

Comparison of Colour Properties of Polypropylene and Poly-(Lactic) Acid Fibres Dyed With Photoluminescent Dye

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Abstract

Every manufacturer wants to protect their textile products and their brand. A possible solution is, for example, the insertion of fibres with special pigments visible under irradiation by UV light into the final product. The paper focused on the study of the structure and colourimetric properties of polypropylene (PP) and poly-(lactic) acid (PLA) fibres modified with photoluminescent dye and halloysite (HNT) modified with photoluminescent dye. The photoluminescent dye and HNT modified with photoluminescent dye affected the structure of PP and PLA fibres differently. Increasing the HNT content up to 0.15 % increased the orientation of the PP fibres. In the case of PLA fibres, the increased content of photoluminescent dye in PLA fibres increased their orientation in the observed concentration area. PLA-based knitted fabrics showed better light stability, where there was no visible degradation of the knitted fabric, only its darkening. Likewise, PLA-based knitted fabric showed luminescence in UV light even after accelerated light aging.

Keywords

polypropylene and poly-(lactic) Acid Fibres, photoluminescent dye, colour properties, mechanical properties and structure.

1. Introduction

In our current times branding is typical. People like brands. However, many branded products of higher value are facing the problem of counterfeiting, hence these products are more imitated and copied. Some copies are hard to be distinguished from originals at first glance and can only be recognised by an expert. Every manufacturer wants to protect their product and their brand. One of the options is to incorporate protective elements into the product, ones which would also not disturb the product or its visual impression. One of the solutions is, for example, the insertion of fibres with special pigments which are only visible under irradiation by light of a certain wavelength. The protective element can be applied either to the whole product or to a particular location or brand logo.

These special fibres must be made from material which must be resistant and suitable to form a mixture with special additives such as photoluminescent pigments. Polypropylene (PP) is very suitable for preparation of photoluminescent fibres. PP is one of the

plastic materials most used. Polypropylene is a semi-crystalline thermoplastic polymer with wide applications. PP has very good mechanical properties, it can be easily processed at low costs, and it is resistant to externalities. Due to its properties, it is suitable to be used as a polymer matrix for the preparation of fibres incorporating special pigments [1]. On the other hand, the resistance of polymers has a negative impact on the environment due to the growing production of polymers and subsequent accumulation of waste. The increasingly serious environmental problems require the replacement of synthetic polymers. As an alternative, biodegradable polymers and polymers from renewable sources can be applied. Biodegradable polymers can be defined as polymers that decompose into low-molecular products by the action of microorganisms and their enzymes. By combining the production of polymers from renewable sources and their biodegradability, the possibility of extending the lifecycle of plastic products has emerged [2-6].

Poly-(lactic) acid (PLA) is a highly universal, biodegradable, aliphatic

polyester derived from 100% renewable resources. It is a thermoplastic polymer which may be partially crystalline or completely amorphous depending on the polymer backbone stereochemistry. It is characterised by low flammability and high strength, is colourless and colour-stable, as well as resistant to UV radiation [7]. PLA is a unique polymer which, in many ways, behaves like polyethylene terephthalate (PET) but also has many similarities to polypropylene (PP) [8]. Many published works deal with the dyeing of PLA threads [9-14]. PLA is a polyester of hydrophobic character because disperse dyes are used for their dyeing as well.

The incorporation of photoluminescent pigments represents a cost-acceptable solution for the protection of original products. Photoluminescence is a form of luminescent radiation where materials emit light of specific wavelengths [15]. Based on the time of radiation emissions, photoluminescence can be divided into fluorescence with a short luminescence decay time (a few nanoseconds) and phosphorescence, which has a long luminescence decay time (a few minutes

or hours) [16]. Today, it is possible to prepare inorganic photoluminescent pigments which can emit light in a precisely defined pattern for the applications required [17]. Fluorescent dyes are used in various applications, such as in solar systems, lasers, LEDs and for the dyeing of textiles [18].

The most promising direction for providing the special properties of fibres for garments and fabrics is fibre modification with various additives or nanoadditives (surface modification and modification in the mass). Additives and nanoadditives are substances that in some way improve certain properties of another substance or mixture. One of the most widely used nanoadditives is currently halloysite (HNT). Halloysite has a high degree of biocompatibility and very low cytotoxicity and is therefore suitable for use in the textile, medical and agricultural industries [19]. Halloysite is natural hydrated aluminosilicate clay of hollow cylindrical geometry. Because of this structure, it is used as a carrier in most applications [20].

On the basis of the similarity of polypropylene and poly-(lactic) acid, these two polymers were selected as a matrix for special fibres containing photoluminescent dyes. As a dye, HNT modified with special photoluminescent dye inside its tube was applied. It is believed that the dye incorporated in halloysite could have greater stability in the fibre in terms of the colouristic characteristics together with a little change in mechanical properties. The use of unmodified and modified halloysite with photoluminescent dyes can be very significant in terms of the development of new functional polymeric nanocomposite fibres.

The aim of this study was to observe the structure, mechanical and colourimetric properties of PP and PLA fibres modified with photoluminescent dye and HNT modified with photoluminescent dye. This paper also presents a comparison of PP and PLA fibres containing photoluminescent dye and HNT modified with photoluminescent dye regarding the stability after exposure to light.

2. Experimental Part

2.1. Materials

2.1.1. Characterisation of used materials

In this paper, pure polypropylene TATREN HT 2511 (PP, produced by Slovnaft Co., Slovakia) prepared by Ziegler-Natta catalyst with the melt flow index MFI = 27.6 g/10 min, and poly-(lactic) acid INGENO™ Biopolymer 6202D (PLA, produced by NatureWorks LLC., USA) with MFI = 15-30 g/10 min. at 201°C were used for the preparation of PP and PLA fibres, respectively. Polymer fibres were dyed by photoluminescent dye only, or by HNT nanotubes modified with photoluminescent dye. Radglo CFF-X-02 UV Blue (CF, produced by Radiant Colour NV, Belgium) was applied as an ultra-violet responsive fluorescent dye. Fluorescent nanotubes (HNTCF) were prepared using halloysite (HNT, Aldrich Chemistry, product USA) $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2 \text{H}_2\text{O}$ nanotubes with a molecular weight of 294.19 g·mol⁻¹, diameter of 30-70 nm and length of 1-3 µm.

2.1.2. Modification of nanoadditive

Halloysite is an inorganic nanoadditive consisting of one-dimensional long nanotubes or fibrous crystals. Their structure allows modification by special additives (e.g. photoluminescent dyes) into nanotubes. Dissolved Radglo CFF-X-02 UV Blue (CF) dye was added to the activated HNT. After the dye absorption, the modified HNT was dried.

The modification of HNT with CF was confirmed by ATR-FTIR analysis. In the FTIR spectrum of PP modified by HNTCF was observed an absorption band at 1035 cm⁻¹, which corresponds to the Si-O stretching band of halloysite nanotubes (*Figure S1*. in supplement) [21].

2.1.3. Preparation of dyed PP and PLA fibres

The PP and PLA fibres modified with CF and modified HNTCF dye were

prepared in two steps – the preparation of masterbatches (PP/CF and PP/HNTCF as well as PLA/CF and PLA/HNTCF) and that of modified fibres. Masterbatches with an optimal concentration of additives (CF, HNTCF) in PP and PLA and the required filterability were prepared using a laboratory twin-screw extruder - Werner-Pfleiderer with a screw diameter of 28 mm, at a constant screw rotation speed of 250 min⁻¹. The extrudate was then cooled and pelletised.

The pellets of PP or PLA masterbatches were mechanically mixed with pure PP or PLA so that PP/CF, PP/HNTCF, PLA/CF and PLA/HNTCF mixtures with the required concentration (0.005, 0.01, 0.05, 0.1, 0.15, 0.2 and 0.3 wt %) of CF dyes or the modified HNTCF additive were obtained. These mixtures were further used to produce fibres.

PP fibres dyed in mass were prepared from individual mixtures of the PP and PP masterbatch using a laboratory line with a single screw extruder having a diameter of 32.0 mm, with a spinning nozzle of 2x25 holes of 0.3 mm diameter, at a spinning temperature of 220°C and final spinning process speed of 1500 m·min⁻¹. The fibres prepared were drawn at a drawing ratio of $\lambda=2.0$, at a drawing temperature of 130°C and final drawing process speed of 100 m·min⁻¹.

PLA fibres dyed in mass were prepared from individual mixtures of PLA and PLA masterbatch using a laboratory line with a single screw extruder having a diameter of 32.0 mm, with a spinning nozzle array containing 2x25 holes of 0.3 mm diameter, at a spinning temperature of 210°C, and final spinning process speed of 1500 m·min⁻¹. The fibres prepared were drawn at a drawing ratio $\lambda=2.0$ and at a drawing temperature of 80°C.

From the PP/CF, PP/HNTCF, PLA/CF and PLA/HNTCF fibres prepared, knitted fabrics were prepared on a knitting machine by a classic technique.

2.1.4. Accelerated aging of fibres

Light aging in the Q-SUN Xenon test chamber Xe-1-S (Q-Lab, Inc. Cleveland,

OH, USA) was performed under the following conditions: window glass filter, blackbody temperature - 65 °C; irradiance - 420 nm 1.1 W·m⁻²; E = 89 000 lx; irradiance in the region 300–800 nm 494 W m⁻², ageing time - 72 h.

2.2. Methods

2.2.1. Supramolecular structure

2.2.1.1. Fibre birefringence

The orientation degree of polymer chains in the fibre characterises the level of anisotropy of oriented polymers e.g. fibre. One of methods for determination of the orientation degree is the measurement of fibre birefringence (Δn) by the compensation method. The refractive indexes of light in the fibre axis as well as in the perpendicular direction of fibre were determined. From these values the fibre birefringence was calculated according to the equation (1):

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

where n_{\parallel} is the refractive index of light in the fibre axis and n_{\perp} the refractive index of light in the perpendicular direction of fibre.

2.2.1.2. Sound speed in fibres

The sound speed in substances depends on their internal structure arrangement. A higher arrangement of the substance structure gives a higher sound speed. It is used for determination of the level of fibre anisotropy characterising the supramolecular structure of fibres. The sound speed in fibres is obtained from the ratio of fibre length and the time needed for the transfer of acoustic nodes across this length (named c and expressed in km·s⁻¹).

The sound speed in dyed PP and PLA fibres was measured by a Dynamic Modulus Tester PPMR (USA).

2.2.2. Mechanical properties

The mechanical properties are represented by the tenacity at break - σ , elongation at

break - ε and Young's modulus - E_{γ} . The mechanical properties of dyed PP and PLA fibres were measured using Instron 3343 equipment (USA). Measuring conditions were a fibre 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, Young's modulus and elongation at break) were determined in accordance with Standard ISO 2062:1993.

2.2.3. UV-VIS spectroscopy

The reflectance spectra in the UV-VIS region (200 – 800 nm) were measured by a spectrophotometer CECIL-CE-3055 (Cecil Instrument Limited, Cambridge, UK), using an integration sphere. Calibration was performed with the white Spectralon® standard.

2.2.4. Colourimetric measurements

The CIELAB system was used to evaluate the colourimetric coordinates (a , b), and the lightness (L) of the samples by a spectrophotometer - Spectrodens (TECHKON GmbH, Königstein, Germany) with M0 measuring conditions. Colourimetric data were acquired with the application of D65 standard illumination and 10° standard observer.

The total colour difference ΔE_{ab} was calculated from the well-known Eq. (2) [22]:

$$\Delta E_{ab} = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2} \quad (2)$$

Where the L -axis gives the lightness, a white object has an L value of 100, and the L value of a black object is 0. The so-called achromatic colours, shades of grey, are on the L -axis. Chromatic colours are described using the axes in the horizontal plane. The a -axis is the green-red ($-a$, $+a$) axis and the b -axis goes from blue ($-b$) to yellow ($+b$). Each colour is represented by a colour point (L , a , b) in the colour

space. The total colour difference ΔE_{ab} is the colour difference between colours of the sample and the reference.

2.2.5. Luminescence characteristics

Luminescence properties were measured by an Aminco Bowman Series 2 spectrometer. The excitation light beam was at an angle of 20°, and the emission was recorded at - 70 °C from the surface normal. The band-pass of emission and excitation monochromator was set to 4 nm. The excitation and emission spectra were recorded for 6 repetitions at a speed of 20 nm·s⁻¹. Emission spectra were measured at a wavelength corresponding to the maximum excitation, and vice versa. In order to compare the intensity of luminescence between samples, the voltage at the photomultiplier was kept constant for all measurements.

3. Results and Discussion

3.1. Supramolecular structure and mechanical properties

A lot of products from the textile industry are imitated and copied. This causes financial losses and the possibility of using products with dangerous effects. One of the options for protecting products is incorporating fibres which after UV radiation are active. Our goal was the preparation of polypropylene and poly-(lactid) acid fibres dyed with photoluminescent dye and HNT modified with photoluminescent dye in mass with the required structure and mechanical and colour properties. It was necessary to compare the stability of the colour photoluminescent effect of the dye and dye incorporated in HNT used for the preparation of PP and PLA fibres.

In the first step we prepared undrawn PP and PLA fibres dyed with CF or HNTCF in the mass by classical discontinuous spinning from the melt at a spinning temperature of 220°C (PP) and 210°C (PLA) and final spinning process speed of 1500 m·min⁻¹. The fibres prepared

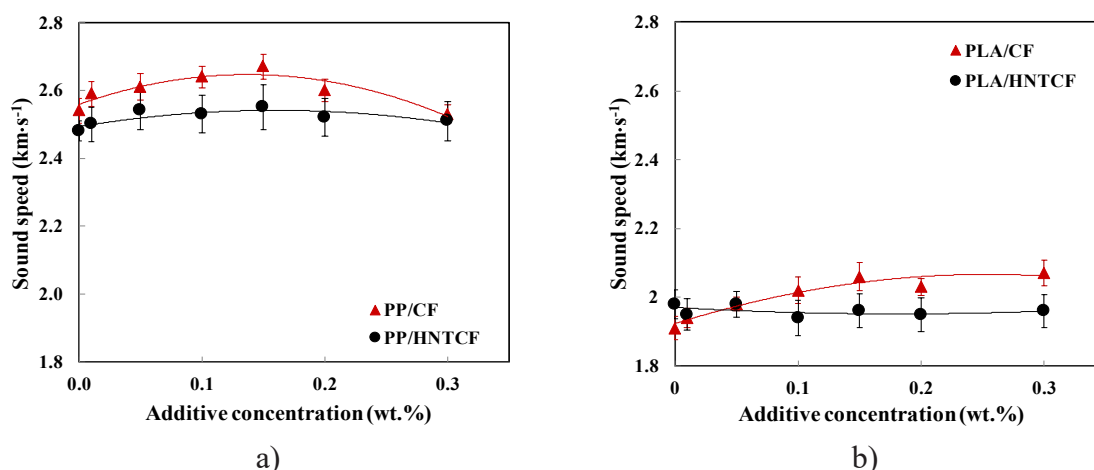


Fig. 1. Dependences of fibre sound speed on the concentration of CF and HNTCF in the PP (a) and PLA (b) fibres dyed in mass

were drawn at a drawing ratio of $\lambda=2.0$, at a drawing temperature of 130°C (PP) and 80°C (PLA), and at a final drawing process speed of 100 m·min⁻¹. The structure was observed based on the determination of the birefringence and sound speed and mechanical properties (tenacity and elongation at the break, Young's modulus) of the PP and PLA fibres prepared (Figures 1.-5.). The CF concentration in all fibres dyed with pure CF dye as well as HNT modified with CF dye was 0.005, 0.01, 0.05, 0.1, 0.15, 0.2 and 0.3 wt % dye in the fibre. The changes in the structure and mechanical properties, which are not the same for the PP and PLA fibres, were observed

The speed of sound in the fibres and birefringence are presented in Figure 1. and Figure 2. respectively. In PP fibres, both parameters increase with the concentration of CF and HNTCF additives within the range of 0–0.15 wt %. The change is more pronounced in the case of CF modified fibres. With a concentration above 0.15 wt %, the value of both parameters drops down to the level of pure PP fibres.

From the results it can be concluded that at their lower content, the CF and HNTCF additives improve the oriented structure of the dyed PP fibres. Even if the fibre speed and birefringence of the dyed PP fibres with a higher content of additives decrease the level of orderliness of the structure of the dyed PP fibres, it

does not fall below that of pure PP fibres (Figures 1.a and 2.a).

Another situation can be observed in the case of PLA fibres (Figures 1.b and 2.b). The fibre sound speed and birefringence of PLA fibres dyed with CF increased in the whole concentration range observed. The changes in the sound speed of PLA fibres with HNTCF is within the measurement error. More significant changes were observed in the birefringence of PLA fibres with HNTCF, which were about 10 %. The sound speed of fibres characterises only their surface orientation and the birefringence the orientation of the full bulk of the fibre cross-section. The effect of more inert inorganic particles of HNTCF is higher in the surface layers of the dyed fibres than in the full bulk dyed fibres. The effect of inert inorganic particles of HNTCF on the structure of modified PLA fibres is negligible in comparison with CF particles in the sound speed as well as in the birefringence.

Mechanical properties of PP and PLA fibres also differ in regard from types of additives, e.g. CF or HNTCF. Generally, additives of solid particles in the mass of oriented fibres make their tenacity at the break and elongation at break worse in comparison with pure PP or PLA fibres, as shown in Figures 3., 5.

The tenacity at break of PP fibres with CF as well as HNTCF decreases in the full concentration range in comparison with

the tenacity at break of pure PP fibres. The PP fibres with inorganic HNTCF particles have lower tenacity than the PP fibres with CF dye (Figure 3.a). This can be caused by the lower orientation ability of polymer chains in the area of particles, followed by the break of fibres. On the other hand, the fluorescent dyes, CF and HNTCF, do not cause distinct changes in the Young's modulus of the PP fibres with additives. The Young's modulus of PP fibres modified with HNTCF is a little higher than that of PP fibres modified with CF at a concentration of 0.1 wt % (Figure 4.a). The reinforced effect of inorganic particles was not confirmed. Taking into account mainly the elongation at break of the PP fibres observed (Figure 5.a) and variability of data obtained, it can be concluded that the additives used in the preparation of PP fibres do not change the mechanical properties. Generally, the tenacity at break decreases with increasing elongation at break. The elongation at break of the PP fibres prepared with CF and HNTCF is the result of the drawing of these fibres. The drawing process of the PP fibres prepared is blocked by additive particles in the bulk mass of fibres and orientation of polymer chains, or the crystal elements of these fibres are more pronounced.

The improved oriented structure of PLA fibres with CF and HNTCF, characterised mainly by higher birefringence, did not show in the mechanical properties of these PLA fibres (Figures 3.b, 4.b and 5.b). The change in mechanical properties

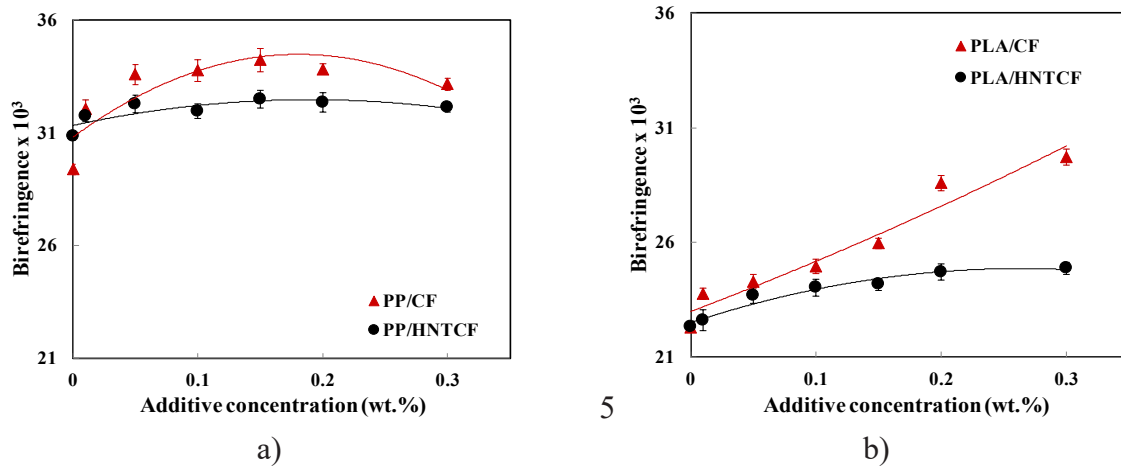


Fig. 2. Dependences of fibre birefringence on the concentration of CF and HNTCF in the PP (a) and PLA (b) fibres dyed in mass

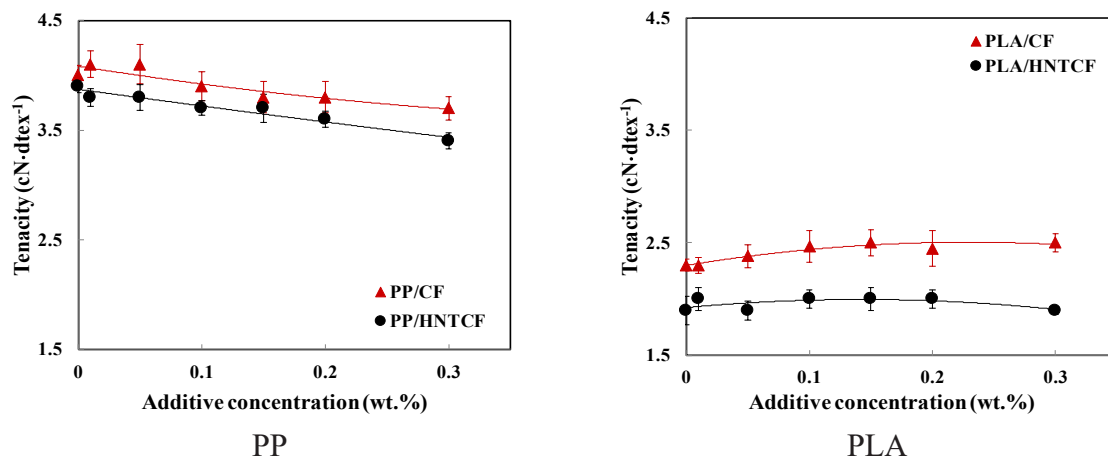


Fig. 3. Dependences of tenacity at break on the dye concentration of CF and HNTCF in PP (a) and PLA (b) fibres dyed in mass

– tenacity at break, Young's modulus and elongation at break – is in the range of measurement precision. The mechanical properties of PLA fibres with CF and HNTCF are comparable with those of pure PLA fibres.

From the results of structure and mechanical properties obtained, it is possible to state that the PP and PLA fibres prepared with fluorescent dye CF and HNT modified with CF have the required properties and comply with the processability requirements of fibres in textile technology.

3.2. Colourimetric properties

For evaluation of reflectance, colourimetric and fluorescent properties only knitted fabrics prepared from PP and

PLA fibres with the addition of 0.2 wt % of CF and HNTCF were selected.

In order to determine the light stability of the samples prepared, they were subjected to accelerated aging in a Q-sun chamber for 72 hours. This time could not be extended as the material degraded, especially for PP, which was associated with the decomposition of the material (*Figure 7*), which illustrates the appearance of aged PP and PLA knitted fabrics with and without the addition of CF and HNTCF additives. With respect to the appearance, no fluorescence was observed in the case of PP knitted fabrics after aging.

The samples were characterised by colourimetry (*Table 1*) and UV-VIS spectroscopy. The addition of fluorescent dye CF led to a change in the b^* coordinate

more into the blue region as well as to an increase in the L^* coordinate; the samples were lighter. Compared to samples dyed with CF only, those that contained HNT in addition to CF showed smaller colour difference between coloured and uncoloured samples.

Colourimetry and UV-VIS spectroscopy were used to evaluate the light stability of the samples. Significant changes in colour coordinates were observed during accelerated aging in the Q-sun chamber over 72 hours (see *Table 1*). In the case of both types of knitted fabrics without dye (PP and PLA), there was mainly a decrease in the L^* coordinate, which was associated with darkening of the samples; similar changes were recorded for PLA knitted fabrics with dye. In PP coloured knitted fabrics, there was a significant

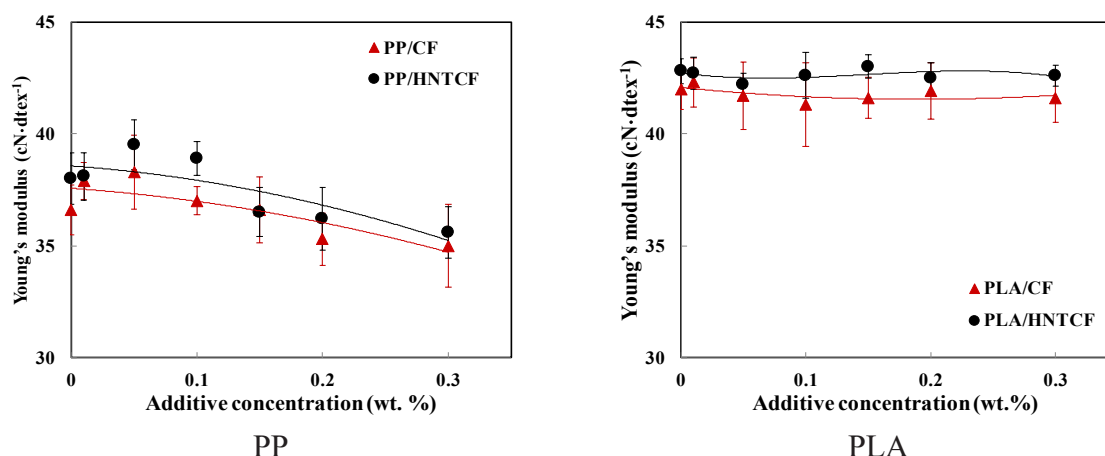


Fig. 4. Dependences of Young's modulus E_y on the dye concentration of CF and HNTCF in PP (a) and PLA (b) fibres dyed in mass

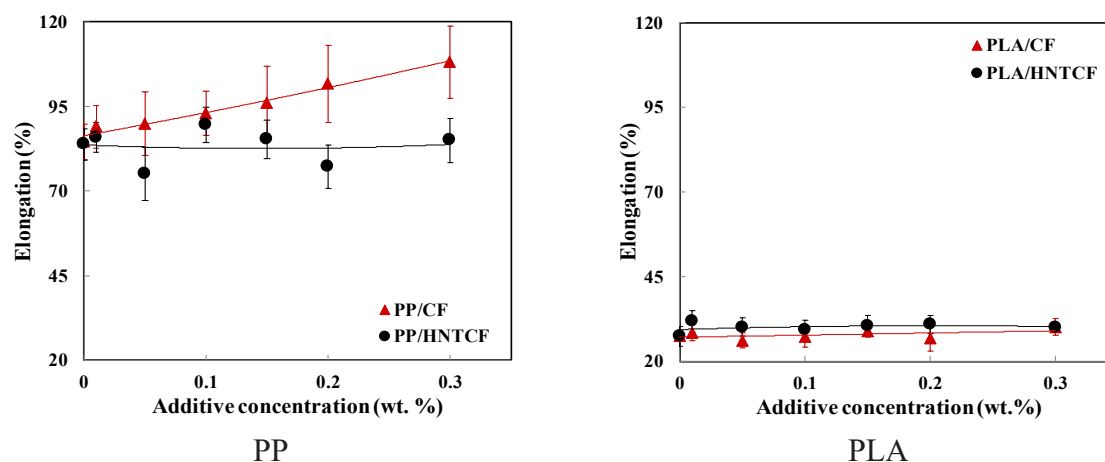


Fig. 5. Dependences of elongation at break e on the dye concentration of CF and HNTCF in PP (a) and PLA (b) fibres dyed in mass

Table 1. CIELab parameters (L , a , b) of PP and PLA knitted fabrics dyed in mass before (0 h) and after light ageing (72 h); $(\Delta E_{ab})_1$ represents changes between non-coloured and coloured samples before aging and $(\Delta E_{ab})_2$ represents changes due to aging

Sample	Unaged				aged			
	L	a	b	$(\Delta E_{ab})_1$	L	a	b	$(\Delta E_{ab})_2$
PP	79.3	0.12	-0.44		66.5	-1.43	-1.84	12.9
PP/CF	81.3	0.78	-3.9	4.05	78.1	-1.50	8.06	12.7
PP/HNTCF	80.3	0.2	-0.9	1.1	75.3	-1.14	5.87	8.5
PLA	75.8	-1.88	-2.40		72.3	-0.43	-0.99	4.3
PLA/CF	80.5	1.34	-4.87	6.2	71.9	0.75	-2.57	9.8
PLA/HNTCF	80.1	1.01	-3.7	5.3	65.5	0.93	-2.17	14.7

increase in the b^* coordinate associated with yellowing of the samples during aging. Although the addition of HNT resulted in a decrease in the ΔE_{ab} value compared to the coloured sample without HNT, it accelerated the degradation of PP (Figure 6). No degradation of the material was visually observed in the

PLA-based knitted fabric. However, in FTIR spectra an increase in carbonyl bands was observed, indicating oxidative degradation of the PP and PLA materials (see Supplement Figure S2 and S3).

Reflection spectra of aged and non-aged samples were also measured (Figure 7).

The addition of fluorescent dye caused a significant increase in reflexion for both PP and PLA knitted fabrics for wavelengths under 400 nm. with the values measured exceeding 1. This phenomenon is related to the emission of fluorescent dye in the fibres that is added over the reflectance of the sample

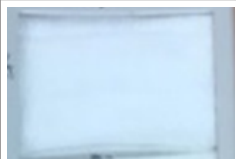
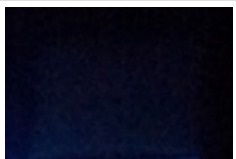

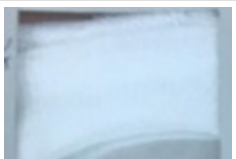





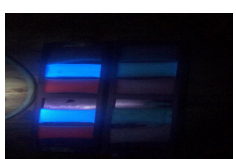


	Under visible light	Under UV light	Under UV light	Under visible light	
PP					PLA
PP/CF					PLA/CF
PP/CF/ HNT					PLA/CF/ HNT

Fig. 6. Samples under visible (outdoor fields) and UV light (indoor fields)

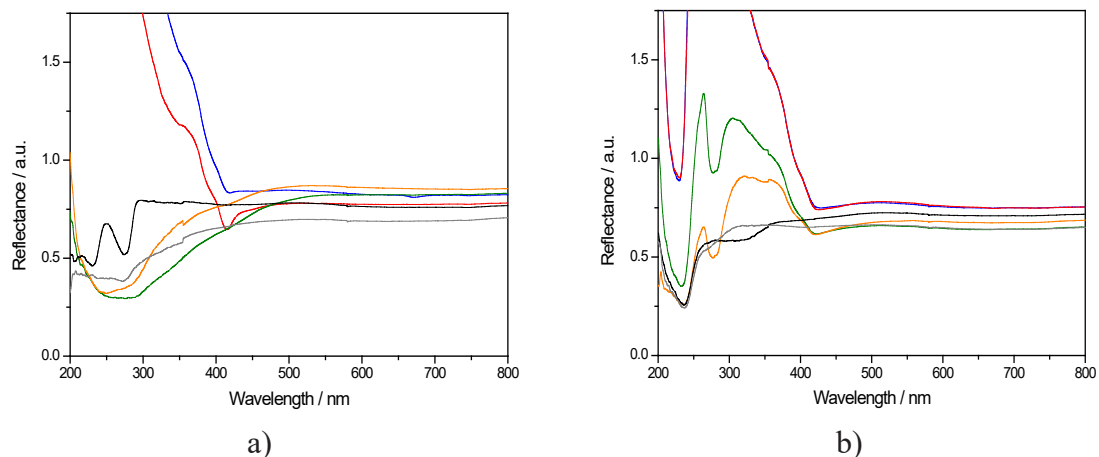


Fig. 7. Reflexion spectra of PP (a) and PLA (b) knitted fabrics without dye (not aged – black line, aged 72 h in the Q-sun chamber – gray line), with CF (not aged – blue line, aged 72 h in the Q-sun chamber – green line) and with CF and HNT (not aged – red line, aged 72 h in the Q-sun chamber – orange line)

measured. In this case fluorescent additives were excited by a deuterium lamp that is used as the radiation source in the spectrophotometer. We observed this phenomenon repeatedly and the reflexion depended on the amount of fluorescent dye added. During accelerated aging, the reflectance in the UV region decreases, indicating decomposition of the fluorescent additive. After 72 hours of aging, the reflectance of both types of dyed PP samples resembles the spectrum of aged polypropylene without fluorescent dye. In the case of PLA samples, the decrease in reflectance in the short wavelength region is not so strong. Even after 72 hours of accelerated aging, the

maximum wavelength of approximately 310 nm could be observed. In the case of PLA with CF a signal higher than 1 was obtained. We can state that aged coloured PP fibres show no fluorescence, while PLA fibres with CF fluoresce exhibit more significant fluorescence in coloured samples without halloysite. This fact is also confirmed in **Figure 6.**, where we can see a significant difference between coloured PP and PLA samples under a UV lamp.

Analysis of the luminescence spectra (**Figure 8.**) of the dyed fibres reveals that the excitation maximum of the textiles prepared is at 399 ± 1 nm, and the emission

maximum is at 433 ± 1 nm. The aging of PP fibres with fluorescent additives in the Q-sun chamber resulted in a reduction in luminescence to almost negligible values regardless of the presence of halloysite content. On the other hand, the decrease in luminescence in the case of aged PLA fibres is not as large. PLA unaged samples with halloysite content exhibit stronger luminescence than those without it. On the contrary, ageing by light has a stronger effect on PLA/HNTCF samples – the luminescence drops by about 50 %, whereas the luminescence of PLA/CF drops by only 20 %. The luminescence of aged PLA/CF samples is then higher than that of PLA/HNTCF samples.

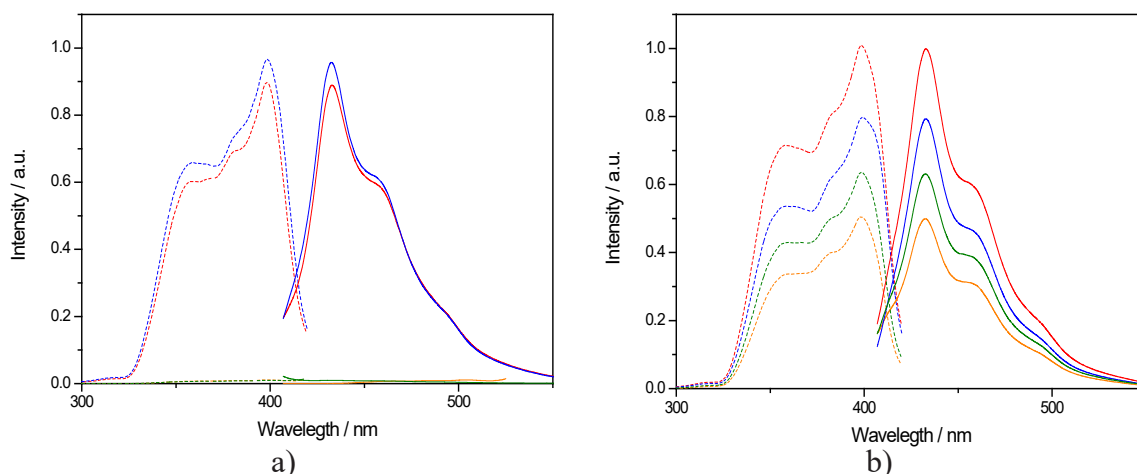


Fig. 8. Emission (full lines) and excitation (dashed lines) spectra of PP (a) and PLA (b) knitted fabrics with CF (not aged – blue line, aged 72 h in the Q-sun chamber – green line) and with CF and HNT (not aged – red line, aged 72 h in the Q-sun chamber – orange line)

The change in luminescence properties complements the results obtained by the reflectance measurements mentioned above (Figure 7.). As seen in Figure 6., the PLA/HNTCF aged more in comparison to the PLA/HNTCF sample as evaluated by appearance. There was also a larger colour difference between the unaged and aged samples of PLA/HNTCF (see Table 1.).

4. Conclusion

In the experimental work, PP and PLA fibres were modified either with photoluminescent dye or with HNT modified with photoluminescent dye. Their structure, mechanical and colouristic properties were investigated.

The photoluminescent dye and HNT modified with photoluminescent dye affected the structure of PP and PLA fibres differently. Increasing the content

of HNT with photoluminescent dye up to 0.15 % in PP fibres increased the sound speed and birefringence, but a higher content of HNT with photoluminescent dye in PP fibres caused a decrease in these parameters. The growth of photoluminescent dye content in PLA fibres increased the sound speed as well as the birefringence in the concentration area observed. The effect of HNT modified with photoluminescent dye on the birefringence was very low. The maintenance or mild loss of mechanical properties (tenacity at break, Young's modulus E_V , elongation) were observed in PP and PLA modified fibres, except for the tenacity or elongation of commercial PP fibres.

Compared to PP, PLA-based knitted fabrics showed better light stability, where there was no visible degradation of the knitted fabric, only its darkening. Likewise, PLA-based knitted fabric showed luminescence in UV light even

after accelerated aging for 72 h in the Q-sun chamber.

The addition of HNT modified with photoluminescent dye was not beneficial with respect to the light stability of the materials. In the case of PP, it contributed to a faster degradation of the material compared to PP dyed without HNTCF. In the case of PLA, the PLA samples dyed with HNTCF initially showed higher luminescence; however, after accelerated aging for 72 h, the luminescence decrease was more significant compared to the PLA samples without HNTCF.

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Supplement

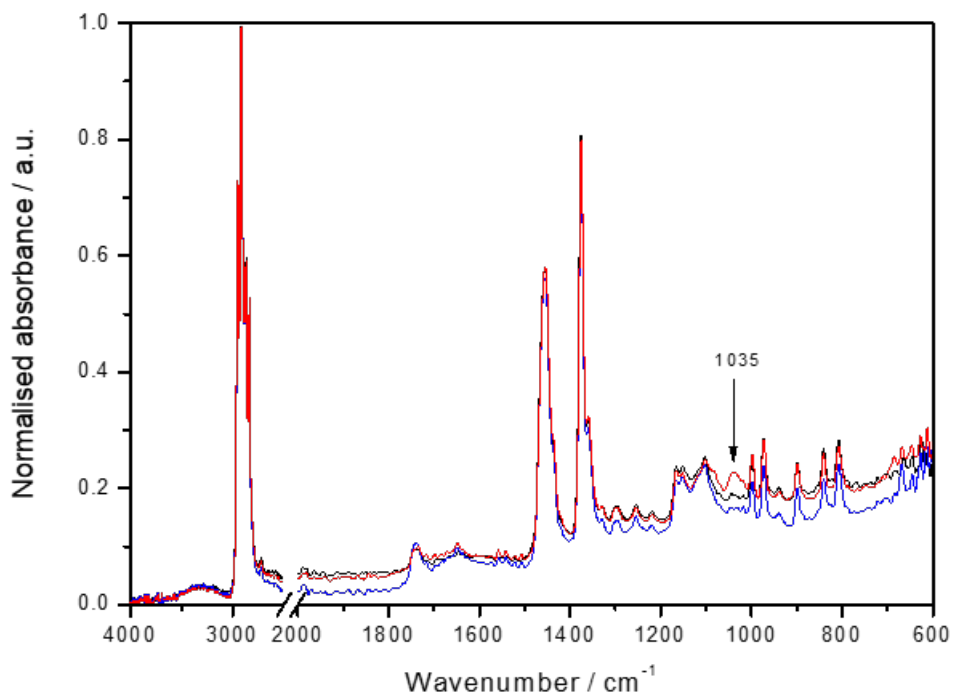


Fig. S1. Normalised FTIR spectra of PP (black line), PP modified by CF (blue line) and PP modified with HNTCF (red line)

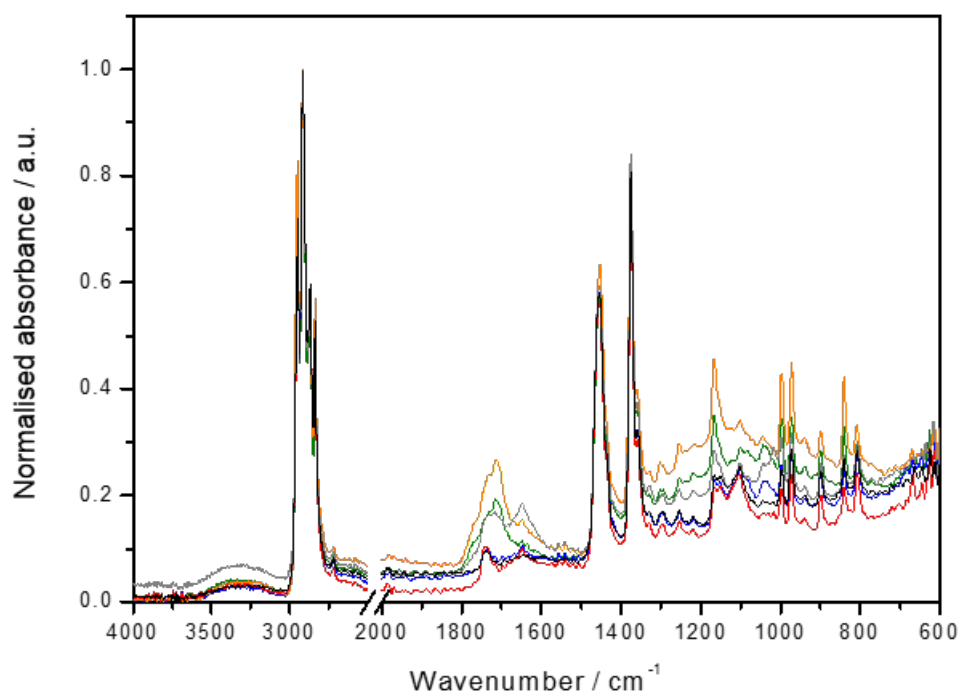


Fig. S2. Normalised FTIR spectra of PP samples without dye (not aged – black line, aged 72 h in the Q-sun chamber – gray line), with CF (not aged – blue line, aged 72 h in the Q-sun chamber – green line) and with CF and HNT (not aged – red line, aged 72 h in the Q-sun chamber – orange line)

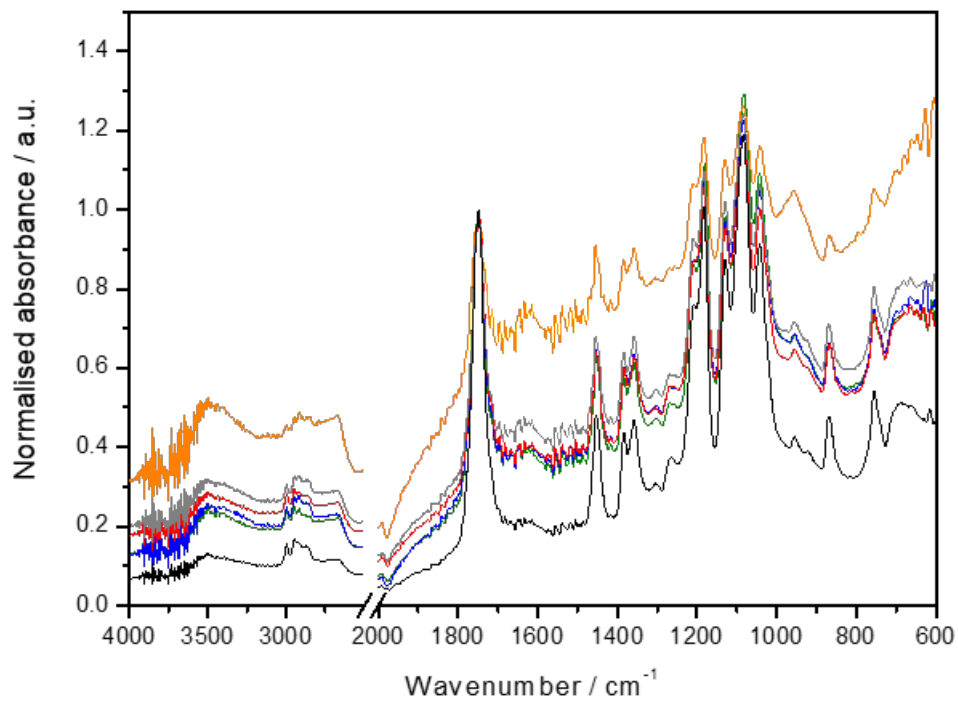


Fig. S3. Normalised FTIR spectra of PLA samples without dye (not aged – black line, aged 72 h in the Q-sun chamber – gray line), with CF (not aged – blue line, aged 72 h in the Q-sun chamber – green line) and with CF and HNT (not aged – red line, aged 72 h in the Q-sun chamber – orange line)