HALLOYSITE NANOTUBES MODIFIED BY REPELLENT IN POLYPROPYLENE FIBRES: INFLUENCE ON SUPERMOLECULAR STRUCTURE AND MECHANICAL PROPERTIES

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Abstract: *Nowadays, there is a growing request for smart fibres therefore modification of classic fibre types is essential. Modification of the mass or surface of fibres by nanotechnologies is one of the most prospective ways how to ensure the special properties of clothing and technical textiles. This article is focused on the study of modified halloysite nanotubes by repellent (HN-R) used in polypropylene fibres (PP). The halloysite nanotubes are natural nanoadditive with porous inner surface which can be used as the carrier of chemically and biologically active agents. The influence of different content of modified halloysite nanotubes in undrawn and drawn nanocomposite polypropylene fibres on the supermolecular structure (birefringence, sound velocity in fibres, and crystallinity index), fineness and basic mechanical properties (Young´s modulus, tenacity at break and elongation at break) was investigated. The obtained experimental results of nanocomposite fibres were compared with results of supermolecular structure and mechanical properties of PP fibres without additive content prepared under the same technological conditions.*

Keywords: *halloysite nanotubes, PP nanocomposite fibres, structure, mechanical properties.*

1 INTRODUCTION

Linear polypropylene (PP) is widely used thermoplastic material because it offers a unique combination of desirable chemical and physical properties, recyclability and low cost. The advantages of PP are: the high flexural strength as a consequence of semicrystalline nature, high resistance to moisture, good chemical resistance over a wide range of bases and acids, good impact strength and good fatigue resistance, and also a good electrical resistance [1-3]. However, PP lacks the melt strength and strain hardening in extensional flow required for many industrial processes as well as the absence of functional groups and low polarity makes PP difficult to dye. From chemical point of view PP is susceptible to oxidation and UV degradation; it has a high flammability and poor resistance to chlorinated solvents and aromatics [4-6]. For above mentioned properties there is still much scientific and industrial interest in modifying PP for improving its processability and properties required for more demanding applications [7, 8]. Polypropylene except to the conventional plastic applications also lends itself well in fiber applications including: ropes, carpets, upholstery, clothing what gives it a wider range of uses [3, 9]. Although the fibre production has experienced the slowest growth in the last 3 years to about 106 million tons, the man-made fibre business still continues its 10-year expansion in spite of the worsening of economic climate. For example, the filament yarns recorded the highest grow rate in 3 years to 48 million tons (PET +4.0%, PA -0.5%, CV +1.8%, PP +1.5%) [10]. This is largely due to much research which has been done in the field of fibres modification including also PP fibres. Fibre manufacturers must keep pace with the development of new polymer modifications and combinations, enabling such further functionalization of the product. The man-made fibre market needs new “intelligent” materials to continue with its growth [11].

One of the most promising ways how to ensure sophisticated properties of textiles is modification of polymer matrix by nanoparticles during fibre extrusion. Procedure, how mono- or multi- functional properties of fibres can be achieved even at low concentrations of nanoadditives, which is also very beneficial in economic terms [12]. Nanocomposite systems based on natural layered silicates, particularly montmorillonite and halloysite belongs to the most significant studied polymer nanocomposites [13-15]. Halloysite nanotubes (HN) are types of naturally occurring 1:1 clays with nanotubular structures and similar chemical composition to kaolin.

Due to various characteristics such as nanoscale lumens, high length to diameter ratio, relatively low hydroxyl group density on the surface, etc., numerous exciting applications have been discovered for this unique clay. The results of studies suggest that these nanocomposites exhibit remarkable performance such as reinforcing effects, enhanced flame retardancy and reduced thermal expansion [15]. The shape of halloysite – the hollow nanotubes with the porous inner surface, can be used as the carrier of chemically and biologically active agents [16].

In our research we used the synthetic compound DEET (N,N-diethyl-meta-toluamide) as the most effective and widely used insect repellent (R) in the world [17].

In this study, the influence of halloysite nanotubes content modified by repellent (HN-R) together with uniaxial deformation on the supermolecular structure as well as basic mechanical properties of polypropylene fibres was investigated. The repellent lost by washing were also investigated. The undrawn and drawn PP fibres modified with HN-R were prepared by discontinuous technological process of spinning and drawing. Obtained results of modified PP fibres were compared with PP fibres without HN-R nanoadditive prepared under the same technological conditions.

2 EXPERIMENTAL AND METHODS

2.1 Materials

Isotactic granulated polypropylene (PP), produced by Slovnaft Company, Slovak Republic, with MFR 27.6 g/10 min (230°C/2.16 kg) and nanoadditive - halloysite nanotubes 685445 modified by repellent N,N-diethyl-m-toluamide (HN-R), prepared by company A1Synth, Ltd., Slovak Republic, were used. The content of repellent (R) inside the hollow nanotubes was 20 wt.%. The masterbatch with 10 wt.% of HN-R, developed by Research Institute for Man-made fibres, a.s. Svit, where Elvax 150W (ethylene-vinyl acetate copolymer resin) produced by DuPont Packaging & Industrial Polymers (USA), was used as a polymer carrier of HN-R during the fibre preparation process.

Preparation of modified nanoadditive halloysite nanoclay 685445 by repellent N,N-diethyl-m-toluamide (HN-R)

The halloysite nanotubes modified with repellent (HN-R) was prepared as follows:

Repellent was dried in the three steps before modification of halloysite nanotubes (HN). HN was activated before modification in vacuum dryer under pressure 0.1 mbar and temperature 60°C during 8 hours. Subsequently, HN was modified as follows: the activated halloysite in dry diethyl ether was stirred in a sulphonation flask by a mechanical stirrer under an argon atmosphere. Repellent was slowly added dropwise in dry diethyl ether after 30 min. The contents were stirred at slow speed for 60 minutes. The contents of the flask were transferred to an argonated closed frit and the solvent was allowed to flow slowly into a round flask of so-called "Schlenk method". After filtration, the solvent was again poured onto a frit. Finally, the solvent was filtered off, the filter cake was washed with dry diethyl ether and dried on a rotary evaporator. The resulting sample was dried in a vacuum oven. From the resulting experimental measurements, adsorption of additives about 20% into activated halloysite was evident.

2.2 Fibre preparation

The modified PP fibres with content of HN-R from 0.25 to 2.00 wt.% (PP/HN-R) from mechanical mixture of PP granulated polymer and 10 wt.% masterbatch HN-R were prepared using the classical discontinuous process of spinning and drawing. The laboratory discontinuous line has an extruder with diameter of D=32 mm, with a discontinuous one-step drawing process. The constant processing conditions - spinning temperature of 220°C, spinning die plate of 25 holes with diameter of 0.3 mm, final spinning process speed of 1500 $m.min^{-1}$, the drawing ratio λ=2.0, the drawing temperature of 130°C and final drawing process speed of 100 $m.min^{-1}$ were used.

2.3 Methods

The fibre birefringence - total orientation of fibres

The orientation of macromolecular chains in fibre expresses the level of anisotropy of oriented polymer system (fibre). The total orientation of prepared unmodified and modified PP fibres was evaluated using polarization microscope DNP 714BI. The refractive indexes of light in fibre axis ($n_{\|}$) and in perpendicular direction of fibre ($n_{\perp}$) were determined. From refractive indexes of light the fibre's birefringence was calculated according to equation 1:

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

The sound speed in fibres

The sound speed in fibres is given by the ratio of fibre length and time needed for transfer of acoustic nodes across this length (expressed in $km.s^{-1}$). It is dependent on internal structure of fibre arrangement (expressed by supermolecular structure parameter) and may be served as a measure of fibre anisotropy. The sound speed in fibres was measured by Dynamic Modulus Tester PPMSR.

Crystallinity index (FT-IR)

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} (*Ai840*) characterizing the regularity of macromolecular chains segments arrangement and integrated absorbance of absorption band of 2723 cm^{-1} (*Ai2723*) as the internal standard influencing the degree of crystallinity, (Equation 2):

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

Crystallinity index of modified PP/HN-R fibres and unmodified PP fibres was evaluated by FT-IR spectrophotometer 8400 Shimadzu.

Mechanical properties of fibres

The mechanical properties (tenacity at break, elongation at break and Young's modulus) of unmodified and modified PP fibres were measured using Instron 3343 equipment (USA) in accordance with the STN EN ISO 2062:2010. A gauge length of 125 mm and clamping rate of 500 mm/min were used. The average of at least 10 individual measurements was used for each fibre. The fineness was measured in accordance with the STN EN ISO 2060:1998.

Washing test

For estimation of repellent stability in fibre we determined the weight loss of repellent after 5 and 20 washes. The washing conditions were: temperature 40°C, concentration of washing agent 5 g/l and washing time 30 min. After washing fibres were rinsed two times in distilled water, then in flowing water and finally they were air-dried.

The weight loss (*UR*) of repellent after the washing procedure was calculated as the weight difference between weight before washing m_0 and weight after washing *m* (5 and 20 washes) from 10 repetitions for one fibre according to the following equation 3:

$$UR = \frac{m_0 - m}{m_0}.100 \quad (3)$$

For reliable estimation of repellent with nanotubes in modified PP/HN-R fibres there were determined the relevant weight loss calculated as difference between final weight loss of drawn modified PP/HN-R fibre and final weight loss of drawn PP standard fibre including also the soluble amorphous or low molecular part of PP.

3 RESULTS AND DISCUSSION

Stability of the spinning and drawing process of the studied system PP/HN-R in concentration range of HN-R 0.25 - 2.0 wt.% was evaluated and compared with stability unmodified PP standard.

It was found that the studied system PP/HN-R (spinning speed of 1500 $m.min^{-1}$) is fibre forming in the whole range of HN-R concentration and comparable with stability of unmodified PP standard, but process is stable only to 1 wt.% HN-R, over this content the slight odor under spinneret was felt. It was caused by the release of the repellent from halloysite nanotubes at higher HN-R content in PP matrix.

For following discontinued drawing process and the next evaluations only concentration range of HN-R from 0.25 to 1.0 wt.% in PP matrix of the studied system PP/HN-R was used. The drawing process of modified PP/HN-R fibres on the drawing ratio λ=2.0 was stable and comparable with stability of unmodified PP standard fibre.

By spinning and drawing processes PP/HN-R fibres were prepared to study their supermolecular structure parameters and basic mechanical properties which were compared with the unmodified PP standard.

Figures 1 and 2 show the effect of various content of halloysite nanotubes modified by repellent on the supermolecular structure parameters of undrawn and drawn modified PP fibres.

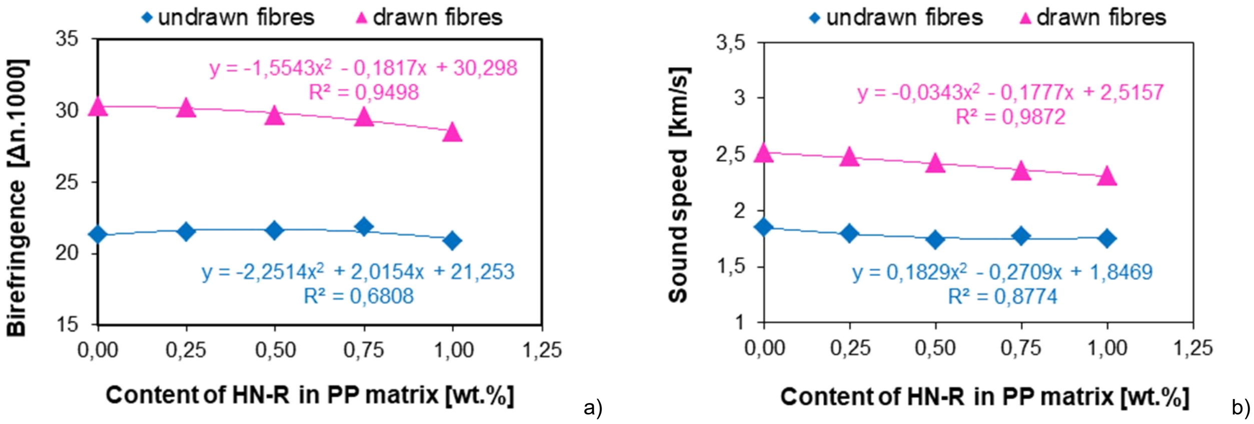


Figure 1 Dependence of birefringence (a) and sound speed (b) of undrawn and drawn (λ=2.0) modified PP fibres on halloysite nanotubes modified by repellent (HN-R) content

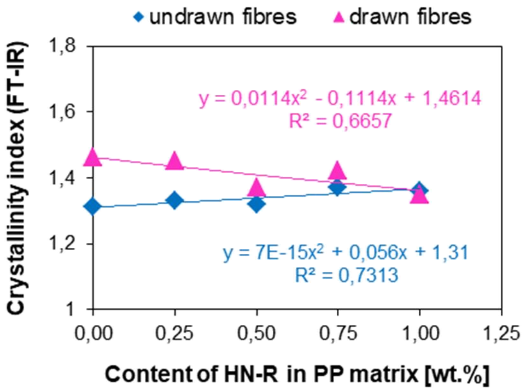


Figure 2 Dependence of crystallinity index I_k of undrawn and drawn (λ=2.0) modified PP fibres on halloysite nanotubes modified by repellent (HN-R) content

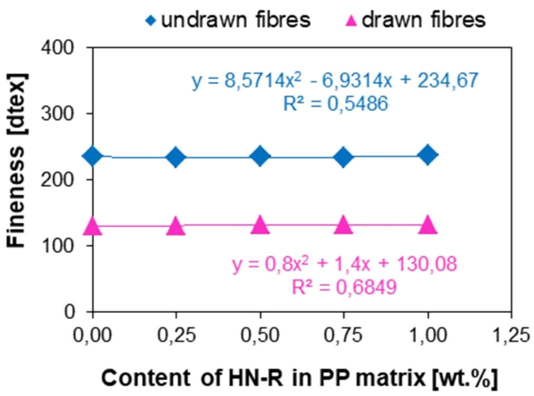
In case of undrawn modified PP fibres the total average orientation of macromolecular chains segments (birefringence) due to growing content of HN-R in the PP matrix was practically unchanged up to 0.75 wt.% content of HN-R. On the other side a slight decrease in birefringence with increasing HN-R content in PP fibers was observed in drawn fibers (Figure 1a) what can be the result of the steric braking effect of halloysite nanotubes modified by repellent on the orientation of macromolecular chains segments in the polymer matrix in the direction of fibre axis during the drawing process.

Similarly, also decrease of the orientation of PP macromolecular chains segments in surface layers (sound speed; Figure 1b) with growing content of HN-R significantly have been showed in drawn PP/HN-R fibres and in undrawn PP/HN-R fibres sound speed was slightly decreased only in comparison with unmodified PP standard.

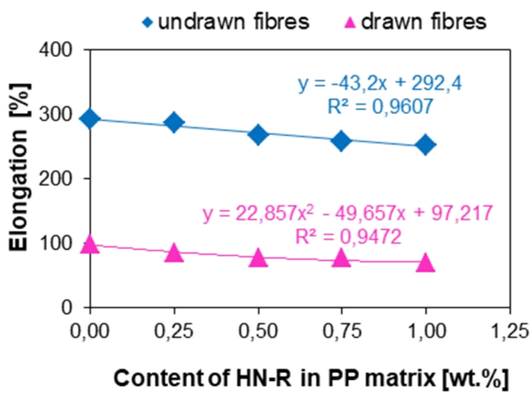
From Figure 2 it is evident that the fraction of crystalline phase (crystallinity index FT_{IR}) of undrawn PP/HN-R fibres is slightly growing with an increase of nanoadditive content. It can be the result of nucleating effect of HN-R particles on the PP matrix in the spinning process. In contrary, due to uniaxial deformation occurs the crystalline phase fraction is decreased in PP/HN-R fibres, what may be caused by steric braking effect of halloysite nanotubes modified by repellent as mentioned above.

Figures 3 and 4 show the effect of various HN-R content on the basic mechanical properties of undrawn and drawn modified PP/HN-R fibres. It was found that the content of nanoadditive HN-R from 0.25 to 1.0 wt.% in the PP matrix of fibre does not affect the fineness of undrawn and drawn modified PP/HN-R fibres (Figure 3a).

Tenacity at break respective Young's modulus of undrawn modified PP/HN-R fibres slightly decreases (up to about 20% and up to about 30%) with increasing content of modified nanoadditive, while the elongation of fibres decreases slightly (up to 40% absolute) Tenacity at break and Young's modulus for drawn modified PP fibres also decrease with growing content of modified nanoadditive (up to max 25%) as well as their elongation at break (up to approximately 30 % absolute). The decline of elongation at break together with tenacity at break in undrawn and drawn modified PP/HN-R fibres with growing content of modified nanoadditive can be a result of rising content of ethylene-vinyl acetate copolymer matrix of masterbatch in modified PP fibres.

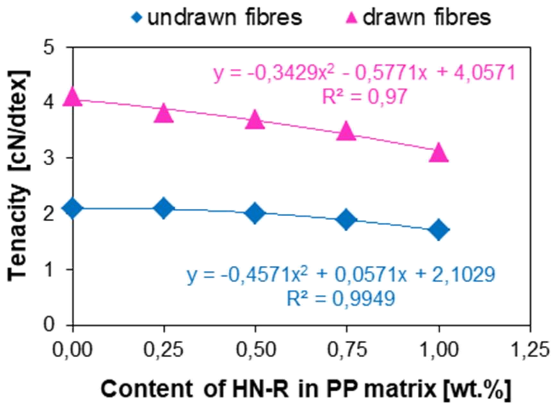


a)



b)

Figure 3 Dependence of fineness (a) and elongation at break (b) of undrawn and drawn (λ=2.0) modified PP fibres on halloysite nanotubes modified by repellent (HN-R) content



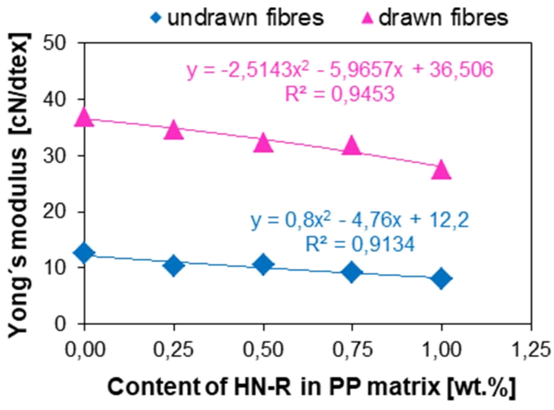


Figure 4 Dependence of tenacity at break (a) and Young's modulus (b) of undrawn and drawn (λ=2.0) modified PP fibres on halloysite nanotubes modified by repellent (HN-R) content

The change of mechanical properties is also governed by the drawing process (see Figures 1-4). Uniaxial deformation of undrawn modified PP/HN-R fibres significantly increased the total average orientation of macromolecular chains segments (birefringence, Figure 1a) up to 42% and the orientation of PP macromolecular chains in surface layers (sound speed, Figure 1b) up to 38%, causing higher tenacity at break about twice (Figure 4a) and Young's modulus of elasticity about three times (Figure 4b) over the entire evaluated range of HN-R nanoadditive content.

The crystallinity index has different of trends curves undrawn and drawn fibres with increasing content of modified nanoadditive (Figure 2).

In the case of undrawn fibres the growing tendency of curve was observed with increasing content of modified nanoadditive and in the case of drawn fibres the decreasing tendency with increasing content of HN-R was observed. These results show that only up to 1 wt. % of HN-R the uniaxial deformation has positive influence on increase of the crystallinity index. In this point the curves intersect. On the other hands fall of elongation at break (Figure 3b) due to uniaxial deformation was expected, because it's generally known, that the elongation at break is reciprocal value to tenacity at break. The fineness (Figure 3a) also decreased due to uniaxial deformation of undrawn fibres.

From the obtained results it is evident, that the mechanical properties of modified PP/HN-R fibres are in good correlation with their supermolecular structure parameters.

From industrial point of view, it is important to know what quantity of a repellent is released from the fibers after washing, therefore washing test of modified PP/HN-R fibres was performed. Percentual weight decrement was calculated after 5 and 20 washing cycles (Table 1). It is evident that loss weight after 5 and 20 washing cycles was observed already at PP standard fibre. It could be related to the content of finishes as well as oligomers of polypropylene which can also migrate into the water. For that reason, the reduced weight loss was calculated and was supposed that reduced loss weight of fibres during their washing tests is connected with loss of repellent content from drawn modified PP/HN-R fibres. But from the experimental results it is obvious that the values of reduced weight loss are almost higher as the values of repellent content in fibres (Table 1). This is associated with further release of finishes as well as oligomers of polypropylene, therefore loss of fibres weight during their washing is not directly proportional by the content of repellent in halloysite nanotubes. It is evident from reduced weight loss that the part of repellent stayed in nanotubes halloysite after spinning process.

Table 1 Relative weight loss after 5 and 20 washes of modified PP/HN-R fibres and unmodified PP standard fibre

Carrier/ modified nanoadditive content	Repellent content in modified PP fibres	5 washes		20 washes	
		Weight loss [%]	Reduced weight loss [%]	Weight loss [%]	Reduced weight loss [%]
PP standard	-	0.72	-	0.61	-
PP/HN-R/0.25%	0.05	0.91	0.19	0.76	0.15
PP/HN-R/0.50%	0.10	0.76	0.04	0.77	0.16
PP/HN-R/0.75%	0.15	0.75	0.03	0.74	0.13
PP/HN-R/1.00%	0.20	0.99	0.27	0.80	0.19

Weight loss [%] is final weight loss of fibre calculated after washing. Reduced weight loss [%] is calculated as difference between final weight loss of drawn modified PP/HN-R fibre and final weight loss of drawn PP standard fibre

4 CONCLUSION

The nanoadditive - halloysite nanoclays modified by repellent, has been prepared with the content of repellent to 20 wt.%. Influence of different content (0.25 - 2.0 wt.%) of modified nanoadditive HN-R in PP matrix during the discontinuous spinning and drawing process was investigated and compared with the stability of unmodified PP standard. It was found that content of HN-R only up to 1 wt.% in PP matrix of the studied system PP/HN-R (spinning speed of 1500 m.min^{-1}) is fibre forming and stable but over this content the slight odor under spinneret was felt. By discontinued drawing process at drawing ratio λ=2.0 and in the concentration range of HN-R from 0.25 wt.% to 1.0 wt.% in PP matrix the drawn PP fibres were prepared for evaluation of supermolecular structure and basic mechanical properties.

Addition of modified halloysite HN-R into PP matrix led to the decrease in structure parameters (birefringence, sound speed and crystallinity index) as well as in basic mechanical properties (tenacity at break, elongation at break and Young's modulus) of drawn modified fibres in comparison to drawn unmodified PP standard fibre. In undrawn modified PP fibres the results are not so unambiguous.

The content of repellent in PP modified fibres has been verified by washing process. Reduced loss weight showed that halloysite nanotubes protected some amount of repellent during spinning process because the final weight loss of modified PP fibres is higher than final weight loss of PP standard fibre, but on the other side it was found that loss of fibres weight during their washing tests is not directly proportional by content of repellent in halloysite nanotubes. Based on our result we can state that the halloysite nanotubes protect components inside hollow tubes.

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