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Thermal Properties of Functionalised Metallocene Polypropylene Fibres

Abstract
In this contribution blend metallocene polypropylene (mPP) fibres modified with 4, 8, 12 wt.% of copolyamide A and 4, 8, 12 wt.% of compatibiliser L were prepared. Copolyamide A consists of 85 wt.% of ε-caprolactam and 15 wt.% of nylon salt of adipic acid and diethylenetriamine. Compatibiliser L is low molecular isotactic polypropylene grafted with maleineanhydride. Thermal properties of the components, blends and modified mPP fibres were evaluated. Fibres modified with both copolyamide A and compatibilizer were successfully spun and drawn, with the opposite being the case for mPP fibres modified only with copolyamide A without compatibiliser L, which were not spun, confirming the positive role of compatibiliser L. The modified fibres conserve their thermal characteristics - melting temperature, melting enthalpy and entropy in the whole interval of both additive concentrations evaluated. The positive influence of the compatibiliser was found from the point of melting enthalpy and melting entropy.

Key words: *metallocene polypropylene, copolyamide, compatibilizer, modification, thermal properties, modified polypropylene fibres.*

Introduction

The preparation of blends from commercial polymers is well-known and easy, being usually more advantageous than the synthesis of new (co)polymers with suitable properties. At the same time, the application of blends in industry is cheaper, although it needs highly effective mixing of components.

The modification of non-polar fibre-forming polypropylene (isotactic iPP or metallocene mPP) with the aim of improving some of its properties is often possible with a certain amount of another (polymer) additive. If a more polar additive is used, usually worse mechanical properties of the products modified are obtained. Polypropylene/polyamide (PP/PA) blends are interesting because both components are relatively cheap, with versatile advantageous properties and being easily processable by melting. The modification of polypropylene is also possible with copolymers such as copolyamideureas and copolyamides.

1 – 5 wt.% of copolyamideureas based on CL containing 1,4-bis(3-aminopropyl) piperazine as additives to iPP brings better sorptive and electrostatic properties of the iPP fibres modified, but with a lower tensile strength and elongation at break [1].

iPP fibres blended with 4 - 15 wt.% of alkaline copolyamides (which are crystalline polymers [2]) based on CL, containing –NH- groups from diethylenetriamine [3, 4] or 8 wt.% of copolyamide containing piperazine cycles from 1-(2-aminoethyl)piperazine, [5] exhibit better sorptive and electrostatic properties and dyeability.

Their lower tensile strength and changed elongation at break are the consequence of a lack of compatibility with more polar (polymer) additive.

The improved properties of iPP products with a higher amount of polar additive can be assured when a compatibiliser is added. The compatibiliser itself can change the thermal characteristics of blend components, and its application can bring better rheological, thermal, mechanical and other properties due to the better adhesion of blend components. Moreover, chemical modification allows considerable adhesion advancement.

For improvement of the interfacial interaction and mechanical properties of iPP/PA blends, block or grafted copolymers of polypropylene (or its copolymers) are effective. A frequently used compatibiliser is PPgMA i.e. isotactic polypropylene grafted maleic anhydride

A small addition of PPgMA (equal to 0.2 wt.%) in the PP melt influences the crystallisation of iPP and leads to a reduction in homogeneous nucleation at high cooling rates and to an increase in the number of effective nuclei, meaning that PPgMA acts as a nucleating agent in the iPP phase. From the results reported it can be concluded that PPgMA crystallises mainly via heterogeneous nucleation at all the cooling rates examined, while iPP crystallizes via both heterogeneous and homogeneous nucleation, which is noticeable when the cooling rate is high [6].

The crystallisation and melting behaviour of polypropylene and PPgMA blends at different cooling temperatures was investigated. The blends of iPP/PPgMA 50/50 show either single (at low cooling rate) or double (at a rapid cooling rate) fusion endotherms, depending on their previous crystallisation conditions. The double peaks correspond well to the melting points of pure iPP and PPgMA, respectively, implying the separate melting of different lamellar crystals, while the single peak indicates the dominance of co-crystals in the blend system [7].

In the blends 70 wt.% (iPP+PPgMA) + 30 wt.% PA 6 with different weight fractions of PPgMA, the formation of a new copolymer at the interface between the domains of PA 6 and the matrix of PP was investigated. It was proved that a reaction between PA 6 and PPgMA occurs and both components (iPP and PA 6) exhibit miscibility with the PPgMA [8].

iPP/PA 6 blends with weight fractions equal to 70/30, 50/50 and 30/70 containing 2 wt.% of thermoplastic maleic anhydride were processed. While increasing the amount of polyamide in the blend compatibilised with MA, the tensile strength and water absorptivity increase [9].

Polypropylene and polyamide blends 70/30 wt.% have been studied with and without the addition of PPgMA at different levels: 1, 3, 5 and 10 wt.%. The isothermal crystallisation of the PA component is influenced by the presence of iPP, reducing the crystallisation rate due to the diluent effect originated by this polymer. On the other hand the crystallisation rate of iPP in the blends is

higher than the corresponding value for pure iPP. This effect is higher in blends without a compatibilizer, this behaviour being related to the nucleating activity of the PA component [10].

Copolymers based on mostly ε-caprolactam (CL) containing some polar functional comonomers are at least as polar as PA 6, and from a chemical point of view the metallocene polypropylene is the same as isotactic polypropylene, thus knowledge in the references mentioned above can be used for study of the compatibilisation of blends of metallocene polypropylene/copolyamide.

■ Experimental

Materials used

Metallocene polypropylene PP HM 562 R: abbreviated as mPP, chips and ground, MFI = 26.6 g/10 min, producer: LyondellBasell, Italy.

Copolyamide: abbreviated as A, binary copolyamide from 85 wt.% of ε- caprolactam and 15 wt.% of nylon salt ADETA (adipic acid + diethylenetriamine), synthesised by authors according to [34, 35], devoided of low-molecular compounds by 2 hours of extraction in hot water, and finally dried, T_m = 192 °C, [η] = = 73 g.ml-1 (96% H_2SO_4, 25 °C). Comparable commercial PA 6 from Nylstar Humenné, Slovakia has at the same conditions T_m = 221 °C, [η] = 153 g·ml-1.

Compatibilizer **Licomont AR 504:** abbreviated as L, low molecular isotactic polypropylene grafted with maleineanhydride, producer: Clariant GmbH, yellowish chips (fine grain), softening temperature: 154 - 158 °C, approximate density: 910 kg.m-3, viscosity of melt at 170 °C about 800 mPa·s. Other characteristic are in source [11].

The thermal stability of all three components used is very good [11,12].

Preparation of blends and fibres

For the preparation of blends without Licomont L, chips of dried copolyamide and chips of mPP were used. In the blends containing compatibiliser Licomont L in the form of fine grain, the PP was ground.

Three sets of modified mPP fibres were prepared. The first set contained only 4 wt.% A, 8 wt.% A and 12 wt.% A, the second one - 4 wt.% A + 2 wt.% L,

8 wt.% A + 4 wt.% L and 12 wt.% A + + 6 wt.% L, and the third one - 4 wt.% A + + 4 wt.% L, 8 wt.% A + 8 wt.% L and 12 wt.% A + 12 wt.% L.

Relevant components of the blends were mechanically mixed and melted in a single-screw ribbon extruder - GÖTTFERT (Germany) at the temperature of its 3 zones: $T_1 = T_2 = T_3 = 200$ °C. The blended ribbon was cooled down in cold water and cut into chips. The air-dried blend chips were finally vacuum-dried for 2 hours at T_4= 105 °C and used for fibre preparation.

Spinning of the dried blend chips was performed with lubricant using laboratory spinning equipment with an extruder of D = 16 mm at T_5 = 210 ° C, feeding weight - 15.6 g/10 min, take up speed - 150 m.min-1, and a spinneret nozzle with 13 fibrils. After spinning, the fibres were drawn at T_6 = 110 ° C and drawing ratio of $λ_1$ = 3. Fibres from the mPP + A blends without compatibiliser L could not be prepared due to the absence of the compatibiliser.

The thermal experimental characteristics, T_m, T_c, $ΔH_{m1exp}$, $ΔH_{m2exp}$ and $ΔH_c$, of the blends and fibres were determined using a DSC 7 Perkin Elmer at 10 K·min-1 the heating and cooling rates. Three cycles were applied (heating – cooling – heating) for comparison of thermal properties. The melting entropy $ΔS_m$ was calculated according to the relationship: $ΔS_m = ΔH_m/T_m$. The thermal characteristics calculated, $ΔH_{m1c}$ and $ΔH_{m2c}$, were found according to the additive method. All characteristics measured and calculated are given in *Tables 1* and *2*.

■ Results and discussion

Evaluation of the thermal properties of components (mPP, copolyamide A and compatibilizer L) and mPP + copolyamide A blends

Melting and crystallisation temperatures

The melting temperatures, T_{m1} and **T_{m2},** of mPP and compatibiliser L (as low molecular isotactic polypropylene grafted with maleineanhydride) are very close. The same is in the case of the T_{m2} values. The melting temperature of copolyamide is higher (*Table 1*). The addition of copolyamide A into mPP matrix does not influence the melting temperature of the blends when its amount is 4

and 8 wt.%. The amount 12 wt.% of copolyamide is manifested moreover by its own crystalline peak $ΔH_{m1}$= 3.9 J/g and melting temperature close to this of pure copolyamide.

The crystallisation temperatures T_c of mPP and the blends are very close (within 112.5 – 113.5 °C, *Figure 1* - see page 27). In the blend with 12 wt.% of copolyamide its own crystallization temperature turned out to have a value close to that of pure copolyamide. Hence the melting and crystallisation temperatures of the mPP/copolyamide blends practically do not depend on the amount of copolyamide.

Melting enthalpies

From the values in *Table 1* it is clear that all three components, i.e. metallocene polypropylene, copolyamide A and compatibilizer L are crystalline. Metallocene polypropylene is a highly crystalline polymer with $ΔH_{m1}$= 72.6 J/g. Compatibiliser L as a low molecular isotactic polypropylene grafted with maleineanhydride has a melting enthalpy about half of that of mPP – $ΔH_{m1}$= 35.2 J/g. Copolyamide A is a highly crystalline copolymer, as proven by $ΔH_{m1}$= 70.8 J/g.

The effect of blending to the crystallinity level can be evaluated by the $ΔH_{m1}$ values of the blends compared with the $ΔH_{m1}$ value of non modified mPP i.e. as value X. The $ΔH_{m1}$ values for the blends, calculated according to the additive rule from the amount of components (i.e 72.5 and 72.4 J/g), are practically the same as for non modified mPP (i.e. 72.6 J/g) because the $ΔH_{m1}$ values of mPP and copolyamide A are very close; however, the experimentally measured $ΔH_{m1}$ values for the blends are significantly lower as a consequence of mPP and copolyamide A incompatibility, which is seen in the drop when the amount of copolyamide increases from 4 to 8 wt.% and reaches X_{m1} = 75% and 66% of the value for non modified mPP. At these lower amounts copolyamide A does not exhibit any crystallisation peak due to its dispersion in the matrix of mPP. It is probable that a lower amount of copolyamide is dispersed completely in the matrix of mPP and no part of the copolyamide can crystallise. At the amount of 12 wt.% of copolyamide A in the blend, with a certain part of it manifested by its own crystallisation peak ($ΔH_{m1}$= 3.9 J/g), the total level of blend crystallinity increases and the X_{m1} value increases to 73%.

Table 1. *Thermal properties of mPP, copolyamide A, compatibiliser Licomont L and blends mPP + A;* [a] *partial values (ΔH_{m11}, ΔH_{m12}): (49.1+3.9) J/g,* [b] *partial values (ΔS_{m21}, ΔS_{m22}): (0.031+0.064) J/g.K,* [d] *partial values (ΔH_{m21}, ΔH_{m22}): (56.3 + 2.8) J/g,* [e] *partial values (ΔH_{m21}, ΔH_{m22}): (12.8 + 27.0) J/g,* [f] *partial values (ΔS_{m11}, ΔS_{m12}): (0.126+0.008) J/g.K,* [g] *partial values (ΔS_{m21}, ΔS_{m22}): (0.135+0.006) J/g.K, m – experimentally measured value, c - value calculated according to the additive method, X_m - experimental value, X_c – calculated value, $X_{m1} = (\Sigma \Delta H_{m1\ blend}/\Sigma \Delta H_{m1\ PP}) \times 100$, $X_{m2} = (\Sigma \Delta H_{m2\ blend}/\Sigma \Delta H_{m2\ PP}) \times 100$.*

System	T_m, °C	ΔH_{m1}, m, J/g, c	ΔS_{m1}, J/g.K	X_{m1} % X_r	T_c, °C	$-\Delta H_c$, J/g	T_{m2}, °C	ΔH_{m2}, m, J/g, c	X_{m2}, %	ΔS_{m2}, J/g.K
mPP	145.8	72.6	0.173	-	112.6	70.2	145.7	64.1	-	0.153
A	192.0	70.8	0.152	-	150.1	43.2	195.4	35.0	-	0.075
L	148.7	35.2	0.083	-	101.3	55.9	137.2/148.7	39.8[e]	-	0.095 [b]
96% mPP + 4% A	144.8	54.7 72.5	0.131	75.3 90.3	113.5	67.2	145.2	58.8 62.9	93.5	0.141
92% mPP + 8% A	145.5	48.2 72.5	0.115	66.4 83	113.1	64.6	145.7	51.5 61.8	83.3	0.123
88% mPP + 12% A	145.7 196.3	53.0[a] 72.4	0.134[f]	73 88	112.5 154.3	68.6 4.6	144.9 195.9	59.1[d] 60.6	97.5	0.141[g]

Table 2. *Thermal properties of mPP fibres non modified and modified with copolyamide A and compatibiliser L; λ3 – drawing ratio, ch – chips, m – experimentally measured value, c - value calculated according to the additive method, $X = (\Sigma \Delta H_{m1\ blend}/\Sigma \Delta H_{m1\ PP}) \times 100$.*

System	T_{m11}, °C	ΔH_{m1}, J/g m	c	-δ	ΔS_{m1}, J/g.K	X, %	T_{c1}, °C	$-\Delta H_c$, J/g	T_{m2}, °C	ΔH_{m2}, J/g	ΔS_{m2}, J/g.K
mPP ch	145.8	72.6			0.173	100	112.6	70.2	145.7	64.1	0.153
mPP λ0	144.2	53.9	-	-	0.129	74.2	111.8	75.3	143.9	53.1	0.127
mPP λ3	145.0	63.3			0.151	87.2	106.1	73.7	143.0	58.8	0.141
96 PP + 4A + 0L ch	144.8	54.7	63.4	8.5	0.131	75.3	113.5	67.2	145.2	58.8	0.141
96 PP + 4A+ 0L λ0	144.8	56.2	63.4	7.2	0.134	104.3	111.5	71.7	144.5	51.9	0.124
96 PP + 0A + 4L λ3	142.8	59.6	62.2	2.6	0.143	94.2	104.0	74.6	142.4	42.6	0.102
94 PP + 4A + 2L λ3	143.7	62.8	63.0	0.2	0.151	99.2	103.8	75.1	142.9	51.4	0.124
92 PP + 4A + 4L λ3	142.7	57.4	62.6	4.8	0.138	90.7	103.3	72.8	142.2	36.5	0.088
92 PP +8A +0L ch	145.5	48.2	52.4	3.2	0.115	66.4	113.1	64.6	145.7	51.5	0.123
92 PP +0A + 8L λ3	143.3	61.8	61.5	-0.3	0.148	97.6	103.6	76.6	142.9	43.6	0.105
88 PP +8A + 4L λ3	144.2	63.2	65.5	2.3	0.151	99.8	103.1	72.3	142.2	44.1	0.106
84 PP +8A + 8L λ3	143.7	57.3	63.5	6.2	0.137	90.5	103.1	72.7	142.0	42.6	0.102
88 PP+12 A+0L ch	145.7 196.3	53.0	55.8	2.8	0.126	73	112.5	68.6	144.9 195.9	59.1	0.140
88 PP +0A + 12L λ3	143.5	60.0	60.7	0.7	0.144	94.8	103.1	73.9	141.9	42.0	0.101
82 PP+ 12A + 6L λ3	143.8	62.4	63.0	0.6	0.150	98.6	103.3	75.3	142.4	48.1	0.115
76 PP+12A +12L λ3	144.3	62.3	61.9	-0.4	0.149	98.4	103.1	73.4	142.0	42.4	0.102

This effect of crystallisation promotion is supported by the values of the melting enthalpy of the second heating ΔH_{m2}, which are higher than those of the first heating ΔH_{m1}.

The experimentally measured melting enthalpies of the blends are theoretically composed of the melting enthalpies of the components, i.e. mPP and copolyamide A. For the blends containing 4 and 8 wt.% of copolyamide A, there are no contributions of copolyamide A, hence the melting enthalpy of these blends can only be obtained at 96 and 92 wt.% of mPP. If index X_{m1} is calculated up to these amounts of mPP, a more correct, real X_r value is obtained which expresses the amount of crystallised mPP in relationship with pure mPP. These values demonstrate that only 90.3, 83 and 88% crystallinity is achieved in comparison with the 100% crystallinity of pure mPP; thus copolyamide A defends to the maximal possible crystallisation of mPP. The same reflection can be used for the evaluation of copolyamide action in the blend.

In the blend containing 12 wt.% of copolyamide, this amount was manifested with an enthalpy contribution equal to ΔH_{m1A}= 3.9 J/g. At the condition where this amount behaves in the mPP matrix exactly the same as pure copolyamide (with ΔH_{m1}= 70.8 J/g), one can conclude that the contribution ΔH_{m1A}=3.9 J/g corresponds to 44.8% of all the amount of copolyamide A in this blend manifested by crystallites; hence more than 50% of the copolyamide is dispersed in the matrix as an amorphous phase.

The second heating brings about changes in the melting enthalpy of all three components. Copolyamide A has ΔH_{m2} = 35 J/g, rather lower than ΔH_{m1}= 70.8 J/g. This higher value demonstrates the contribution of the enthalpy of crystallites formed during primary crystallisation in the cooling of its melt after the synthesis and simultaneously contribution of crystallites formed during secondary crystallization which occurs in the period after the synthesis until DSC measurement. Its melting enthalpy during the second heating,

ΔH_{m2}= 35 J/g, proves this assumption because it is the demonstration of crystallites formed only during the cooling of the DSC measurement. From the difference $\Delta H_{m1} - \Delta H_{m2}$ = 35.8 J/g (i.e. 70.8 J/g – 35 J/g), the big role of secondary crystallisation at ambient temperature for copolyamide A is confirmed.

For mPP its melting enthalpy in the second heating, ΔH_{m2} = 64.1 J/g, is also lower in comparison with that of the first heating - ΔH_{m1}= 72.6 J/g and points to a similar but lower influence of the second crystallisation.

During cooling after the first heating, compatibiliser L forms two crystalline modifications: one with a lower melting temperature 137.2 °C and ΔH_{m21}= 12.8 J/g, and another one with ΔH_{m22}= 27.0 J/g and with the former melting temperature. The possibility to form two types of crystals is probably the reason that the melting enthalpy of the second heating, ΔH_{m2}= 39.8 J/g, is higher than that of the first heating ΔH_{m1}= 35 J/g.

The second heating brings about a positive effect for the melting enthalpies of the blends. The melting enthalpies of the second heating are higher than those of first, which is possible to explain by the positive nucleation effect of copolyamide on the crystallisation of the blend during cooling after the first heating. The reason for this effect is the higher crystallisation temperature of copolyamide A (T_c = 150 °C), where the solid particles of copolyamide A can promote the crystallisation of mPP crystallites formed at a lower crystallization temperature (T_c = 113 °C, **Figure 1**), and homogeneous or heterogeneous crystallisation of mPP can occur. The X_{m2} index increases and reaches values of 93.5, 83.3 and 97.5% of pure mPP crystallinity fibres also due to the lower ΔH_{m2} values of mPP and copolyamide. The previous tendency for X_{m1} is also valid for the X_{m2} index. Hence for both the first and second heating, the melting enthalpy of the mPP/copolyamide blends is lower in comparison with that of pure mPP, this difference being lower for values of the second heating.

Crystallization enthalpies
Crystallisation enthalpies show the level of crystallinity occurring during cooling after the first heating and can be compared with the melting enthalpies of the first heating. The crystallisation enthalpy ΔH_c of mPP compared with the melting enthalpy ΔH_{m1} is practically the same, hence the levels of crystallinity are similar before the first heating and after cooling. The crystallisation enthalpy of copolyamide A is rather lower and exhibits lower crystallisation kinetics during cooling (at a given rate of cooling), with the absence of secondary crystallisation. The crystallisation enthalpy of compatibiliser L is higher in comparison with its melting enthalpy ΔH_{m1} probably as a consequence of the formation of two crystalline modifications, which consume more energy than one crystalline modification present before DSC measurement.

Melting entropies
The melting entropy documents the level of the macromolecular system arrangement, with a higher value expressing the better arrangement of the system. From this point of view, crystalline polymers mPP and copolyamide A have a highly organised structure and compatibiliser a L lower one, when the two are compared. The melting entropies of the blends are lower compared with that of mPP. It is interesting that the highest value of ΔS_{m1}
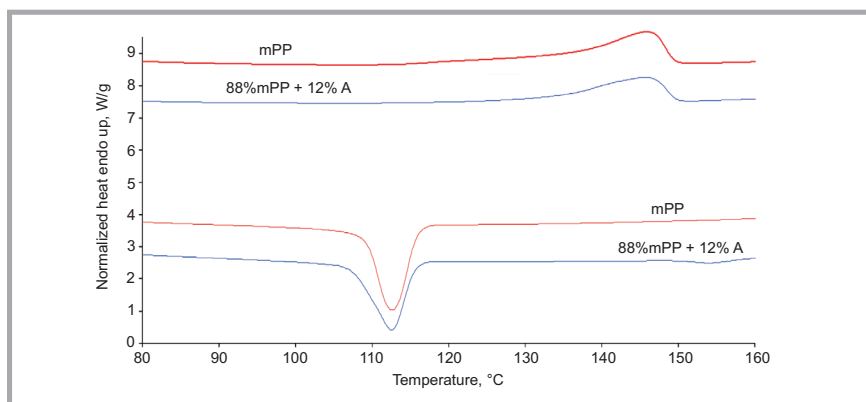

Figure 1. *DSC thermograms of mPP and blend 88 wt.% PP + 12 wt.% A.*
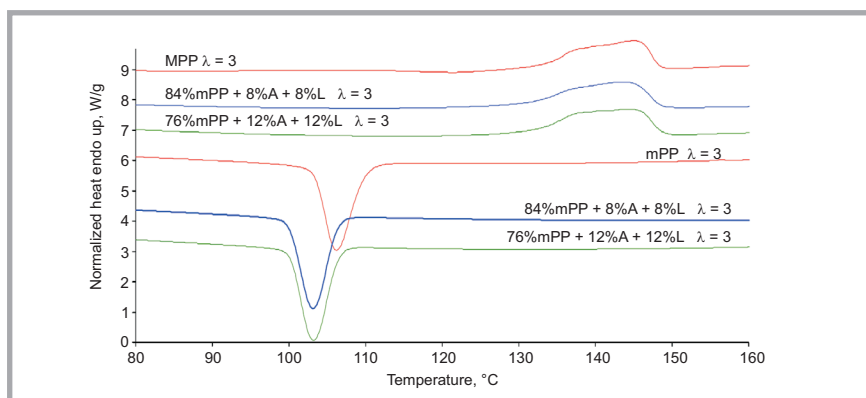

Figure 2. *DSC thermograms of non modified and modified mPP fibres (first heating and cooling).*

is shown by the system 88 wt.% mPP + 12 wt.% copolyamide A, hence the system with the highest amount of non-compatible copolyamide as an additive in the polypropylene matrix, which is probably a consequence of the fact that only about 50% of this amount is dispersed in the mPP matrix, with the remaining part forming its own crystallites with a high level of order, which thus contributes to the high value of blend melting entropy. Therefore the melting entropies of the mPP/copolyamide blends are much lower in comparison with that of pure mPP, and the blend systems are more poorly organised in comparison with pure mPP .

Evaluation of the thermal properties of modified mPP fibres

For evaluation of the thermal properties of the fibres, only values T_{m1}, ΔH_{m1}, ΔS_{m1} and ΔH_c respectively, can be used because all other values do not characterise the fibres due to their non isotropic structure (influencing thermal characteristics), only the blend of all components formed after the first melting and cooling. Differences in the values from the first and second heating highlight changes occurring after the melting of fibres.

Melting and crystallisation temperatures
All thermal characteristics concerning the fibres are given in **Table 2**.

The melting temperatures of non modified and modified mPP fibres are very close, and there is no evidence of the influence of copolyamide A or compatibiliser L or a tendency regarding the amount of copolyamide A or compatibiliser L with respect to these values.

The drawn non modified mPP fibres have T_c = 106.1 °C, and all modified mPP fibres have lower but very close T_c values (within 103.1 – 104.0 °C, **Figure 2**). Probably the recrystallisation and creation of other types of crystallites during the drawing process and the presence of additives are the reasons for this change.

The crystallization temperatures of pure mPP, the blends and non-drawn fibres consisting of 96 wt.% mPP + 4 wt.% copolyamide are at approximately the same level, but those modified with only the compatibiliser or both copolyamide A and compatibiliser L have about a 10 °C lower temperature. Compared with the

accuracy of the DSC measurement [13], this difference is not negligible and could be caused by the common influence of both additives. The amount of either copolyamide A or compatibilizer does not influence the crystallisation temperature of drawn modified mPP fibres.

Melting and crystallisation enthalpies, and the melting entropy

From the values of the melting enthalpies of the modified mPP fibres, it is clear that they are crystalline (*Table 2*). The differences in melting enthalpies are higher than the accuracy of DSC measurements, given in [13].

The ΔH_{m1} values of mPP chips, non drawn and drawn mPP fibres are different. The melting enthalpy of mPP chips is the highest (primary and secondary crystallisation). Fibres have lower ΔH_{m1} values due to quick cooling during spinning. mPP fibres drawn to $\lambda = 3$ have a higher ΔH_{m2} value compared with the enthalpy of non drawn fibres because the drawn fibres underwent drawing after spinning, enabling further (re)crystallisation.

Comparison of the melting enthalpy ΔH_{m1} of the blends and fibres with $\lambda = 0$ shows that the fibres have a higher ΔH_{m1} value, hence they have a higher level of crystallisation, which is logical because the components of the blend are once more mixed in a molten state; thus the additives can be better dispersed, displaced and moved into the amorphous part of the matrix.

Modified fibres drawn at a drawing ratio of $\lambda = 3$ have an even higher value as a consequence of further (re)crystallisation and a higher arrangement during the quick process of drawing above the glass temperature T_g.

All drawn modified fibres ($\lambda = 3$) containing only compatibiliser L have experimental ΔH_{m1m} values very close or even higher than calculated ΔH_{m1c} values, thus compatibiliser L alone does not negatively influence the crystallization ability of mPP fibres.

Drawn mPP fibres modified "only" with compatibiliser L have a lower experimental ΔH_{m1} value (in *Table 2*, denoted as m) in comparison with those modified with copolyamide A and half the amount of compatibiliser L (4 wt.% A + 2 wt.% L, 8 wt.% A + 4wt.% L and 12 wt.% A + 6 wt.% L), and even those modified with

12 wt% A + 12 wt.% L, which means that modified fibres containing copolyamide A and compatibiliser L crystallise better than those containing only compatibiliser L. If the modified fibres contain an equal amount of copolyamide A and compatibiliser L, the melting enthalpy decreases even at 12 wt.% of copolyamide A and 12 wt.% of compatibiliser L; this difference being negligible.

The theoretical values ΔH_{m1} calculated for modified mPP fibres (in *Table 2*, denoted as c) show a hypothetic state when all components crystallise as pure constituents without a negative influence on each other, hence with the maximal melting enthalpy possible. Comparison of the experimental (measured) values ΔH_{m1} with those calculated shows that they are close to each other, with the difference δ being small. In other words, the lower the difference δ, the better the compatibility of components, or at least the components can crystallise to the highest degree. If the value of δ reaches even a negative value, it means that the components of the system form more crystallites with a higher melting enthalpy than the summary of the melting enthalpies of all components alone, and the components of the system do not negatively influence each other.

This situation is also explained by the value X as the ΔH_{m1} value of the modified fibres compared with the ΔH_{m1} value of non modified mPP fibres. If the level of the ΔH_{m1} value for non modified mPP fibres is 100%, mPP fibres modified with 4 wt.% A + 2 wt.% L reach X = 99.2%, when modified with 8 wt.% A + 4 wt.% L they reach 99.8%, and those modified with 12 wt.% A + 6 wt.% L reach 98.6% of the value for non modified mPP fibres. mPP fibres modified with 12 wt.% A + 12 wt.% L have almost the same ΔH_{m1} value than those with half the amount of compatibiliser L.

One can divide modified mPP fibres into two categories: The melting enthalpies of mPP fibres modified with 4 and 8 wt.% of copolyamide A and half the amount of compatibiliser L are higher than those modified with copolyamide A and the same amount of compatibiliser L. The highest amount of copolyamide (i.e. 12 wt.% A) has comparable melting enthalpy characteristics for both amounts of compatibiliser L.

The values of ΔS_{m1} confirm this effect because at the same composition of modified mPP fibres they are the highest and reach the value of non modified mPP fibres.

mPP fibres modified only with 4, 8 and 12 wt.% of copolyamide A (without compatibilizer L) could not be spun, thus we do not have the possibility to compare their characteristics with those of fibres modified with couple copolyamide A + compatibiliser L; however, the results of the fibres last mentioned show that this modification was successful at least in the preparation of the modified fibres and in the thermal characteristics i.e. melting temperature and melting enthalpy.

■ Conclusions

1. It was not possible to spin modified mPP fibres only with copolyamide A.
2. The spinning and drawing of mPP fibres modified with different amounts of copolyamide A and compatibiliser L were successful.
3. The positive role of compatibiliser L was confirmed i.e. low molecular isotactic polypropylene grafted with maleineanhydride.
4. The fibres modified conserve their thermal characteristics - melting temperature, melting enthalpy and entropy in the whole interval of both additive concentrations evaluated, mainly when the amount of compatibiliser L forms half the amount of copolyamide A.
5. According to the melting enthalpy, a higher effectivity of compatibiliser L in the fibres modified was found when its amount equalled half the copolyamide amount i.e . 4 wt.% A + 2 wt.% L, 8 wt.% A + 4wt.% L and 12 wt.% A + 6 wt.% L and modified with 12 wt% A + 12 wt.% L.
6. The melting entropies of the fibres have the same tendency and are the same or nearly the same as for non modified mPP fibres, which confirms that the macromolecular arrangement of the blend system is not negatively influenced by modification with copolyamide when a compatibiliser is used.

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