

Michal Krištofič,
Mária Dulíková,
Iveta Vassová,
Jozef Ryba

Slovak University of Technology in Bratislava,
Faculty of Chemical and Food Technology,
Institute of Polymer Materials,
Department of Fibres and Textile Chemistry
812 37 Bratislava, Radlinského 9, Slovak Republic,
e-mail: michal.kristofic@stuba.sk

PA 6 / Copolyamide / Layered Silicate Fibres

Abstract

The modification of PA 6 fibres with macromolecular modifiers in order to improve their sorptive and electric properties was studied. Modifiers consisting of binary, high molecular, semicrystalline copolyamides (from ϵ -caprolactam as a major component and 5, 17 and 30 wt.% of nylon salt from adipic acid + diethylenetriamine) and PA 6 homopolyamide were synthesised in the presence of nanoadditive montmorillonite, and the basic characteristics of the modifiers were evaluated. Synthesised modifiers of 10, 20, 30 and 50 wt.% were used for the preparation of blended M/F poly- ϵ -caprolactam/modifier fibres and the fibres' properties were evaluated. The electric and sorptive properties of PA 6 fibres modified with modifiers containing montmorillonite were improved; their tensile strength (mainly with lower amount of modifiers) decreased only negligibly.

Key words: polyamide fibres, copolyamide, layered silicate, modification, properties.

Introduction

The modification of fibre-forming polymer with the aim of obtaining a raw material for fibres which improves their properties is topical these days. The modification can be chemical, physical or combined. Polyamides are easily modified by copolyreaction when a suitable comonomer is used.

The introduction of same polar atoms or groups (like -O-, -SO₂-, piperazine rings etc.) into a polyamide chain assures a higher water sorption ability [1 - 4] and these polymers can be used as additives to improve the sorptive and electric properties of fibre-forming polymers and fibres made from them.

For ϵ -caprolactam (CL) polyreaction many initiators can be used. If water or the acid ϵ -aminocaproic (AA) are used, polyamide 6 is obtained. The main reason for the application of AA is to shorten the time of polyreaction. Nylon salt with general formula $H_2N-R_1-NH_3^+ \cdot \bar{O}OC-R_2-COOH$ can be used as an initiator as well, and in this case a copolyamide is the main polymer obtained. The reason for nylon salt application is the preparation of a functional copolyamide and fibres with some special end-use properties (chemical modification). Like AA, the nylon salts shorten the time of polyreaction as well. The copolyamides prepared can be used as additives to PA 6 as well (physical modification). By this physical modification of a blend, M/F modified PA 6 fibres are obtained with better properties in a certain domain. If the functional comonomer – nylon salt contains hydrophilic, the polar atoms or groups and it is used for the preparation of copolyamide, it can be applied as an additive into neat PA 6 and modified

PA 6 fibres with better sorptive (of water vapour and dyestuffs) and electric properties can also be prepared.

Polymers or copolymers like polyetherureas [5] with an oxygen atom in the chain, or copolyamides and copolyamideureas containing a tertiary atom -N= or -NH- group from piperazine derivatives [6] or diethylenetriamine [7, 8] improve the above-mentioned properties of polyamide 6 (PA 6) and even polypropylene modified fibres [9, 10]. The properties of copolyamides based on CL and ADETA nylon salt from adipic acid (A) and diethylenetriamine (DETA), including thermal ones [11], are suitable for use as additives.

The introduction of a functional copolymer into basic fibre-forming PA 6 usually brings about worse mechanical properties of PA 6 modified fibres.

The preparation of polyamide or copolyamide strengthened by nanoadditive is a perspective to prepare modified PA 6 fibres with better end-use properties without a drop in their mechanical properties.

In this contribution, modifiers from ϵ -CL, nylon salt of adipic acid and diethylenetriamine and layered silicate – organophilic montmorillonite according to Kojima, Usuki et al [12, 13] were prepared. After their adaptation (extraction of low molecular compounds) they were used for modification of fibre-forming PA 6 and preparation of modified PA 6 fibres. The electric, sorptive and mechanical properties of these fibres were evaluated and discussed.

Experimental

Material used

- poly- ϵ -caprolactam, i.e. PA 6c, commercial, Nylstar Slovakia, Humenné,
- ϵ -caprolactam, CL, Nylstar Slovakia, Humenné,
- organophilic montmorillonite Bentonite 11958, Fluka,
- adipic acid, p.a., A, Fluka,
- ϵ -aminocaproic acid, p.a., AA, Fluka,
- diethylenetriamine, DETA, vacuum distilled,
- sulphuric acid, 96 %, p.a.,
- ethanol, p.a., 96 %,
- ADETA nylon salt from adipic acid and diethylenetriamine,
- M0, M5, M17, M30 modifiers.

Synthesis of modifiers and evaluation of their properties

Four modifiers (according to reference 11) were synthesised and designated according to the concentration *c* of ADETA nylon salt in the mixture at the beginning of the synthesis:

M0 – (92 wt.% of CL + 5 wt.% of AA) + 3 wt.% of MMT + 0 wt.% of ADETA

M5 – 92 wt.% of CL + 5 wt.% of ADETA + 3 wt.% of MMT

M17 – 80 wt.% of CL + 17 wt.% of ADETA + 3 wt.% of MMT

M30 – 67 wt.% of CL + 30 wt.% of ADETA + 3 wt.% of MMT

The influence of (lower) molecular weight of copolyamides in M0, M17 and M30 modifiers on the mechanical properties of modified fibres can be appreciated when PA 6 homopolymer + MMT (i.e.

modifier M0 with a molecular weight comparable with the molecular weight of modifiers M5, M17 and M30) is used as a modifier in the same manner as other functional copolyamides containing comonomer ADETA and MMT. So polyamide 6 with polyreaction initiator - 5 wt.% ϵ -aminocaproic acid (instead of nylon salt ADETA) and 3 wt.% of MMT was synthesized and used.

The powdered components: ϵ -caprolactam, nylon salt ADETA and montmorillonite were mechanically mixed and put into a glass apparatus immersed in the thermostated oil bath and heated to a temperature of about 120 °C. The mixture melted and a mechanical stirrer was installed. The temperature of oil bath was gradually increased with time to a temperature of 270 °C at the end of the reaction time.

At the end of the reaction time the modifier was poured onto a metallic plate and cut into chips. The chips were extracted in boiling water for over 2 hours in order to remove water soluble low-molecular compounds, LMC. The modifiers extracted were dried out at 80 °C for 3 hours in a vacuum oven and stored in a desiccator. The amount of LMC was determined gravimetrically from the difference of weights before and after extraction and drying.

Both η_r and intrinsic viscosity $[\eta]$ values were determined viscosimetrically in the solution of H₂SO₄ 96% p.a. at 25 °C according to the formula:

$$\eta_r = t/t_0 \text{ and } [\eta] = \frac{2}{c} \cdot \left(\sqrt{\frac{t}{t_0}} - 1 \right)$$

valid for concentrations $c \leq 0.5$ g/100 ml and calculated for $c_1 = 0.5$ g/100 ml, where t is the flow time of the polymer solution and t_0 is the flow time of the pure solvent i.e. H₂SO₄. The melting temperature T_m was estimated as an average of 5 measurements on a Kofler block. The polymerisation schedule and basic properties of PA 6c and modifiers are presented in Table 1.

Preparation of blends

Modified PA 6 blends containing 10, 20, 30 and 50 wt.% of extracted and dried modifiers M0, M5, M17 and M30 were prepared by melting a mixture of PA 6 + relevant modifier in a GÖTTFERT single-screw ribbon extruder at a temperatures of zones $T_1 = T_2 = T_3 = 250$ °C. The blended ribbon was cooled down in cold water and cut into chips. The air-dried chips were finally vacuum dried

Table 1. Polymerisation schedule and basic properties of PA 6c and modifiers.

Polymer, modifier	Amount of ADETA MMT, wt. %		Time of polymerisation, min	Properties of modifier			
				LMC, wt. %	$[\eta]$, ml.g ⁻¹	η_r	T_m , °C
PA6c	0	0	-	8-12	121.5	1.70	227
M0	0	3	470	15	101.8	1.55	226
M5	5	3	245	10,9	103.7	1.59	224
M17	17	3	200	9,5	76.2	1.42	210
M30	30	3	280	10,6	97.0	1.54	175

Table 2. Composition and viscosity η of blends and electric properties, U_{max} , $t_{1/2}$, water vapour sorption, S and tensile strength, TS of modified PA 6 fibres.

Blend, fibre	CL, wt. %	ADETA, wt. %	MMT, wt. %	Viscosity η , Pa·s	U_{max} , kV	$t_{1/2}$, s	S , wt. %	TS , cN/dtex
PA6c	100	0	0	179	30	16	4.53	2.56
PA6 + 10% M0	99.7	0	0.3	155	22.5	10	4.60	2.40
PA6 + 20% M0	99.4	0	0.6	134	28.5	8	4.30	2.30
PA6 + 30% M0	99.1	0	0.9	113	29.5	23	4.56	2.34
PA6 + 50% M0	98.5	0	1.5	94	15.5	28	4.70	2.24
PA6 + 10% M5	99.2	0.5	0.3	168	23.2	2	4.96	2.31
PA6 + 20% M5	98.4	1.0	0.6	148	27.5	5	4.85	2.29
PA6 + 30% M5	97.4	1.5	0.9	128	29.0	18	5.06	2.29
PA6 + 50% M5	96.0	2.5	1.5	115	22.5	25	5.07	2.07
PA6 + 10% M17	98.0	1.7	0.3	144	16.5	23	4.78	2.34
PA6 + 20% M17	96.0	3.4	0.6	130	26.5	3	4.64	2.13
PA6 + 30% M17	94.0	5.1	0.9	115	30.0	6	4.85	2.10
PA6 + 50% M17	90.0	8.5	1.5	86	30.0	4	4.96	1.63
PA6 + 10% M30	96.7	3	0.3	155	27.5	-	5.30	2.40
PA6 + 20% M30	93.4	6	0.6	125	30.0	9	5.63	2.09
PA6 + 30% M30	90.1	9	0.9	94	29.5	14	5.95	1.9
PA6 + 50% M30	84.0	15	1.5	49	-	-	-	-

at 105 °C and used for spinning. From output (m), geometry of orifice (diameter R , length L), pressure (P), density (ρ) the viscosity η of the melt was calculated according to the relationships:

$$\eta = \frac{\tau}{\dot{\gamma}} \text{ where: } \tau = \frac{P \cdot R}{2 \cdot L} \text{ and } \dot{\gamma} = \frac{4 \cdot m}{\rho \cdot \pi \cdot R^3}$$

Preparation of modified PA 6 fibres

The spinning of dried blend chips was performed by laboratory spinning equipment with an extruder $\Phi = 16$ mm at $T = 250$ °C, take up speed of 150 m·min⁻¹ with and without lubricant (13 fibrils, diameter of each spinning hole $d = 5 \cdot 10^{-5}$ m). After spinning, the fibres were drawn to the $\lambda_1 = 2$ (nonlubricated fibres) and $\lambda_2 = 3$, respectively (lubricated ones). Fibres drawn to $\lambda_2 = 3$ had a linear density T_d in an interval 298 – 326 dtex.

Evaluation of the fibres' properties

The electric properties of non-lubricated fibres with $\lambda_1 = 2$ were measured by two apparatus:

1. The fibres were rolled up on a metal frame (about 10 × 12 cm) mechanically to a uniform surface and the frame with the fibre thus arranged was fixed to a STAT-CHARGE FD 28 table. The fibre's surface was charged to the maximum potential U_{max} by friction of the slider moving on it.
2. The measurement by Polystat 1 consists in the charging of a sample (about 1 - 1.4 cm²) to the maximum potential by corona charge. The fibre surface was prepared with fibres rolled up on the metal plate. After the potential reached the maximum, its drop was continuously recorded until the charge achieved zero potential. The half time of discharging $t_{1/2}$ was obtained from this time dependence.

The fibres hydrophilicity was evaluated gravimetrically at a temperature $T = 21.7$ °C and a 65% relative humidity using lubricated fibres with $\lambda_2 = 3$. Tensile strength was measured by Instron 3334 apparatus. Electric and sorptive characteristics and tensile strength values are listed in Table 2.

Results and discussion

The synthesis of modifiers M5 – M17 containing ADETA nylon salt was completed in a shorter time than the synthesis of homopolymer PA 6 i.e. modifier M0 (with ϵ -aminocaproic acid AA without ADETA nylon salt, both as activators of polyreaction). The better catalytic influence of ADETA nylon salt ADETA compared with ϵ -aminocaproic acid AA is clear mainly from the comparison of modifiers M0 and M5. Both compositions contain the same amount of polyreaction initiator i.e. 5 wt. % of AA (M0) and 5 wt. % of ADETA (M5). At the same time the molar mass of M5 is a little higher (according to $[\eta]$ and η_r values) and the polyreaction time is rather lower (245 min versus 470 min). If the amount of ADETA is higher, the molar characteristics are lower, but simultaneously the polyreaction time is rather shorter. In the given conditions of polyreaction it was not possible to extend the polyreaction time due to high melt viscosity. The other advantages of modifiers are lower amounts of low-molecular compounds for all 3 copolyamides and not much lower melting temperatures T_m mainly for M5 and M17 modifiers as well in comparison with the synthesized homopolymer-modifier M0 (Table 1).

The preparation of blends shows the effect of the 'dilution' of homopolymer PA 6 caused by the lower density of intermolecular bonds and lower compatibility (or incompatibility) between "free" PA 6 and the structures polyamide or copolyamide + nanoadditive MMT, but it did not bring about any problems. The influence of the lower molecular weight and lower melting temperature of modifiers M17 and M30 was manifested by a drop in melt viscosity, radical mainly at 50 wt.% of the modifier M30 (Table 2), and due to this fact the blend 50/50 PA6/M30 was not spinnable in the applied spinning conditions at all.

The properties of modified PA 6 fibres are especially influenced by the fact the modifiers containing more polar copolyamide with lower molecular weight and nanoadditives were added. The other fact which can not be omitted is the lower compatibility among PA 6, copolyamide and structures formed by polymers and nanoadditive. Higher polarity of copolyamide positively influences hydrophilicity and electrostatic properties, lower compatibility and lower molecular weight of modifiers negatively influence the

tensile strength of modified PA 6 fibres but only when there is a higher amount of modifiers.

Despite the modified PA 6 fibres being charged nearly to the same maximal value as nonmodified PA 6 fibres, the value of half time of discharging is essentially lower mainly for fibres modified by modifiers M5, M17 and M30 containing comonomer ADETA (Table 2).

A higher amount of polar, hydrophilic groups –NH- and more 'open' internal structure (lower compatible components) of a blend system are the main reasons that the water vapour sorption of modified PA 6 fibres is positively influenced mainly by modifiers with a higher content of polar ADETA comonomer in the modifier and a higher amount of modifier in the blended fibres (Table 2).

It is possible to suppose that a part of the comonomer polymerised between galleries of MMT and those (exfoliated or intercalated) structures of MMT + homopolyamide or/and copolyamide contribute to the strengthening of the blended fibres and in other parts polymerised as 'free' polyamide and copolyamide outside MMT. Moreover, the part of MMT which was not swollen by CL during the polyreaction and is not the component of exfoliated or intercalated structures that can occur in the blend as microparticles and can deteriorate the mechanical properties of modified fibres. So the negative influence of the lower molecular weight of modifiers (copolyamides) and lower compatibility as well can be, to a certain extent, compensated with the positive influence of MMT-homopolyamide or/and copolyamide nanostructures. From this point of view, the drop in tensile strength is negligible mainly if the tensile strengths of comparable fibres are considered i.e. when the tensile strengths of PA 6 fibres modified with functional modifiers M5, M17 and M30 are compared with those of fibres PA 6 modified with synthesized modifiers M0 consisting of homopolyamide PA 6 + MMT. This is valid mainly for modified fibres with a lower amount of modifier (10 wt. % of M17 and M30 and 10 – 30 wt. % of M5). With a higher amount of ADETA nylon salt in these modifiers the drop in tensile strength is a little bit higher (Table 2).

Conclusions

1. The synthesis of modifiers is easy and quick. ADETA Nylon salt has a posi-

tive influence on the polyreaction time (lower values).

2. Modifiers have high molecular weight (however, lower than PA 6c), a comparable amounts of low molecular compounds and lower T_m corresponding inversely to the amount of ADETA nylon salt in copolyamide.
3. The preparation of blends, spinning and drawing of modified PA 6 fibres is without problems.
4. The electrostatic properties of modified PA 6 fibres are much better especially if modifiers M17 and M30 with a higher amount of polar comonomer ADETA are used.
5. The water vapour sorption of modified fibres shows the same tendency.
6. Tensile strength is not negatively influenced mainly with a lower amount of modifiers.

Acknowledgment

The support of the National Grant Agency of Slovakia APVV – Grant No 20-011404 and VEGA 1/2475/05 is appreciated.

References

1. *Encyclopedia of Polym. Sciences*, 1967, Vol 10, John Wiley & Sons Inc., New York, pp. 526, 527.
2. USA pat. 3 143 527, 1964.
3. Beaman, R. G., Cramer, F. B.: *J. Polymer Sci.*, Vol. 21(1956) pp. 223-235.
4. Jap. pat. 72 32753.
5. Krištofič M., Pikler A., Beniska J.: *Buletinul Institutului Politehnic DIN IASI*, 1980, XXVI, Fasc. 1-2, Sectia II Chimie si Inginerie Chimica, pp. 25-30, Romania.
6. Krištofič M., Marcinčin A., Borsig E.: *Polym. Adv. Technol.*, Vol. 10(1999) pp. 179-186.
7. M. Krištofič, A. Marcinčin, A. Ujhelyiová and A. Murárová: *Chem. Papers*, Vol. 54(2000) pp. 53-58.
8. Krištofič M., Karabcová N.: *3rd CEC Conference named Fibre-Grade Polymers, Chemical Fibres and Special Textiles, Proceedings on CD-ROM, doc. 9, Sept. 10-12. 2003, Portorose, Slovenia.*
9. CS. Pat. 234 283, 1987.
10. CS. Pat. 235 156, 1987.
11. Krištofič M., Ujhelyiová A.: *Fibres and Textiles in Eastern Europe*, Vol. 14(2006) No. 4(58), pp. 21-24.
12. Kojima Yo., Usuki A., Kawasumi M., Okada A., Kurauchi T., Kamigaito O.: *Synthesis of Nylon 6-Clay Hybrid by Montmorillonite Intercalated with ϵ -Caprolactam*, *J. Pol. Sci., Part A, Pol. Chemistry*, Vol. 31(1993) pp. 983-986.
13. Usuki A., Kojima Yo., Kawasumi M., Okada A., Fukushima Yo., Kurauchi T., Kamigaito O.: *J. Mater. Res.*, Vol. 8(1993) pp. 1479-1184.

Received 15.11.2007 Reviewed 15.01.2008