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Thermal Behaviour of Oriented and Un-oriented Polymer Blends from Metallocene Polypropylene

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Abstract

In this paper the effect of various polyethylenes (PE) as well as Ziegler-Natta polypropylene (ZNPP) on thermal behaviour of metallocene polypropylene (mPP) in the oriented and un-oriented polymer blend fibres is presented. The DSC 7 apparatus (Perkin Elmer) for measurement of thermal properties of these fibres was used. The oriented and un-oriented mPP/PE blends and fibres are characterised by individual melting temperatures of both components with deviation of the basic thermal quantities in comparison with mPP and PE. The decrease of the total melting enthalpy of the blend indicates a partial compatibility of mPP and PE at a temperature above the melting point of the components at low concentration of PE. The mPP/ZNPP fibres are compatible polymer blends with one melting temperature in the range of melting temperature of mPP and ZNPP.

Keywords: polymer blend fibres and blends, metallocene and Ziegler-Natta polypropylene, low density polyethylene, thermal behaviour

Introduction

Fibre-forming polymer blends are used for preparation of synthetic fibres with the special applications. Two or more components in the fibre-forming blend provide the variability of properties in fibres as well as their functionalities. The polyamide 6 (PA 6) and polyesters (PES) in the polypropylene/polyamide 6 (PP/PA 6) and polypropylene/polyesters (PP/PES) blend fibres improve their dyeability at the exhaust dyeing from bath (Ondrejmiška 1944). The lower melting temperatures of branched polyethylene (LDPE) and its high adhesion to many polymers mainly to polypropylene (PP) is preferably used in the thermobonding textile

technology for preparation of nonwoven textiles for home and technical application (Vogel 1996).

Nonwoven textiles are produced by various processes such as spunbonding and meltblowing directly from fibres while spinning from molten plastics. The spun fibres are deposited on a moving belt where they are bonded mechanically, thermally or chemically. The thermal bonding of the prepared fibres depends on the structure and properties of fibres which result from the processing conditions used. In thermal point bonding commercially the most commonly used method fibre-to-fibre fusion depends on both the used temperature and pressure. The mechanical properties of nonwoven textiles increase with bonding temperature to the optimal value (Bhat 2002).

The preparation of blended fibres from various polyolefins with different (mainly lower) melting temperatures could provide a way of the preparation of nonwoven textiles - fabrics with optimal properties at the lower bonded temperature and pressure.

The very low Tg's and exceptionally low crystallinity of metallocene catalysts' copolymers and polymers remain free flowing due to their narrow composition distribution. These two properties combined allow them to be used as efficient impact modifiers for rigid matrices such as polypropylene. The ductile-brittle transition temperature of PP modified with a homogeneous ULDPE decreases linearly with the density of the ULDPE. The presence of the more crystallisable polyethylene within the ULDPE domains strengthens the interface between the particle and the matrix and thus reduces the ductile-brittle transition compared with homogeneous modifiers of equal density. The extent of the coupling increases as the crystallinity of the polyethylene increases (Khare 2000).

Most of fibre-forming polymer blends are thermodynamically incompatible and form heterogeneous systems with certain miscibility level, blend stability, various size and shape of dispersed phase (Schäfer 1995). The structure of heterogeneous system depends on the processing conditions which strongly influence the supermolecular and morphological structure of fibres (Marcinčin 1996, Shanks 2000). The processing conditions are related with the molecular structure and rheological properties of fibre-forming polymers used in the fibre preparation.

One of the parameters of supermolecular and morphological structure of polymer blends is the crystallinity and the type of crystals formed. The crystallization of PP was demonstrated in different types of PE and indicated that the PP is only soluble in the LLDPEs. While crystallizing from a phase-separated mixture the crystallization of PP is similar to phase separation of bulk PP though each phase is expected to contain some amount of the

polymer. The crystallization of PP from the solution in LLDPE is very slow and because the minor PP in the solution can form crystals throughout the full volume and also a continuous structure of very fine sparse crystals (Shanks 2000).

The crystallization of LDPE and PP in the blend fibres is influenced by the amount of the components in the system. The low amount of one component in the LDPE/PP blended fibres increases the crystallization ability of other component. The component with the low amount behaves as a nucleation agent for the major component (Ujhelyiova 2005).

It is also well known that melting temperatures and equilibrium crystallinity in LLDPE may be strongly influenced by the branching distribution. The distribution of crystallisable sequence lengths is found to have profound influences on the viscoelastic properties of LLDPEs during crystallization and melting. Non-isothermal crystallization by slow cooling gives a narrower solidification interval for the highly heterogeneous copolymer ZN-LLDPE than for the homogeneous M-LLDPE. Crystallites formed by almost linear molecules have higher melting temperature and they form the backbone of supermolecular structures (Gelfer 2003).

In this paper the effect of various low density polyethylenes as well as Ziegler-Natta polypropylene on the thermal behaviour mPP in the oriented and un-oriented polymer fibres and blends is presented.

Experimental

Materials used

The metallocene polypropylene HM562R (mPP), Lyondell Basell Co., Italy, MFI = 25 g/10 min, Ziegler-Natta polypropylene HT 2511 (ZNPP), MFI = 27.6 g/10 min and low density polyethylenes BRALEN FB2-30 (LDPE FB2), MFI = 2 g/10min and BRALEN SA 200-22 (LDPE SA 200), MFI = 22 g/10 min from Slovnaft, a.s. Bratislava, Slovak Republic were used at the preparation of fibres.

Preparation of LDPE/mPP fibres

The mPP/PE and mPP/ZNPP blends were prepared within a concentration range of 0 – 100 % wt.. Chips of both polymers were mechanically mixed. The undrawn mPP/PE and mPP/ZNPP fibres were prepared by classical procedure of spinning from mechanical mixture using laboratory pilot plant with the screw ϕ = 16 mm at a temperature of 200^{o}C with the take-up

speed at the spinning 2.5 $m.s^{-1}$. The prepared undrawn fibres were drawn on the drawn ratio 2.0 at a laboratory temperature.

Methods used

The thermal characteristics – melting (T_m) temperature and melting (ΔH_m) enthalpies of mPP/LDPE fibres were measured using DSC 7 Perkin Elmer at the following conditions: The original samples of fibres were heated with the rate of 10 °C.min^{-1} from 50°C to 180°C. Thus, a melting endotherm of the original fibre with the melting temperature T_m and melting enthalpy ΔH_m was obtained. The peak widths at half height (W) and in the baseline (HW) as well as the peak height (H) were estimated from the endotherm obtained at the first heating, too. Then, the sample was cooling with the rate of 10 °C.min^{-1} to the 50 °C and consequently it was heated to the 180°C marked such as 2nd heating of isotropic un-oriented blends. The measurement was made in the inert gas atmosphere (nitrogen).

The calculated melting enthalpies of mPP in the mPP/LDPE fibres and blends were estimated from the experimental enthalpy of individual polypropylene deduced to its weight fraction in the blend

$$\Delta H_{mcalcPP} = \Delta H_{mexpPP} * w_{PP} \quad (1)$$

where w is weight fraction of polypropylene in given mPP/LDPE fibres or isotropic blends and ΔH_{mPP} is the experimental melting (ΔH_m) enthalpy of pure mPP.

The calculated melting enthalpies of mPP/ZNPP in the mPP/ZNPP fibres and blends were defined as the additive value from experimental enthalpies of individual mPP and ZNPP deduced from their weight fraction in the blend

$$\Delta H_{mcalcmPP/ZNPP} = \Delta H_{mexpmPP} * w_{mPP} + \Delta H_{mexpZNPP} * w_{ZNPP} \quad (2)$$

where w_{mPP}, w_{ZNPP} are weight fractions of mPP or ZNPP in given mPP/LDPE fibres or isotropic blends and $\Delta H_{mexpmPP}$, $\Delta H_{mexpZNPP}$ are the experimental melting enthalpies of mPP or ZNPP.

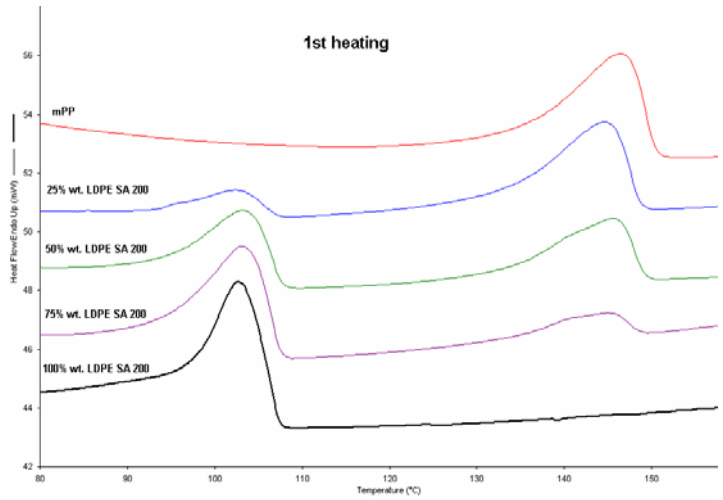
Results and Discussion

The endotherms of anisotropic and isotropic mPP/LDPE and mPP/ZNPP fibres and blends obtained at the 1st and 2nd heating are on the Figs. 1-2. The basic thermal parameters – melting (T_m) temperature, width, half width as well as height of peak of observed mPP/LDPE fibres and blends evaluated from endotherms are listed in the Tables 1 – 2.

The endotherms obtained at the 1st heating (scanning 10 °C.min^{-1}) of anisotropic mPP/LDPE fibres content two single-peaks the melting temperatures of which correspond with melting temperatures of individual mPP and LDPEs (Figs. 1a, 2a). The endotherms obtained at the 2nd heating of these isotropic blends have similar shape compared to those in the first heating (Figs. 1b, 2b).

These results show that the observed blends at the conditions of preparation used are processing compatible but are not thermodynamically compatible. These change only the shape of mPP and LDPE melting peaks such as width, half width and height on the dependence of LDPE content (Tables 1-2).

The melting temperatures of mPP/LDPE fibres reveal individual behaviour of the polymer components in the anisotropic blends. Experimental melting temperatures of LDPE FB2 or LDPE SA 200 component in blends are comparable with those of homopolymers (Table 1) and do not change on the LDPE SA 200 as well as the FB2 content in the fibres. Increasing the LDPE amount in the mPP/LDPE anisotropic fibres for both types of LDPE (SA 200 and FB2) there is a change in the width, half width and height of melting peak. The half width of both LDPE peaks decreases and the height and width of melting peaks increase with the increase of LDPE content in the fibres. But the heights are lower and the widths are higher for the mPP/LDPE fibres with SA 200 than with the FB2. It is related with the crystallization ability of LDPE component in the observed anisotropic fibres. These parameters of mPP in the mPP/LDPE anisotropic fibres are not different for both types of PE but they decrease with the mPP content in these observed fibres.



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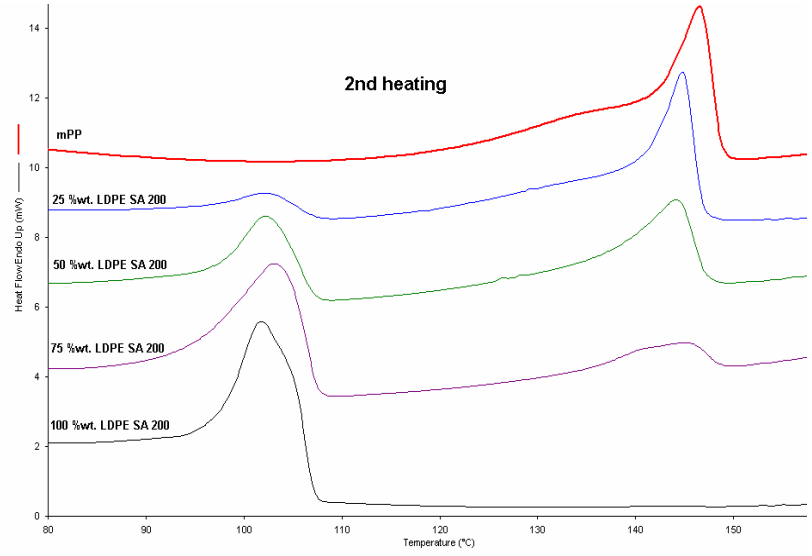

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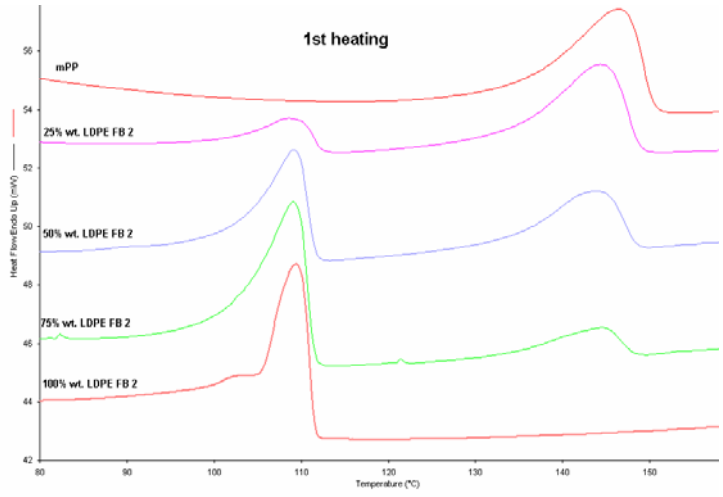
Fig. 1. Endotherms of mPP/LDPE SA 200 fibres and blends obtained at the 1st (a) and 2nd (b) heating



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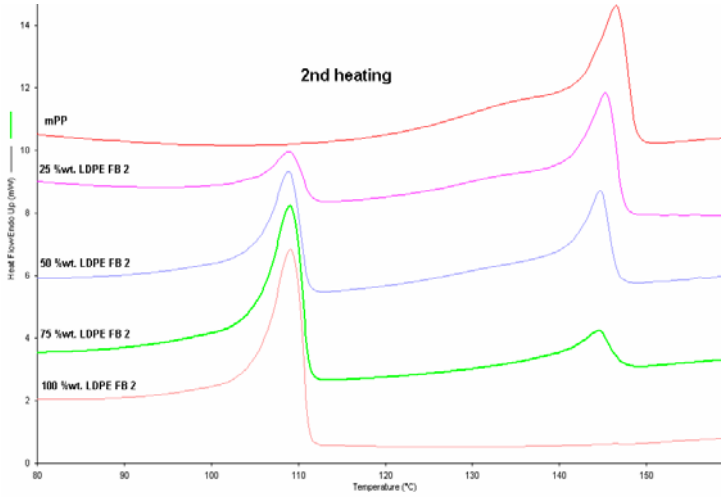

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Fig. 2. Endotherms of mPP/LDPE FB2 fibres and blends obtained at the 1st (a) and 2nd (b) heating

The difference in the thermal behaviour of anisotropic and isotropic mPP/LDPE blends is in the shape, size and area of endotherms obtained (Figs. 1-2, Tables 1-2). At the 2nd heating these were found the melting peaks with the lower half width for the both LDPEs as well as for mPP but with the higher heights for all observed components in the mPP/LDPE blends.

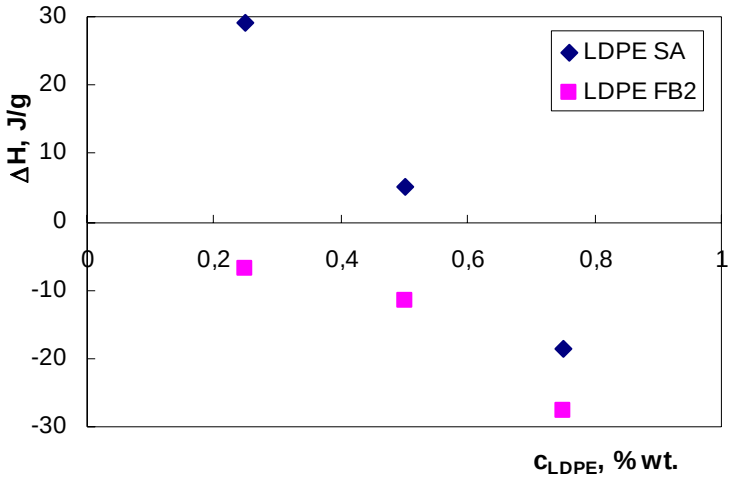
Table 1. Melting temperature (T_m), half width (HW), width (W) and height (H) of melting peak of components in anisotropic mPP/LDPE fibres obtained at the 1st heating (heating rate = 10 °C.min^{-1})

C_{LDPE} / (% wt.)	LDPE				mPP			
	T_m / (°C)	HW / (°C)	H / (mW)	W /(°C)	T_m / (°C)	HW / (°C)	H / (mW)	W /(°C)
LDPE SA 200								
0	-	-	-	-	146.5	8.1	3.44	27.0
0.25	102.5	7.1	0.84	14.0	144.7	8.0	2.97	22.7
0.50	103.3	6.9	2.44	19.5	145.5	8.9	2.08	22.6
0.75	103.3	7.0	3.58	21.4	145.0	6.3	0.70	19.7
1.00	102.8	5.6	4.58	20.9	-	-	-	-
LDPE FB2								
0	-	-	-	-	146.5	8.1	3.44	27.0
0.25	109.5	5.0	1.01	16.4	144.3	4.7	2.91	22.1
0.50	109.2	4.5	3.65	19.1	144.8	7.1	1.90	22.4
0.75	109.2	4.9	5.40	22.1	144.5	6.9	0.93	19.5
1.00	108.8	3.4	5.57	18.3	-	-	-	-

The changes in the melting enthalpies of mPP/LDPE blends confirm the thermal demonstration of the components during the crystallization and also the mPP and LDPE interaction in creating the supermolecular structure of the mPP/LDPE blends (Figs. 1-2).
The different thermal behaviour of mPP/LDPEs with the various types of LDPE (SA 200 and FB2) also confirms the dependencies of difference experimental and calculated melting enthalpies on the LDPE content in oriented as well as in un-oriented blends (Fig. 3). At the preparation of anisotropic mPP/LDPE with the major mPP content the LDPE SA 200 supports the growth of mPP crystallization. At the minor mPP content the mPP crystallization decreases below the crystallization ability of pure mPP (Fig. 3a). The LDPE FB2 decreases the mPP crystallization ability at the preparation of anisotropic blends in the process of direct orientation in comparison with the crystallization of pure mPP. The mPP crystallization in isotropic mPP/LDPE blends with both types of LDPE achieves the negative deviation in comparison with the pure mPP crystallization (Fig. 3b).

Table 2. Melting temperature (T_m), half width (HW), width (W) and height (H) of melting peak of components in the isotropic mPP/LDPE blends obtained at the 2nd heating (heating rate = 10 °C.min^{-1})

C_{LDPE} / (% wt.)	LDPE				mPP			
	T_m / (°C)	HW / (°C)	H / (mW)	W /(°C)	T_m / (°C)	HW / (°C)	H / (mW)	W / (°C)
LDPE SA 200								
0	-	-	-	-	146.5	4.1	4.38	36.1
0.25	102.2	5.9	0.64	13.5	144.7	3.4	4.18	21.7
0.50	102.4	5.2	2.19	16.4	144.2	5.8	2.34	21.6
0.75	103.0	5.3	3.27	20.1	144.7	3.5	0.89	13.8
1.00	101.9	5.3	4.53	14.8	-	-	-	-
LDPE FB2								
0	-	-	-	-	146.5	4.1	4.38	36.1
0.25	109.0	3.2	1.38	12.5	145.2	3.6	3.77	25.6
0.50	108.9	3.1	3.65	19.3	144.7	3.0	2.87	24.4
0.75	109.0	3.5	5.37	19.9	144.5	3.8	1.12	20.3
1.00	109.2	3.2	5.80	14.5	-	-	-	-



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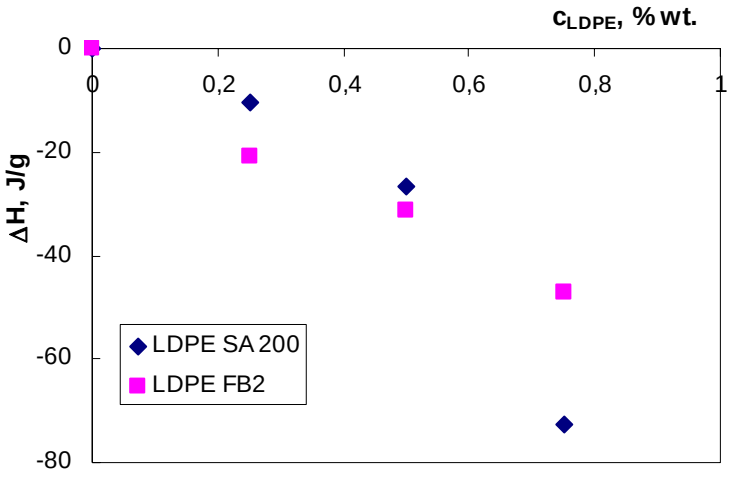
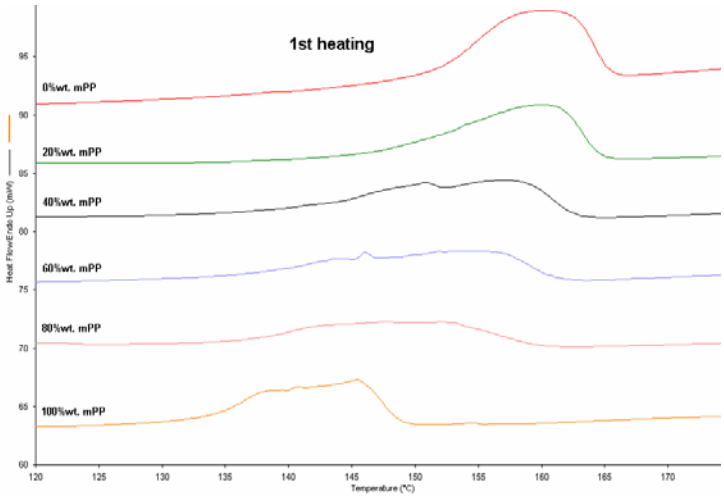


b)

Fig. 3. Dependencies of difference between the calculated and experimental melting enthalpies on the LDPE content in the oriented and un-oriented mPP/LDPE blends obtained at the 1st (a) and 2nd (b) heating

From the obtained endotherms of anisotropic and isotropic mPP/ZNPP fibres and blends it can be seen that these prepared fibres have the processing as well as thermodynamic compatibility (Fig. 4). It has been confirmed from the obtained endotherms with the single peak in the range of melting temperatures of mPP and ZNPP. At the preparation of anisotropic oriented fibres with the major ZNPP in the blend the PP forms the crystals with higher melting temperature than the equivalent additive temperature (Table 3). The half width and width of melting PP peaks rise with the increase of mPP content (to the 80 %wt. - HW, to the 60 % wt. - W) in the blend and then drops to the original level. The height of melting PP peaks is inversely proportional to the width. The height decrease with the mPP content in the fibres to the 70 % wt. and then against rises but do not achieve the height of pure ZNPP. The same thermal behaviour is also observed for isotropic mPP/ZNPP blends.



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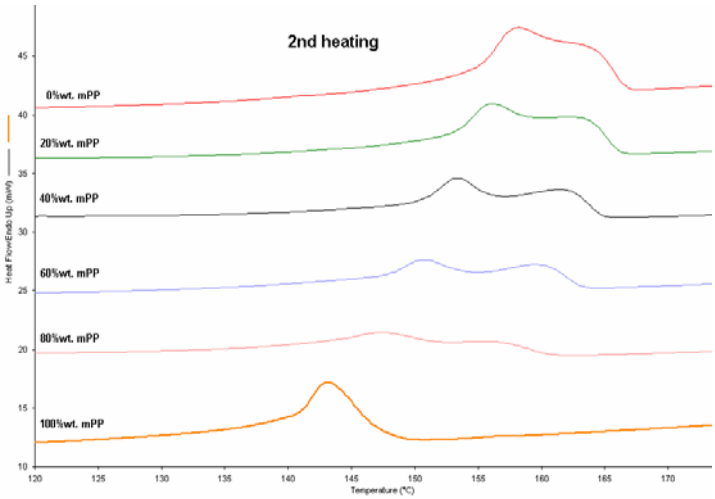

b)

Fig. 4. Dependencies of difference between the calculated and experimental melting enthalpies on the mPP content in the oriented and un-oriented mPP/ZNPP blends obtained at the 1st and 2nd heating

Table 3. Melting temperature (T_m), half width (HW), width (W) and height (H) of melting peak of components in anisotropic and isotropic mPP/ZNPP fibres and blends obtained at the 1st and 2nd heating (heating rate = 10 °C.min^{-1})

C_{mPP} / (% wt.)	1st heating				2nd heating			
	T_m / (°C)	HW / (°C)	H / (mW)	W / (°C)	T_m / (°C)	HW / (°C)	H / (mW)	W / (°C)
0	160.2	14.1	5.30	17.4	158.2	12.4	5.17	17.9
0.10	160.5	15.5	4.51	17.8	157.9	13.3	3.82	18.8
0.20	160.0	14.5	4.07	22.0	156.2	13.7	3.34	18.7
0.30	158.7	16.8	3.47	21.1	154.4	14.9	3.10	23.5
0.40	157.3	17.1	2.96	23.8	153.4	14.6	2.74	19.1
0.50	157.8	20.2	2.31	20.7	151.9	18.2	1.40	20.9
0.60	154.8	17.0	1.83	25.0	150.5	15.7	1.63	18.8
0.70	152.5	21.0	1.98	23.9	147.9	15.6	1.77	18.3
0.80	152.2	21.4	2.24	23.5	147.5	18.7	1.87	21.5
0.90	146.8	18.0	2.80	22.0	146.7	14.6	2.24	17.9
1.00	145.3	14.9	3.78	17.2	143.2	6.5	3.72	10.1

The PP crystallization ability in the anisotropic and isotropic mPP/ZNPP blends is different. It results from the endotherms obtained at the 1st and 2nd heating (Fig. 5). At the direct orientation the difference between the experimental and calculated melting enthalpies decreases with the mPP content to the 50 %wt. and then it increases again but it do not achieve the crystallization ability of the additive value of pure PP. At the crystallization of isotropic mPP/ZNPP blends the difference between the experimental and calculated melting enthalpies decrease in the whole range of the mPP content.

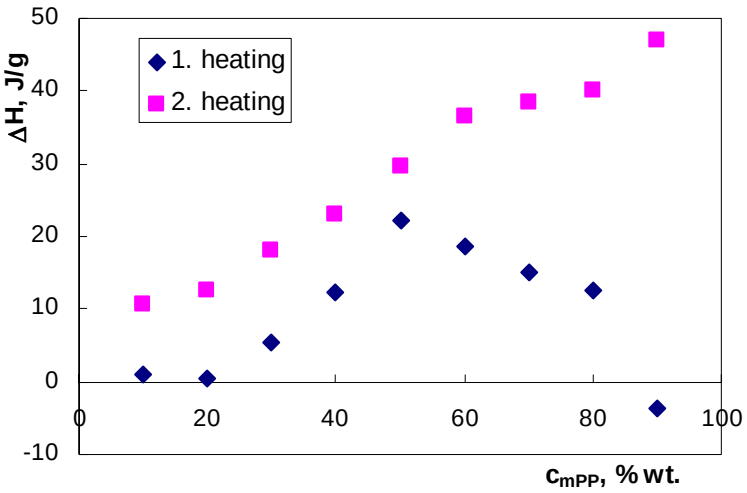

Fig. 5. Dependencies of difference calculated and experimental melting enthalpies on the mPP content in the oriented and un-oriented mPP/ZNPP fibres and blends obtained at the 1st and 2nd heating

Conclusion

The mutual interactions of the metallocene polypropylene with low density polyethylenes with different MFI (2 and 200 g/10 min) as well as with ZNPP in fibres and blends were studied by DSC method. It was found:

mPP and LDPE manifest the individual phase transition in the blend fibres with individual peaks on thermograms

1. The decrease of the difference of calculated and experimental melting enthalpies of the fibres and blends indicates a partial compatibility of mPP and LDPE SA 200 at a temperature above the melting point of components of minor concentration of LDPE
2. The increase of the difference of calculated and experimental melting enthalpies of the fibres and blends indicates a partial compatibility of mPP and LDPE FB2 at a temperature above the melting point of components in the whole LDPE concentration range
3. LDPE with low MFI exhibits higher mPP crystallinity in mPP/LDPE fibres and blends
4. mPP and ZNPP are thermodynamically compatible with forming of one melting peak on the endotherms
5. The PP crystallization ability is different in the oriented and un-oriented mPP/ZNPP fibres and blends.

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