

STRUCTURAL AND PHYSIOLOGIC PROPERTIES OF PA 6 FIBRES FUNCTIONALIZED WITH COPOLYAMIDES AND NANOCCLAYS

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Abstract

The contribution deals with hydrophilicity, orientation factor and barrier properties of PA 6 fibres physically modified with 5, 10 and 20 wt. % of concentrates. Each concentrate contains 95 wt. % of copolyamide + 5 wt. % of one nanoclay Bentonite 11958 or Cloisite 15A and was synthesized in the melt. Comonomers of copolyamide are ϵ -caprolactam, nylon salt of adipic acid and 1-(2-aminoethyl)piperazine and nylon salt of adipic acid and diethylenetriamine. Total amount of nylon salts in copolyamides is either 10.7 or 21.4 wt. %.

Hydrophilicity is positively influenced by higher amount of concentrates in modified PA 6 fibres and mainly if concentrates contain higher amount of nylon salts.

Fibres' orientation factors increase with increased drawing ratio and decrease with increased amount of concentrates in modified fibres and it is not or only slightly negatively influenced when PA 6 fibres are modified with concentrates having lower amount of comonomers and nanoclay Cloisite.

Barrier properties are better only in the case of AC and DC concentrates, mainly at 10 wt. %

From the point of nanoclay used Cloisite 15 A is more effective in comparison with Bentonite 11958.

Key words: polyamide fibres, modification, copolyamide, nanoclay, hydrophilicity, orientation factor, barrier properties

Introduction

The use of modified polymers and fibres will continue to grow. The modification is chemical, physical or combined. The most simple one is blending of basic fibre-forming polymer with two or more materials, one of them being filler or/and compatibilizer. Compatibilizer can be successfully replaced by copolymer having its structure similar to this of basic polymer and they are at least partially compatible like in the case of a polyamide + a copolyamide, both based on the same monomer. This blend assures good processability and properties of modified PA 6 fibres as well [1]. PA 6 fibres modified with copolyamides based on ϵ - caprolactam and polar functional nylon salts exhibit better electric and sorption properties but they have usually lower mechanical properties [2].

Nowadays polymers and fibres may be over-engineered by application of nanoclay and their mechanical properties are maintained or better. Introduction of nanoclay into polymer blend is either by simple compounding or by preparation polyamide 6-based nanocomposites [3].

PA 6 fibres modified with copolyamide 6-based nanocomposites (mentioned in abstract) have better electric and sorptive properties [4] and interesting mechanical properties [5].

Experimental

Materials

Polyamide 6, PA 6, commercial, $\eta_{rel} = 2.58$, $T_m = 221$ °C, Nylstar Humenné, Slovak Republic,

ϵ - caprolactam commercial, abbreviation CL, Nylstar Humenné, Slovak Republic, 1-(2-aminoethyl) piperazine, abbreviation N2, Aldrich, vacuum distilled,

Diethylenetriamine, abbreviation DETA, Aldrich, vacuum distilled,

Nylon salt AN2, prepared from adipic acid and 1-(2-aminoethyl)piperazine (N2),

Nylon salt ADETA prepared from adipic acid and diethylenetriamine,
 Nanoclay Bentonite 11958, Fluka, abbreviation Ben,
 Nanoclay Cloisite 15A, Southern Clay Products, Inc., USA, abbreviation Clo.

Preparation of concentrates

The nylon salts AN2 and ADETA were prepared by mixing of 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 concentrates were prepared through a polyreaction in a melt under nitrogen atmosphere. Powdered CL, nylon salt AN2 (for concentrate DX) or both nylon salts AN2 and ADETA and one of nanoclays were mechanically mixed and put in a glass apparatus immersed in a thermostatted oil bath. Temperature was gradually increased to 260 – 270 ° C. The melting, homogenization 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 chips. All synthesized concentrates (DX, A, AC, D, DC) contain the same amount i.e. 5 wt. % of one nanoclay and their compositions are below:

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

Preparation of modified PA 6 chips and fibres

PA 6 chips and chips of concentrates were dried 3 hours at 120 °C and were mechanically blended and melted:

1. Either in a single-screw ribbon extruder GÖTTFERT (Germany) at the temperature of its 3 zones $T_1 = T_2 = T_3 = 250$ °C (concentrate D), or by
2. Twin-screw ribbon extruder Lab Tech Engineering Company Ltd at the temperatures of its 10 zones $T_1 - T_{10} = 250$ °C (concentrates AC and DC), and they were cut into chips.

Mechanical blends of PA 6 and 5, 10 a 20 wt. % of concentrates A and DX were spun directly from the mechanical mixture of PA 6 chips and concentrates A and DX dried in a vacuum oven 2 hours at 80° C before spinning.

All PA 6 modified fibres containing 5 wt. %, 10 wt. % and 20 wt. % of each concentrate were prepared at semi-industrial spinning equipment with an extruder $\Phi = 32$ mm at $T_{11} - T_{15} = 260, 255, 255, 255$ and 260 °C, spinneret nozzle with 40 fibrils, each with diameter $d = 0.5$ mm, take up speed $800 \text{ m}\cdot\text{min}^{-1}$ with lubricant. After spinning drawn fibres were prepared by two

manners. Drawing manner α (optimized semi-industrial one) has primary feeding speed of fibre motion on the first godet $v_1 = 40 \text{ m}\cdot\text{min}^{-1}$ and speed of fibre on the secondary godet $v_2 = 120 \text{ m}\cdot\text{min}^{-1}$ (drawing ratio $\lambda_1\alpha = 3$). Length of the heater of drawing equipment equals to 20 cm and at $\lambda_1 = 3$ and the retention time on the heater is 0.0375 s. Manner β (experimental one) with primary feeding speed of fibre motion on the first godet $v_3 = 16.66 \text{ m}\cdot\text{min}^{-1}$ and speed on the

secondary godet corresponding to drawing ratios $\lambda_1\beta = 3$, $\lambda_2\beta = 3.5$ (all fibres) and $\lambda_3\beta = 4$ (only those modified with concentrates D, AC and DC). Length of the heater of drawing equipment equals to 30 cm and at $\lambda_1 = 3$, the retention time is 0.541s. Both drawing manners were made at the same temperature $T = 110^\circ \text{C}$.

Methods used

Water vapour sorption was evaluated gravimetrically at the temperature $T = 21.7^\circ \text{C}$ and at the 65 % relative humidity using lubricated fibres drawn to $\lambda_1 = 3$. The results are listed in Tables 2 and 3.

The fibres' orientation factor f was calculated according to the equation $f = 1 - C_n^2/C^2$ where C_n is the speed of sound in the absolutely non oriented fibre being equal to $1.25 \times 10^3 \text{ m.s}^{-1}$ and C is the speed of sound in the fibre measured by a PPM-5 Dynamic Modulus Tester (H.M. Morgan Co. Inc., Norwood, USA). The results are indicated in Table 4.

Barrier properties of fibres were measured using a "Libra S12" spectrophotometer and evaluated by modified Standard STN EN 13758-1/2001. Measured spectrum was in interval of wavelength $\lambda = 200 - 400 \text{ nm}$ so it involves all UVA and UVB spectrum and part of UVC spectrum. Each value was evaluated from 20 measurements. The modification of Standard STN consists in preparation of measured sample. Textile material was prepared from fibres wound on small metallic frame equipped with cuts distant 0.75 mm in two directions: longitudinal and perpendicular. Consecutively the transmittance through this layer was measured in the UV range and UPF was calculated by standard specification according to following equation:

$$UPF = \frac{\sum_{\lambda=290}^{\lambda=400} E(\lambda) \times S(\lambda) \times \Delta(\lambda)}{\sum_{\lambda=290}^{\lambda=400} E(\lambda) \times S(\lambda) \times T(\lambda) \times \Delta(\lambda)}$$

Where UPF – ultraviolet protection factor, $E(\lambda)$ – relative erythermal spectral effectiveness in $\text{W/m}^2.\text{nm}$, $S(\lambda)$ – solar UVR spectral irradiance (Melbourne), $T(\lambda)$ – spectral transmittance of the sample, $\Delta(\lambda)$ – bandwidth in nm, λ – wavelength

Results and discussion

Modified PA 6 fibres are the blend of PA 6 and concentrate. Concentrate is the complex component consisting of macromolecules of copolyamide and nanoclay in the form of nano- or micro- particles. During synthesis of concentrate, preparation of modified PA 6 chips and spinning of modified fibres the exfoliated or intercalated structures of nanoclay and macromolecules of copolyamides and polyamide 6 can be formed. These structures are characterized by high stiffness and molecular weight and the proportion between free particles of nanoclay and exfoliated or intercalated structures influence properties of PA 6 modified fibres.

Copolyamides have different regularity of their macromolecules due to the presence of one comonomer (concentrate DX) or two comonomers (all other concentrates) in copolyamide and due to different amount of comonomers in copolyamide' macromolecules. It influences the compatibility of blend components and deformability of blend fibres. Factors influencing properties of modified fibres are mainly:

1. The total amount of concentrate in modified fibres (5, 10 and 20 wt. %),

2. the total amount of comonomers in copolyamide of concentrate (10.7 and 21.4 wt. %),
 3. the type of nanoclay (Ben or Clo), and
 4. the manner of drawing process - temperature, equipment and velocity.
1. Amount of concentrates influences all characteristics of modified PA 6 fibres though the total amount of functional comonomers in copolyamides is rather small [5] and copolyamides are very similar in their chemical structure to neat homopolyamide 6. It is due to the fact the amount of concentrate in modified fibres increases 4 times from 5 wt. % to 20 wt. %. The same validates for nanoclays.
2. Prepared concentrates have two amounts of comonomers(s). Concentrates A, AC and DX contain copolyamides with lower content (10.7 wt. %) of functional comonomers. Concentrates D and DC with higher content of functional comonomers i.e. 21.4 wt. % have more polar macromolecules of copolyamides and influence effectively sorptive properties of modified fibres. In addition their macromolecules have higher flexibility and influence maximal drawing ratio of modified fibres.
3. Nanoclay influences mainly maximal drawing ratio and fibres' orientation factor.
4. Two manners of drawing (semi-industrial α manner and experimental β manner) were realized at different drawing speed and different length of the heater of drawing equipments.
- All above mentioned factors functions in complexity. E.g. PA 6 fibres modified with concentrates AC, D and DC and drawn by β manner can be drawn to the highest drawing ratio $\lambda_{3\beta} = 4$ even though concentrate AC contains copolyamide with lower amount of functional comonomers but as well as the concentrate DC (with higher amount of functional comonomers) contain Cloisite as nanoclay. Despite of this concentrate D contains higher amount of functional comonomers but nanoclay Bentonite. It supports the assumption about good compatibility of major matrix polymer and concentrates and focusses to the plasticizing effect of concentrates having either higher amount of comonomers in copolyamide' macromolecules or positively influencing nanoclay Cloisite as well.
- Sorption of water vapor of experimental non- and -modified PA 6 fibres spun at semi-industrial spinning equipment and drawn by two α and β manners to the drawing ratio $\lambda_1 = 3$ are gathered in Table 1 and drawn to the higher drawing ratios by β manner are gathered in Table 2. From values in Tables 1 and 2 it is clear that sorption of water vapor always increases with increased amount of concentrates (5 \rightarrow 20 wt. %) in modified PA 6 fibres. Levels of water vapor sorption for fibres prepared by α and β manners are different and higher for fibres drawn by α manner i.e. by semi-industrial spinning equipment. It points out to different internal structure of semi-industrial fibres with their less oriented internal structure proved by lower orientation factors given in Table 3.
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- PA 6 fibres modified with concentrates D and DC have higher water vapor sorption than those modified with concentrates A, AC and DX mainly at the amount 10 and 20 wt. % of these concentrates.
- Concentrates D and DC contain higher amount of functional comonomers and higher amount of hydrophilic atoms of nitrogen and $-\text{NH}-$ groups therefore they are characterized by higher sorption of water vapor. It can be stated that lower amount of comonomers causes lower

hydrophilicity, while higher amount of comonomers and presence of nanoclay Cloisite assures higher hydrophilicity.

Sorption of water vapor is influenced mainly by the amount of hydrophilic atom and groups introduced into copolyamides of concentrates and by drawing ratio.

Fibres' orientation factors of non- and modified PA 6 fibres drawn by both manners and at the same temperature are gathered in Table 3. They are influenced by drawing ratio and amount of additives. Their comparison shows unambiguous increase with increased drawing ratio as a consequence of higher tension which naturally contributes to higher orientation of all macromolecular components in the fibre system. From the point of modification the fibres' orientation factor of modified fibres is the same as for non modified ones or decreases with increased amount of concentrates.

Different conditions of drawing manners α and β bring about difference in fibres' orientation factors. Basic difference between α and β manner is the speed of drawing process and consecutively the retention time spent on the heater of drawing equipment i.e. time spent above T_g of polymer components forming blend when they can crystallize. Comparison of fibres drawn to the same drawing ratio $\lambda_1 = 3$ prepared by both manners shows that fibres prepared by experimental manner β have much higher fibres' orientation factor due to higher retention time on the heater of drawing equipment. These retention times are $t_\beta = 0.541$ s for experimental manner β and $t_\alpha = 0.0375$ respectively for semi-industrial manner α , i.e. more than 14 times longer for experimental manner β . Due to higher retention time macromolecular components in experimental manner β have enough time to reach higher level of orientation.

According to fibres' orientation factor modified fibres form two groups:

- First group is formed by PA 6 fibres modified with concentrates A, DX and AC having more uniform internal structure with lower amount of comonomers (10.7 wt. %) in copolyamide' macromolecules. They have higher fibres' orientation factor.

- Second group involves PA 6 fibres modified with concentrates D and DC with less regular internal structure due to higher amount of comonomers (21.4 wt. %) in copolyamide' macromolecules. They have lower fibres' orientation factor.

Fibres' orientation factor of the first group of modified fibres PA 6 have the same or little lower values in comparison with non modified PA 6 fibres. The highest orientation factors exhibit fibres modified with concentrate AC having the same orientation factor as non modified PA 6 fibres in all concentrations interval and drawing ratios $\lambda_2 = 3.5$ and $\lambda_3 = 4$. Fibres modified with concentrates DX and A have fibres' orientation factor equal or lower (but very close) to this of non modified PA 6 fibres. This validates for all drawing ratios and both manners of drawing α and β . The explanation is that concentrates AC and A with lower amount of comonomers have more regular structure of copolyamides' macromolecules, more similar to homopolymer PA 6 macromolecules and less "hamper" during crystallization and orientation processes i.e. spinning and drawing. In addition, concentrate AC permits drawing to the higher drawing ratio $\lambda_3 = 4$ what focus to the better influence of nanoclay Cloisite. Better influence of nanoclay Cloisite is evident from values of orientation factors exhibiting lower decrease in comparison with orientation factors of fibres modified with Bentonite. PA 6 fibres modified with concentrate AC exhibit synergic effect of lower amount of comonomers in copolyamide macromolecules and presence of nanoclay Cloisite and have the same fibres' orientation factor as non modified PA 6 fibres. Fibres' orientation factors of PA 6 fibres modified with concentrates D and DC having higher amount of comonomers (21.4 wt. %) are lower.

Table 1 Sorption of water vapor, S, of modified PA 6 fibres, manners α and β , $\lambda_1 = 3$

Amount of concentrate [wt. %]	α					β				
	Type of concentrate									
	A	D	DX	AC	DC	A	D	DX	AC	DC
	S [wt. %]									
PA 6	5.24					4.96				
5	5.43	5.56	5.25	5.55	5.56	5.20	5.18	5.13	5.32	5.34
10	5.52	5.89	5.21	5.60	5.60	5.34	5.39	5.17	5.33	5.51
20	-	6.25	5.42	5.58	5.87	-	5.84	5.42	5.41	5.82

Table 2 Sorption of water vapor, S, of modified PA 6 fibres, manner β , $\lambda_2 = 3.5$ and $\lambda_3 = 4$

Amount of concentrate [wt. %]	$\lambda_2 = 3.5$					$\lambda_3 = 4$
	Type of concentrate					
	A	D	DX	AC	DC	D
	S [wt. %]					
PA 6	4.87					4.59
5	4.81	5.15	4.84	4.98	5.06	4.94
10	5.07	5.21	5.13	5.05	5.23	5.12
20	-	5.44	5.19	5.12	5.54	5.53

Higher amount of comonomers in copolyamide macromolecules (concentrate D) or synergic effect of higher amount of comonomers in copolyamide macromolecules and presence of Cloisite assure higher plasticity of blend system and capability to draw them to higher drawing ratio $\lambda_3 = 4$. High fibres' orientation factor assures good mechanical properties of such modified PA 6 fibres [5].

Generally fibres' orientation factor is influenced by:

- drawing manner. Higher retention time on the heater of drawing equipment is advantageous.
- Amount of concentrate in modified fibres. Its lower amount permits higher fibres' orientation factor.
- Drawing ratio. The higher is the drawing ratio the higher is the fibres' orientation factor.
- Regularity of copolyamide macromolecular backbone. Higher regularity i.e. lower amount of functional comonomers assures higher fibres' orientation factor and
- nanoclay used. Cloisite is more effective than Bentonite.

Barrier properties are characterized by UPF factor expressing resistance of fibrous materials against penetration of UV light to the skin i.e. the light with wavelengths 100 – 400 nm. The higher is value of UPF factor the higher is resistance of material against UV penetration. Partial characteristics - UVA, UVB and UVC factors express transmission of light with certain wavelengths through the material. These wavelengths are 315- 400 nm for UVA, 290 – 315 nm for UVB and 100 – 290 nm for UVC.

According to the definition the lowest are these factors the higher is the protection efficiency and less UV light penetrates through the material. Values of UPF, UVA, UVB, UVC and their coefficients of variance, CV, are gathered in Table 4. According these values the efficiency of concentrates can be compared and it is evident that the best barrier properties have PA 6 fibres modified with concentrates AC and DC i.e. modified with concentrates containing nanoclay Cloisite. For such modified PA 6 fibres values of UPF are higher and these of UVA, UVB a UVC are lower than these for non modified PA 6 fibres, mainly at the amount 5 and 10 wt. %

concentrate AC and 10 and 20 wt. % concentrate DC. Barrier properties are improved only by concentrates containing nanoclay Cloisite.

Conclusion

1. PA 6 fibres modified with concentrates containing 0.54 - 4.24 wt. % of functional comonomers (AN2 + ADETA) and 0.25 - 1 wt. % of both nanoclays, exhibit standard or better properties.
2. Higher plasticity of concentrates D, DC with higher amount of comonomers in copolyamide and/or nanoclay Cloisite in AC and DC) assures higher drawing ratio.
3. The higher is the amount of functional comonomers in copolyamide, the higher is the amount of concentrate in modified PA 6 fibres and the lower is drawing ratio the higher is hydrophilicity of modified fibres. Nanoclay does not play any important role.
4. Lower speed of drawing assures much higher fibres' orientation factor.
5. Higher drawing ratios assure maximal fibres' orientation factor of modified PA 6 fibres and these modified with concentrate AC (10.7 wt. % of comonomers + nanoclay Cloisite 15A) have the same fibres' orientation factor as non modified PA 6 fibres.
6. Barrier properties are improved only by concentrates AC and DC containing Cloisite 15A.
7. From the point of all three evaluated properties the concentrates AC (fibres' orientation factor and barrier properties) and DC (hydrophilicity and barrier properties) are the most effective.

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References

1. Krištofič M., Marcinčin, A. and Ujhelyiová A., *J Therm Anal Cal*, 60, pp. 357-369, 2000,
2. Krištofič, M., Marcinčin, A. and Borsig E.: Preparation, *Polym Adv Technol* 10, pp. 179-186, 1999,
3. Kojima Y. et al, *J Polym Sci Part A, Polymer Chem* 31, pp. 983-986, 1993,
4. Krištofič, M., Dulíková, M., Vassová, I. and Ryba, J., *Fibres & Textiles in Eastern Europe*, 15, 5-6, pp. 34-36, 2007,
5. Krištofič M., Ujhelyiová A., Vassová I., Michlík P., Brejka O. and Ryba J., *Fibres & Textiles in Eastern Europe*, accepted as No 2995,

Table 3 Speed of sound, C and fibres' orientation factor, f, of modified PA 6

Amount and type of concentrate [wt. %]	C [km.s ⁻¹]				f			
	Manner of preparation							
	α	β			α	β		
	$\lambda_1 = 3$	$\lambda_2 = 3.5$	$\lambda_3 = 4$		$\lambda_1 = 3$	$\lambda_2 = 3.5$	$\lambda_3 = 4$	
PA 6	2.06	2.27	2.39	2.49	0.65	0.71	0.73	0.75
5 A	2.04	2.26	2.39	-	0.64	0.70	0.73	-
10 A	2.02	2.24	2.35	-	0.62	0.69	0.72	-
5 D	2.00	2.22	2.31	2.41	0.61	0.68	0.71	0.73
10 D	1.98	2.20	2.31	2.37	0.60	0.67	0.71	0.72
20 D	1.95	2.17	2.26	2.36	0.59	0.66	0.70	0.72
5 DX	2.02	2.24	2.38	-	0.64	0.69	0.73	-
10 DX	2.00	2.22	2.34	-	0.61	0.68	0.72	-
20 DX	1.99	2.19	2.30	-	0.60	0.67	0.71	-
5 AC	2.06	2.27	2.40	2.49	0.65	0.71	0.73	0.75
10 AC	2.03	2.27	2.39	2.47	0.62	0.70	0.73	0.75
20 AC	1.98	2.23	2.38	2.47	0.59	0.69	0.73	0.75
5 DC	2.02	2.24	2.35	2.42	0.62	0.69	0.72	0.73
10 DC	2.01	2.23	2.30	2.41	0.61	0.68	0.71	0.73
20 DC	1.97	2.22	2.29	2.37	0.59	0.68	0.71	0.72

Table 4 Barrier properties of modified PA 6 fibres modified, manner α , $\lambda_1 = 3$

Amount and type of conc. [wt. %]	UPF	CV _{UPF} [%]	UVA	CV _{UVA} [%]	UVB	CV _{UVB} [%]	UVC	CV _{UVC} [%]
PA 6	10.5	30	0.10	28	0.10	25	0.08	30
5 A	9.9	48	0.12	35	0.12	35	0.10	39
10 A	8.5	45	0.14	30	0.13	32	0.12	36
5 D	10.5	36	0.11	27	0.11	27	0.09	31
10 D	8.5	24	0.12	22	0.12	23	0.11	25
20 D	9.9	33	0.11	27	0.11	30	0.10	33
5 DX	10.9	27	0.10	27	0.10	28	0.08	33
10 DX	9.4	34	0.12	28	0.12	33	0.10	38
20 DX	9.6	27	0.11	25	0.11	27	0.10	31
5 AC	11.8	29	0.09	29	0.09	28	0.08	35
10 AC	13.5	28	0.08	29	0.08	30	0.07	37
20 AC	10.8	45	0.11	31	0.10	33	0.09	38
5 DC	10.9	46	0.11	30	0.10	33	0.09	39
10 DC	12.4	20	0.09	20	0.08	20	0.07	23
20 DC	11.7	29	0.09	20	0.09	22	0.08	25