THE STRUCTURE AND PROPERTIES OF POLYPROPYLENE-MODIFIED HALLOYSITE NANOCLAY FIBRES

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Abstract: *Due to the dominance of Asian production of standard man-made fibres in the world, a necessity for the sophistication of European fibres and textiles arises. Bulk or surface modification of materials by nanoadditives is one of the most prospective ways how to ensure special mono- and multi-functionality of fibres in clothing and technical textiles. Natural nanotubes of halloysite nanoclay can be modified (M-HNT) by a chemically, biologically and physically active substances like photoluminescent pigments which emits light after the absorption of photons (electromagnetic radiation). In this work, M-HNT nanotubes modified by organic protective photoluminescent pigment have been used. The article presents results of the study of influence of M-HNT content as well as the influence of uniaxial deformation on the supermolecular structure (birefringence, sound velocity in fibres, crystallinity index and crystallinity) and mechanical properties (fineness, Young´s modulus, tenacity and elongation at break) of modified nanocomposite polypropylene (PP) fibres (PP/M-HNT fibres). Color performance of above mentioned PP/M-HNT fibres was investigated under day light (D65) and after illumination with UV lamp. The obtained experimental results undrawn and drawn of PP/M-HNT fibres were compared with PP fibres modified by organic protective photoluminescent pigment and unmodified PP fibre (standard), both prepared under same technological conditions. Our results confirmed that the nanoadditive halloysite nanoclay can be used as a potential carrier of organic protective photoluminescent pigment for PP nanocomposites, including nanocomposite PP fibres with acceptable impact on structure and mechanical properties of modified nanocomposite fibres.*

Keywords: *modified halloysite nanoclay, photoluminescent pigment, PP nanocomposite fibres, structure, mechanical properties, color performance*

1 INTRODUCTION

The global world production of textile fibres increased in 2016 by 1.7% to 95.3 million tons [1]. This includes an increase of 2.8% in the chemical fibre sector to 70.4 mil tons while natural fibres dropped -1.4% to 24.9 mil tons. The production of PP fibres increased in 2016 by 3.0% to 5.5 million tons [2]. In the future, the increase in textile market is expected to reach 106 mil tons in 2020 and almost 139 mil tons in 2030. This amounts to per capita consumption of 13.9 kg in 2020 and 16.7 kg in 2030 and further increase in the volume of world production of man-made fibres up to 75 mil tons in 2020, at an average annual increase of 4% [3, 4].

The 2016 world survey continues to underscore the dominance of Asia in the fibre business. In 2016 Asia accounted for 88.5% of the worldwide chemical fibre production and holds the dominant position in the world production of standard man-made fibres [1]. This implies the necessity of sophistication of European fibre and textile products in today´s highly competitive environment. It particularly concerns the development of special, modified, mono and multi-functional active fibres and textiles necessarily characterized by high functionality, diversification, flexibility and highly effective and environmentally acceptable production [5, 6]. The most perspective way to ensure sophisticated properties of textiles is modification of their mass or surface by nanotechnologies [5, 6]. The most important nanotechnological procedures in the area of textiles include nano-treatment of their surface and nanoadditive addition of the fibres mass during their extrusion (nanocomposite fibres). By these procedures, mono or multi-functional properties of textiles even at low concentrations of nanoadditives can be achieved, which is very beneficial from an economic aspect as well. The world nanocomposites market is highly prospective and its volume in 2015 was estimated to have reached 7.3 billion US$ [6, 7].

Nanocomposite systems based on natural layered silicates, particularly montmorillonite and halloysite nanoclay (HNT), belong to the most significant studied polymer nanocomposites [8-10]. The advantage of halloysite is the shape of the hollow nanotubes with porous inner surface, which makes them suitable to be used as the carrier of chemically and biologically active substances for polymer nanocomposite systems [11, 12]. This article presents some results from the study of influence of content natural nanoadditive halloysite nanoclay modified by organic protective photoluminescent pigment as well as the influence of uniaxial deformation on the supermolecular structure and basic mechanical properties of undrawn and drawn modified nanocomposite PP fibres prepared by discontinuous technological process. The obtained experimental results of modified nanocomposite PP fibres were compared with the supermolecular structure and mechanical properties of undrawn and drawn PP fibres modified by organic protective photoluminescent pigment prepared under same technological conditions.

2 EXPERIMENTAL AND METHODS

2.1 Materials

Isotactic granulated polypropylene PP (Slovnaft Company) with MFR=27.6 g/10 min; inorganic nanoadditive halloysite nanoclay 685445 - HNT (Applied Minerals Inc.); inorganic nanoadditive HNT modified by organic protective photoluminescent pigment A (content 20.0 wt.%) - M-HNT in cooperation with A1Synth Ltd. Company; PP/M-HNT masterbatch developed by Research Institute for Man-Made Fibres a.s., Svit (M-HNT content 5.0 wt.%, MFR=28.3 g/10 min); PP masterbatch of organic protective photoluminescent pigment A (Radiant Color NV) developed by Research Institute for Man-Made Fibres, a.s. Svit (pigment content 2.0 wt.%, MFR=20.9 g/10 min) were used during fibre preparation process.

2.2 Fibre preparation

The modified nanocomposite PP/M-HNT fibres were prepared from mechanical mixture of PP granulated polymer and PP/M-HNT masterbatch using the classical discontinuous process of spinning and drawing. The laboratory discontinuous line had an extruder with diameter of D=32.0 mm, with a discontinuous one-step drawing process. There were used constant processing conditions as the spinning temperature of 220°C, spinning die 2x25 holes with diameter 0.3 mm, final spinning process speed of 1500 m.min^{-1}, the drawing ratio λ=2.0, the drawing temperature of 132°C and final drawing process speed of 100 m.min^{-1}. The modified PP/A fibres which were used for comparison, have been prepared from mechanical mixture of PP granulated polymer and PP masterbatch of organic protective photoluminescent pigment A under same processing conditions.

2.3 Methods used

<u>Orientation of fibre (the fibre´s birefringence)</u>

The orientation of macromolecular chains segments in fibre expresses the level of anisotropy of oriented polymer system (fibre). The total orientation of prepared modified nanocomposite PP fibres was evaluated using a DNP 714BI polarization microscope, where the refractive indexes of light in the fibre axis ($n_{//}$) and in the perpendicular direction of the fibre ($n_{\perp}$) were identified. The fibre's birefringence (Δn) was calculated from these values using Equation 1 below:

$$\Delta n = n_{//} - n_{\perp} \quad (1)$$

<u>The sound velocity in fibres</u>

The sound velocity in fibres is given as the ratio of fibre length to the time needed for the transfer of acoustic nodes along that length (expressed in km.s^{-1}). It is dependent on the internal structure arrangement of fibres (expressed by a supermolecular structure parameter) and may serve as a measure of fibre anisotropy. The sound velocity in fibres was measured using a PPMSR Dynamic Modulus Tester (USA).

<u>Crystallinity index (FT-IR)</u>

Crystallinity index I_k of PP fibres represents the fraction of the crystalline phase in PP fibres. It is determined as the ratio of integrated absorbance of absorption band of 840 cm^{-1} (A_{i840}) characterizing the regularity of the arrangement of macromolecular chains segments and integrated absorbance of absorption band of 2723 cm^{-1} (A_{i2723}) as the internal standard influencing the degree of crystallinity:

$$I_k = \frac{A_{i840}}{A_{i2723}} \quad (2)$$

Crystallinity index of modified nanocomposite PP fibres was evaluated by FT-IR spectrophotometer 8400 Shimadzu.

<u>Crystallinity of fibres</u>

Crystallinity β represents the crystalline portion of fibres and may be evaluated by various methods. In this work DSC 4 apparatus Perkin Elmer was used for the evaluation of thermal properties of modified nanocomposite PP fibres and modified PP fibres according to the STN EN ISO 3146/AC. In this procedure the non-isothermal process of analysis was performed. A sample of original fibre was heated by rate of 10°C.min^{-1} from 50 to 260°C. All measurements were carried out in nitrogen atmosphere. Melting enthalpy (ΔH_m) from melting endotherm of 1st heating was determined and was used for the calculation of crystallinity β using the equation 3:

$$\beta = \frac{\Delta H_m}{\Delta H_{m,0}} \cdot 100\% \quad (3)$$

where $\Delta H_{m,0}$ = 198.11 kJ.kg^{-1} is the melting enthalpy of PP with the 100% crystallinity.

Mechanical properties of fibres

The mechanical properties of modified nanocomposite PP fibres and modified PP fibres were measured using Instron 3343 equipment (USA) with a gauge length of 125 mm and clamping rate of 500 mm.min^{-1}. The average of at least 10 individual measurements was used for each fibre. The mechanical characteristics (tenacity at break, elongation at break and Young's modulus) were determined according to ISO 2062:1993 and fineness according to the STN EN ISO 1973.

3 RESULTS AND DISCUSSION

From experimental spinning and drawing tests of the studied modified nanocomposite PP system it follows that the PP/M-HNT nanocomposite is fibre forming in over the entire evaluated concentration range of the modified nanofiller (0.05-1.50 wt.%). The discontinuous spinning and drawing processes at drawing ratio λ=2.0 of PP/M-HNT nanocomposite fibres are stable, comparable to unmodified PP standard. The supermolecular structure parameters and basic mechanical properties of pure and nanocomposite undrawn and drawn PP fibres were evaluated.

The obtained results in Tables 1-4 show the effect of the modified nanoadditive (M-HNT) content on the supermolecular structure parameters and mechanical properties of undrawn and drawn nanocomposite PP fibres. It was found, that evaluated concentration range of 0.05-1.5 wt.% of the modified nanofiller M-HNT does not influence significantly the birefringence of undrawn nanocomposite PP fibres (Table 1 - Δn). With an increase of M-HNT content it slightly decreases the crystalline portion β, which is a result of steric braking effect of nanoadditive particles (in nanotubes form) on orientation of segments of PP macromolecular chains into the direction of the fibre axis in the spinning zone. This also implies a slight decrease in the crystalline portion β (Table 1 - β) of PP matrix of undrawn nanocomposite fibres with an increased content of the nanoadditive in the mass of fibres. At the same time, there is slight increase of the sound velocity (Table 1 - average orientation c), as well as conformational regularity of their crystalline regions (Table 1 - crystallinity index I_k). It is probably a result of the nucleating effect of nanofiller particles in the process of formation of undrawn nanocomposite PP fibres in the spinning zone.

The uniaxial deformation of undrawn nanocomposite PP fibres significantly increases total average orientation of macromolecular chains of polymer matrix and orientation of macromolecular chains in surface layers (Table 2 - Δn, c), as well as crystalline portion β and conformational regularity of crystalline regions (Table 2 - β, I_k) of PP matrix of drawn nanocomposite fibres.

In comparison with drawn unmodified PP fibre, evaluated concentration range 0.05-1.5 wt.% of the modified nanofiller M-HNT in the drawn nanocomposite PP fibres does not influence significantly on the total average orientation of macromolecular chains of polymer matrix and orientation of macromolecular chains in surface layers (Table 2 - Δn, c) of drawn nanocomposite PP fibres. At the same time the increased nanoadditive content in the drawn nanocomposite PP fibres results in the decrease in conformational regularity of crystalline regions, as well as crystalline portion β (Table 2 - I_k, β) of drawn nanocomposite fibres. It is probably a result of a steric braking effect of nanoadditive particles (nanotubes form) on orientation of segments of PP macromolecular chains in the direction of the fibre axis in the drawing process of nanocomposite fibres.

Table 1 Supermolecular structure parameters of undrawn PP/M-HNT nanocomposite fibres

Content of M-HNT [wt.%]	$\Delta n.10^3$	$CV_{\Delta n}$ [%]	c [km/s]	CV_c [%]	I_k (FT-IR)	CV_{Ik} [%]	β
-	21.68	1.0	1.88	1.1	1.04	4.0	0.426
0.05	21.66	1.0	1.85	1.2	1.01	3.7	0.425
0.25	21.74	1.2	1.86	1.5	1.05	1.6	0.422
0.50	22.37	0.8	1.90	1.6	1.16	1.8	0.421
0.75	22.34	1.0	1.93	0.7	1.21	4.0	0.416
1.0	22.45	1.1	1.95	1.1	1.22	2.0	0.409
1.5	21.49	1.2	1.94	0.9	1.23	9.6	0.406

Table 2 Supermolecular structure parameters of drawn PP/M-HNT nanocomposite fibres

Content of M-HNT [wt.%]	$\Delta n.10^3$	$CV_{\Delta n}$ [%]	c [km/s]	CV_c [%]	I_k (FT-IR)	CV_{Ik} [%]	β
-	30.26	1.1	2.61	1.8	1.27	3.7	0.448
0.05	29.68	0.9	2.56	1.3	1.27	4.9	0.445
0.25	30.34	1.1	2.58	1.9	1.23	1.2	0.440
0.50	30.59	1.1	2.59	1.8	1.25	1.1	0.435
0.75	30.64	1.6	2.61	1.8	1.17	3.8	0.432
1.0	30.66	1.7	2.62	1.5	1.12	1.4	0.427
1.5	30.51	1.9	2.60	1.9	1.09	0.7	0.423

Table 3 Mechanical properties of undrawn PP/M-HNT nanocomposite fibres

Content of M-HNT [wt.%]	Fineness [dtex]	CV_F [%]	Tenacity [cN/dtex]	CV_T [%]	Elongation [%]	CV_E [%]	Young´s modulus [cN/dtex]	CV_{YM} [%]
-	460.8	0.6	2.1	4.2	268.7	5.6	11.4	8.5
0.05	460.2	0.9	2.1	4.6	285.8	5.5	12.2	8.6
0.25	459.5	1.1	2.1	3.8	288.3	6.3	12.9	8.6
0.50	460.3	0.9	2.0	3.4	271.2	5.1	14.7	8.7
0.75	462.3	1.3	2.0	4.6	279.2	5.1	17.0	4.2
1.0	461.5	0.9	1.9	4.4	279.0	6.7	17.6	5.3
1.5	462.5	1.3	1.9	3.1	282.8	5.0	18.8	7.8

Table 4 Mechanical properties of drawn PP/M-HNT nanocomposite fibres

Content of M-HNT [wt.%]	Fineness [dtex]	CV_F [%]	Tenacity [cN/dtex]	CV_T [%]	Elongation [%]	CV_E [%]	Young´s modulus [cN/dtex]	CV_{YM} [%]
-	255.7	2.4	4,1	2.3	103.4	3.9	40.1	3.2
0.05	258.3	1.2	4,0	1.6	100.4	3.7	39.8	3.5
0.25	258.6	0.9	3,9	2.1	95.4	6.2	40.6	3.5
0.50	257.7	1.2	3,9	2.4	94.2	6.5	38.7	2.3
0.75	259.6	1.2	3,7	2.9	90.1	5.6	38.9	4.5
1.0	260.4	0.8	3,6	2.1	92.5	7.4	38.4	3.8
1.5	259.8	1.4	3,5	1.2	92.2	4.8	36.2	3.7

The fineness of undrawn PP/M-HNT nanocomposite fibres was found constant and does not depend on M-HNT content in the fibres (Table 3). The slight increase in their elongation (up to 20% absolute) and slight decrease in their tenacity (up to 10%) when compared to unadditivated standard was found. An increase in Young’s modulus with increased M-HNT content in the mass of undrawn fibres (up to 20%) is mainly related to the increase in the conformational regularity of their crystalline areas (Table 1 - I_k).

The fineness of drawn PP/M-HNT nanocomposite fibres was found constant in dependence of M-HNT content in the fibres (Table 4). The process of uniaxial deformation of undrawn nanocomposite fibres significantly increases the tenacity and Young´s modulus and decreases elongation of drawn fibres. It is the result of a significant increase in total average orientation of macromolecular chains of polymer matrix and orientation of macromolecular chains in surface layers (Table 2 - Δn, c), crystalline portion β also the crystallinity index of PP matrix (Table 2 - β, I_k) of drawn nanocomposite fibres.

With increased nanoadditive content in the mass of drawn PP/M-HNT nanocomposite fibres slight decreases the tenacity (up to 15 %), the elongation (up to 15 % absolute) and the Young’s modulus (up to 10 %) of drawn fibres (Table 4). It is mainly related to the decrease in conformational regularity of crystalline areas and crystaline portion β (Table 2 - I_k, β) of drawn nanocomposite fibres.

Obtained values of the basic mechanical properties of PP/M-HNT nanocomposite fibres are in good correlation with evaluated parameters of their supermolecular structure.

Figures 1 and 2 show the effect of the modified nanofiller M-HNT content on the color performance of undrawn and drawn nanocomposite PP/M-HNT fibres under daylight D65 (a) and under a UV lamp.

a) b)

Figure 1 The influence of modified nanofiller M-HNT with a content 0.05; 0.25; 0.50 and 1.50 wt.% on the color performance of undrawn nanocomposite PP fibres compared with unmodified PP fibre (first from the left) under daylight D65 (a) and under a UV lamp (b)

a) b)

Figure 2 The influence of modified nanofiller M-HNT with a content 0.05; 0.25; 0.50; 1.00 and 1.50 wt.% on the color performance of drawn nanocomposite PP fibres compared with unmodified PP fibre (first from the left) under daylight D65 (a) and under a UV lamp (b)

Figures 1a and 2a clearly show that all prepared PP/M-HNT nanocomposite fibers are white under the daylight D65. Under the UV lamp there is no shine to only in the case of unmodified PP fibre (Figures 1b and 2b) while the nanocomposite PP fibres with M-HNT turn blue. Color intensity increases as the content of modified nanofiller M-HNT in nanocomposite PP fibres is increased. It is evident from Figures 1b and 2b that even at low content of M-HNT (about 0.05 wt.%, samples 2 from left to right) a clearly visible color change under the UV lamp is provided.

From the experimental spinning and drawing tests of the modified PP/A fibres which were used for comparison it follows that the modified system is fibre forming in over the entire evaluated concentration range 0.01-0.30 wt.% of photoluminescent pigment A in the mass of PP/A fibre. The discontinuous spinning and drawing processes at drawing ratio λ=2.0 of PP/A modified fibres are stable, comparable to unmodified PP standard. The supermolecular structure parameters and basic mechanical properties of pure and modified undrawn and drawn PP fibres were evaluated.

The obtained results in Tables 5-8 show the effect of the photoluminescent pigment A content on the supermolecular structure parameters and mechanical properties of undrawn and drawn PP/A modified fibres.

In the case of undrawn PP/A modified fibres a slight increasing in dependence of birefringence and sound velocity (Table 5 - Δn, c) and slight decreasing in dependence of crystalline portion β and conformational regularity of crystalline regions (Table 5 - β, I_k) on the photoluminescent pigment A content was found.

The uniaxial deformation of undrawn PP/A modified fibres significantly increases total average orientation of macromolecular chains in polymer matrix and orientation of macromolecular chains in surface layers (Table 6 - Δn, c), as well as crystalline portion β and conformational regularity of crystalline regions (Table 6 - β, I_k) in PP matrix of drawn modified fibres.

In comparison with drawn unmodified PP fibre, the evaluated concentration range 0.01-0.30 wt.% of the photoluminescent pigment A in the drawn PP/A modified fibres slightly increases total average orientation of macromolecular chains in polymer matrix (Table 6 - Δn). At the same time, the increased pigment A content in the drawn modified PP fibres results in the slight increase in conformational regularity of crystalline regions and decrease the crystalline portion β (Table 6 - I_k, β) of drawn modified fibres. It is probably the result of a plasticizing effect of organic photoluminescent pigment A on orientation of PP macromolecular chain segments in the direction of the fibre axis in the drawing process of modified fibres.

Table 5 Supermolecular structure parameters of undrawn PP/A modified fibres

Content of pigment A [wt.%]	$\Delta n.10^3$	$CV_{\Delta n}$ [%]	c [km/s]	CV_c [%]	I_k (FT-IR)	CV_{Ik} [%]	β
-	20.48	2.1	1.79	0.6	1.10	0.4	0.425
0.01	20.71	1.2	1.86	0.5	1.20	0.2	0.422
0.05	21.00	1.1	1.87	1.0	1.13	0.1	0.420
0.10	21.37	0.9	1.87	0.3	1.16	0.1	0.419
0.15	21.69	1.5	1.88	0.7	1.04	0.1	0.417
0.20	22.12	0.8	1.89	0.9	1.01	0.1	0.413
0.30	21.86	1.4	1.88	1.4	1.04	0.1	0.410

Table 6 Supermolecular structure parameters of drawn PP/A modified fibres

Content of pigment A [wt. %]	$\Delta n.10^3$	$CV_{\Delta n}$ [%]	c [km/s]	CV_c [%]	I_k (FT-IR)	CV_{Ik} [%]	β
-	29.37	0.8	2.54	1.4	1.45	0.4	0.451
0.01	32.07	1.2	2.59	1.4	1.46	0.7	0.448
0.05	33.57	1.3	2.61	1.5	1.54	0.3	0.443
0.10	33.75	1.4	2.64	1.2	1.64	0.3	0.442
0.15	34.21	1.5	2.67	1.4	1.72	0.1	0.441
0.20	33.81	0.7	2.60	1.3	1.63	0.1	0.435
0.30	33.15	0.8	2.53	1.1	1.54	0.1	0.430

Table 7 Mechanical properties of undrawn PP/A modified fibres

Content of pigment A [wt. %]	Fineness [dtex]	CV_F [%]	Tenacity [cN/dtex]	CV_T [%]	Elongation [%]	CV_E [%]	Young´s modulus [cN/dtex]	CV_{YM} [%]
-	450.6	1.0	2.1	3.1	284.1	6.6	10.6	16.7
0.01	444.2	1.0	2.1	5.2	276.7	8.3	11.1	16.5
0.05	448.5	1.3	2.1	2.7	297.8	4.9	11.4	15.3
0.10	445.1	0.5	2.1	3.1	291.0	6.7	12.6	5.9
0.15	443.5	0.5	2.1	2.6	307.6	4.8	13.5	7.8
0.20	444.4	0.7	2.0	5.0	309.8	7.3	15.3	6.7
0.30	442.5	0.8	1.9	4.1	311.5	9.4	17.4	6.6

Table 8 Mechanical properties of drawn PP/A modified fibres

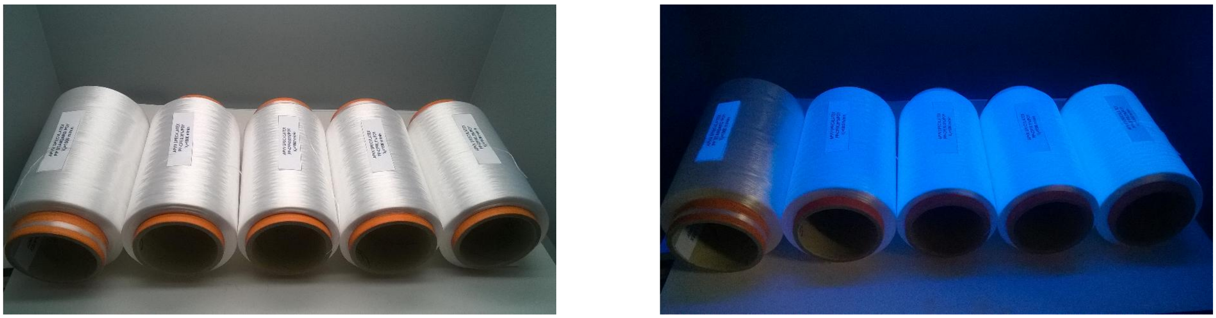
Content of pigment A [wt. %]	Fineness [dtex]	CV_F [%]	Tenacity [cN/dtex]	CV_T [%]	Elongation [%]	CV_E [%]	Young´s modulus [cN/dtex]	CV_{YM} [%]
-	247.8	1.5	4.0	2.3	84.6	6.2	38.6	3.0
0.01	245.5	2.4	4.1	3.0	89.0	7.0	37.9	2.2
0.05	245.4	1.6	4.1	4.4	89.9	10.5	38.3	4.3
0.10	245.8	0.5	3.9	3.4	93.0	7.1	37.0	1.7
0.15	243.3	0.8	3.8	3.8	96.0	11.3	36.6	4.0
0.20	244.7	1.8	3.8	3.8	101.8	11.2	35.3	3.3
0.30	242.3	0.7	3.7	2.9	108.2	9.9	35.0	5.3

The fineness of undrawn PP/A modified fibres was found constant in dependence of pigment A content in the fibres (Table 7). The slight increase in their elongation (up to 25% absolute) and slight decrease in their tenacity (up to 10%) when compared to unmodified standard was found. An increase in Young’s modulus with increased pigment A content in the mass of undrawn fibres is probably related to the slight increase of their birefringence and sound velocity (Table 5 - Δn, c).

The fineness of drawn PP/A modified fibres was found constant in dependence of pigment A content in the fibres (Table 8), as well. The process of uniaxial deformation of undrawn PP/A modified fibres significantly increases the tenacity and the Young´s modulus of drawn fibres. It is the result of a significant increase in total average orientation of macromolecular chains of polymer matrix and orientation of macromolecular chains in surface layers (Table 5 - Δn, c), crystalline portion β also the crystallinity index of PP matrix (Table 5 - β, I_k) of drawn nanocomposite fibres.

With increased pigment A content in the mass of drawn PP/A modified fibres slightly decreases the tenacity (up to 8%), the Young’s modulus (up to 10%) and slightly increases the elongation (up to 20% absolute) of drawn modified fibres (Table 8).

Figures 3a and 4a show that all prepared PP/A modified fibers under the daylight D65 are white. Under the UV lamp there is only unmodified PP (Figures 3b and 4b) not shiny, while the modified PP fibres with photoluminescent pigment A turn to blue. Color intensity increases as the content of photoluminescent pigment A in modified PP fibres is increased. It is evident from Figures 3b and 4b that even the lowest pigment A content (about 0.01 wt.%, samples 2 from left to right) provides a clearly visible color change under the UV lamp.



a) b)

Figure 3 The influence of photoluminescent pigment A with content 0.01; 0.05; 0.10 and 0.30 wt.% on the color performance of undrawn PP/A modified fibres compared with unmodified PP fibre (first from the left) under daylight D65 (a) and under a UV lamp (b)

a) b)

Figure 4 The influence of photoluminescent pigment A with content 0.01; 0.05; 0.10; 0.20 and 0.30 wt. % on the color performance of drawn PP/A modified fibres compared with unmodified PP fibre (first from the left) under daylight D65 (a) and under a UV lamp (b)

4 CONCLUSION

The results from the study of the spinning, drawing, supermolecular structure and mechanical properties of modified PP/M-HNT nanocomposite fibres presented in this article have showed that the modified nanocomposite system PP/modified halloysite is fibre forming using discontinuous technological process in the whole evaluated range 0.05-1.50 wt.% of modified halloysite nanoparticles. The technological conditions for stable spinning and drawing were found. The basic dependences of the influence of modified nanoadditive content and uniaxial deformation on the supermolecular structure parameters and basic mechanical properties of undrawn and drawn modified nanocomposite PP fibres were evaluated. Addition of modified halloysite into PP fibres does not influence significantly the total average orientation of macromolecular chains of polymer matrix, at the same time reduces the crystallinity, as well as the conformational regularity of crystalline regions of oriented nanocomposite fibres. This led to the slight decrease in the tenacity (up to 15%), the elongation (up to 15% absolute) and the Young's modulus (up to 10%) of drawn nanocomposite fibres. Influence of content 0.05-1.50 wt.% of modified halloysite by the photoluminescent pigment A (M-HNT) on the supermolecular structure and mechanical properties drawn PP fibres is practically comparable with the influence of content 0.01-0.30 wt.% of photoluminescent pigment A in drawn PP fibres.

An important result is also the finding that the color performance under the UV light is clearly visible even at lowest modified halloysite content (0.05 wt.%) in modified PP/M-HNT nanocomposite fibres. Color intensity increases as the content of modified halloysite M-HNT in nanocomposite PP fibres is increased. Their color performance under the UV lamp there is comparable with the color performance of PP fibres modified by the photoluminescent pigment A with content of 0.01-0.30 wt.%. Therefore, it can be used as a tool for protection of original PP fibres and textile products.

Based on the obtained results it can be stated that the evaluated nanoadditive halloysite nanoclay proves to be a potential carrier of chemically and biologically active modifying substances for PP nanocomposites, including nanocomposite PP fibres with acceptable impact on structure and mechanical properties of modified nanocomposite fibres.

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5 REFERENCES

1. An.: Global fiber production, Man-Made Fiber Year Book 2017, 67, 2017, pp. 27-29
2. An.: Global fiber production, Chemical Fibers International, 67(4), 2017, pp. 195-197
3. Engelhardt, A.: Analysis of per capita fiber consumption, International Fiber Journal, 27(5), 2013, pp. 4-8
4. An.: Man-made fiber production 2020, Chemical Fibers International*,* 63(1), 2013, p. 20
5. Purvis, C.: Challenges in the global man-made fibers market, Proceedings of 49th Dornbirn Man-Made Fibers Congress - Congress-Guide, Dornbirn, September 2010, p. 48
6. De Schrijver, I. et al: Nanotechnology in demanding textile applications, Proceedings of 48th Dornbirn Man-Made Fibers Congress - Congress-Guide, Dornbirn, September 2009, p. 63
7. Sezen, M.: Nanotechnology and nanotextiles: technologies, markets, economics and future trends, Proceedings of 48th Dornbirn Man-Made Fibers Congress - Congress-Guide, Dornbirn, September 2009, p. 66
8. Joussein, E. et al: Halloysite clay minerals – A review, Clay Minerals, 40(4), 2005, pp. 383-426, ISSN 0009-8558
9. Du, M. et al: Newly emerging applications of halloysite nanotubes: A review, Polymer Int., 59(5), 2010, pp. 574-582
10. Lvov, Y; Abdullayev, E: Functional polymer-clay nanotube composites with sustained release of chemical agents, Progress in Polymer Science, 38(10-11), 2013, pp. 1690-1719
11. Khunová, V. et al: The effect of halloysite modification combined with in situ matrix modifications on the structure and properties of polypropylene/halloysite nanocomposites, eXPRESS Polymer Letters, 7(5), 2013, pp. 471-479
12. Liu, M et al: Recent advance in research on halloysite nanotubes-polymer nanocomposite, Progress in Polymer Science, 39(8), 2014, pp. 1498-1525