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Functionalisation of Polypropylene. Part I. Mechanical, Electric and Sorptive Properties of PP Fibres Modified with Concentrates Consisting of Copolyamides and Nanoclay

Abstract

Concentrates of copolyamides consisting of copolyamide (ε -caprolactam + nylon salt of adipic acid and diethylenetriamine and nylon salt of 1-(2-aminoethyl) piperazine and adipic acid) and the nanoadditive Bentonite were prepared, characterised and used for the preparation of blend polypropylene (PP) fibres. PP fibres modified with 4, 8 and 12 wt.% of the three types of concentrates prepared were spun without a compatibiliser by the standard melting process and drawn at three drawing ratios. Mechanical properties of the modified PP fibres, i.e. tenacity and Young's modulus, are better mainly at lower amounts of each concentrate and at higher drawing ratios. The electric properties of the modified PP fibres are positively influenced by all three concentrates. The higher their amount in the modified PP fibres, i.e. the sorption of water vapour and disperse dyestuffs, are much better in comparison with non modified PP fibres.

Key words: *polypropylene, copolyamide, Bentonite, modification, mechanical, electric, sorptive properties.*

Introduction

Due to excellent mechanical properties, high chemical stability and processability, polypropylene fibres are often used in different fields. However, because of a low surface energy, lack of reactive sites and sensitivity to photo and thermal oxidation, their polymer properties are insufficient for some applications. To improve their chemical and physical properties, hydrophobic polypropylene fibres can be modified by several techniques e.g. plasma treatment, chemical or physical modification, etc. Physical modification by the compounding of polypropylene with suitable additive(s) is a very simple way, as reported in many references.

Improvement of polypropylene affinity to polar agents such as water and dyestuffs can be effectively made with more polar (polymer) additives, such as polyamideureas and copolyamides. Hence 8 wt.% of copolyamides based on ε-caprolactam and nylon salt of 1-(2-aminoethyl)piperazine with adipic acid [1] or 5 wt.% - 15 wt.% of copolyamides based on ε-caprolactam and nylon salt of diethylenetriamine with adipic acid [2] or 1 - 5 wt.% of copolyamideureas based on ε-caprolactam, urea and nylon salt of 1-(2-aminoethyl)piperazine with adipic acid [3] used as additives without a compatibiliser improve the sorption of water vapour, dyeing from a bath and the antistatic properties of modified polypropylene (PP) fibres; however, these negatively influence their mechanical properties.

Standard PP fibres modified with 25 - 30 wt.% of polyamide 6 and polypropylene-grafted maleineanhydride as a compatibiliser or with 15 - 30 wt.% of polyethylene terephthalate and amide of stearic acid and alkylphthalate as a compatibiliser can be prepared and effectively dyed from a bath with disperse dyes without a carrier [4].

If the polymer additive has a lower molecular weight and no compatibiliser is added, lower mechanical properties of the modified fibres are usually obtained [5]. On the other hand, the addition of a polymer additive with a high molar weight (e.g. nanoadditive) can improve the mechanical properties of blends and fibres prepared therefrom. Moreover this nanoadditive can form an intercalated or exfoliated hybrid with the polymer additive. It is important to note that the molecular weight of the nanoadditive platelets is considerably greater (cca 1.3 \times 10⁸) than that of typical commercial polymers. In addition, platelets are not totally rigid but have a degree of flexibility [6]. The substantial enhancement of the nanocomposite properties is attributed to the ultra fine phase dimensions of the filler in the polymer matrix, which can be observed in the swelling of nanoclay with the monomer and synthesis of the polymer additive in the presence of the nanoclay, permiting the direct formation of polymer among the galleries of clay [7 - 10].

Rheological measurements have proved that nanocomposites with a copolyamide matrix have a higher afinity to MMT than to homopolymer PA 6 [11].

If the components of the blend system contain dyeable amino groups, its dyeing from a bath is improved with disperse dyestuffs and decreased with acid and metallocomplex dyestuffs due to the fact that nanoclay is bonded to amino groups and does not allow to fix acid or metallocomplex dyestuff [12].

To ensure a higher compatibility of components and better mechanical properties of polymer blend systems, compatibilisers are often used. Compatibiliser PPgMA improves the compatibility of PA 6, PP and organically modified nanoclay [13].

Nanocomposites PP/PA 6 were prepared by intercalation from the melt blending of PP, PA and organophilic montmorillonite in the presence of compatibiliser PPgMA. The composition of the blend and sequence of mixing influenced the dispersability of MMT, forming a crystalline structure and crystallization rate. Self-agregated structures were noted in the PP and PA 6 composites [14].

The application of PPgMA of different molar weight showed that the best mechanical properties of the nanocomoposite samples were found for composites containing PPgMA of the highest molar weight [15].

According to [16], montmorillonite is the most effective clay for use in nanocomposites due to its low levels of loading, high aspect ratio, cation exchange capability, and natural abundance.

The aim of this work was the preparation of modified fibres from blends of PP and concentrates consisting of copolyamide and organically modified montmorillonite without a compatibiliser, as well as the evaluation of their electrical, mechanical and sorptive properties.

Materials and methods

Materials used

Polypropylene commercial PP TG 920, PP, Slovnaft Bratislava, T_m = 166 °C, MFI = 10.5 g/10 min,

- ε-caprolactam commercial, (CL), Nylstar Humenné, $T_m = 70$ °C,
- Adipic acid, Fluka,
- 1-(2-aminoethyl)piperazine, (N2), Fluka,
- Diethylenetriamine, (DETA), Fluka,
- Nylon salt (AN2) from 1-(2-aminoethyl)piperazine and adipic acid,
- Nylon salt (ADETA) from DETA and adipic acid,
- Nanoadditive Bentonite, type 11958, organically modified, i.e layer wise mineral with sodium ions and quaternary ammonia ions between the layers, (Ben), Fluka Concentrates:

A 84.3 wt.% CL + 5.35 wt.% AN2 + 5.35 wt.% ADETA + 5.0 wt.% Ben, $T_{m1,2}$ =191 and 204 °C, η_{rel} = 1.49, total amount of nitrogen 11.89 wt.%, total amount of

- comonomers 10.7 wt.%, D 73.6 wt.% CL + 10.7 wt.% AN2 +10.7 wt.% ADETA + 5.0 wt.% Ben, $T_m = 187$ °C, $\eta_{rel} = 1.42$, total amount of nitrogen 12.07 wt.%, total amount of comonomers 21.4 wt.%,
- For comparison, the commercial homopolymer PA 6 (Nylstar Humenné) has the following properties: $\eta_{rel} = 1.68$ and $T_m = 221$ °C.

Preparation of nylon salt and concentrates A, B and D

Both nylon salt AN2 and nylon salt ADE-TA were prepared by mixing equimolar ethanolic hot solutions of 1-(2-aminoethyl) piperazine and adipic acid (AN2) or ethanolic hot solutions of diethylenetriamine and adipic acid (ADETA). After removing the maximum amount of ethanol, the viscous solution crystallised for several days. The crystallised nylon salt was then pulverised and dried in a vacuum oven [17, 18].

Concentrates A, B and D, from copolyamides with a nanoadditive, were prepared from ε -caprolactam, relevant nylon salts AN2 and ADETA, and Ben by the poly(addition-condensation) reaction 'in situ' in a melt and N₂ atmosphere. The mixture of powdered CL, AN2, ADETA and Ben was heated in a glass apparatus immersed in a thermostated oil bath. During the first 10 min, the temperature was raised so that the nylon salt melted and homogenised in the molten CL. Some time later the polyreaction started (evaporation and condensation of reaction water), and the viscosity of the melt gradually increased over time to a temperature of 270 - 280 °C at the end of the reaction time. The concentrate was poured in a cylindrical form onto a metallic plate and cut into chips [19].

Methods used

Low molecular compounds created during the poly(addition-condensation) reaction were removed and evaluated gravimetrically before and after extraction in hot demineralised water. The relationship water/concentrate i.e. the bath ratio was 200/1 g of polymer, and the extraction was a simple process lasting 2 hours.

The relative viscosity η_{rel} of the copolyamide solution was measured viscosimetrically in 96% H₂SO₄ p.a at 25 °C. Melting temperatures were determined using a DSC 7 Perkin Elmer at a heating rate of 10 K·min⁻¹.

The total amount of nitrogen was evaluated using an elemental CHNS-O Flash EA analyser, type NCHS42-WO3.mth.

Chips of dried concentrate and chips of mPP were used for the preparation of blends containing 4, 8 and 12 wt.% of concentrates A, B and D. All blends were mechanically mixed well, and the mixtures were melted in a Göttfert single-screw ribbon extruder at the temperature of three zones $T_1 = T_2 = T_3 = 250$ °C. The blend ribbon was cooled down in cold water and cut into chips. The airdried chips were finally vacuum-dried at $T_4 = 105^{\circ}$ C.

The spinning of the dried blend chips was performed by laboratory spinning equipment with an extruder of $\Phi = 0.016$ m at $T_1 = 250$ °C, and at a take-up speed of 150 m.min⁻¹ with and without a lubricant (spinneret nozzle with 13 fibrils). After spinning, the fibres were drawn at the following drawing ratios: $\lambda_I = 2$ (without lubrication), $\lambda_2 = 3$, $\lambda_3 = 3.5$ and $\lambda_4 = 4$ (lubricated fibres).

The linear density T_d was measured 10 times as the weight of 10 m of fibres, and the mean of these 10 measurements was calculated.

Table 1. Composition of PP fibres modified with concentrates A, B and D.

Amount and type of concentrate, wt.%	Amount of components in fibre, wt.%								
	DAG	Total amount	Components of concentrate						
	FA 0	of concentrate	CL	ADETA	AN 2	BEN			
PP	100	-	-	-	-	-			
4 A	96	4	3.372	0.214	0.214	0.20			
8 A	92	8	6.744	0.428	0.428	0.40			
12 A	88	12	10.116	0.642	0.642	0.60			
4 B	96	4	2.864	0.200	0.736	0.20			
8 B	92	8	5.728	0.400	1.472	0.40			
12 B	88	12	8.592	0.600	2.208	0.60			
4 D	96	4	2.944	0.428	0.428	0.20			
8 D	92	8	5.888	0.856	0.856	0.40			
12 D	88	12	8.832	1.284	1.284	0.60			

Table 2. Linear density T_d , tenacity σ , elongation ε , Young's modulus E and coefficients of variance CV of PP fibres modified with concentrates A, B and D, $\lambda_2 = 3$.

Amount and type of concentrate, wt.%	T _d , dtex	CV _{Td} , %	σ, cN·dtex-1	CV _σ , %	ε, %	CVε, %	E, cN·dtex-1	CV _E , %
PP	268	5	2.2	8	90	6	23	8
4 A	252	4	2.3	8	98	8	35	14
8 A	272	7	1.9	10	61	19	28	10
12 A	278	5	1.7	4	54	25	26	8
4 B	265	6	2.2	3	93	12	31	8
8 B	264	7	1.8	5	71	18	27	11
12 B	266	7	1.6	8	70	10	30	9
4 D	269	3	2.3	4	82	10	31	8
8 D	271	6	2.0	5	58	27	28	8
12 D	283	4	1.6	11	70	22	26	12

Table 3. Linear density T_d , tenacity σ , elongation ε , Young's modulus E and coefficients of variance CV of PP fibres modified with concentrates A, B and D, $\lambda_3 = 3.5$.

Amount and type of concentrate, wt.%	T _d , dtex	CV _{Td} , %	σ, cN·dtex-1	CV _σ , %	ε, %	CVε, %	YM, cN·dtex-1	СV _{ҮМ} , %
PP	236	7	2.5	8	51	29	30	11
4 A	196	9	2.6	6	31	14	34	8
8 A	223	6	2.4	7	34	41	33	8
12 A	232	9	2.3	6	26	24	34	5
4 B	199	13	2.5	5	26	10	34	5
8 B	227	8	2.3	8	44	27	29	15
12 B	237	12	2.1	7	25	23	35	7
4 D	203	6	2.5	6	28	18	30	10
8 D	230	13	2.4	7	25	36	30	13
12 D	236	12	2.1	7	27	25	29	9

Table 4. Linear density T_d , tenacity σ , elongation ε , Young's modulus E and coefficients of variance CV of PP fibres modified with concentrates A, B and D, $\lambda_4 = 4$.

Amount and type of concentrate, wt.%	T _d , dtex	CV _{Td} , %	σ, cN·dtex-1	CV _σ , %	ε, %	CVε, %	E, cN.dtex ⁻¹	CV _E , %
PP	218	5	2.7	4	20	12	34	13
4 A	190	4	3.0	9	26	13	47	10
8 A	209	6	2.9	4	20	16	39	6
12 A	213	5	2.7	6	20	21	38	10
4 B	190	6	2.7	4	27	22	37	9
8 B	218	8	2.5	9	20	10	36	9
12 B	223	6	2.4	10	19	8	40	9
4 D	190	2	3.0	6	23	27	43	11
8 D	197	5	2.8	9	22	9	45	13
12 D	199	4	2.6	10	21	11	40	12

The mechanical properties of the lubricated modified PP fibres were measured 20 times by an Instron 3343, and the tenacity σ , elongation at break ϵ , Young's modulus E and their variation coefficients CV were evaluated from these values. The clamping length was 0.25 m and the speed of clamps - 0.5 m/min.

Electrostatic properties of the modified and non modified PP fibres were measured with EP 02 apparatus. Fibres without lubtication ($\lambda = 2$) were rolled up on a metal frame (about 10 × 12 cm) as a uniform surface, and the frame with fibres thus arranged was fixed onto the moving part of the apparatus. The fibre surface was charged to the maximum potential U_{max} by the friction of the slider moving on it. The discharging of fibres was measured until the potential equalled zero or till 1800 s, after which a discharging curve was constructed and the half time of discharging t_{1/2} evaluated.

The fibre sorption of water vapour was evaluated gravimetrically at temperature $T_5 = 21.7$ °C and at 65% relative humidity using lubricated fibres at a drawing ratio of $\lambda = 3$.

Results and discussion

The composition of the modified PP fibres is documented in *Table 1*.

The linear densities and mechanical properties of PP fibres modified with concentrates A, B and D, drawn at three different drawing ratios, are given in *Tables 2 - 4*.

The linear density of the modified PP fibres is influenced by two factors: the drawing ratio and the amount of concentrate in the modified fibres. For a drawing ratio of $\lambda_4 = 4$, practically all the linear densities of the modified PP fibres are lower in comparison with those of non modified PP fibres, which is as a consequence of their lower internal arrangement (or higher internal "free volume"). From the point of fibre density, concentrates with lower molecular regularity and voluminous piperazine cycles hamper more at higher drawing ratios ($\lambda_4 = 4$), as at lower drawing ratios ($\lambda_2 = 3$ and $\lambda_3 = 3.5$) where the linear densities of the modified PP fibres are lower at the lowest amount of concentrate, gradually increasing even over that of non- modified fibres. The coefficients of variance CV_{Td} for non-modified PP fibres are 5 - 7%,

whereas those for the modified ones are in the range ofl 2-8 ($\lambda_2 = 3$ and $\lambda_4 = 4$) and 6-13 ($\lambda_3 = 3.5$), hence not very different. Moreover,, from the point of view of linear density, the modified PP fibres are relatively even.

The tensile strength of fibres modified with concentrates is influenced mainly by the morphological structure of elements formed by the nanoadditive and copolyamide, by their compatibility with the basic polymer i.e. polypropylene, by the molar weights of the copolyamide and nanoadditive, and by the amount of concentrate in the fibre.

It was shown that if the molar weights of components of the blend (copolyamide and compatibilizer) are not high enough (comparable with the molar weight of the matrix), they have a negative influence on the tenacity of the modified fibres [5]. Mechanical properties are more negatively influenced the higher the amount of polymer additive there is, with a lower molar weight of fibres. In our contributiuon the molar weights of concentrates are lower (in comparison with commercial PA 6, with $\eta_{rel} = 1.68$). A sufficient amount of nanoclay in an effective form (exfoliated or intercalated) can improve mechanical properties. It should also be noted that PP fibres modified with 4 wt.% of the concentrate contain 0.2 wt.% of Bentonite nanoclay; those with 8 wt.% of each concentrate contain 0.4 wt.%, and those with 12 wt.% of the concentrate contain 0.6 wt.% of nanoclay (Table 1). Hence the amount of nanoclay is rather small, but from the lowest to the highest amount of concentrate in the modified fibres, it increased twice or tripled, which can effectively contribute to the improvement of tenacity. The lower molar weights of concentrates have an opposite influence on nanoclay at higher amounts.

From the values in *Tables 2 - 4*, it is evident that the tenacity is not negatively influenced by 4 wt.% of all three concentrates at all three drawing ratios. At $\lambda_2 = 3$, higher amounts of concentrates i.e. 8 and 12 wt.% rapidly negatively influence the tenacity of modified PP fibres (*Table 2*). At higher drawing ratios e.g. $\lambda_3 = 3.5$, an elevated amount of each concentrate does not have such a negative influence, and even PP fibres modified with 4 wt.% of concentrates A and B have a higher tenacity than non modified PP fibres; at higher amounts the tenacity is not dramatically lowered (*Table 3*). At the high-

FIBRES & TEXTILES in Eastern Europe 2011, Vol. 19, No. 2 (85)

Table 5. Maximum potential U_{max} , potential after a time of 1800s, U_{1800} , half time of discharging $t_{1/2}$, and time of discharging to a zero potential t_{sum} of modified non lubricated *PP* fibres, $\lambda_1 = 2$.

Amount and type of concentrate, wt.%	U _{max} , kV	t _{1/2} , s	U ₁₈₀₀ , kV	t _{sum} , s
PP	12.5	>1800	11.8	>1800
4 A	9.5	>1800	8.9	>1800
8 A	5.0	>1800	3.9	>1800
12 A	3.4	600	1.3	>1800
4 B	6.1	>1800	4.7	>1800
8 B	3.7	>1800	2.8	>1800
12 B	2.7	1200	1.1	>1800
4 D	8.0	>1800	5.0	>1800
8 D	4.8	900	3.0	>1800
12 D	3.2	900	1.8	>1800

Table 6. Take-up of dyestuffs from the bath T, concentration of dyestuff in the fibre c_{f_i} and water vapour sorption S of the modified PP fibres, $\lambda_2 = 3$.

Amount and type of concentrate, wt.%	Terasil Blau		Ostacet yellow		S,%		
	Т, %	c _f , mg/g	Т, %	c _f , mg/g	λ = 3	λ =3.5	λ =4
PP	3.1	0.61	27.5	5.51	0.12	0.11	0.11
4 A	9.6	1.93	29.6	5.93	0.34	0.28	0.17
8 A	18.2	3.63	47.2	9.43	0.60	0.49	0.39
12 A	20.2	4.04	51.0	10.2	0.81	0.77	0.64
4 B	11.9	2.37	30.1	6.01	0.36	0.30	0.26
8 B	13.7	2.73	48.8	9.76	0.59	0.54	0.48
12 B	18.8	3.76	51.2	10.2	0.87	0.72	0.60
4 D	12.6	2.51	34.6	6.91	0.35	0.31	0.23
8 D	17.2	3.44	41.9	8.39	0.66	0.57	0.45
12 D	19.1	3.81	47.0	9.40	1.08	0.84	0.59

est drawing ratio - λ_4 = 4, concentrates A and D positively influence the tenacity of modified PP fibres in all ranges of their amount (*Table 4*). The coefficients of variance CV_{σ} are in the range of 4 - 11% (for non modified PP fibres 4 - 8%), showing practically the same evenness in this respect.

The higher tenacity of PP fibres modified with concentrates (of copolyamide and a nanoadditive) is probably caused by the fact that the system is comprised of two non- compatible components, one being oriented macromolecules of PP and the other - oriented structures consisting of the nanoadditive with copolyamides. These two components conserve the separated phase boundary and oriented structures of the nanoadditive with copolyamides, having a much higher molecular weight than the 'reinforced network'' in the matrix of PP.

Young's modulus is positively influenced at all three drawing ratios, more at $\lambda_1 = 3$ (with an increase of 13 - 52%) and at $\lambda_4 = 4$ (6 - 38%), and the least at $\lambda_3 = 3.5$ (up to 17%). The coefficients of variance

are more dispersed, reaching values of 6 - 14%.

Because the lower molar weight of additives of different chemical structure negatively influence the mechanical properties of blends, better mechanical properties of the PP fibres presented must be acquired by the nanoadditive used.

The elongation at break of the modified fibres at $\lambda_2 = 3$ and $\lambda_3 = 3.5$ is lower than that for non modified PP fibres, and higher values of the coefficients of variance confirm the blend character of the modified fibres.

It is known that if the maximal electrostatic charge is higher than 5 kV, it can cause an explosion of combustible vapour and gases. Values higher than 3 kV cause unpleasant electrical shocks, and those lower than 1 kV cause that the textile material has a very low soil-release property.

From *Table 5* it is evident that all the modified PP fibres have a certain potential, even after 1800 s; hence only the three remaining characteristics can be used for the evaluation of electric prop-

erties, and only two of them (Umax and U₁₈₀₀) give expressive differences. From the values of these two characteristics, it follows that modifying PP fibres with all three concentrates has a positive effect on their electrical properties. In comparison with non- modified PP fibres, the electrical properties of the modified PP fibres are better even at the lowest amount of, equal to 4 wt.%, the effectivness of which increases with an increase in the amount of the concentrates. The maximum potential reached as well as that after 1800 s decrease with an increase in the amount of concentrates A, B & D, and for 8 wt.% and 12 wt.% they are in the range 1 - 5 kV, which is the most advantageous from a physiological and maintainance point of view. All this is a consequence of the higher amount of copolyamide in the concentrates, which have macromolecules with a higher concentration of polar nitrogen and higher water vapour sorption, bringing about a higher conductivity and dissipation of electric charge.

PP fibres are hydrophobic, hence their sorption of water vapour is very low. All three concentrates as additives markedly increase the hydrophilicity of the modified PP fibres (Table 6, see page 21). Two factors contribute to a higher hydrophility: The first is the presence of copolyamides (in concentrates) with their polar groups in the blend fibres and the second is the more "opened" internal structure due to the lower compatibility of PP and copolyamide. Though concentrates A, B & D contain different partial and total amounts of both comonomers, it is not possible to evaluate the contributions of each one. Moreover, from these different amounts a higher or lower geometrical arrangement of copolyamides can result. The higher the amount of all three copolyamides, the higher the water vapour sorption. A higher drawing ratio causes a more tightened internal structure, as a result of which water vapour sorption decreases at a higher drawing ratio.

The dyeability of the modified PP fibres with disperse dyestuffs Terasil Blau 3RL and Ostacet Yellow E-L5R is much better mainly at an amount of 8 wt.% and 12 wt.% of all three concentrates - A, B & D. The reason is the same as for the improvement of water vapour sorption i.e. a higher amount of polar groups in the modified PP fibres and, as usual, a more opened internal structure of the blend fibres. Although concentrates A, B & D contain different partial and total amounts of comonomers, the results obtained do not allow to quantify the contribution of each comonomer nor its amount in relation to the properties examined.

Conclusion

- 1. PP fibres modified with 4, 8 and 12 wt.% of concentrates A, B & D, consisting of copolyamides and nanoadditive Bentonite, can be spun even without a compatibiliser by the standard melting process and drawn at high drawing ratios.
- 2. The mechanical properties of the modified PP fibres, i.e. the tenacity and Young's modulus, are better mainly at lower amounts of each concentrate and at higher drawing ratios.
- 3. The electric properties of the modified PP fibres are positively influenced by all three concentrates. The higher their amount in the modified PP fibres, the better the electrostatic properties.
- 4. The sorptive properties of the modified PP fibres i.e. the sorption of water vapour and disperse, dyestuffs are much better in comparison with non modified PP fibres.

Acknowledgment

This work was supported by the Slovak Research and Development Agency under contract No APVT -20-011440 and by the VEGA Agency under contract 1/0406/08

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- Received 25.11.2009 Reviewed 01.06.2010