

# Thermal properties of PA 6 and PA 6 modified with copolyamides and layered silicates

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**Abstract** This article focuses on the thermal properties of PA 6 and additives, i.e. ternary copolyamides, concentrates consisting of binary or ternary copolyamides + nanoadditive montmorillonite Bentonite 11958 or Cloisite 15A and PA 6 fibres modified with Bentonite, copolyamide and concentrate. The copolyamides are prepared from  $\epsilon$ -caprolactam as a major comonomer and nylon salts AN2 from adipic acid + 1-(2-aminoethyl)piperazine and ADETA from adipic acid + diethylenetriamine. All copolyamides and concentrates exhibit lower melting temperatures  $T_m$  and lower melting enthalpies  $\Delta H_m$  compared to neat PA 6. PA 6 fibres modified with 0.25–2.5 wt% MMT exhibit higher melting enthalpies in comparison with unmodified PA 6 fibres. PA 6 fibres modified with 10 wt% of ternary copolyamide containing 21.4 wt% of comonomers AN2 and ADETA have higher melting enthalpy as well. PA 6 fibres modified with 10 and 20 wt% of concentrate containing the same ternary copolyamide + 5 wt% of MMT have higher melting enthalpies and higher tensile strength in comparison with these characteristics of unmodified PA 6 fibres.

**Keywords** DSC · Copolyamides · Nanoadditives

## Introduction

Thermal analysis is a useful tool for investigation of the properties of polymers, blends and polymer/clay

nanocomposites and mechanisms of improvement of their thermal properties [1]. Thermal characteristics of all thermoplastic polymers processed by moulding, injection or spinning at elevated temperatures are very important. Thermal characteristics are important as well for fibre-forming polymers and their additives mainly in assessing the behaviour in the blend and during processing to products. Homopolymers and copolymers based on the same comonomer may form the blend material for products with better end-use properties. Copolymers are able to improve many properties, including thermal ones [2, 3].

Copolymers have a great advantage—a good compatibility with relevant homopolymer. Segments of semicrystalline block copolymers can even cocrystallize with homopolymer, form several types of crystals with various sizes and level of perfection and similar segments of copolymer can form their own crystallites [4, 5]. Copolyamides and copolyamideureas based on  $\epsilon$ -caprolactam (CL) with other functional comonomer(s) can be applied as compatible additives for modified polyamide (PA 6) fibres [6, 7].

Crystallization ability of copolyamides based on CL depends mainly on the amount, chemical nature and molecular length of other functional comonomer which determine the longitudinal (dis)order of the copolyamide macromolecules [8]. In certain cases, however, the crystallinity is not reduced because the segment of the comonomer is similar in size to that which is being replaced and we can suppose that segments with (not very) different chemical nature but with similar length could cocrystallize or at least to have a good compatibility each other.

Homopolymer poly- $\epsilon$ -caprolactam contains a crystalline portion as a consequence of the regular spatial order of its macromolecules and intermolecular bonds. Due to copolyreaction, higher longitudinal disorder usually reduces crystallinity as a rule. Addition of such copolymer to

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the homopolymer can bring about worse mechanical properties [9].

CL, DETA and N2 molecules are very similar to those of adipic acid and terephthalic acid in their chemical nature and molecular length [10, 11]. This presumes the possible isomorphous and crystalline character of copolyamides consisting of CL and nylon salts AN2 and ADETA from adipic acid + 1-(2-aminoethyl) piperazine and from adipic acid + diethylenetriamine. Higher disorder and bulky piperazine rings can bring about a lower number of intermolecular bonds and a decrease of some characteristics (e.g.  $\Delta H_m$ ,  $T_m$ , etc.). Usually, the higher the amount of minor comonomer, the higher is the probability of a higher disorder of the macromolecules and the possibility of decreasing the level of crystallization as well. This is valid in the case of random copolymers and in the situation when the minor comonomer cannot cocrystallize, i.e. its length and spatial arrangement is not close to that of a major comonomer. In the case of block copolymers, the situation would be different and a higher amount of the minor comonomer enables the formation of longer different segments of both comonomers and two or more types of crystals as well. The asymmetrical molecule of 1-(2-aminoethyl) piperazine is probably the reason why crystals built with various arrangements and more crystalline forms can be present in the macromolecule of copolyamide containing nylon salt AN2, mainly when the amount of this comonomer is higher [12].

To avoid the negative phenomena of simple polymer blends and to improve their properties, the nanocomposites can be prepared by either in situ polymerization [13, 14] or melt-blending process [15]. Comparison of these two ways showed that in situ polymerized nanocomposites exhibited higher melt viscosity and higher tensile ductility than the melt-blended nanocomposites which was related to improved dispersion and polymer-layered silicate interactions [16].

Polyamides synthesized in the presence of nanoadditive exhibit better properties of end products, mainly from the point of mechanical properties [17, 18]. Addition of 5 wt% of commercial organophilic montmorillonite, MMT, (Cloisite 30B) modified with various surfactants brings about no variation of melt temperature and crystallinity of LDPE but significant increase of the air thermal stability [19]. The results of testing the flammability of polyimideamide nanocomposite fibres containing 3 wt% of modified montmorillonite justify to characterize them as flame-retardant fibres [20].

Several thermal methods, including DSC, were used for the examination of thermal properties of polyamide 6/clay (Cloisite 10A and Cloisite 20A) and PA 6/thermoplastic polyurethane/clay blends. It has been proved that the thermal stability and tensile properties of these systems were

better when the clay was present within the polymer matrix and depend on both the clay loading and its type [21].

The main aim of this study was to synthesize copolyamides from CL with different amount of nylon salts ADETA and AN2 and concentrates with the same composition of CL, ADETA and AN2 plus equal amount of nanoadditives, and to judge the influence of comonomers AN2, ADETA and nanoadditives to copolyamide's and concentrate's properties. Therefore, copolyamides and relevant concentrates were studied and compared together and with commercial homopolyamide PA 6 from the point of their thermal properties. PA 6 fibres modified with different amount of chosen concentrate were prepared and their mechanical properties were evaluated as the third objective.

## Experiment

### Materials used

Polyamide 6, PA 6, commercial,  $\eta_{rel} = 2.58$ ,  $T_m = 221$  °C, Nylstar Humenné, Slovakia. Polyamide 6, PA 6P, commercial polymer moulded in extruder GÖTTFERT,  $\eta_{rel} = 2.56$ ,  $T_m = 221$  °C.  $\epsilon$ -caprolactam commercial, CL, Nylstar Humenné, Slovakia, major comonomer Adipic acid, anal. grade, Aldrich. 1-(2-aminoethyl)piperazine, N2, Aldrich, vacuum distilled. Diethylenetriamine DETA, Aldrich, vacuum distilled. Nylon salt AN2 prepared from adipic acid and 1-(2-aminoethyl)piperazine (N2), minor comonomer. Nylon salt ADETA prepared from adipic acid and diethylenetriamine, minor comonomer. Nanoadditive Bentonite 11958, organophilic montmorillonite, i.e. layered mineral with sodium ions and quaternary ammonia ions between the layers, Fluka, Nanoadditive Cloisite 15A, organophilic montmorillonite, ditallowdimethylammonium salts with Bentonite 100%, Fluka,

### Copolyamides:

1.  $\alpha$ —89.3 wt% CL + 5.35 wt% AN2 + 5.35 wt% ADETA
2.  $\delta$ —78.6 wt% CL + 10.7 wt% AN2 + 10.7 wt% ADETA
3.  $\beta$ —76.6 wt% CL + 18.4 wt% AN2 + 5 wt% ADETA

### Concentrates:

- DX—84.3 wt% CL + 10.7 wt% AN2 + 0 wt% ADETA + 5.0 wt% Bentonite  
 A—84.3 wt% CL + 5.35 wt% AN2 + 5.35 wt% ADETA + 5.0 wt% Bentonite  
 AC—84.3 wt% CL + 5.35 wt% AN2 + 5.35 wt% ADETA + 5.0 wt% Cloisite  
 D—73.6 wt% CL + 10.7 wt% AN2 + 10.7 wt% ADETA + 5.0 wt% Bentonite

DC—73.6 wt% CL+10.7 wt% AN2 + 10.7 wt% AD-ETA + 5.0 wt% Cloisite  
 B—71.6 wt% CL + 18.4 wt% AN2 + 5.0 wt% ADE-TA + 5.0 wt% Bentonite

The nylon salts AN2 and ADETA were prepared by mixing hot equimolar solutions of adipic acid and distilled either 1-(2-aminoethyl)piperazine or diethylenetriamine in 96% ethanol. By gradual evaporation of ethanol, the solution became thicker. When it reached the honey-like consistency it was poured into Petri dishes and residual ethanol was evaporated in a fume chamber for several days. During drying, the nylon salt crystallized. Then, the nylon salt was pulverised and vacuum dried to remove quantitatively the residual ethanol.

The copolyamides and concentrates were prepared through a polyreaction in a melt under nitrogen atmosphere. Powdered CL, and both nylon salts AN2 and ADETA (for copolyamides  $\alpha$ ,  $\beta$  and  $\lambda$ ) and powdered CL, one or both nylon salts AN2 and ADETA and nanoadditive (for concentrate DX, A, AC, D, DC and B) were mechanically mixed and put in a glass apparatus immersed in a thermostatted oil bath. The melting, homogenization and poly(addition–condensation) reaction were completed within 90–220 min (copolyamides) and 230–340 min (concentrates). The nylon salts act as the activators of the polyreaction of CL so that longer polyreaction time for copolyamide with lower amount of nylon salts was used. At the end of the polyreaction, the copolyamides were poured onto a metallic plate and cut into chips.

All synthesized concentrates contained 5 wt% of nanoadditive.

## Methods used

In order to evaluate the influence of additives (nanoadditives, copolyamides and concentrates), the physical mixtures of commercial PA 6 chips with chips of copolyamide or concentrate and commercial powdered PA 6 with Bentonite (0.25–2.5 wt%) were prepared and melted in the single-screw extruder GÖTTFERT at the temperatures of zones  $T_1 = T_2 = T_3 = 250$  °C. The ribbon was cooled down in the cold water and cut into chips. In order to eliminate low-molecular compounds, the chips of copolyamides and concentrates were extracted in boiling water for 2 h and dried at 105 °C for 2 h. The air-dried chips were finally dried in vacuum oven at 105 °C for 2 h and used for spinning.

The spinning of dried blend chips was performed by a laboratory spinning equipment with an extruder  $\Phi = 16$  mm at  $T_4 = 250$  °C, take-up speed 150 m min<sup>-1</sup> with lubricant (spinneret nozzle with 13 fibrils). After spinning, the fibres were drawn to the drawing ratio  $\lambda = 3$ .

The thermal properties, melting temperature,  $T_m$ , crystallization temperature,  $T_c$ , melting enthalpies of the first and second heating,  $\Delta H_{m1}$ ,  $\Delta H_{m2}$ , and enthalpy of crystallization,  $\Delta H_c$  were determined using DSC 7 Perkin Elmer at 10 K min<sup>-1</sup> the heating and cooling rates. The heating—cooling—heating cycles were applied for the study of thermal properties.

Mechanical properties, i.e. tensile strength and elongation at break, were measured by INSTRON 1122. Clamping length was 100 mm, deformation rate was 200 mm min<sup>-1</sup>.

## Results and discussion

In the first part, thermal characteristics of ternary copolyamides and concentrates consisting of binary and ternary copolyamides with nanoadditives Bentonite or Cloisite were studied. In the second part, thermal characteristics of PA 6 fibres modified with the only Bentonite, one copolyamide and one concentrate were evaluated.

$T_m$  and  $\Delta H_m$  characteristics are usually evaluated from the second heating. The comparison between thermal characteristics of the first and second heating can be used for evaluation of crystallization process and its dependency on factors like time and speed of cooling. For fibres, the primary structure is destroyed during the first heating so that the subsequent second heating reveals only the characteristics of polymer not of the fibres. The thermal characteristics of the first heating show the situation after long term (primary and secondary) crystallization or recrystallization, respectively. Comparison of melting enthalpy of the first heating  $\Delta H_{m1}$  with melting enthalpy of the second heating  $\Delta H_{m2}$  shows the ability of system (either copolyamide or concentrate) to crystallize in a long time after its preparation. The difference between  $\Delta H_{m1}$  and  $\Delta H_{m2}$  focuses to the role of secondary crystallization. Therefore, from DSC measurements, melting and crystallization temperatures, enthalpies of melting and crystallization were determined. Other characteristics like general macromolecular order and secondary crystallization can be judged from primary characteristics indirectly.

In order to evaluate the influence of remoulding on the DSC characteristics of homopolyamide PA 6, two DSC measurements of polyamide 6 were carried out. One for the primary commercial PA 6 and the second for commercial PA 6 once moulded with extruder GÖTTFERT and designated as PA 6P. Thermal characteristics of commercial PA 6 and once melted commercial PA 6 designed as PA 6P are very similar so remoulding of PA 6 does not change practically its thermal characteristics (Table 1). Values of melting enthalpies  $\Delta H_{m1}$  for the first heating are practically the same for both polyamides 6. Differences observed after the second heating are the consequence of formation of two structural modifications. In the first heating only one structural

**Table 1** Thermal properties of commercial PA 6 and ternary copolyamides (no Bentonite)

Polymer	Amount of com./wt%	$T_{m1}/^{\circ}\text{C}$	$\Sigma\Delta H_{m1}/\text{J g}^{-1}$	X/%	$\Delta S_{m1}/\text{J g}^{-1}\text{K}^{-1}$	$T_c/^{\circ}\text{C}$	$-\Delta H_c/\text{J g}^{-1}$	$T_{m2}/^{\circ}\text{C}$	$\Delta H_{m2}/\text{J g}^{-1}$	$\Sigma\Delta H_{m2}/\text{J g}^{-1}$	Y/%	$\Delta S_{m2}/\text{J g}^{-1}\text{K}^{-1}$	Z/%	Q/J g <sup>-1</sup>	R/J g <sup>-1</sup>
PA 6	0	221	77.9	-	0.158	186	75.4	222	62.6	62.6	-	0.126	80.4	2.5	15.3
PA 6P	0	221	78.0	-	0.158	186	74.1	212, 220	24.2, 38.4	62.6	-	0.127	80.3	3.9	15.4
$\alpha$	10.7	204	67.3	86.3	0.141	155	60.4	190, 202	9.3, 34.3	43.6	69.6	0.092	64.8	6.9	23.7
$\delta$	21.4	180	58.6	75.1	0.129	135	43.2	178	32.3	32.3	51.6	0.072	55.1	15.4	26.3
$\beta$	23.4	182	59.4	76.2	0.131	128	49.5	184	34.4	34.4	55.3	0.076	57.9	9.9	25.0

modification appeared with melting temperature  $T_{m1} = 221$  °C. In the second heating two structural modifications have manifested with melting temperatures  $T_{m21} = 212$  °C and  $T_{m22} = 220$  °C.

The first structural modification with  $T_{m21}$  is characterized by its melting enthalpy  $\Delta H_{m21} = 24.2$  J g<sup>-1</sup> and the second one with  $T_{m22}$  is characterized by melting enthalpy  $\Delta H_{m22} = 38.4$  J.g<sup>-1</sup> but the sum  $\Sigma\Delta H_{m2} = 62.6$  J g<sup>-1</sup> is the same as the value  $\Delta H_{m1} = 62.6$  J g<sup>-1</sup>.

Melting entropies of the first heating  $\Delta S_{m1}$  of both PA 6 and PA 6P are the same ( $\Delta S_{m1} = 0.158$  J g<sup>-1</sup> K<sup>-1</sup>) and these of the second heating are very close, equal to 0.126 and 0.127 J g<sup>-1</sup> K<sup>-1</sup> so the macromolecular order is practically at the same level in both types of PA 6 (Table 1).

The thermal characteristics of copolyamides  $\alpha$ ,  $\delta$  and  $\beta$  depend mainly on the total amount of comonomers as well as on the presence of nanoadditive used (Tables 1, 2). The type and the amount of each comonomer in copolyamide are not decisive. All copolyamides and concentrates have lower melting and crystallization temperatures  $T_m$ , and  $T_c$ , melting and crystallization enthalpies  $\Delta H_m$ , and  $\Delta H_c$  in comparison with homopolymer PA 6 or PA 6 P.

#### Evaluation of melting temperature, $T_m$

Regarding the melting temperature  $T_m$  (Tables 1, 2), copolyamides and concentrates can be divided into two groups. The copolyamide  $\alpha$  and concentrates with lower amount of both comonomers (i.e. A and AC) and concentrate DX with the only minor comonomer have higher  $T_m$ , concentrates even with two melting temperatures (except concentrate DX).

Copolyamide  $\alpha$  with the total amount 10.7 wt% of comonomers has melting temperature  $T_m = 204$  °C, other two copolyamides  $\delta$  and  $\beta$  with higher total amount of comonomers (21.4 and 23.4 wt%) have the melting temperatures 180 and 182 °C.

Concentrates DX and AC with lower total amount of comonomers 10.7 wt% have the highest melting temperatures 191–206 °C and those with higher amount of comonomers have melting temperatures from the interval 185–189 °C. In the case of concentrate DX, it is a consequence of the most regular molecular structure, and in the case of concentrate AC, it is the influence of Cloisite. The better influence of Cloisite is evident as well from the comparison of both concentrates AC and DC containing Cloisite with concentrates A and D containing Bentonite. Concentrates AC and DC have higher  $T_m$  and  $\Delta H_{m1}$  values.

#### Evaluation of melting enthalpy $\Delta H_{m1}$

The value of  $\Delta H_{m1}$  expresses melting enthalpy of crystallites formed after the synthesis. It consists of two

**Table 2** Thermal properties of commercial PA 6 and concentrates consisting of copolyamides and Bentonite or Cloisite 15A

System	$T_{m1}/^{\circ}\text{C}$	$\Delta H_{m1}/\text{J g}^{-1}$	$\Sigma\Delta H_{m1}/\text{J g}^{-1}$	$\Delta S_{m1}/\text{J g}^{-1}\text{K}^{-1}$	$X/\%$	$T_d/^{\circ}\text{C}$	$-\Delta H_d/\text{J g}^{-1}$	$T_{m2}/^{\circ}\text{C}$	$\Delta H_{m2}/\text{J g}^{-1}$	$\Delta H_{m2}/\text{J g}^{-1}$	$\Sigma\Delta H_{m2}/\text{J g}^{-1}$	$\Delta S_{m2}/\text{J g}^{-1}\text{K}^{-1}$	$Y/\%$	$Z/\%$	$Q/\text{J g}^{-1}$	$R/\text{J g}^{-1}$
PA 6P	221	78.0	78.0	0.158	–	186	75.4	212, 220	24.2, 38.4	62.6	62.6	0.127	–	80.3	2.5	15.4
DX	198, 206	48.3, 23.2	71.5	0.151	91.2	161	56.7	204	44.7	44.7	44.7	0.094	71.4	62.5	14.8	26.8
A	191, 204	29.7, 33.3	63.1	0.134	81	157	53.7	197, 203	20.2, 21.8	42.0	42.0	0.089	67.1	66.6	9.4	21.1
AC	198, 205	51.0, 17.3	68.3	0.144	87.7	161	54.8	193, 204	11.7, 34.8	46.5	46.5	0.098	74.3	68.1	13.5	21.8
D	187	54.3	54.3	0.118	69.7	137, 126	43.2 <sup>a</sup>	181	26.9	26.9	26.9	0.059	43	49.5	11.1	27.4
DC	189	58.7	58.7	0.127	75.4	138	44.8	182, 188	16.5, 13.7	30.2	30.2	0.066	48.2	51.4	13.9	28.5
B	185	57.6	57.6	0.126	73.9	128	41.6	183	30.8	30.8	30.8	0.067	49.2	53.5	16.0	26.8

<sup>a</sup> = (20.6 + 22.6) J g<sup>-1</sup>

contributions. The first one is the melting enthalpy of crystallites formed during the cooling of ribbon of synthesized additive and expresses the primary crystallization. The second contribution expresses the secondary crystallization as the melting enthalpy of crystallites formed in the period from primary crystallization till DSC measurement.

From the point of melting enthalpy  $\Delta H_{m1}$  (Tables 1, 2), one can observe a concentration dependence for copolyamides and concentrates as well. The melting enthalpy  $\Delta H_{m1}$  of neat additives can be compared with melting enthalpy of PA 6 directly either by relevant  $\Delta H_{m1}$  values or as the quotient of the melting enthalpy  $\Delta H_{m1}$  of homopolyamide to melting enthalpy of PA 6 (column X in Tables 1, 2). X means the quotient melting enthalpy of additive to melting enthalpy of PA 6 at the first heating calculated as

$$X = \left( \frac{\sum \Delta H_{m1\text{additive}}}{\sum \Delta H_{m1\text{PA6}}} \right) \times 100$$

Copolyamides have lower melting enthalpies  $\Delta H_{m1}$  compared to PA 6 and they decrease with amount of minor comonomers as a consequence of decreasing regularity of the macromolecular backbone. Copolyamide  $\alpha$  with lower amount of minor comonomers has the highest  $\Delta H_{m1}$  value and  $X = 86\%$  of PA 6. Two copolyamides with higher amount of comonomers in copolyamide, i.e. the copolyamide  $\delta$  and  $\beta$ , have practically the same melting enthalpies and crystallization ability with  $\Delta H_{m1} = 59.4$  and  $58.6 \text{ J g}^{-1}$  and  $X = 76$  and  $75\%$ .

Melting enthalpies of concentrates can be divided into two groups. Comparison of three concentrates containing copolyamides with the amount of comonomers equals to 10.7 wt% and two different nanoadditives Bentonite and Cloisite (i.e. A, AC and DX) show that  $\Delta H_{m1}$  value of concentrate A (two comonomers + Bentonite) is lower than this for copolyamide  $\alpha$  ( $X = 81$  vs.  $86\%$ ). Concentrate AC (two comonomers + Cloisite) has this value higher ( $X = 88$  vs.  $86\%$ ) and concentrate DX containing copolyamide with only one minor comonomer has the highest  $\Delta H_{m1}$  value and  $X = 91\%$ . Therefore,  $\Delta H_{m1}$  value is positively influenced by higher regularity of copolyamide macromolecules arrangement and by the nanoadditive Cloisite as well. Concentrates with higher amount of minor comonomers (i.e. D, DC and B) have lower  $\Delta H_{m1}$  values in comparison with concentrates having lower amount of both minor comonomer(s). Their level of  $\Delta H_{m1}$  values is  $X = 70\text{--}75\%$  of  $\Delta H_{m1}$  PA 6 value.

General comparison of presented results shows that from the point of melting enthalpy the highest values  $\Delta H_{m1}$  are reached by concentrates DX and AC and copolyamide  $\alpha$ . Therefore, concentrate DX with 10.7 wt% of the only one comonomer AN2 containing Bentonite has the value  $X = 91\%$ , concentrate AC with lower amount of both

comonomers i.e. 5.35 wt% of AN2 + 5.35 wt% of ADETA + 5 wt% of Cloisite 15A as nanoadditive has the value  $X = 88\%$  and copolyamide  $\alpha$  containing 5.35 wt% of AN2 + 5.35 wt% of ADETA, without any nanoadditive has the value  $X = 86\%$ .

The increase of  $T_m$  but the drop of  $\Sigma\Delta H_{m1}$  values of concentrates with higher total amount of comonomers in copolyamide in comparison with copolyamides containing the same amount of comonomers are remarkable and show the influence of nanoadditive used. Concentrates, i.e. copolyamides + nanoadditive with higher amount of comonomers causing lower organized copolyamide macromolecules, do not prefer crystallization of the system so  $\Delta H_{m1}$  values are lower. However, this drop is the lowest in the case of nanoadditive Cloisite so Cloisite maintains high values of melting enthalpy.

#### Evaluation of crystallization enthalpy $\Delta H_c$

It follows from values  $\Delta H_c$  of copolyamides and values  $Q$  ( $Q = \Delta H_m - \Delta H_c$ ) that the higher level of crystallization after the first heating is reachable by copolyamides, and concentrates have a higher value of  $Q$ , so their possibility to crystallize to the primary level is lower.  $Q$  expresses the difference of total system melting enthalpy  $\Delta H_{m1}$  and crystallization enthalpy  $\Delta H_c$  according to:

$$Q = \Sigma \Delta H_{m1} - \Delta H_c.$$

According to absolute values of  $\Delta H_c$  the highest value is observed for the copolyamide  $\alpha$  with the low amount of comonomers and without nanoadditive, lower values of  $\Delta H_c$  have concentrates with low amount of comonomers and nanoadditives, and the lowest values  $\Delta H_c$  have copolyamides and concentrates with higher amount of comonomers.

From these two statements, it follows that all three copolyamides have higher macromolecular mobility in comparison with aggregates of copolyamide macromolecules and nanoadditive in concentrates at the cooling conditions due to higher rigidity of these aggregates with nanoadditive. Higher amount of comonomers in copolyamides, either without or with nanoadditive, restrains to reach higher crystallization level.

Copolyamide  $\alpha$  with the lowest amount of comonomers and with the most regular macromolecular structure has the highest value  $\Delta H_c = 60.4 \text{ J g}^{-1}$ . Copolyamide  $\beta$  ( $\Delta H_c = 49.5 \text{ J g}^{-1}$ ) with higher portion of one comonomer and even with higher total amount of all comonomers has higher  $\Delta H_c$  value in comparison with copolyamide  $\delta$  containing lower total amount of comonomers and equal amount of comonomers. It is due to higher amount of similar macromolecular segments (of one comonomer i.e.

AN2) in the case of copolyamide  $\beta$  and so the possibility to crystallize to the higher level is higher.

Concentrates DX, A and AC with 10.7 wt% of total amount of nylon salts have very close  $\Delta H_c$  values in interval  $53.7\text{--}56.7 \text{ J.g}^{-1}$  what is lower than the value for the copolyamide  $\alpha$ . Concentrates D, DC and B with higher amount of nylon salts have lower  $\Delta H_c$  values as a consequence of lower  $\Delta H_{m1}$  value.

#### Evaluation of melting enthalpy $\Delta H_{m2}$

Melting enthalpy of the second heating gives a view to the crystallinity of sample acquired after the DSC cooling i.e. at primary crystallization. This value  $\Delta H_{m2}$  is connected mainly with the speed of cooling and macromolecules regularity and mobility. From Tables 1 and 2, it follows that all melting enthalpies  $\Delta H_{m2}$  of the additives are lower in comparison with PA 6 as it is evident according to both values  $\Delta H_{m2}$  and  $Z$  where  $Z$  expresses the quotient of  $\Delta H_{m2}$  to  $\Delta H_{m1}$  in percentage reached at the second heating:

$$Z = \left( \frac{\Sigma \Delta H_{m2PA6}}{\Sigma \Delta H_{m1PA6}} \right) \times 100 \quad \text{or}$$

$$Z = \left( \frac{\Sigma \Delta H_{m2additive}}{\Sigma \Delta H_{m1additive}} \right) \times 100$$

According to this criterion, copolyamides and concentrates with lower amount of comonomers in copolyamide have approximately the same level of crystallinity and influence of nanoadditive Cloisite is manifested by higher  $\Delta H_{m2}$  value of concentrate AC in comparison with concentrate A containing the nanoadditive Bentonite.

Concentrates with higher amount of comonomers have this value significantly lower with higher  $\Delta H_{m2}$  value for concentrate AC compared with A which confirms influence of Cloisite again.

$\Delta H_{m2}$  exhibits the melting enthalpy of crystalline portion formed after the cooling so it can be said that it expresses the primary crystallization of the sample and  $Z$  expresses this crystallinity level in % as the share to the  $\Delta H_{m1}$  value according to:

$$Z = \left( \frac{\Sigma \Delta H_{m2PA6}}{\Sigma \Delta H_{m1PA6}} \right) \times 100 \quad \text{or}$$

$$Z = \left( \frac{\Sigma \Delta H_{m2additive}}{\Sigma \Delta H_{m1additive}} \right) \times 100$$

For PA 6, the value  $Z$  is 80%. According to the criterion  $Z$ , all additives can be divided into 3 groups: additive with lower total amount of comonomers, i.e. copolyamide  $\alpha$  and concentrates DX, A and AC, where the value  $Z$  is from interval 62–68%, copolyamides  $\beta$  and  $\delta$  with  $Z = 55\text{--}58\%$  and concentrates D, DC and B with higher total amount of

comonomers and the lowest values  $Z$  from the interval 49–54%.

From these values, one can state that the highest macromolecular mobility have the concentrates AC and A with lower amount of comonomers and nanoadditive Cloisite and Bentonite, even a little bit higher compared to copolyamide  $\alpha$  with the same copolyamide constitution but without nanoadditive. It can be said that the nanoadditive contributes to higher organization of existing structures.

From these differences, one can conclude the great influence of secondary crystallization to the level of  $\Delta H_m$  and as well to state that PA 6, copolyamides and systems copolyamide + nanoadditive crystallize even at the ambient temperature. This property is lower for homopolymer PA 6 and higher for additives.

#### Evaluation of difference of melting enthalpies

$$\Delta H_{m1} - \Delta H_{m2}$$

The difference  $R = \sum \Delta H_{m1} - \sum \Delta H_{m2}$  as the difference between melting enthalpy of the first heating and that of the second one evaluates the successive secondary crystallization and can be explained by the higher period of sample crystallization (i.e. the period from its synthesis until the time of DSC measurement) and speed of cooling during DSC measurement. It focuses to the mobility of copolyamide macromolecules depending on a glass temperature  $T_g$ . If  $\sum \Delta H_{m1} \gg \sum \Delta H_{m2}$  the combination of the cooling rate and lower mobility of macromolecules brings about the essentially lower crystallization during cooling. The time during cooling is not sufficient for complete crystallization when the mobility of macromolecules or structures of system is lower. Probably, both aspects influence lower value of  $\Delta H_{m2}$  in comparison with  $\Delta H_{m1}$  for presented samples. From this difference  $R$  and from values  $Z$ , one can conclude the mobility of sample structures. If values  $R$  of additives are higher than that for PA 6 it insinuates better mobility of macromolecules (in copolyamides) or structures (in concentrates).

Since the speed of cooling for all PA 6 and additives is the same, the percentage  $Z = \left( \frac{\sum \Delta H_{m2PA6}}{\sum \Delta H_{m1PA6}} \right) \times 100$  or  $Z = \left( \frac{\sum \Delta H_{m2additive}}{\sum \Delta H_{m1additive}} \right) \times 100$  (Tables 1, 2) as well as value  $R = \sum \Delta H_{m1} - \sum \Delta H_{m2}$  express the ability of macromolecules to arrange themselves into crystallites and to reach a certain level of crystallinity. For PA 6 and PA 6P, the value  $Z = 80\%$  and for all additives–copolyamides as well as concentrates this value is lower than this for PA 6 so additives have lower crystallization ability in comparison with neat homopolymer PA 6 under the conditions applied. According to the value of  $R$ , the secondary crystallization of blend systems is the most negatively influenced with

concentrates D, DC and B containing higher amount of comonomers and nanoadditive ( $R = 25\text{--}29 \text{ J g}^{-1}$ ) and the least with copolyamide  $\alpha$  and concentrate A and AC with the lowest amount of comonomers and nanoadditive ( $R = 21\text{--}24 \text{ J g}^{-1}$ ).

Therefore, while  $\Delta H_{m1}$  values express the primary crystallization, the difference  $R = \sum \Delta H_{m1} - \sum \Delta H_{m2}$  expresses mostly the secondary crystallization. This difference can be lower when the macromolecules mobility is higher and they are able to crystallize during the DSC cooling to a higher level, and  $\Delta H_{m2}$  value approaches to the  $\Delta H_{m1}$  value.

#### Evaluation of crystallization temperature $T_c$

Temperatures of crystallization  $T_c$  and crystallization enthalpy  $\Delta H_c$  of copolyamides and concentrates as well are falling. Lower amount of comonomer(s) in copolyamide brings about better arranged macromolecules and higher crystallization enthalpy  $\Delta H_c$ . Higher amount of comonomers in copolyamides and lower level of arrangement leads to lower crystallization enthalpy and lower temperature of crystallization as well. Comparison of temperatures of crystallization  $T_c$  shows lower crystallization temperatures for copolyamides with higher amount of comonomers.

Considering the concentrates, the situation is similar. Concentrates with lower amount of comonomers in copolyamide have both enthalpies of crystallization  $\Delta H_c$  and crystallization temperatures  $T_c$  higher and approximately similar, concentrates with higher amount of comonomers in copolyamide have  $\Delta H_c$  values and crystallization temperatures  $T_c$  lower and close as well.

#### Evaluation of glass temperature $T_g$

It is known that the dependence of the speed of crystallites growth on temperature is the Gauss curve along the temperature  $T_c$  with maximum at maximal speed of crystallites growth and with margin limits  $T_m$  and  $T_g$ . Since  $T_m$  of copolyamides drops with amount of comonomers, one can conclude that  $T_g$  of copolyamides drops as well. The other aspect which supports this confirmation is that copolymers have generally always lower  $T_g$  in comparison with homopolymers due to their lower macromolecular regularity and lower number of intermolecular bonds. The same is valid for concentrates, especially for those with higher amount of comonomers.

#### Evaluation of melting entropy $\Delta S_m$

The level of system order can be evaluated by values of melting entropy  $\Delta S_m$  as well, calculated according to the relationship:

$$\Delta S_m = \sum \frac{\Delta H_m}{T_m} \text{ or}$$

$$\Delta S_m = \sum \frac{\Delta H_{mi}}{T_{mi}}$$

if there are more crystalline modifications.

Comparison of  $\Delta S_{m1}$  values demonstrates that macro-molecular system organization is highest for PA 6 where  $\Delta S_{m1} = 0.158 \text{ J g}^{-1} \text{ K}^{-1}$ . Differences among copolyamides are evident. Copolyamide  $\alpha$  with lower amount of comonomers has higher value  $\Delta S_{m1} = 0.141 \text{ J g}^{-1} \text{ K}^{-1}$ , copolyamides with higher amount of comonomers (i.e.  $\beta$  and  $\delta$ ) have a lower  $\Delta S_m$  values equal to  $0.129 \text{ J g}^{-1} \text{ K}^{-1}$  and  $0.131 \text{ J g}^{-1} \text{ K}^{-1}$ . In general, concentrates with lower amount of comonomers have much higher  $\Delta S_{m1}$  values than concentrates with higher amount of comonomers in copolyamide and mainly concentrate DX with only one minor comonomer has the highest  $\Delta S_{m1}$  value. Comparison between concentrate A with nanoadditive Bentonite and concentrate AC with nanoadditive Cloisite 15A focuses again to the better influence of Cloisite 15A to the system organization. These two concentrates have their  $\Delta S_{m1}$  values even higher than  $\Delta S_{m1}$  value of copolyamide  $\alpha$  without nanoadditive what shows that in these concentrates A and AC nanoadditive did not play any negative role.

The same tendency can be observed for  $\Delta S_{m2}$  values with one big difference: all  $\Delta S_{m2}$  values are much lower than  $\Delta S_{m1}$  what is the prove that the reachable level of system organization is after the first heating and cooling much lower than primary state before first heating.

Therefore, it can be said that the best system organization exhibits concentrate DX with lower amount of the only one comonomer, concentrate AC with lower amount of two comonomers and nanoadditive Cloisite 15A and copolyamide  $\alpha$  with lower amount of two comonomers and without nanoadditive.

#### Thermal properties of PA 6 fibres modified with Bentonite

For evaluation of the nanoadditive influence to the thermal properties PA 6, the fibres modified only with 0.25–2.5 wt%

of Bentonite were prepared. As it is demonstrated in Table 3, the nanoadditive increases values of  $\Delta H_{m1}$  and  $\Delta H_{m2}$ , maximal at the amount of 1 wt%. Melting temperatures,  $T_m$  and crystallization temperatures,  $T_c$  are influenced negligibly; the crystallization enthalpy  $\Delta H_c$  is higher in comparison with that of PA 6 fibres. The only important difference is the formation of three melting temperatures instead of two in the second heating, while the third  $T_m$  is lower than two others.

#### Thermal properties of PA 6 fibres modified with copolyamide $\delta$

Table 4 documents the influence of copolyamide  $\delta$  and concentrate D on the thermal and mechanical properties of PA 6 fibres modified with these two additives.

Copolyamide  $\delta$  influences thermal properties of modified PA 6 fibres. The amount of 10 wt% increases slightly  $\Delta H_{m1}$  and  $\Delta H_{m2}$  values as well as  $\Delta H_c$ .  $T_m$  and  $T_c$ , are slightly lower. It can be concluded that 10 wt% of copolyamide  $\delta$  does not interfere crystallization of PA 6 and higher  $\Delta S_{m1}$  value focuses to the better organization of this blend system than it is in unmodified PA 6 fibres.

The amount of 30 wt% of this copolyamide  $\delta$  decreases all these characteristics.

#### Thermal properties of PA 6 fibres modified with concentrate D

Thermal properties of PA 6 fibres modified with 10 and 20 wt% of concentrate D are better, the best at 20 wt% of D. Crystallization ability evaluated by  $\Delta H_{m1}$  and  $\Delta H_{m2}$  values is higher, higher  $\Delta S_{m1}$  value shows better organization of the systems. The amount of 30 and 50 wt% concentrate D exhibit progressive drop of  $\Delta H_{m1}$ ,  $\Delta H_{m2}$  and  $\Delta H_c$ , values as well as  $\Delta S_{m1}$  value and only slight drop of  $T_m$  and  $T_c$  values.

Influence of copolyamide  $\delta$  and concentrate D on the tensile strengths of modified PA 6 fibres is demonstrated in Table 4 as well. PA 6 fibres modified by 10 and 20 wt% of the concentrate D have higher or equal tensile strength compared with non modified PA 6 fibres while copolyamide  $\delta$  without nanoadditive negatively influences

**Table 3** Thermal properties of PA 6 fibres and PA 6 fibres modified with Bentonite (0–2.5 wt%),  $\lambda = 3$

System	$T_{m1}/^{\circ}\text{C}$	$\Sigma\Delta H_{m1}/\text{J g}^{-1}$	X/%	$T_c/^{\circ}\text{C}$	$-\Delta H_c/\text{J g}^{-1}$	$T_{m21}, T_{m22}, T_{m23}/^{\circ}\text{C}$	$\Sigma\Delta H_{m2}/\text{J g}^{-1}$	Y/%	Z/%	Q/J $\text{g}^{-1}$
PA 6P	221	68.2	–	187	65.2	212, 218	54.3	–	79.6	3.0
0.25% BEN	222	73.7	108.1	189	72.9	214, 220	58.2	107.3	79	0.8
0.5% BEN	222	74.6	109.4	189	64.9	204, 219, 221	56.3	103.7	75.5	9.7
1% BEN	220	78.2	114.7	189	71	206, 213, 219	60.4	111.2	77.2	7.2
1.5% BEN	221	71.9	105.4	188	68.8	206, 213, 219	54.9	101.1	76.4	3.1
2.5% BEN	221	73.2	107.3	188	73	207, 213, 219	57.9	106.6	79.1	0.2



**Table 4** Thermal properties, tensile strength,  $\sigma$ , and elongation at break,  $\epsilon$ , of PA 6 fibres modified with copolyamide  $\delta$  and with concentrate D,  $\lambda = 3$

System	$T_m/^\circ\text{C}$	$\Sigma\Delta H_{m1}/\text{J g}^{-1}$		$X/\%$	$\Delta S_{m1}/\text{J g}^{-1}\text{K}^{-1}$	$T_c/^\circ\text{C}$	$-\Delta H_c/\text{J g}^{-1}$	$T_{m21}, T_{m22}/^\circ\text{C}$	$\Sigma\Delta H_{m2}/\text{J g}^{-1}$		$Y/\%$	$Z/\%$	$Q/\text{J g}^{-1}$	$\sigma/N \text{ tex}^{-1}$	$\epsilon/\%$
		Exp	Calc						exp	calc					
		$\Delta_1$	$\Delta_2$												
PA 6P	221	68.2	-	-	0.138	187	65.2	212, 218	54.3	-	-	79.6	3.0	0.24	62
PA 6+10% $\delta$	219	70.7	66.2	4.5	0.144	186	70.5	211, 218	55.1	52.1	3.0	101.5	0.2	0.21	58
PA 6+30% $\delta$	219	66.2	63.3	1.0	0.129	184	57.1	209, 217	46.3	47.7	-1.4	85.3	6.2	0.18	70
PA 6+10%D(0.5%BEN)	220	70.9	66.8	4.1	0.144	186	65.5	212, 219	64.6	51.6	13.0	119	5.4	0.26	77
PA 6+20%D(1% BEN)	220	72.4	65.4	7.0	0.147	183	63.4	210, 223	56.4	48.8	7.6	103.9	9.0	0.24	82
PA 6+30%D(1.5%BEN)	219	64.6	64.0	0.6	0.131	183	60	208, 217	52.4	46.1	6.3	96.5	4.6	0.20	74
PA 6+50%D(2.5%BEN)	219	56.7	61.3	-4.6	0.115	181	49.8	206, 216	41.8	40.6	1.2	77	6.9	0.15	71

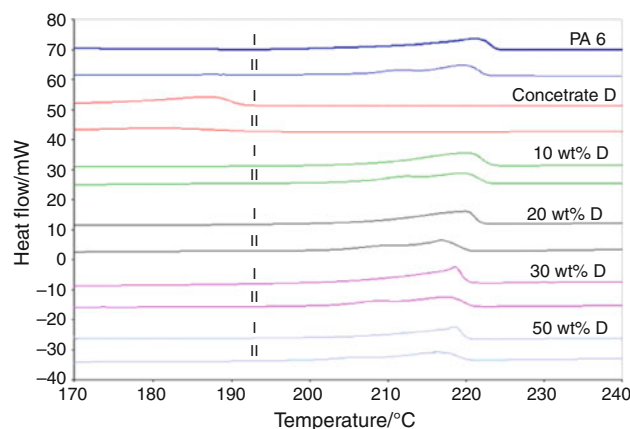
X quotient of additive  $\Delta H_{m1}$  to PA 6H  $\Delta H_{m2}$  value in %, Y quotient of additive  $\Delta H_{m2}$  value to PA 6H  $\Delta H_{m2}$  value in %

Z quotient of additive  $\Delta H_{m2}$  value to additive  $\Delta H_{m1}$  value in %, Q difference  $\Sigma \Delta H_{m1} - \Delta H_c$ , R =  $\Delta H_{m1} - \Delta H_{m2}$

tensile strength of modified PA 6 fibres even at the amount 10 wt%. The higher the amount of copolyamide  $\delta$  in blend PA 6 fibres the lower their tensile strength. So it is evident that nanoadditive Bentonite positively influences tensile strength of PA 6 fibres modified with 10 and 20 wt% concentrate D. Elongation at break of PA 6 fibres modified either with copolyamide  $\delta$  or with concentrate D is generally a little bit higher in comparison with non modified PA 6 fibres.

The only one melting peak assumes one crystalline structure is present or two or several crystalline modifications occur which are ‘hidden’ in the present melting peak if it is ‘large enough’. Comparing first and second heating of PA 6 fibres and PA 6 fibres modified with 10, 20, 30 and 50 wt% concentrate D (Fig. 1) one can state that PA 6 and concentrate D are (at least partially) compatible because temperature intervals of first and second heating of PA 6 and all modified fibres are very resembling each other nevertheless modified PA 6 fibres contain 10 or 50 wt% of concentrate D. If melting curves of unmodified PA 6 and neat concentrate D are considered it is evident that concentrate’s D melting interval is shifted to much lower temperature than that of PA 6 (157–193 °C versus 195–225 °C at the first heating and 158–193 °C versus 197–223 °C at the second heating—Table 5) but melting intervals of PA 6 fibres modified with 10–50 wt% of concentrate D are not shifted to much lower temperature. Though at the second heating two peaks have appeared they are always in the primary melting temperature interval.

Crystallization of a sample is characterized by experimentally measured melting enthalpy but it can be as well calculated as the contributions of crystallization of all components according to equation



**Fig. 1** DSC diagram of PA 6, concentrate D and PA 6 fibres modified with 10, 20, 30, 40 and 50 wt% of concentrate D, I first heating, II second heating

**Table 5** Melting intervals of non modified and modified PA 6 fibres

Sample	I Heating/°C		II Heating/°C	
	Interval of melting	Peak	Interval of melting	Peak
PA 6P	195–225	221	197–223	212, 219
Concentrate D	157–193	187	158–193	181
90% PA 6 + 10% D	196–223	220	185–223	212, 219
80% PA 6 + 20% D	193–222	220	193–220	209, 217
70% PA 6 + 30% D	189–220	219	195–221	209, 217
50% PA 6 + 50% D	187–220	218	195–220	208, 217

$$\Delta H_{\text{mcalc}} = \sum_{i=1}^n \Delta H_{\text{mi}} \times w_i$$

where  $\Delta H_{\text{mi}}$  is experimentally measured melting enthalpy of each neat component, and  $w_i$  is weight fraction of each component.

The comparison of these two values can clarify the ability of blend crystallization. If the experimentally obtained melting enthalpy of the blend is higher than the calculated value, one can state that this blend crystallizes better than it follows from contributions of elementary components. Therefore, components of the blend do not interfere each other but positively contribute to the crystallization of the blend. Since it is not possible to determine melting enthalpy of nanoadditive for calculated values  $\Delta H_{\text{mcalc}}$  only melting enthalpies of two components, PA 6 and copolyamides or concentrates, were used. Differences

$$\Delta_1 = \sum \Delta H_{\text{m1exp}} - \sum \Delta H_{\text{m1calc}} \text{ and } \Delta_2 = \sum \Delta H_{\text{m2exp}} - \sum \Delta H_{\text{m2calc}}$$

$\Delta_1$  values for PA 6 fibres modified with copolyamides and concentrates (Table 4) show that experimental values of melting enthalpies  $\Delta H_{\text{m1}}$  are higher for blend fibres containing 10–30 wt% of copolyamide  $\delta$  and concentrate D. Copolyamide  $\delta$  and concentrate D in above mentioned amounts helps to reach higher level of crystallization.

The same validates for difference of melting enthalpies of second heating but the difference  $\Delta_2$  is lower for blends with copolyamide and higher for blends with concentrate.

These statements confirm positive effect of nanoadditive Bentonite in concentrate to the process of crystallization of modified PA 6 fibres.

## Conclusions

Melting temperatures of additives (copolyamides and concentrates) with lower amount of minor comonomers are higher than these with higher total amount of both minor comonomers and all are lower than melting temperature of polyamide 6.

Melting temperatures and crystallization ability of concentrates containing nanoadditive Cloisite 15A are higher than these with nanoadditive Bentonite.

All additives are semicrystalline though less than PA 6. Additives with lower total amount of minor comonomers have higher melting enthalpies  $\Delta H_{\text{m1}}$  and  $\Delta H_{\text{m2}}$  in comparison with additives containing higher total amount of minor comonomers.

Differences  $\Delta H_{\text{m1}} - \Delta H_{\text{m2}}$  *i.e.* values  $R$  focus to the great role of secondary crystallization.

Melting entropies  $\Delta S_{\text{m}}$  additives with lower amount of comonomers are lower in comparison with PA 6 but higher in comparison with additives containing higher total amount of minor comonomers.

Melting enthalpies  $\Delta H_{\text{m1}}$  and  $\Delta H_{\text{m2}}$  of PA 6 fibres modified with Bentonite alone are higher in comparison with these of non modified PA 6 fibres, with maximal value at its amount of 1 wt%.

Copolyamide  $\delta$  and concentrate D at concentrations 10–30 wt% positively influence the process of crystallization of modified PA 6 fibres and these fibres reach higher experimental melting enthalpies than calculated according to the rule of additivity.

Tensile strength is positively influenced by modification of PA 6 fibres with 10 and 20 wt% of concentrate D *i.e.* system containing copolyamide  $\delta$  + nanoadditive Bentonite.

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