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Modification of PP Fibres with Alkaline Copolyamides

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Summary: Copolyamides with 5.9-19.7 wt.% of nylon salt ADETA (adipic acid + diethylenetriamine) and 94.1-80.3 wt.% of ε-caprolactam were synthesized and their properties were estimated. Blended polypropylene/copolyamides fibres containing 5-15 wt.% of copolyamides were prepared and their properties were evaluated. The electrical properties, hydrophilicity and especially dyeability of modified PP fibres are positively influenced by a higher amount of the copolyamide in the PP and also by a higher amount of the nylon salt ADETA in the copolyamide.

Introduction

Polypropylene (PP) fibres belong to the most produced synthetic fibres. They have many useful properties, some of which, however, do not satisfy requirements of customers. These requirements involve e.g. electrical and sorption properties as well as the dyeability by exhaustion processes. An absence either of the higher sorption of water vapors and dyestuffs or of the higher conductivity can be explained by the hydrophobic nature of PP macromolecules without any polar groups. Introduction of the sufficient amount of efficient polar groups into PP macromolecules (chemical modification) or into a PP material (physical modification) gives the possibility to prepare modified PP fibres with improved properties.

Commercial polar polymers (like polyamides or poly(ethyleneterephtalate)) or copolymers developed as additives to poly(ε-caprolactam) (PA 6) fibres can also be used for the modification of PP fibres[1-5], either without or with compatibilizers. Their introduction into PP allows one to employ their special properties and also to improve the blended PP/copolyamides fibre properties. Polyamides characterized by a high concentration of polar -NH- groups in the backbone, have a strong affinity to water that make them water-soluble[6]. Introduction of the less polar comonomer (such as ε-caprolactam, CL) leads to the water-insoluble copolyamides whose affinity to water (vapor) or the affinity to other polar compounds is higher than that for homopolymer PA 6.

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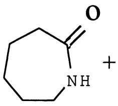
Copolyamides can be prepared eventually as block copolyamides (diblock, multiblock or ABA type[7]) and can assure the sufficient compatibility in the case of the blended PA 6 - copolyamide system.

Copolyamides prepared by the poly(addition-condensation) reaction e. g. from ε-caprolactam and the nylon salt (of adipic acid and 1-(2-aminoethyl) piperazine or 1,4-bis(3-aminopropyl) piperazine or hexamethylenediamine) are block copolymers which are compatible with PA 6[8]. Copolyamides prepared from ε-caprolactam, diethylenetriamine and adipic acid are insoluble in water and can be used as additives to polyamide fibres[9] as well. This enables their utilization in blends with PA 6.

The compatibility of PP and copolyamide is not as good as in the PA 6/copolyamide system and therefore their processability (spinning, drawing) can more difficult. For this reason it is necessary to evaluate also these characteristics and properties of the PP fibres modified by copolyamides.

In our contribution the copolyamides prepared from ε-caprolactam, adipic acid and diethylenetriamine (Scheme 1) were used as additives to PP:

m  $+ \text{n } HOOC(CH_2)_4COOH + \text{n } H_2N(CH_2)_2NH(CH_2)_2NH_2$

$\rightarrow 2\text{ n } H_2O + \text{-}[HN(CH_2)_2\,NH(CH_2)_2\,NHOC(CH_2)_4\,CO]_n\text{-}\,[NH\,(CH_2)_5\,CO]_m\text{-}$

Scheme 1

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 of CL with a beforehand prepared nylon salt ADETA from adipic acid and DETA.

The nylon salt ADETA was prepared by mixing the 70 °C hot solutions of adipic acid and diethylenetriamine in ethanol in a glass apparatus immersed in the thermostated bath. After mixing these two parts the main part of ethanol was distilled off. The concentrated solution of ADETA (honey like appearance) was poured onto Petri dishes. The complete evaporation of ethanol resulted in crystallization of the nylon salt ADETA, which was pulverized and vacuum-dried.

Polyreaction of the mixture of CL and ADETA was performed in a glass apparatus immersed in the thermostated bath. The temperature of the reaction mixture was gradually increased to 280 °C at the end of the reaction time RT according to Table 1. The beginning of the polyreaction was indicated by an intense releasing of the reaction water. At the end of the polyreaction the copolyamide was poured onto the metallic plate and cut into granules. Copolyamides were marked by the wt. % of the nylon salt ADETA in the mixture at the beginning of the polyreaction:

KOPA 5. 9 = 5. 9 wt. % of ADETA and 94.1 wt. % of CL
KOPA 9. 9 = 9. 9 wt. % of ADETA and 90.1 wt. % of CL
KOPA 13.7 = 13.7 wt. % of ADETA and 86.3 wt. % of CL
KOPA 19.7 = 19.7 wt. % of ADETA and 80.3 wt. % of CL

The granules were extracted in boiling water {T =100 °C} in order to determine the content of the low molecular compounds, where w_1 represents the low molecular compounds (in wt. %) extracted after 1hr at the polymer/water ratio 1g/100g and w_2 is the the weight portion of low molecular compounds extracted after 2x1hr at the polymer/water ratio 1g/8g.

The extracted copolyamides were dried out at T = 105° C in a vacuum oven and stored in the atmosphere without water vapor. Intrinsic viscosity $[\eta]$ values were determined viscosimetrically in a solution of H_2SO_4, 93 % at T = 25 °C.

The thermal characteristics of PP and copolyamides were estimated by the differential thermal analysis method, DTA, using a Derivatograph Q-1500D (MOM Budapest, Hungary). The melt temperature T_m, weight loss of the sample at certain temperatures (Δm_{100}, Δm_{200}, Δm_{300} and Δm_{400} at T = 100, 200, 300 and 400 °C, respectively) and the decomposition temperature T_d (50 wt. % of copolyamide was decomposed) were obtained from a relevant TG curve.

The mass fraction of nitrogen in the copolyamide, w_3 , was determined by an elemental CHNS-O EA 1108 analyser (Carlo Erba, Milano, Italy). The characteristics of PP and copolyamides are given in Table 1.

Table 1. Characteristics of PP and copolyamides

Polymer Characteristic	PP	KOPA 5.9	KOPA 9.9	KOPA 13.7	KOPA 19.7
RT / min	CP	150	150	150	60
w_1 / wt.%	-	10.3	10.5	12.7	12.5
w_2 / wt.%	-	13.5	13.3	15.0	13.5
$[\eta]$ / ml.g^{-1}	MFI	52	31	21	46
T_m / ° C	159	206	194-197	190	184
Δm_{100} / wt.%	0	2.5	2.7	2.9	2.1
Δm_{200} / wt.%	0.2	5.7	7.1	6.9	5.5
Δm_{300} / wt.%	4.2	7.4	9.9	9.6	9.0
Δm_{400} / wt.%	35	29	39.7	35.7	36.2
T_d / ° C	415	417	408	411	413
w_3 / wt. %	0	13.06	13.35	13.50	14.22

RT- reaction time (time of preparation)

CP - commercial product PP TI 903 from Slovnaft Bratislava

MFI - melt flow index = 25g/10min (at T = 190 °C and 2.6 kg)

Preparation of fibres

The concentrate containing 20 wt. % of the dried copolyamide in PP was prepared by melting in a single-screw ribbon-die extruder at the temperatures of zones T = 240 – 250 °C, T = 250 – 260 °C and T = 260 °C. The blended ribbon was cooled down in the cold water, cut into granules, air-dried and finally vacuum-dried at T = 105 °C. The blended fibres containing 5 wt. %, 10 wt. % and 15 wt. % of copolyamide in PP were prepared by mixing the PP with the 20 wt. % copolyamide concentrate immediately before spinning.

The spinning of mixtures was performed on the laboratory model equipment (Institute of Man-Made Fibres, Svit, Slovak Republic) at the temperatures of three zones T = 250 °C with and without lubricant (13 fibrils). After spinning, the fibres were drawn (T = 120 °C) to the drawing ratio $\lambda_1 = 3$ and $\lambda_2 = 4$. Their total linear density T_{dt1} and T_{dt2} were in the range 201 – 247 dtex ($\lambda_1 = 3$) and 172 – 181 ($\lambda_1 = 4$) dtex respectively. During drawing the non-lubricated fibres were permanently wetted with water.

Evaluation of the fibres properties

The electrical properties of non-lubricated fibres were measured be:

a) the Polystat 1 equipment (JZD Jizera, Predmerice nad Jizerou, Czech Republic). The fibre sample (λ_l= 3) with a surface of about 1-1.4 cm^3 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 the half-time of discharging, $t_{1/2}$, was estimated. The results are shown in Table 2.

b) the electromer, type 610 C (Keithley Instrument). The sample was fixed between 2 electrodes. After switching on the stable potential U = 500 V the current intensity I was measured and the resistance of the sample was calculated as R = U / I.

The fibres hydrophilicity was evaluated gravimetrically as the water vapor sorption WS at temperature T = 21.7 °C and 65 % RH using lubricated fibres (λ_l= 3). The results are shown in Table 2.

Table 2. Electrical Properties and Water Vapour Sorption, WS, of Non-modified and Modified PP Fibres

	KOPA	**U_{max}**	**$t_{1/2}$**	**t_{0v}**	**R / Ω**		**WS**
System	**wt.%**	**V**	**s**	**s**	**RH = 25%**	**RH = 65%**	**wt.%**
PP	**0**	180	12	780	$1.2x10^{13}$	$3.5x10^{13}$	0.39
	5	480	35	1500	$9.8x10^{14}$	$1.0x10^{13}$	0.56
PP+KOPA 5.9	**10**	350	3	1200	$1.4x10^{15}$	$4.9x10^{13}$	0.59
	15	-	-	-	-	-	0.89
	5	480	39	1500	$1.7x10^{15}$	$5.6x10^{13}$	0.60
PP+KOPA 9.9	**10**	470	27	1200	$6.4x10^{15}$	$4.8x10^{13}$	0.71
	15	450	7	900	$5.6x10^{14}$	$8.0x10^{12}$	0.99
	5	350	3	600	$4.6x10^{11}$	$3.4x10^{9}$	0.61
PP+KOPA 13.7	**10**	150	2	480	$4.2x10^{14}$	$1.1x10^{13}$	0.94
	15	30	1	1	$4.2x10^{9}$	$7.7x10^{8}$	1.11
	5	370	5	1080	$1.3x10^{16}$	$3.7x10^{13}$	0.65
PP+KOPA 19.7	**10**	430	16	1380	$2.6x10^{15}$	$1.1x10^{13}$	0.96
	15	420	7	1140	$1.1x10^{13}$	$4.2x10^{11}$	1.25

Mechanical properties i.e. tensile strength, TS, elongation, E, and elastic deformation, ε°, respectively were measured using the Instron 1112 apparatus. The fibres orientation factor, f, was calculated according to the equation [10]:

$$f = 1 - C_n^2 / C^2$$

where C_n is the speed of sound in the non-oriented fibre equal to 1.25×10^3 m / s and C is the speed of sound in the fibre measured by a PPM - 5 Dynamic Modulus Tester (H. M. Morgan Co. Inc., USA). The results are given in Table 3.

Table 3. Tensile strength, TS, elongation, E, Elastic Deformation, ε°, and Orientation Factor, f, of Non-modified and Modified PP Fibres

	Property	$\lambda_1 = 3$			$\lambda_2 = 4$				
	KOPA	T_{dt1}	TS_1	E_1	T_{dt2}	TS_2	E_2	ε°	f
System	**wt.%**	**dtex**	**$cN.dtex^{-1}$**	**%**	**dtex**	**$cN.dtex^{-1}$**	**%**	**%**	
PP		230.0	2.40	153.4	172.8	3.73	29.6	64.7	0.68
PP+KOPA 5.9	**5**	214.6	1.87	99.0	176.1	3.41	34.8	60.6	0.61
	10	202.4	2.14	98.6	166.8	3.55	29.6	56.7	0.63
	(λ=2) 15	327.9	1.13	98.9	-	-	-	-	-
PP+KOPA 9.9	**5**	221.4	2.08	98.9	172.4	3.39	37.8	69.0	0.60
	10	229.6	2.00	98.8	173.3	3.33	34.2	77.8	0.62
	15	228.2	2.01	99.2	180.8	2.99	31.4	59.9	0.63
PP+KOPA 13.7	**5**	222.4	1.94	98.9	173.3	3.39	35.6	73.2	0.61
	10	201.0	1.89	97.9	168.4	3.36	35.4	77.9	0.60
	15	238.1	1.81	98.2	180.9	3.02	32.1	74.0	0.59
PP+KOPA 19.7	**5**	218.0	1.98	98.4	160.3	3.19	35.8	56.4	0.53
	10	246.6	1.79	98.6	180.0	3.11	31.2	75.6	0.56
	15	235.9	1.92	98.5	173.5	3.12	36.2	74.4	0.55

The dyeability of PP fibres (λ_1= 3, lubricated) was evaluated by dyeing with the apparatus AHIBA 1000 using:

C. I. Acid Red 160 (Supranobriliantrot GBW), soluble in ethanol and

C. I. Acid Red 211,.both soluble in hot water

Two types of dyeing were carried out :

(i) dyeing of the same fibres at different concentration of the dyestuff in the bath, i. e. 0.05, 0.1, 0.5, 1.0, 1.5, and 2 wt. % of dyestuff per 1 g of fibres (Table 4) and

(ii) dyeing of the different fibres at the same concentration of the dyestuff in the bath, i.e.2 wt. % of dyestuff per 1 g of fibre (Table 5)

Table 4. Dyeability of PP Fibres Modified by 5 wt.% of KOPA 5.9 and 5 wt.% of KOPA 9.9, respectively, with C. I. Acid Red 160 (I) and C. I. Acid Red 211 (II), $\lambda_1 = 3$

Concentration of dye / wt.%	I		II		I		II	
	PP + 5 wt.% of KOPA 5.9				PP + 5 wt.% of KOPA 9.9			
	K/S	Ex	K/S	Ex	K/S	Ex	K/S	Ex
0.05	0.621	0.191	1.086	0.044	0.804	0.202	1.181	0.051
0.10	0.632	0.223	1.264	0.071	0.813	0.249	1.422	0.249
0.50	0.875	0.259	1.542	0.410	1.026	0.285	1.914	0.579
1.00	0.954	0.307	2.129	0.996	1.173	0.391	3.010	1.524
1.50	1.103	0.449	2.717	1.446	1.362	0.511	3.486	1.878
2.00	1.076	0.482	2.794	1.452	1.346	0.524	3.674	1.923

Table 5. Dyeability of Modified PP Fibres in the Dyeing Bath with 2 wt.% of C.I. Acid Red 160 (I) and 2 wt.% of C.I. Acid Red 211 (II), respectively, $\lambda_1 = 3$

KOPA System	wt.%	I		II	
		K / S	Ex	K / S	Ex
PP	0	0.457	0.326	1.629	0.517
PP+KOPA 5.9	5	0.898	1.498	4.705	1.830
	10	1.895	1.652	4.801	1.920
	15	4.156	2.406	7.709	2.184
PP+KOPA 9.9	5	1.309	1.588	4.722	1.938
	10	3.135	1.867	5.573	2.472
	15	5.423	2.579	9.138	3.048
PP+KOPA 13.7	5	1.124	1.738	3.007	2.132
	10	4.169	2.201	6.832	2.682
	15	8.891	3.363	10.926	3.534
PP+KOPA 19.7	5	1.553	2.147	3.652	2.818
	10	4.220	2.936	8.500	3.102
	15	10.736	3.479	11.966	3.738

The shade of the dyed fibres was evaluated by K/S values measured with the apparatus Macbeth-Color-Eye. K is the coefficient of absorbancy and S is the coefficient of scattering from the well-known Kubelka-Munk relationship in the form K/S = A.c where A is the constant and c is the concentration of the absorbed dyestuff. The dyestuff consumed from the dyeing bath was estimated from the difference of extinction values, Ex, before and after dyeing with the apparatus Spekol at the wavelength 540 nm. The results are shown in Tables 4 and 5.

Conclusion

1. It is possible to synthesize the copolyamides from ε-caprolactam and the nylon salt ADETA (adipic acid and diethylenetriamine) with the sufficiently high molecular weight. Their properties indicate the possibility to use them as additives to PP fibres and their thermal stability is comparable with that of PA 6 and PP.
2. The processability of the PP fibres modified with copolyamides is not negatively influenced up to 15 wt.% of copolyamide.
3. Electrical properties of modified PP fibres, evaluated by two methods, are better than those of non-modified PP fibres mainly in case of the highest amount of the copolyamide (15 wt.%) with a higher concentration (13.7 wt.%) of the nylon salt ADETA in the copolyamide.
4. The higher the amount of copolyamide and the concentration of the nylon salt ADETA in the copolyamide the higher is the water vapour sorption, WS, of the modified fibres.
5. Tensile strength of the modified fibres declines with the increased amount of the copolyamide (as it is usual for blended fibres). The drop of tensile strength is apparent, but not very high at the amount of 5 wt. % and the next drop of tensile strength is noticeable at 15 wt. % of copolyamides KOPA 5.9 - 13.7. The lowest tensile strength is manifested in PP fibres modified by 5-15 wt. % of copolyamide KOPA 19.7. Elongation of the modified PP fibres, E, is generally a slightly higher than that of non-modified PP fibres. Elastic deformation, ε°, does not exhibit an unambiguous tendency. In the PP fibres blended with 10 - 15 wt. % of copolyamides KOPA 13.7 and KOPA 19.7 (of ADETA) this property exhibits approximately a 15% increase as a consequence of the presence of copolyamide with the block character. The orientation factor, f, expresses the general tendency in blends of the incompatible polymers i.e. it decreases, as the structure

of copolyamide is becoming less ordered and less similar to the structure of the main polymer (PP).

6. Dyeability of the modified PP fibres is positively influenced by copolyamides with polar groups. The dyestuff concentration of 1.5 wt. % seems to be sufficient for good dyeability of PP fibres containing 5 wt. % of KOPA 5.9 and 5 wt. % of KOPA 9.9.
7. Dyeability of the modified PP fibres is better, if copolyamides with higher amount of the ADETA salt are used (i.e. KOPA 13.7 and 19.7). The increased amount of the copolyamide in the polypropylene results in a better dyeability.

It is possible to conclude that the higher amount of the copolyamide with the higher concentration of the nylon salt ADETA in the copolyamide improves to a great extent the end-use properties such as hydrophilicity, dyeability and electrical properties of the PP fibres.

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