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PROPERTIES OF POLYAMIDE 6 FIBRES MODIFIED BY SILICATE NANOPARTICLES

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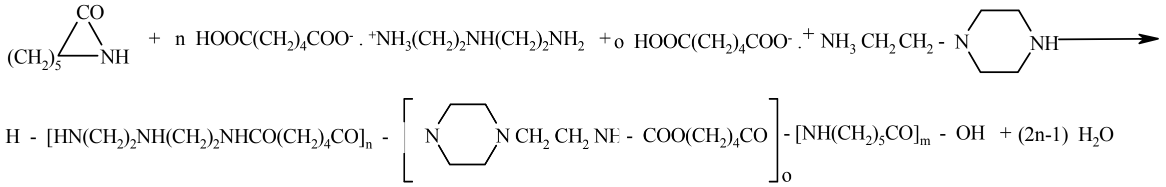
The first part of contribution is focused to the synthesis of ternary copolyamides containing layered silicate (i.e. Bentonite 11958 or Cloisite 15A). Concentrates were prepared from the basic comonomer, ε-caprolactam and minor polar comonomers, nylon salt AN 2 from adipic acid and 1-(2-aminoethyl)piperazine and nylon salt ADETA from adipic acid and diethylenetriamine in the total amount of 10.7 and 21.4 wt.%. Amount of layered silicates in the concentrates is always the same, 5 wt.%.

Reaction scheme of synthesis of copolyamide



The second part of contribution deals with the preparation of polyamide 6 (PA 6) fibres non-modified and modified by concentrates and determination of some properties (i.e. mechanical, sorptive, barrier and thermal properties) of modified fibres, too.

Keywords: Polyamide 6, layered silicate, concentrates, properties

Introduction

Polyamide fibres have many useful properties, but some of them such as electrostatic and sorptive ones do not meet the requirements of customers. Chemical and physical modifications are the basic methods for an improvement of these properties. Chemical modification is application of comonomers at the preparation of copolyamides. Addition of concentrates, i.e. copolyamides containing layered silicate into PA 6 is a physical modification of PA 6.

Introduction of the new comonomer, with some polar atoms or groups into the backbone of poly-ε-caprolactam is the possibility to prepare copolyamides which can be used as modifiers for PA 6 as well. Many polyamides and polyamide fibres containing the derivatives of piperazine or piperidine are characterized by higher sorption of water vapour than PA 6 [1-3]. Binary copolyamides based on ε-caprolactam and a nylon salt of adipic acid and 1-(2-aminoethyl)piperazine or 1,4-bis-(3-aminopropyl)piperazine are crystalline copolymers with good compatibility with PA 6 [4]. PA 6 fibres modified with binary copolyamides have better electrostatic and sorptive properties [5].

Concentrates such as binary or ternary copolyamides based on poly-ε-caprolactam containing polar comonomers from adipic acid + 1-(2-aminoethyl)piperazine (AN 2), adipic acid + diethylenetriamine (ADETA) and organoclay would be effective modifiers for PA 6.

Materials

Polyamide 6, PA 6, Nylstar Slovakia, Slovak Republic, $\eta_{rel} = 2.642$ in HCOOH, $\eta_{rel} = 1.68$ in H_2SO_4, 96%, 25 °C, at the concentration c = 0.5 g of polymer / 100 ml solution, $T_m = 227$ °C

ε-caprolactam, CL, Nylstar Slovakia, Slovak Republic

Nylon salt AN 2, AN2, SUT, Department of Fibres and Textile Chemistry, Slovak Republic, it is prepared from adipic acid, A + 1-(2-aminoethyl)piperazine, N 2

Nylon salt ADETA, ADETA, SUT, Department of Fibres and Textile Chemistry, Slovak Republic, it is prepared from adipic acid, A + diethylenetriamine, DETA

Layered silicate – organophilic montmorillonite, MMT:

- Bentonite 11958, BEN, Aldrich, USA, it contains sodium and quartery ammonium ions between layers

- Cloisite 15A, CLO, Gonzales, USA, it is MMT modified with quartery ammonium salt, i.e. ditallowdimethylammonium salt of Bentonite

Preparation of modifiers

Concentrates of ε-caprolactam, nylon salts AN 2 and ADETA and layered silicate were prepared by the poly (addition-condensation) reaction proceeding in melt in the N_2 atmosphere. The powdered CL, AN 2, ADETA mixture with MMT was heated in the glass apparatus. During the first 10 minutes the temperature was raised so that the nylon salts melted and homogenized in the CL. Later the polyreaction started – reaction water evaporated and condensed and the viscosity of the melt increased with time to the temperature of 270-280 °C at the end of the reaction time. The concentrates were poured into the cylindrical form onto the metallic plate and cut into granules. Concentrates were designed by the symbols A, B and C according to different concentration of the nylon salts.

Their composition and main characteristics are:

A – 73.6% KL + 10.7% ADETA + 10.7% AN 2 + 5.0% MMT

B – 84.3% KL + 10.7% AN 2 + 5.0% MMT

C – 73.6% KL + 10.7% ADETA + 10.7% AN 2 + 5.0% CLO 15A

Preparation of modified PA 6 fibres

Modifiers were extracted in hot water to remove low-molecular compounds and dried.

The blends of PA 6 containing 5, 10 and 20 wt.% of concentrate A, B and C were prepared in a single-screw ribbon extruder at the temperature of zones $T_1 = T_2 = T_3 = 250$ °C.

The spinning of blends was performed on the experimental equipment at the temperature of zones $T_1 = 260$ °C, $T_{2\text{-}4} = 255$ °C and $T_5 = 260$ °C with lubricant.

After spinning the fibres were drawn at the temperature 110 °C to the drawing ratio $\lambda = 3$ and 3.5.

Methods used for the evaluation of the fibres properties

The mechanical properties, i.e. tensile strength of PA 6 fibres were measured by Instron 3343.

The hydrophilicity of fibres was evaluated gravimetrically at the temperature $T_8 = 21.7$ °C and at the 65% relative humidity.

The barrier properties, i.e. ultraviolet protection factor of fibres ($\lambda = 3$) were measured by spectrophotometer with deuterium lamp, Libra S12.

The thermal properties of these fibres ($\lambda = 3$) were measured by Perkin-Elmer DSC 7 equipment. The conditions of measurement were:

- heating 50 °C → 250 °C
- cooling 250 °C → 50 °C

with heating and cooling rate 10 °C/min in N_2 atmosphere.

Results and discussion

Amount of low molecular compounds of concentrates *(Table 1)* are at the same level as for PA 6. Relative viscosity and melting temperature of concentrates (Table 1) decrease with amount of comonomers, but these are lower than in the case of PA 6.

Tensile strength of fibres *(Table 2)* increases with drawing ratio, but it decreases with the amount of concentrates in fibres. Modified fibres have smaller tenacity than PA 6 fibre. Fibres modified by concentrate C have the best tensile strength in comparison with other modified fibres, particularly when the amount of concentrate in fibres is lower, i.e. 5 and 10 wt.% and at the drawing ratio 3.5.

Values of water vapour sorption (Table 2) increases with amount of concentrates in fibres and it decreases in dependence on higher drawing ratio due to higher orientation in fibres. Fibres modified by concentrates A and C have better sorptive properties than fibres modified by concentrate B, because they contain higher amount of polar, hydrophilic comonomers, which improve hydrophility of fibres, because they are able to fix molecules of water vapour.

If UPF value is higher, then less ultraviolet radiation is transmitted through material. UPF of modified fibres (Table 2) depends on type of used layered silicate (Bentonite or Cloisite 15A). UPF is better in the case of fibres modified by concentrate C, which contains Cloisite 15A.

Melting temperatures of modified PA 6 fibres *(Table 3)* are lower in comparison with non-modified PA 6 fibre, but their crystallization temperatures (Table 3) are similar.

Melting entalphies and enthalphies of crystallization of modified PA 6 fibres (Table 3), mainly with lower amount of concentrates A, B and C, i.e. 5 and 10 wt.% are higher or practically the same as for non-modified PA 6 fibre.

Table 1: Time of synthesis, t, amount of low molecular compounds, LMC, relative viscosity, η_{rel} and melting temperature, T_m of PA 6 and concentrates

CONC	t [min]	LMC [wt.%]	η_{rel}	T_m [°C]
PA 6	≈600	≈12	1.68	227
A	340	10.1	1.42	187
B	360	9.6	1.48	198
C	360	15.1	1.39	189

Table 2: Tensile strength, σ, water vapour sorption, S and ultraviolet protection factor, UPF of PA 6 fibres non-modified and modified with concentrates

Fibres	σ [cN.dtex^{-1}]		S [%]		UPF
λ	3	3,5	3	3,5	3
PA 6	4.04	4.38	4.96	4.87	10.5
5% A	3.46	4.15	5.18	5.15	10.5
10% A	3.45	3.87	5.39	5.21	8.5
20% A	2.81	3.38	5.84	5.44	9.9
5% B	3.71	4.32	5.13	4.84	10.9
10% B	3.39	4.24	5.17	5.13	9.4
20% B	3.23	3.77	5.42	5.19	9.6
5% C	3.64	4.49	5.34	5.06	10.9
10% C	3.39	4.43	5.51	5.23	12.4
20% C	2.98	3.93	5.82	5.54	11.7

Table 3: Thermal properties, i.e. melting and crystallization temperatures and entalphies of PA 6 fibres non-modified and modified with concentrates, λ = 3

Fibres	Heating		Cooling	
	T_{m1} [°C]	$\Sigma\Delta H_{m1}$ [J/g]	T_{c1} [°C]	$-\Delta H_{c1}$ [J/g]
PA 6	221	79.8	188	72.1
5% A	216	81.4	188	76.0
10% A	218	75.9	187	70.4
20% A	220	69.3	186	64.9
5% B	218	77.9	188	73.7
10% B	218	77.4	188	75.5
20% B	218	76.8	187	71.1
5% C	217	82.4	189	76.6
10% C	219	78.4	189	71.4
20% C	219	71.1	187	67.0

Conclusions

Concentrates reduce a little bit the tensile strength of modified PA 6 fibres in comparison with non-modified ones because of lower orientation in these fibres.

Concentrates improve sorptive properties of modified PA 6 fibres due to their higher hydrophilicity.

UPF depends on the type of layered silicate used for modification of fibres, from which Cloisite 15A proves to be more effective.

Melting temperatures of modified PA 6 fibres are lower in comparison with non-modified ones because of lower melting temperature of concentrates, but their crystallization temperatures are the same or similar. Lower amount of concentrates in PA 6 fibres do not have a significant effect on thermal properties.

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