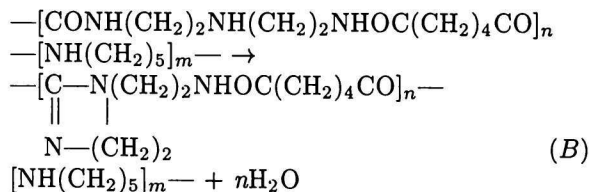


Polyreaction (B) – cyclization of the alkaline copolyamide on the polyamideimidazoline



EXPERIMENTAL

Preparation of Copolyamides and their Properties

Copolyamides from ϵ -caprolactam (CL), adipic acid A, and diethylenetriamine (DETA) were prepared by the poly(addition-condensation) reaction proceeding in melt in the N_2 atmosphere in two steps. The hot DETA solution in ethanol was successively added to the hot solution of adipic acid in ethanol (time 0) contained in a glass apparatus immersed in the thermostated oil bath. After mixing the two parts of Nylon salt, ethanol was gradually distilled off. After the removal of all ethanol, the whole amount of CL was added (time 0–1). Melting and homogenization of CL were completed in the time 2 at 100°C . The temperature of the reaction mixture was rising and the polyreaction started by evaporation and condensation of the reaction water. The first step of the polyreaction was carried out at the atmospheric pressure (time 2–3) and the second one at the gradually reduced pressure (time 3–4). The temperature of the reaction mixture achieved $270\text{--}280^\circ\text{C}$ at the end of the polyreaction (polyreaction time 2–4, the total time of the preparation 0–4).

Copolyamides were designated by the mass fraction w of the Nylon salt ADETA in the mixture at the beginning of the polyreaction and by the letter E in the case when the copolyamide was extracted in hot water before the preparation of the blended fibres

KOPA 21.6: 21.6 mass % of ADETA and 78.4 mass % of CL, nonextracted;

KOPA 21.6E: 21.6 mass % of ADETA and 78.4 mass % of CL, extracted;

KOPA 30.6: 30.6 mass % of ADETA and 69.4 mass % of CL, nonextracted.

To determine low-molecular (water-soluble) compounds (LMC) the amount of about a 5 g granulate of each copolyamide was extracted in hot water for 1 h. The copolyamides extracted were dried at 105°C in a vacuum oven and stored in a desiccator. The amount of LMC was determined from the difference of mass before and after extraction.

The limiting viscosity number (intrinsic viscosity) – $[\eta]$ value of extracted copolyamides was determined viscosimetrically in the solution of 93 % H_2SO_4 , anal. grade, at 25°C , and graphically from the dependences

$$\eta_{\text{sp}}/w_1 = f(w_1) \quad \text{and} \quad \eta_{\text{sp}} = (t - t_0)/t_0$$

where t = flow time of the polymer solution, t_0 = flow time of the pure solvent, and w_1 = polymer mass fraction in the solution.

The nitrogen content w_N in copolyamides was determined by an elemental CHNS-O EA 1108 analyzer (Erba, Milan, Italy). The melting temperature θ_m was estimated as an average of 5 measurements on the Kofler block. Conditions of the preparation and the fundamental properties of PA 6 and copolyamides are indicated in Table 1.

Preparation of Fibres

The dried copolyamides were used for the preparation of blended granules. The mixture consisting of 50 mass % of PA 6 and 50 mass % of copolyamide was melted in a single-screw ribbon extruder at the temperatures of zones $\theta_1 = \theta_2 = \theta_3 = 235\text{--}245^\circ\text{C}$. The blended ribbon was cooled down in the cold water and cut into granules. The air-dried blend was finally vacuum-dried at 105°C and used for spinning. The blended fibres containing 10 mass %, 20 mass %, and 30 mass % of copolyamide were prepared by mixing the PA 6 with

Table 1. Conditions of the Preparation and Some Properties of (Co)polyamide

(Co)polyamide	Step I/min		Step II/min		Time 0–4 min	$[\eta]$ $\text{cm}^3 \text{g}^{-1}$	θ_m $^\circ\text{C}$	LMC mass %	w_N mass %
	Time 0–1	Time 0–2	Time 2–3	Time 3–4					
PA 6	–	–	–	–	–	93	217	–	12.19
KOPA21.6	120	145	180	40	365	56.5	189	5.1	13.32
KOPA21.6E	60	85	120	170	375	41.5	192	5.4 (10.3*)	13.25
KOPA 30.6	80	100	140	140	380	46.5	188	6.3	13.64

*Extraction for (1 + 1) h in the boiling water.

Table 2. Electrical Properties and Sorption of Water Vapour of Nonmodified and Modified PA 6 Fibres

(Co)polyamide	Amount of copolyamide mass %	U_{\max}	$t_{1/2}$	t_{0V}	S
		V	s	s	mass %
PA 6	0	460	7.8	180	4.6
KOPA 21.6	10	480	6.3	385	5.1
	20	370	1.6	75	5.7
	30	420	3.7	35	5.8
	50	230	2.0	10	6.0
	10	440	4.5	110	5.1
KOPA 21.6E	20	390	2.8	45	5.4
	30	315	3.2	30	5.4
	50	340	3.0	25	5.6
KOPA 30.6	10	445	5.5	130	4.9
	20	500	3.0	100	5.2
	30	150	3.0	5	5.5
	50	90	2.9	5	6.1

50 mass % concentrate of copolyamide immediately before spinning. The blended fibres containing 50 mass % of copolyamide were prepared by a direct spinning of the concentrate containing 50 mass % of copolyamide.

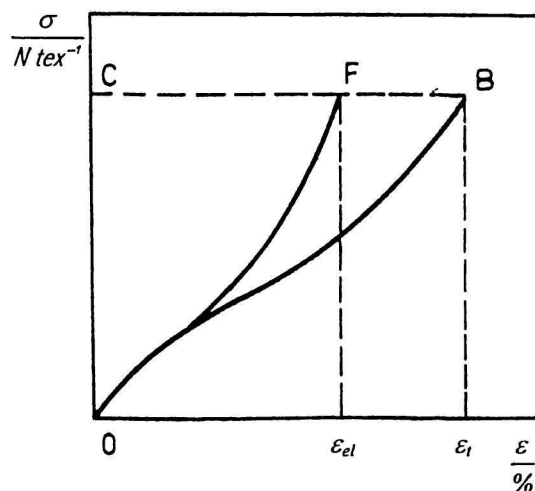
The spinning of blends was performed on the laboratory model equipment at the temperatures of its 3 zones $\theta_4 = \theta_5 = \theta_6 = 250^\circ\text{C}$ with and without a lubricant (13 fibrils). After spinning, the fibres were drawn ($\theta_7 = 120^\circ\text{C}$) to the drawing ratio $\lambda = 3$. Non-lubricated fibres were during drawing permanently wetted with water.

Evaluation of the Fibres Properties

Electrical, mechanical, and elastic properties were studied equally like the hydrophilicity of PA 6 and blended fibres.

The electrical properties of fibres were measured by a POLYSTAT 1. The fibre sample with a surface of about 1–1.4 cm² was charged up to the maximum potential (U_{\max}) and simultaneously the time of achieving the zero potential (t_{0V}) was recorded. From this dependence it was possible to obtain the half-time of discharging $t_{1/2}$. The fibres hydrophilicity (S) was evaluated gravimetrically at the temperature $\theta_8 = 21.7^\circ\text{C}$ and the 65 % relative humidity using lubricated fibres. The results are listed in Table 2.

Mechanical properties were measured on the Instron 1112 apparatus. Clamping length and deformation rate were 100 mm and 500 mm min⁻¹, respectively. Elastic properties were measured on the Instron 1112 apparatus by the method of hysteresis loops at a clamping length of 100 mm and a deformation rate of 200 mm min⁻¹. A diagram of elastic values (Fig. 1) was obtained from hysteresis loops. From this diagram the following quantities were determined: ε_{el} – elastic extension, and ε^0 – elastic deformation in % defined as


Fig. 1. Diagram $\sigma = f(\varepsilon)$ of elastic values.

the ratio of elastic extension ε_{el} to the total extension ε_t according to Fig. 1

$$\varepsilon^0 = (\varepsilon_{el}/\varepsilon_t) \times 100$$

η_{el} – elastic efficiency in % defined as the ratio of elastic deformation work A_{el} (calculated from ε_{el}) to the total deformation work A_t (calculated from ε_t)

$$\eta_{el} = (A_{el}/A_t) \times 100$$

$$A_t = \int_0^{\varepsilon} \sigma d\varepsilon$$

The results are shown in Table 3.

Table 3. Mechanical and Elastic Properties of Nonmodified and Modified PA 6 Fibres

(Co)poly- amide	Amount of copolyamide mass %	TS	E	η_{el}	ϵ^0
		10 N tex ⁻¹	%	%	%
PA 6	0	2.74	107	29	39
KOPA 21.6	10	2.18	100	39	48
	20	1.84	69	40	49
	30	1.66	77	36	46
	50	1.38	70	66	75
	10	2.54	31	47	64
KOPA 21.6E	20	2.06	39	45	58
	30	2.04	30	64	70
	50	1.78	35	50	60
KOPA 30.6	10	2.38	90	33	44
	20	2.04	70	56	60
	30	1.84	102	47	53
	50	1.64	90	54	58

RESULTS AND DISCUSSION

Copolyamides from CL, adipic acid, and diethylenetriamine can be prepared by the polyreaction in melt within 6 h. Conditions and the polyreaction time have an influence mainly on the relative molecular mass (expressed as $[\eta]$) of the copolyamide. The copolyamide preparation involves 2 steps. The first step involves the preparation of the Nylon salt ADETA from the ethanolic solutions of adipic acid and diethylenetriamine and the elimination of ethanol. The second step comprises the adding of CL and the accomplishment of the poly(addition-condensation) reaction. By comparing both methods of the preparation of copolyamide containing the same amount of the Nylon salt ADETA (21.6 mass %) it is possible to maintain that the relative molecular mass (expressed by the intrinsic viscosity $[\eta]$) depends particularly on the time of the first step. The reason is the more competent preparation of Nylon salt (the thorougher elimination of ethanol in the first step) and probably the higher volatility of DETA, *i.e.* the potential loss of DETA during the reduced pressure in the second step, if the whole amount of DETA was not bound before in the Nylon salt or polyreaction product. A loss of DETA disturbs the balance of the reactive groups constituting macromolecules, which leads to a decrease in the relative molecular mass. Conditions for the preparation implemented in the first and second steps were chosen so as to evaluate (at least to a certain extent) their influence on the relative molecular mass of copolyamides and to allow the polyreaction to proceed up to a maximum according to eqn (A).

The obtained relative molecular mass is sufficiently high to characterize copolyamides as polymers, but insufficiently high to achieve their fibre formation. The (LMC) content is comparable to that of the nonextracted PA 6 and their elimination is possible, simi-

larly as in the case of PA 6, by extraction in hot water. Melting temperatures of the copolyamides – θ_m are lower in comparison to PA 6, their difference being 25–29 °C.

The above-indicated characteristics and assumed compatibility of the earlier prepared copolyamides permit their application as additives to the M/F blended fibres containing PA 6 and copolyamide. Neither the lower values of $[\eta]$ or θ_m nor the presence of low-molecular compounds (LMC) in the copolyamide manifested the negative influence on the spinning and drawing of blended PA 6/copolyamide fibres. An elimination of LMC from the finished blended fibres (*e.g.* by washing or shampooing the material) leads to the formation of pores in them, which can (positively) affect further properties of textile products.

By introducing the Nylon salt ADETA into the poly- ϵ -caprolactam chain the content of polar atoms and groups represented by a nitrogen content will increase.

Electrostatic properties of PA 6 fibres (evaluated on the basis of three parameters – U_{max} , t_{0V} , and $t_{1/2}$) improve considerably after adding 20 mass % of copolyamide. By increasing the copolyamide content to the level of 30 mass % and 50 mass % the above properties improve even more. The influence of the nonextracted and extracted copolyamide with the same amount of the Nylon salt ADETA (21.6 mass %) is practically identical. The presence of LMC and the higher relative molecular mass of the nonextracted KOPA 21.6, or the absence of LMC and the relatively lower relative molecular mass of the extracted copolyamide KOPA 21.6E do not have a crucial influence on the electrostatic properties (Table 2).

Water vapour sorption S increases by addition of 10–20 mass % of copolyamide. The content of the extracted KOPA 21.6E which is increased to 30–50 mass % causes only a slight growth of sorption, mean-

while the nonextracted KOPA 21.6 and KOPA 30.6 improve the sorption level to 6–6.1 mass % of the absorbed humidity so as seen in Table 2.

The lower relative molecular mass of copolyamides and the mixed structure of fibres (with all arising consequences) cause a decrease in the tensile strength of modified fibres. This decrease is proportional to the polyamide content in blended fibres and it increases, if the nonextracted types of copolyamides are applied.

The drawing ratio $\lambda = 3$ reflects the relatively higher elongation of unmodified PA 6 fibres ($E = 107\%$). Elongation of the blended fibres modified with nonextracted copolyamide types is positively affected and it even partially decreases ($E = 70\text{--}100\%$). An application of the extracted copolyamide KOPA 21.6E is responsible for a drop in elongation to the level $E = 30\text{--}40\%$.

The below-indicated A_t and A_{el} values lead to the higher values of parameters η_{el} and ε^0 . This suggests that the deformation of blended fibres requires less work than the deformation of unmodified PA 6 fibres, or that the modified fibres are more elastic. It appears that the most pronounced influence on the elasticity has the extracted copolyamide KOPA 21.6E. The improvement of elasticity on applying the 20 mass % copolyamide content, and even higher, ranges between 124 % and 227 % (η_{el}) and 118 % and 192 % (ε^0).

CONCLUSION

1. Copolyamides with a relatively high relative molecular mass can be prepared from ε -caprolactam, adipic acid, and diethylenetriamine. Conditions of the preparation, particularly the different time of step I and II, influence the properties of the prepared copolyamides.

2. Spinning and drawing of the blended PA 6 fibres with a copolyamide are not negatively influenced up to the mass fraction of 50 mass % of copolyamide.

3. Moisture sorption of the modified PA 6 fibres is positively influenced and it increases with a growing copolyamide content; more in the case of an applied nonextracted copolyamide.

4. Electrostatic properties of modified PA 6 fibres which have already the 20 mass % content of any copolyamide are substantially better when compared to nonmodified PA 6 fibres; with an increase of the copolyamide content these properties can be even improved. The highest efficiency is achieved for PA 6 fibres modified to 30 mass % and 50 mass % of the copolyamide with a higher content (30.6 mass %) of the Nylon salt ADETA.

5. Strength of the blended fibres falls down with the growing copolyamide content, meanwhile the elastic efficiency η_{el} and the elasticity degree ε^0 have an upward tendency. The elongation of modified fibres is positively influenced mainly in the case when the extracted copolyamide is applied as an additive.

SYMBOLS

PA 6	poly- ε -caprolactam
CL	ε -caprolactam
A	adipic acid
DETA	diethylenetriamine
ADETA	Nylon salt of adipic acid A and diethylenetriamine DETA
M/F	matrix/fibrils
0—1	step I, time of the reaction from the start till the addition of CL
0—2	step I, time from the start till melting of the mixture and homogenizing of the melt
2—3	step II, polyreaction at the atmospheric pressure
3—4	step II, polyreaction at the reduced pressure
0—4	total time of the copolyamide synthesis
w	concentration of the Nylon salt ADETA in the mixture at the beginning of the synthesis
LMC	low-molecular compounds
w_1	concentration of copolyamide in the solution of H_2SO_4
w_N	concentration of nitrogen in the (co)polyamide
t	flow time of the polymer solution
t_0	flow time of the pure solvent
η_{sp}	specific viscosity
$[\eta]$	limiting viscosity number (intrinsic viscosity)
$\theta_1, \theta_2, \theta_3$	temperatures of zones of a single-screw ribbon extruder
$\theta_4, \theta_5, \theta_6$	temperatures of spinning
θ_7	temperature of drawing
θ_8	temperature of the hydrophilicity measurement
θ_m	temperature of melting
U_{max}	maximum potential of charged fibres
t_{0V}	time within the potential drops from the maximum to the zero value
$t_{1/2}$	half-time of discharging
TS	tensile strength
E	elongation at break
ε_{el}	elastic extension
ε^0	elastic deformation
η_{el}	elastic efficiency
A_{el}	elastic deformation work
A_t	total deformation work

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