of the pure components used for preparation of blends

Material	Comonomer content (wt%)	Weight average MM (kg/mol)	MM polydispersity
HbPE	17.8	88	2.0
LLDPE	7.2	125	4.4
HDPE	not analyzed	5	2.0

### 2.2. Blending

Blends were prepared by dissolving different ratios of components in xylene at 130 °C and stirring for 2 h. After dissolving the mixtures were quenched in liquid nitrogen and then freeze dried in vacuum line for 48 h. Blends were obtained as powders/fluffy materials. Ratios of components in blends were varied: 20/80, 50/50 and 80/20 wt% was taken for LLDPE/HbPE, 20/80 and 80/20 for HDPE/HbPE.

### 2.3. Methods

For all isothermal and non-isothermal experiments at cooling rates 1 °C/min and 10 °C/min Perkin Elmer differential scanning calorimeter DSC-7 was used with nitrogen as furnace purge gas. For non-isothermal experiments at cooling rate 200 °C/min Perkin Elmer Diamond DSC was used with helium as furnace purge gas. Temperature and heat flow calibrations were done with indium and tin standards. To avoid differences in melting and crystallization temperatures caused by variation in sample weight, a sample mass of 1.00 mg ± 0.02 mg was used in all DSC experiments. Samples were manually compressed and packed into aluminium foil to maximize thermal contact between sample and calorimetric furnace.

During non-isothermal measurements the sample was first held at 180 °C for deleting its thermal history. Then it was cooled to -40 °C at cooling rate 1, 10 or 200 °C/min, held at -40 °C for 2 minutes and heated to 180 °C at heating rate 10 °C/min. Degree of crystallinity  $\lambda$  was

calculated from the heat of fusion using the peak area determination method, i.e., by integration of the area under the normalized melting peak after subtraction of an arbitrary straight baseline; a value of  $\Delta H_m^0 = 293$  J/g was used as the reference melting enthalpy of fusion for 100 % crystalline PE.

For isothermal treatment sample was first held at 180 °C, then quenched to an annealing temperature and held there 30 minutes and then heated to 180 °C at heating rate 10 °C/min. Annealing temperatures were between melting temperatures of pure components: 80, 90, 100 and 115 °C.

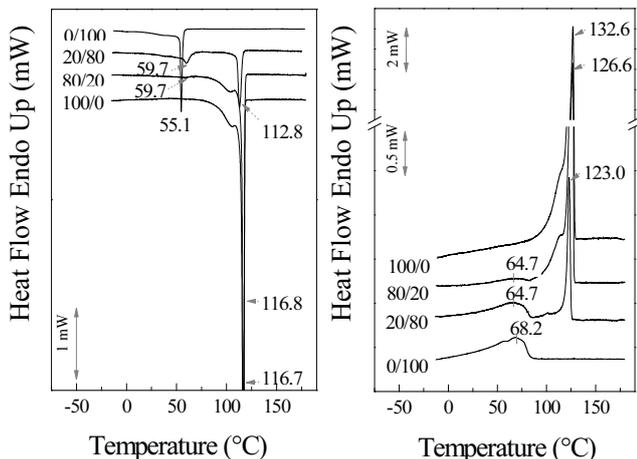
MM and polydispersity were determined by size exclusion chromatography using 1,2,4-trichlorobenzene (TCB) as eluent at 140 °C. Comonomer contents were measured by Fourier transform infrared spectroscopy.

## 3. RESULTS AND DISCUSSION

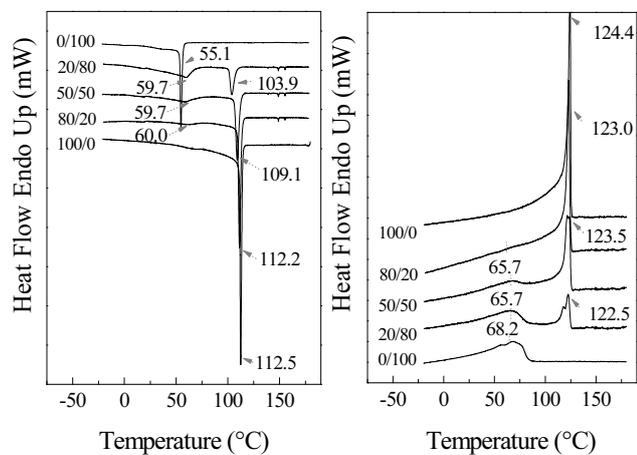
It has been presented elsewhere that blends similar to the blends presented here show extended regions of phase separation (in temperature and composition) in the melt [12–17]. Based on those results it is expected that our blends will show two separate crystal populations. DSC melting endotherms of the blends HDPE/HbPE with various ratios of components are shown in Fig. 1. The heating and cooling rates were 10 °C/min. The DSC result clearly indicates the existence of two crystal populations in these blends. Two melting peaks are found in all studied blends. The mixtures with a high concentration of the high-density polymer (>50 %) show a sharp high-temperature peak with a small peak in the low-temperature region. This low-temperature peak further develops into a well-defined peak for the mixtures with high concentration of the hyper-branched component. The form and position of the low-temperature peak indicates that this peak represents melting of mainly the component rich in HbPE. The high-temperature melting peak seems to represent the HDPE-rich component. It should be noticed that high temperature melting peak has a small shoulder, sub-peak, generated at slightly lower temperature. Similar behavior is detected for all the blends of LLDPE with HbPE, as is obvious from the Fig. 2 where their crystallization and melting thermograms are shown.

The origin of sub-peak observed at high temperatures can be understood from the thermograms of pure components, also presented in Figs. 1 and 2. Pure HDPE component has mainly one melting peak but the shoulder extent to lower temperatures is present, indicating some degree of heterogeneity in sequence lengths. The same is found for pure LLDPE. If the compositional and molar mass (MM) heterogeneity of conventional whole LLDPE is expected, the heterogeneity of HDPE seems to be unusual. As it was mentioned in Experimental part the HDPE used in this study is the first fraction of the whole HDPE obtained by fractionation according to MM. Taken into account that HDPE is catalyzed by Ziegler-Natta technique, first fractions of such polymers after fractionation by MM usually contain branched chains with low MM. The degree of branching in the first fraction is therefore higher than present in whole polymer. Therefore HDPE can contain chains that can be excluded from the

largest lamellae during primary crystallization and generate a secondary crystal population. This can result in an appearance of sub-peak in melting traces. Presence of chains forming the secondary crystals gives the possibility of mixing them with the HbPE chains having very low branch content. As seen from the Figs. 1 and 2, the increase in the amount of HbPE component in the blends results in a better separation of two high-temperatures melting peaks. The position and broadness of these peaks change indicating partial chain segregation of HDPE-rich peak and possibility of a formation of mix crystals.



**Fig. 1.** DSC cooling (left) and melting (right) traces of the HDPE/HbPE blends with various component ratios. Cooling and heating rates are 10 °C/min



**Fig. 2.** DSC exotherms (left) and endotherms (right) of the HDPE/HbPE blends with various component ratios. Cooling and heating rates are 10 °C/min

In order to understand the origin of low temperature and high temperature melting peaks the cooling rate during the cooling scans was varied. The heating rate is constant, 10 °C/min. The thermograms of the blends at 1 °C/min and 200 °C/min cooling rates show identical behavior as it was observed for cooling rate of 10 °C/min. It is clear seen from the Fig. 3 where melting traces of 20/80 HDPE/HbPE and 50/50 LLDPE/HbPE blends at different cooling rates are shown as illustrations. Two main melting peaks with additional sub-peak at high temperature are recorded.

From the heat of fusion, the degree of crystallinity  $\lambda$  by weight was obtained for low and high temperature peak. These values are given in Table 2 for the 20/80

HDPE/HbPE blend as example. First of all the degree of crystallinity of each peak does not depend on scanning rate indicating that the observed peaks are not associated with the recrystallization or reorganization process but consistent with the formation of separate crystals from both components. The other blends of HDPE/HbPE and LLDPE/HbPE are found to possess a similar behavior and the same conclusion can be done for them. Thus, in comparison with HDPE/LLDPE and LDPE/LLDPE discussed in literature [1–14], in our types of blends two crystal populations are forming even in rapidly crystallized mixtures at 200 °C/min similar to slowly cooled samples at 1 °C/min.

**Table 2.** Degree of crystallinities  $\lambda$  for 20/80 HDPE/HbPE blends obtained from melting thermograms at various cooling rates

Cooling rate °C/min	$\lambda$ overall (wt%)		$\lambda$ (low temperature peak) wt%		$\lambda$ (high temperature peak) wt%	
	exptl	calcd	exptl	calcd	exptl	calcd
1	27	37	11	18	16	19
10	26	31	11	12	15	19
200	25	35	10	16	15	19

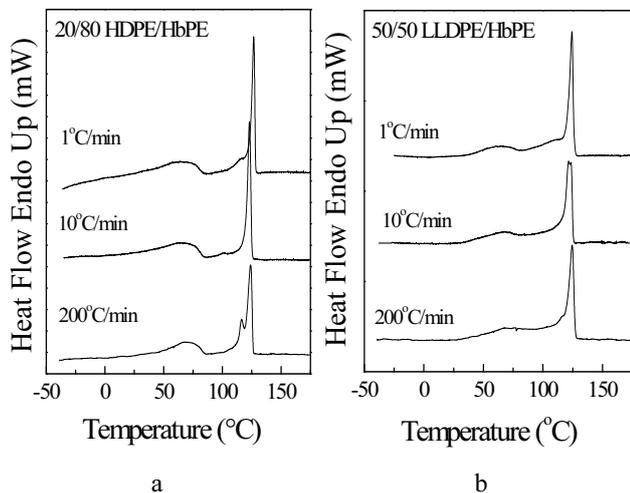
Note. “exptl” means measured from DSC melting endotherms; “calcd” means calculated assuming independently crystallized crystals.

To find out whether the observed melting peaks corresponds to completely separated crystallites, formed independently, the degree of crystallinity of low and high temperature peak was compared with the expected value in the blends if both components had crystallized independently. Table 2 shows that the crystallinity of the HbPE-rich low-temperature peaks is lower than that calculated assuming independent crystallites. Overall degree of crystallinity of both peaks is also lower than that calculated by mentioned above method. Lower crystallinity of the blends compared to the pure blend components has been taken elsewhere as an argument in favor of co-crystallization [3, 7–16]. The observed melting behavior of the blends therefore suggests that slight co-crystallization to some limited extent is present in the blends.

Furthermore, the low-temperature peak in all the blends has almost the same melting point which is around 4 °C lower than observed for the pure HbPE component as also obvious from the Figs. 1 and 2. This result might indicate that even in HbPE there are chain segments that are able to co-crystallize with branched chains of HDPE or LLDPE [17]. In that case remaining HbPE chains, not incorporated in HDPE- (LLDPE-) rich crystals, are suggested to have a higher overall content of branches than the pure HDPE (LLDPE) and should melt consequently at a lower temperature; and this is in fact observed from Figs. 1 and 2.

The melting point of the high-temperature peak in the HDPE/HbPE and LLDPE/HbPE is significantly lower (~10 °C and 2 °C maximum, respectively) compared to that of the pure HDPE and LLDPE component. Other authors have observed a similar depression of the melting temperature of the high-temperature peak in a blend of

LPE/LDPE [13, 19] and LPE/LLDPE [12, 16] and suggest that such behavior can be explained by both the co-crystallization of the branched component into the LPE crystal and a lower lamellae thickness of the LPE component in the blend. Based on this conclusion, the depression of the high-temperature peak in the blends most probably has a complex reason but could be explained, at least partly, from a limited degree of co-crystallization among the blend components.



**Fig. 3.** DSC melting thermograms for 20/80 HDPE/HbPE (a) and 50/50 LLDPE/HbPE (b) blends crystallized at various cooling rates

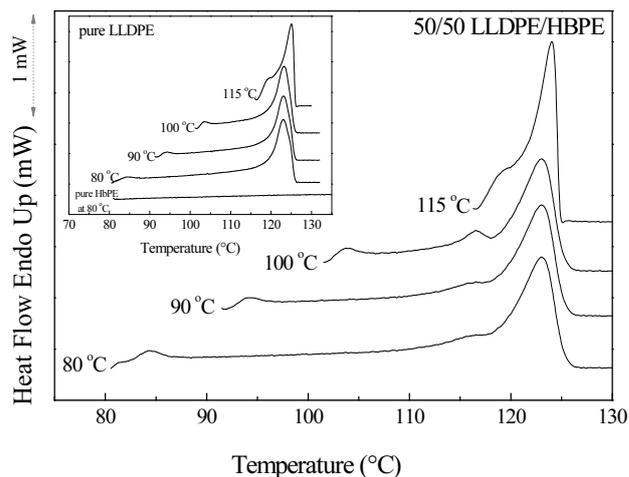
Therefore, a limited degree of co-crystallization is believed to be present in blends used in this work, at least in the blends rich in HbPE ( $\geq 50\%$ ).

One more interesting behavior can be seen from the crystallization traces of the blends. From Fig. 1 it is observed that the crystallization temperature of the HbPE-rich component in separated blends locates at a higher temperature than the crystallization point of the corresponding pure HbPE component. This observation seems to be in a conflict with the observation of melting point behavior. We will explain this effect based on comments and observations made by others [12]. Crystallization curves for both pure blend components show sharp leading edges, characteristic of primary crystallization. Additionally, both components have an extended tail to lower temperatures, reflecting a secondary crystallization process into thinner lamellae. In the blends it is obvious from Figs. 1 and 2 that the HDPE- as well as LLDPE-rich component crystallizes first. The crystallization curves show rather sharp and narrower peak at high temperature. The low-temperature peak, however, reflecting a secondary crystallization process of mainly HbPE-rich component, shows rather broad leading edge very different from the sharp peak observed for pure HbPE. Therefore it was suggested that the primary crystallization in blend is associated with the crystallization of HDPE-rich or LLDPE-rich component in HDPE/HbPE and LLDPE/HbPE blends, respectively. HbPE-rich component crystallizes in a secondary crystallization processes within the structure determined by crystallization of HDPE- or LLDPE-rich component [20]. Therefore as others have suggested the crystallization of HDPE or LLDPE will generate the

crystallization of HbPE at higher temperature than the pure HbPE would otherwise crystallize. The lamellae thickness of the resulting HbPE-rich component in the blends and the subsequent melting behavior indicate that this enhanced crystallization at higher temperature occurs without forming thicker lamellae, as normally would be expected due to higher crystallization temperature.

To confirm the presence of partial co-crystallization in used blends, assuming for the sake of argument that one could initially assign the double melting to the formation of independent LLDPE (or HDPE) and hyper-branched crystal, it follows that isothermal crystallization of blends especially with a high amount of HbPE at temperatures intermediate between both melting peaks should give rise to completely segregated LLDPE (or HDPE) crystals represented by a single peak in DSC thermograms [1].

To test this hypothesis, isothermal crystallizations were carried out in all the blends. The blends were equilibrated in the melt at  $180^\circ\text{C}$  and rapidly cooled to the annealing temperature ( $T_a$ ). The melt endotherms were subsequently recorded starting from  $T_a$ , i.e., without further cooling. The example is shown in Fig. 4 for the 50/50 LLDPE/HbPE blend crystallized at different  $T_a$ . The endotherms of a similar mass of the pure components, crystallized at the same temperatures are demonstrated in the inset to the Fig. 4. The melting after crystallization at different  $T_a \leq 100^\circ\text{C}$  shows two well-defined peaks at about  $116^\circ\text{C}$  and  $123^\circ\text{C}$  and a low-temperature sub-peak in the  $T_a$  region that shifts toward the melting temperature of the main peak. This sub-peak, observed also in scans at  $T_a = 115^\circ\text{C}$ , is often observed for the annealed crystalline polymers: the small crystallites of the size intrinsic of  $T_a$  are generated when the sample is annealed at  $T_a$  [8]. In the heating process these small crystallites melt in the temperature region close to  $T_a$  and can recrystallize into a larger crystallite of the main melting point. In other words, the sub-peaks in Fig. 4 are not considered to come from the co-crystal or phase segregated crystals of the blend.



**Fig. 4.** DSC thermograms measured for 50/50 LLDPE/HbPE blend annealed at various temperatures. Inset shows isothermal DSC thermograms for pure LLDPE and HbPE components

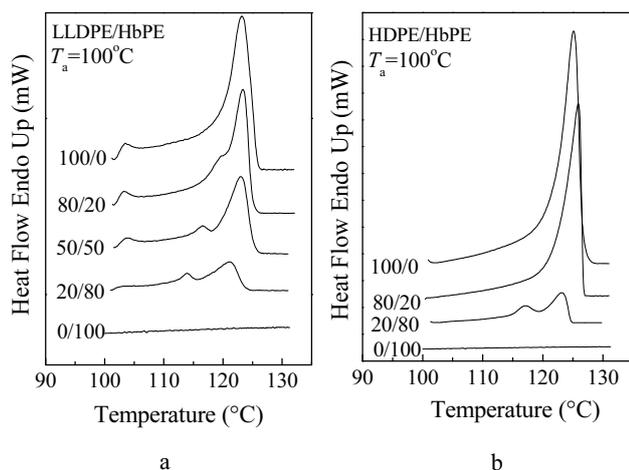
The crystallization at  $T_a$  of the pure HbPE for the same time does not show any melting peak in heating scans as it is clear seen from the inset to the Fig. 4. The pure LLDPE

component shows only one main melting peak at around 123 °C and a sub-peak in  $T_a$  region. Therefore, no chain segregation of LLDPE during annealing is detected. Taken into account the medium peak of the 50/50 blend, around 116 °C, cannot be associated with the melting of segregated crystals formed from the pure HbPE or chain segregated LLDPE. The interesting observation is that the position of medium melting peak of LLDPE/HbPE blend almost does not change with increasing  $T_a$ . Consequently, the peak is believed to be associated with the melting of limited co-crystals formed with molecules from the both components of the blend. The crystallization of shorter sequences of the hyper-branched component, unable to co-crystallize with LLDPE, takes places at lower crystallization temperatures. These crystals melt at  $T < T_a$ . The high peak at ~123 °C is associated with melting of pure LLDPE crystals which probably were formed above  $T_a$  during the cooling process.

The possibility of melting with further recrystallization of a single species during the heating run is believed to be minor for the following reasons. The 50/50 LLDPE/HbPE mixture was crystallized at 100 °C for 30 min and the melting followed at different heating rates (5, 10, and 40 °C/min) was recorded. The relative areas of both melting peaks are practically independent of heating rate within experimental error, indicating that both species are formed mainly during crystallization and not in the melting process [1]. However some degree of recrystallization process is still possible.

High annealing temperatures,  $T_a > 100$  °C, hinder the co-crystallization process; for example, crystallization of the 50/50 mixture at 115 °C (see Fig. 4) results in single melting peaks around 125 °C corresponding to the pure LLDPE species.

These experiments clearly indicate that there is partial co-crystallization of both components in the 50/50 LLDPE/HbPE blend crystallized at temperatures at which the crystallization of the pure hyper-branched component is completely retarded.



**Fig. 5.** DSC thermograms measured for LLDPE/HbPE (a) and blends HDPE/HbPE (b) with different component ratios annealed at 100 °C

A similar behavior is found from the analysis of the melting peaks after isothermal crystallization of the 20/80 and 80/20 LLDPE/HbPE mixtures, and 20/80 HDPE/HbPE

blends, as it is obvious from the Fig. 5. Therefore it is believed that the limited co-crystallization is occurred in all LLDPE/HbPE blends, and in HDPE/HbPE blends rich in hyper-branched component.

HDPE-rich blends did not melt at temperatures indicative of partial co-crystallization. Only a single endotherm was observed for 80/20 HDPE/HbPE blend, see Fig. 5. It is known that for the blends with high concentration of the high-density component, the crystallization rate of the HDPE in the blend is much higher than that of the pure branched polymer [1, 20–22]. Therefore segregation of the components is kinetically favored in 80/20 HDPE/HbPE blend. At high content of HbPE ( $\geq 50$  %) the difference in crystallization rates between HDPE and HbPE becomes smaller, favoring co-crystallization. The results on HDPE/HbPE blends are consistent with the interpretation from the experiments after isothermal crystallization done by other authors for various types of blends [8–10, 17, 21, 22].

#### 4. CONCLUSIONS

The data of rapidly and slowly cooled blends of HDPE and LLDPE with hyper-branched LLDPE indicate that both components form two crystal populations. However, the limited degree of co-crystallization is believed to present in all LLDPE/HbPE blends and HDPE/HbPE blends having the content of HbPE component of 80 %. The DSC thermograms of all mixtures, excepting 80/20 HDPE/HbPE, annealed between the melting temperatures of both components show double melting peaks that were interpreted in terms of partial co-crystallization for all studied blends. 80/20 HDPE/HbPE blend shows only single melting peak in isothermal thermograms, which seems to be associated with completely segregated crystals.

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