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Modification of PA 6 Fibres with Bentonite, Cloisite and Concentrates (Copolyamide + Bentonite)

Abstract
This contribution outlines the preparation and properties of PA 6 fibres modified with two types of montmorillonite - organophilic Bentonite 11958 or Cloisite 15A alone, as well as with concentrates consisting of copolyamides and Bentonite. The concentrates were synthesised with ε-caprolactam (CL) and two minor comonomers - nylon salts from adipic acid + diethylenetriamine (ADETA) and from adipic acid + 1-(2-aminoethyl) piperazine (AN2) in the presence of Bentonite. Three concentrates containing copolyamide from CL + 10.7 wt. %, 21.4 wt.% and 23.4 wt.% of minor comonomers + 5 wt.% of Bentonite were prepared. The basic properties of PA 6 and the concentrates were evaluated. Blends PA 6 + 10 - 50 wt.% of each concentrate, PA 6 + 0.25 – 2.5 wt.% of Bentonite and PA 6 + 0.25 - 5 wt.% of Cloisite were prepared, and the apparent viscosity of the blend melts with Bentonite was measured. Experimental PA 6 fibres modified with Bentonite, Cloisite and the concentrates were prepared and drawn. The mechanical properties – tensile strength, elongation at break and Young's modulus of non-modified and modified PA 6 fibres were compared.

Key words: *PA 6, copolyamides, Bentonite, Cloisite, modified PA 6 fibres, mechanical properties.*

Introduction

The modification of polymers and fibres can be achieved by either the chemical or physical modification of neat polymer. Chemical modification consists in the chemical transformation of homopolymer usually by copolyreactions during or after synthesis (e.g. preparation of copolymers). Physical modification is the addition of suitable modifier(s) and the preparation of matrix/fibril M/F fibres. The combination of both these methods – copolymers as additives - is effective as well. The addition of copolymers brings about a structuralisation of the final product e.g. changes in the morphological fibre structure and thermal characteristics [1, 2], as well as deterioration in the mechanical properties of fibres in most cases [3, 4].

The chemical similarity of 6-aminocaproic acid and nylon salts prepared from diamines and dicarboxylic acids gives a good reason to use nylon salts instead of 6-aminocaproic acid for the same effect to prepare copolyamides for the modification of PA 6 fibres [5]. Copolyamides have a great advantage – enhanced compatibility with PA 6, and their negative influence on mechanical properties can be lowered or even eliminated. Interactions between homopolyamide PA 6 and block copolyamide containing long ε-caprolactam segments [6] enable the preparation of a blend with better compatibility and improved properties of blended products e.g. fibres. Block copolymers can form at least two types of crystallites, two or more peaks of which indicate various crystallites of different sizes and levels of perfection [7].

Homopolymer poly-ε-caprolactam contains a portion of crystalline as a consequence of the regular spatial order of its macromolecules and intermolecular bonds. Due to the copolyreaction, longitudinal disorder and reduced crystallinity result as a rule. In certain cases, however, the crystallinity is not fundamentally reduced because the segment of the comonomer is similar in size to that which is being replaced. In the case of heteropolyamide from dicarboxylic acid and diamine like PA 66 from adipic acid and hexamethylenediamine, both components can be changed. For example, terephthalic acid with a length of 0.59 nm yields polyamides isomorphous to those of adipic acid with a segment of 0.63 nm because of their similar segment lengths [8]. Thus, copolymers of PA 66 and PA 6T are crystalline and do not have an eutectic in the melt temperature-composition curve. In contrast, when PA 610 is copolymerised with PA 6T, the eutectic effect is marked [9].

Comparison of the chemical structures and length of ε-caprolactam, CL, diethylenetriamine, DETA, and 1-(2-aminoethyl) piperazine molecules, N2, with those of adipic and terephthalic acids show that the segments of all the mono-mers are very similar concerning their length. This presumes the isomorphous and crystalline character of copolyamides containing CL, nylon salt AN2 consisting of adipic acid and N2, and nylon salt ADETA from adipic acid and DETA. Derivatives of piperazine in the macromolecules further improve thermal stability and dyeability [10].

Nanoclays are able to increase the mechanical properties of fibres, hence their utilisation can help to maintain or even increase the mechanical properties of modified fibres. Usuki et al. invented a method of doing this for polyamides, in which it was proved that an intercalative polyreaction in the presence of layered silicate is an advantageous technique for the preparation of polymer-layered silicate nanocomposites [11, 12].

6-minocaproic acid acts as an accelerator of polyamide 6 synthesis. Its addition accelerates the polyreaction of ε-caprolactam swollen among galleries of montmorillonite, forming intercalative structures [13]. The chemical similarity and activity of 6-aminocaproic acid and nylon salts allow to use the latter as accelerators of copolyamide synthesis in the presence of nanoadditives and prepare suitable modifiers - concentrates [14].

The aim of this contribution was to evaluate the influence of organophilic montmorillonites Bentonite and Cloisite alone, as well as nanocomposites from ternary copolyamides and Bentonite on the mechanical properties of PA 6 modi-

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fied fibres. For this purpose, the following domains were studied:

- synthesis of concentrates with different amounts of the two nylon salts i.e. nylon salt AN2, and nylon salt ADETA and Bentonite or Cloisite,
- basic properties of the concentrates and neat PA 6,
- preparation of PA 6 fibres modified with Bentonite, Cloisite and concentrates,
- mechanical properties of modified and non-modified PA 6 fibres.

■ Experimental

Material used

- Poly-ε-caprolactam, i.e. PA 6, commercial, T_m = 221 °C, Nylstar Slovakia, Humenné,
- ε-caprolactam, CL, Nylstar Slovakia, Humenné - major comonomer,
- Adipic acid, p.a., Aldrich,
- 1-(2-aminoethyl) piperazine, N2, Aldrich, vacuum distilled once,
- Diethylenetriamine, DETA, Aldrich, vacuum distilled once,
- 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
- Montmorillonite Bentonite 11958, i.e layer wise mineral with sodium ions and quaternary ammonia ions between the layers, Fluka, abbreviation Bentonite or BEN
- Montmorillonite Cloisite 15A, i.e. ditallowdimethylamonium salts with Bentonite 100%, Fluka, abbreviation Cloisite or CLO,
- Concentrates A, B and D

Synthesis of nylon salts and concentrates and an evaluation of their properties

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

Table 1. *Time of preparation t and properties of commercial PA 6 and concentrates A, B & D.*

Polymer	Total amount of comonomers, wt.%	t, min	LMC, wt.%	η_{rel}	[η], ml.g-1	T_{m1}, T_{m2}, °C	$\Delta H_{m1}+\Delta H_{m2}$, $\Sigma\Delta H_m$, J.g-1
PA 6	0	≈ 600	≈ 12	1.68	118	221	77.9
A	10.7	240	10.3	1.49	89	191, 204	29.8 + 33.3, 63.1
B	23.4	230	11.4	1.43	79	185	57.6
D	21.4	340	10.1	1.42	77	187	54.3

Three concentrates - A, B & D - were prepared from ε–caprolactam and nylon salts AN2 and ADETA. The concentrates were prepared via a polyreaction in a melt under a nitrogen atmosphere according to [13]; however, 6-minocaproic acid was replaced with nylon salts. Powdered CL and nylon salts AN2 and ADETA with a nanoadditive were mechanically mixed and put in a glass apparatus immersed in a thermostatted oil bath. The melting, homogenisation and poly(addition–condensation) reaction were completed within 230 – 340 min. At the end of the polyreaction, the concentrates were poured onto a metallic plate and cut into pellets. The composition of the concentration is given bellow:

A - 84.3 wt.% CL + 5.35 wt.% AN2 + + 5.35 wt.% ADETA + 5.0 wt.% BEN
B - 71.6 wt.% CL + 18.4 wt.% AN2 + + 5.0 wt.% ADETA + 5.0 wt.% BEN
D - 73.6 wt.% CL + 10.7 wt.% AN2 + +10.7 wt.% ADETA + 5.0 wt.% BEN

The PA 6 and concentrates were characterised by their preparation, the amount of low-molecular compounds, LMC, the molar weight determined by the solution's relative viscosity and intrinsic viscosity, as well as by thermal characteristics i.e. the melting temperature and melting enthalpy (**Table 1**).

Methods used

The amount of LMC was evaluated gravimetrically before and after extraction in hot demineralised water. The relationship water/concentrate i.e. the bath ratio was 200 ml of water/1 g of polymer, and the extraction was made as a simple extraction during 2 hours. The relative viscosity η_{rel} was measured viscosimetrically in 96% H_2SO_4 p.a. at 25 °C.

The thermal properties (melting temperature T_m and enthalpies of melting ΔH_m) were measured by a Perkin Elmer DSC 7 device at 10 K·min-1 the heating and cooling rates. Three cycles were applied (heating – cooling – heating) for the study of the thermal properties. The

properties and time of preparation of PA 6 and copolyamides are given in **Table 1**.

For evaluation of the influence of Bentonite or Cloisite alone and their concentrates on the viscosity of blend melts and mechanical properties, 3 sets of modified PA 6 pellets were prepared:

1. Physical mixtures of ground PA 6 + 0.25 − 5 wt.% of Bentonite or Cloisite powder were mixed in a mixer at 600 r.p.m for 3 min and processed by a GŐTTFERT single-screw extruder at r.p.m = 50·min-1 , in which the temperatures of zones $T_1 = T_2 = T_3$ = 250 °C - method X. Blend chips containing 5 wt.% of Bentonite or Cloisite, termed BEN concentrate or CLO concentrate, were used in step No 2 and for the preparation of modified PA 6 fibres.
2. Physical mixtures of PA 6 chips and chips of BEN or CLO concentrate containing 0.25 – 2.5 wt.% of Bentonite and 0.25 -5 wt.% of Cloisite were processed by the GŐTTFERT at the same conditions – method Z.
3. Physical mixtures of PA 6 pellets and 10 - 50 wt.% of pellet concentrates A, B and D were processed by the GŐTTFERT at the same conditions.

During the processing with the GŐTTFERT, the pressure p of the melt and the time of molding each sample of known weight were registered. From the time of molding, the known weight of the sample and pressure of the melt, the apparent viscosity of the melt η_{ap} was calculated according to relationships:

$$\eta_{ap} = \frac{\tau}{\gamma} \qquad (1)$$

where:

$$\tau = P_0 \cdot R/2L \text{ and}$$

$$\gamma = 4 \cdot \frac{V}{\pi R^3} = 4 \cdot m/\rho \cdot \pi R^3$$

P_0 - pressure in Pa,
R - radius of the orifice in m,
L - length of the nozzle in m,
V - volume flow of the melt,
m - weight flow of the melt

Table 2. Rheological characteristics of blends PA 6 + BEN prepared by processes X and Z.

Amount of BEN, wt. %	p_a X, bar	η X, Pa.s	p_a Z, bar	η Z, Pa.s
PA 6	61.2	490	61.2	490
0.25	58.6	471	58.3	464
0.5	58.5	468	59.4	478
1.0	60.9	487	59.3	474
1.5	59.5	478	60.9	487
2.5	61.0	487	61.4	494
5.0	65.4	526	-	-

These values of viscosity are not real values, because at the given temperature the correct density of the blend melt is not known; however, the values are useful for comparative purposes. It can be said that these values are apparent viscosities. They were calculated on the assumption that the density ρ of the blend melt is the additive value of PA 6 and concentrate densities, in which the density of the concentrate and its temperature dependence are the same as those of PA 6, which suits the relationship valid for non modified PA 6:

$$\rho_{PA\,6} = 1109.8 - 0.52T \qquad (2)$$

where T is the temperature in °C.

The ribbon of the blend was cooled in cold water and cut into pellets. The air-dried pellets were finally dried in a vacuum oven at 105 °C for 2 hours and used for spinning. The apparent viscosity η_{ap} of the blend melt was calculated for non modified and modified PA 6 according to equation (1). Rheological characteristics of the modified and non- modified PA 6 blend melts are shown in *Table 2*.

The spinning of the dried blend pellets was performed by laboratory spinning equipment with an extruder $\Phi = 16$ mm at T = 250 °C and take up speed of 150 m·min^{-1} with a lubricant (spinneret nozzle with 13 fibrils with a diameter of 0.5 mm). After the spinning, fibres modified with BEN or CLO were drawn at different drawing ratios - λ_1 - λ_5 = 3 − 5, and PA 6 fibres modified with concentrates A, B and C were drawn at the drawing ratio λ_1 = 3. PA 6 fibres modified with concentrate B (having the highest amount of comonomers) were not possible to draw at drawing ratio λ_1 = 3.

The mechanical properties – tensile strength, σ, Young's modulus, E, and elongation at break, ε, of the modified PA 6 fibres were measured 20 times with an INSTRON 3343, in which the clamping length was equal to 250 mm and the

deformation rate - 500 mm/min. The mechanical properties are evaluated graphically in *Figures 1 - 3*.

■ Results and discussion

Properties of the PA 6 and concentrates
The properties of homopolyamide PA 6 and concentrates containing copolyamides and Bentonite are compared in *Table 1*. The time of concentrate preparation is rather lower than that of commercial homopolyamide PA 6, but that of LMC is comparable to that of PA 6. Nylon salts AN2 and ADETA act as activators of the polyreaction of CL, therefore a rather shorter polyreaction time was necessary for copolyamides in comparison with PA 6. Copolyamide in the concentrate is the controlling component with respect to the properties of concentrates. As regards the properties of the concentrates, they can be divided into two groups. Concentrate A has a lower total amount of comonomers, whereas concentrates B and D have a higher total amount of comonomers.

Concentrate A, with the lowest total amount of minor comonomers, has the highest regularity of the macromolecular chain, reaching a higher molar weight in accordance with the relative viscosity η_{rel} or [η]); its thermal properties also reflect this fact. Its melting temperatures (two peaks on the DSC diagram) are lower compared with those of homopolyamide PA 6 but higher compared with the melting temperatures of concentrates B and D, with a higher total amount of comonomers. The melting temperature of concentrates B and D are very close.

The melting enthalpy of concentrate A is the highest due to its higher regularity of macromolecular chains following from the lowest amount of comonomers in the macromolecules of copolyamide. Concentrate B contains 18.4 wt.% of AN2 nylon salt and 5 wt.% of ADETA nylon

salt, thus it is able to form longer segments of CL and AN2 comonomers, and its melting enthalpy is higher in comparison with that of concentrate D, containing an equal amount of both comonomers i.e. 10.7 wt.%.

Rheological and mechanical properties of PA 6 modified with Bentonite only
There are two factors influencing the apparent melt viscosity of the blends. One of them is the formation of exfoliated or intercalated structures, I, of polyamide 6 and the nanoadditive (with their stiffness and high molecular weight) using a part of BEN, and the other one is the presence of nano- or micro- particles of BEN, II.

During the preparation of non modified PA 6 and modified PA 6 blends, the values of pressure p_a registered (for blends and neat PA 6 as well) oscillate in the interval ± 1 bar, hence all values for the blend melts containing 0.25 – 1.5 wt.% are within the margin of error (*Table 2*). From this point of view, it can be said that the amount of BEN does not fundamentally influence the value of the apparent melt viscosity of these blends, neither those prepared directly (method X) nor those from BEN concentrate (method Z), which is only slightly lower in comparison with the apparent melt viscosity of neat PA 6. This can be explained by the fact that probably only a part of BEN forms exfoliated or intercalated nanostructures with macromolecules of PA 6, whereas the other part functions as free nano- or micro- particles "diluting" the system. At 2.5 wt.% and 5 wt.%, the amount of BEN values of the apparent viscosity of blend melts is the same and higher than for neat PA 6. At these amounts of BEN, the portion of exfoliated or intercalated structures increases, the result being a higher apparent melt viscosity.

Comparison of the two methods X and Z shows that one moulding process (method X) or two moulding processes (method Z) does not fundamentally influence the apparent melt viscosity of the blend melt, hence the homogeneity of the blend is the same after one and two homogenisations in the GÖTTFERT.

The processability i.e. the spinning and drawing of fibres modified with BEN, of BEN and CLO concentrates was good, and all fibres were drawn at the maximal drawing ratio λ_5 = 5 without problems.
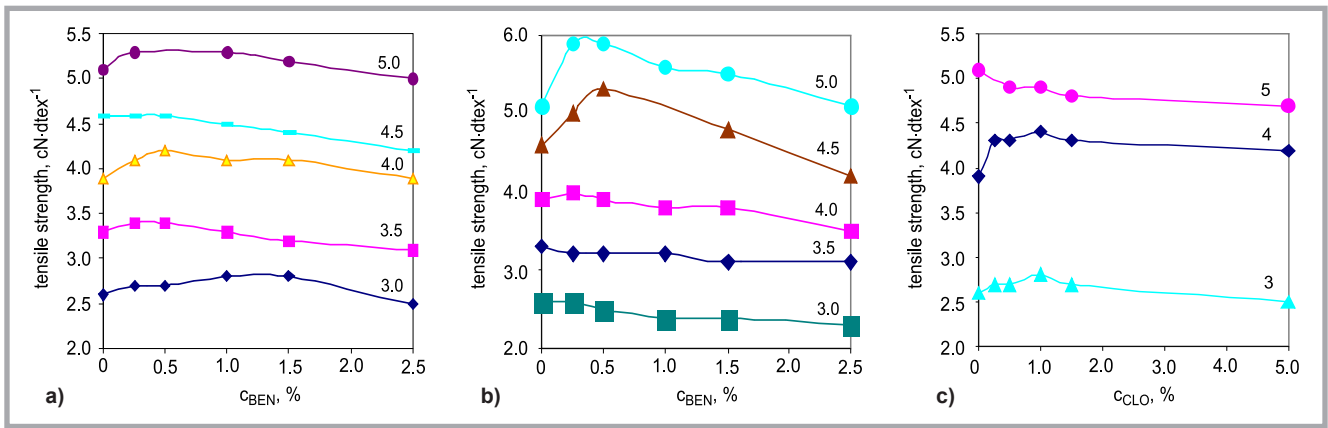
Figure 1. *Dependence of the tensile strength, σ, of PA 6 fibres modified with: a) BEN using method X, b) BEN using method Z and c) CLO using method Z.*
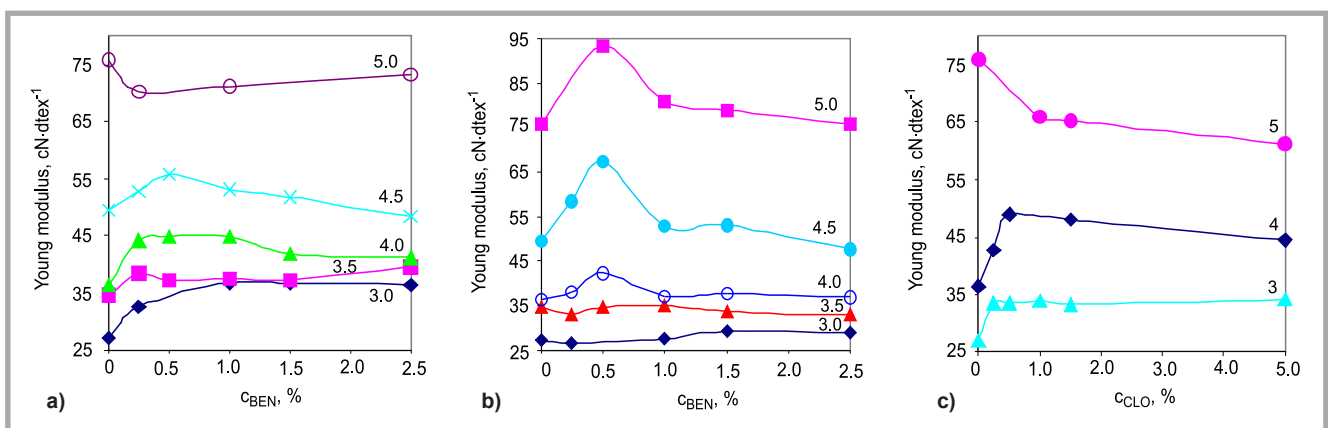
Figure 2. *Dependence of the Young's modulus, E, of PA 6 fibres modified with: a) BEN using method X, b) BEN using method Z and c) CLO using method Z.*
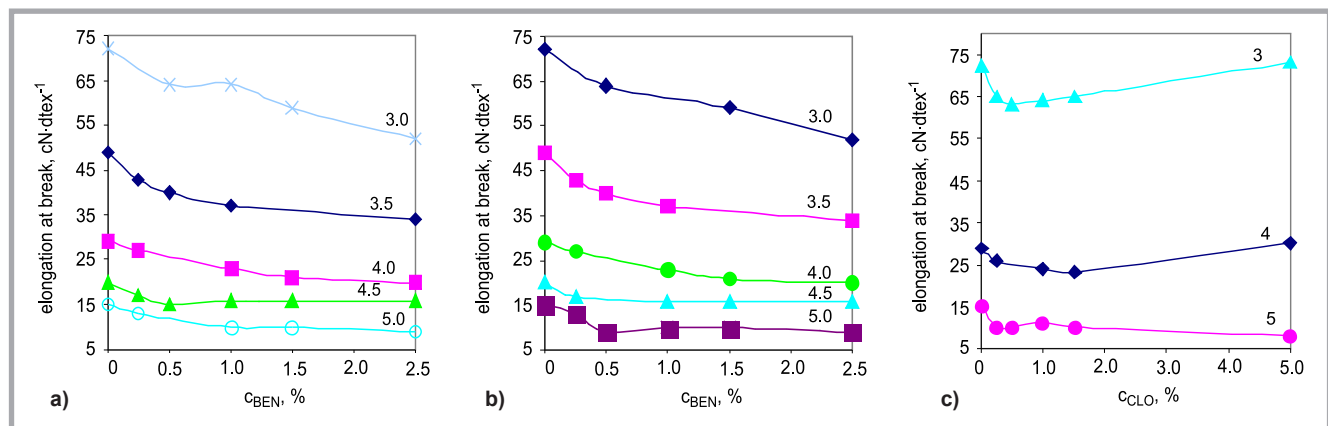
Figure 3. *Dependence of the elongation at break, ε, of PA 6 fibres modified with: a) BEN using method X, b) BEN using method Z and c) CLO using method Z.*

Their mechanical properties - tensile strength, σ, Young's modulus, E, and elongation at break, ε, are evaluated in ***Figures 1 – 3***.

Comparison of the coefficients of variance, CV, of the mechanical properties can give a view of the homogeneity of fibres. The CV values of non-modified PA 6 fibres and PA 6 fibres modified with a nanoadditive are from the same interval, thus it can be stated that the homogeneity and evenness of modified PA 6 fibres is similar to those of non-modified PA 6 fibres.

The tensile strength of PA 6 fibres modified with BEN using the X method is slightly positively influenced mainly at lower drawing ratios $\lambda_1 = 3$ and $\lambda_3 = 4$ in the interval $0.25 – 1.0$ wt.% of BEN, with the maximum at 0.5 wt.% - an increase of about $3 – 8$% (***Figure 1.a***). The Young's modulus of these fibres is higher for all the intervals of BEN amounts and drawing ratios λ_1 - $\lambda_4 = 3$ - 4.5 (***Figure 2.a***). Only at $\lambda_5 = 5$ is the Young's modulus lower for all concentration intervals of BEN. The maximum Young's modulus shifts from the higher amount of

Table 3. *Rheological characteristics and composition of PA 6 blends modified with concentrates A, B & D.*

Composition of blend, wt.%	p_a, bar	η_{ap}, Pa.s	CL, wt.%	ADETA, wt.%	AN 2, wt.%	BEN, wt.%
100 PA 6	51.1	236	-	-	-	-
90 PA 6 + 10 A	39.1	217	8.44	0.53	0.53	0.50
80 PA 6 + 20 A	35.2	195	16.86	1.07	1.07	1.00
70 PA 6 + 30 A	31.1	173	25.3	1.6	1.6	1.50
50 PA 6 + 50 A	30.2	171	42.1	2.7	2.7	2.50
90 PA 6 + 10 B	45.4	197	7.16	0.50	1.84	0.50
80 PA 6 + 20 B	43.7	203	14.32	1.00	3.68	1.00
70 PA 6 + 30 B	38.8	183	21.48	1.50	5.52	1.50
50 PA 6 + 50 B	33.3	179	35.80	2.50	9.20	2.50
90 PA 6 + 10 D	45.2	205	7.36	1.07	1.07	0.50
80 PA 6 + 20 D	43.0	204	14.72	2.14	2.14	1.00
70 PA 6 + 30 D	38.9	183	22.08	3.21	3.21	1.50
50 PA 6 + 50 D	30.7	175	36.80	5.35	5.35	2.50

Table 4. *Mechanical properties of PA 6 fibres modified with concentrates consisting of copolyamides A, B & D, as well as Bentonite, $\lambda = 3$; * $\lambda_6 = 2$ and ** $\lambda_7 = 2.5$.*

Composition of fibres, wt.%	T_d, dtex	CV,%	TS, cN.dtex^{-1}	CV, %	E, %	CV, %	YM cN.dtex^{-1}	CV,%
100 PA 6	303	3	2.4	11	52	21	36.3	7
90 PA 6 + 10 A	302	4	2.2	6	55	16	36.4	6
80 PA 6 + 20 A	308	2	2.1	4	61	14	36.6	5
70 PA 6 + 30 A	310	3	1.9	5	54	11	38.4	5
50 PA 6 + 50 A	315	2	1.7	7	46	24	35.5	6
90 PA 6 + 10 B	303	3	2.2	7	57	17	39.4	5
80 PA 6 + 20 B	313	4	2.1	3	47	14	42.3	4
70 PA 6 + 30 B *	459	3	0.8	9	61	10	27.6	5
50 PA 6+ 50B **	350	6	0.8	14	24	32	29.0	9
90 PA 6 + 10 D	296	3	2.5	7	59	12	39.0	6
80 PA 6 + 20 D	299	3	2.4	10	69	9	39.1	9
70 PA 6 + 30 D	301	3	2.0	9	57	7	37.0	5
50 PA 6 + 50 D	306	3	1.3	15	39	21	34.7	10

BEN (2.5 wt.%) at lower drawing ratios ($\lambda_1 = 3$ and $\lambda_2 = 3.5$) to the amount of 0.5 wt.% of BEN at higher drawing ratios $\lambda_3 = 4$ and $\lambda_4 = 4.5$, with the maximal increase equal to $11 - 36\%$.

The tensile strength of PA 6 fibres modified with BEN using the Z method i.e. the BEN concentrate is fundamentally and positively influenced at higher drawing ratios $\lambda_4 = 4.5$ and $\lambda_5 = 5$ mainly in the interval $0.25 - 1.5$ wt.% of BEN. Maximal increase is reached at 0.5 wt.% of BEN and tensile strength is about $15 - 16\%$ higher in comparison with non modified PA 6 fibres (**Figure 1.b**). The Young's modulus exhibits the same tendency at $\lambda_4 = 4.5$ and $\lambda_5 = 5$, with the maximum at 0.5 wt.% of BEN - an increase of about $23 - 36\%$ (**Figure 2.b**). In addition, it is better for drawing ratio $\lambda_3 = 4$, making an improvement of about 16%.

The tensile strength and Young's modulus of PA 6 fibres modified with CLO from concentrate (method Z) are higher only for interval $0.25 - 1.5$ wt.% and lower drawing ratios $\lambda_1 = 3$ and $\lambda_3 = 4$, with maximal values at $0.5 - 1.0$ wt.%. The improvement in tensile strength reaches $4 - 13\%$ and the Young's modulus - $17 - 35\%$ (**Figures 1.c** and **2.c**).

With an increasing amount of both nanoadditives, the higher stiffness of the blend system causes a decreasing tendency of the elongation at break in all 3 cases (**Figures 3.a – 3.c**).

Comparison of the two different methods of modifying PA 6 fibres with BEN and BEN concentrate shows the difference. Fibres prepared directly from powdered PA 6 with BEN powder (method X) do not exhibit expressively better mechanical properties, whereas those prepared with addition of BEN concentrate (method Z) exhibit better tensile strength and Young's modulus at higher drawing ratios $\lambda_3 - \lambda_5 = 4 - 5$.

The better mechanical properties can be explained by the thermal characteristics of PA 6 fibres modified with $0.25 - 2.5$ wt.% of BEN concentrate, revealing a positive crystallisation effect of BEN. The melting enthalpies of these fibres are higher by about $5 - 15\%$ compared with those of non- modified PA 6 fibres [15].

Rheological and mechanical properties of PA 6 blends and fibres modified with the concentrates

The rheological and mechanical properties of PA 6 modified with concentrates A, B and D are determined by the amount of concentrate in fibres, the relationship of different structures in the concentrates and by the melting temperature of the concentrates (**Table 1**). The concentrates can contain exfoliated or intercalated complex structures of the nanoadditive and polyamide or copolyamide, I, free nano- and micro- particles of the nanoadditive, II, macromolecules of PA 6, III and copolyamide, IV. Important factors are lower molecular weights and lower melting temperatures of the concentrates compared with PA 6.

From the point view of the rheological and mechanical properties of the blends and modified fibres, mainly structures I, II and IV are important. Copolyamides (IV), with lower molecular weight negatively influence the apparent melt viscosity of the blend melt, as well as the mechanical properties of modified fibres, whereas exfoliated or intercalated complex structures (I) increase them. In this case the concentrate has a certain composition of these four structures in the concentrate; its increasing amount in modified fibres brings a higher amount of components II and IV, and the apparent melt viscosity of the blend melt decreases. This trend is confirmed by the values given in **Tables 3**.

The apparent viscosities of blend melts PA 6 + concentrates A, B and D (**Table 3**) are always lower compared with that of PA 6 neat melt. The drop is continuous for all three concentrates, which is a consequence of increasing the amount of concentrate (and copolyamide as well) and the lower melting temperature (**Table 1**) of concentrates, bringing about a lower melt viscosity at a higher processing temperature.

The processability, i.e. spinning and drawing of modified PA 6 fibres was sim-

ilar as this for non modified PA 6 fibres. In the process of drawing, the only difference occurred because it was not possible to draw fibres modified with 30 wt.% and 50 wt.% of concentrate B at drawing ratio $\lambda_1 = 3$. However, fibres modified with concentrate D were drawn even at drawing ratio $\lambda_3 = 4$.

The coefficients of variance, CV, (**Table 4**) evaluated from the 20 tests give a view of the homogeneity of modified fibres. From **Table 4** it is clear that values of CV of the modified fibres are similar to that of non-modified PA 6 fibres, therefore one can state that the homogeneity of the modified fibres is satisfactory.

The mechanical properties of PA 6 fibres modified with concentrates A, B and D (**Table 4**) are influenced mainly by three factors:
- the type,
- the amount, and
- the molecular weight of the concentrate.

An important role is also played by the compatibility of homopolyamide PA 6 and copolyamide in the blend system, mainly at higher amounts of concentrate in the modified fibres [6].

The type of concentrate influences the maximal drawing ratio, therefore concentrate B is not acceptable because higher drawing ratios cannot be achieved.

The higher the amount of concentrate in modified fibres, the lower the tensile strength and Young's modulus as well, as a consequence of the higher negative role of the lower molecular weight of the concentrate [3]. As regards mechanical properties, the most effective is concentrate D because modified PA 6 fibres have the highest tensile strength from all three concentrates used; the tensile strength is higher or equal to non-modified PA 6 fibres at amounts of 10 and 20 wt.%. The values of Young's modulus are higher for all three concentrates up to 30 wt.% of their amount.

This effect can be explained by the thermal characteristics of these fibres. According to [15], the melting enthalpies of PA 6 fibres modified with 10 wt.% and 20 wt.% of concentrate D are higher by about 4 – 6%, the melting temperatures being practically the same. The values of melting enthalpies documented in this reference reveal a positive crystallisation

effect at 10 and 20 wt.% of this concentrate. The higher level of crystallisation can be one of the important factors assuring better mechanical properties. The other positive factor is the high orientation factor of PA 6 fibres modified with lower amount of concentrates A, D and such like [16].

The coefficients of variance, CV, of the mechanical properties of modified and non-modified PA 6 fibres are very close, mainly in the interval 10 – 30 wt.% of the concentrates.

■ Conclusion

1. PA 6 blends modified with Bentonite using both methods have lower melt apparent viscosities compared with neat PA 6 melt.
2. The same is valid for PA 6 modified with concentrates A, B and D i.e. co-polyamide + Bentonite.
3. The spinning of PA 6 fibres modified with Bentonite, Cloisite and concentrates A, B and D was standard.
4. The drawing of the modified fibres prepared was standard for those prepared with both nanoadditives and concentrates A and D.
5. Double moulding is effective because PA 6 modified fibres prepared with Bentonite concentrate (method Z) exhibit better tensile strength and Young's modulus, mainly at higher drawing ratios λ_3 - $\lambda_5 = 4 - 5$, than those prepared with Bentonite using method X, which do not exhibit expressively better mechanical properties.
6. The tensile strength and Young's modulus of PA 6 fibres modified with Cloisite concentrate are positively influenced at lower drawing ratios $\lambda_1 = 3$ and $\lambda_3 = 4$.
7. The optimal amount of nanoadditives is 0.5 wt.%.
8. Mechanical properties - tensile strength and Young's modulus are better or equal to neat PA 6 fibres only for PA 6 fibres modified with 10 and 20 wt.% of concentrate D.
9. The elongation at break decreases with an increasing amount of both nanoadditives for both methods of processing.

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