

PREPARATION, CHARACTERIZATION AND COLOR PERFORMANCE OF PLA PHOTOLUMINESCENT FIBRES

Z. Tomčíková, Š. Krivoš, F. Hrbál' and D. Rerková

Research Institute for Man-Made Fibres a.s., Štúrova 2, 05921 Svit, Slovak Republic
tomcikova@vuchv.sk

Abstract: Polylactic acid (PLA) is one of the fastest growing biodegradable polymers on the market. Consumers' preference of environmentally friendly products from biodegradable polymers but higher costs and lower quality of products may prevent their greater use compared to synthetic products. Therefore, there is an effort to modified PLA properties via different methods like using modifiers, blending, copolymerization and physical treatments. This article presents the preparation process of modified PLA fibres by an organic photoluminescent pigment as well as the preparation of knitted fabrics where the color efficiency of the pigment was detected by UV lamp illumination. For comparison, an unmodified PLA fibre and knitted fabric were prepared in the same manner as modified PLA fibres. To determine the supermolecular structure parameters of the fibres the methods of birefringence, sound velocity in fibres and crystallinity were used. The basic mechanical properties of the modified PLA fibres were expressed through the tenacity and elongation at break. Also, the overall fineness of the fibres has been determined. Results confirmed that the PLA can be used as a carrier of organic protective photoluminescent pigment without any impact on the structure and mechanical properties modified PLA fibres.

Keywords: PLA fibres, photoluminescent pigment, structure, mechanical properties, color performance.

1 INTRODUCTION

Poly(lactic acid) (PLA) is the first viable thermoplastic that can be produced from a plant-based feedstock such as corn or sugar cane, and be processed by the conventional melt processing technologies. Production of PLA requires 25-55% less fossil energy and 20-50% less fossil fuel resources than the production of petroleum-based polymers. PLA polymer is compostable, as it easily degrades by simple hydrolysis under the appropriate conditions (around 60°C and 90% relative humidity) [1]. Therefore PLA successfully bridges the gap between synthetic and natural fibres and finds a wide range of uses. Applications of PLA fibres are mainly in fibrefill (pillows, comforters, mattresses and duvets), nonwoven applications (agricultural and geo textiles, hygiene products, wipes) and less in apparel (sport, active, underwear and fashion wear) [2]. From other areas PLA finds use in the packaging, agriculture, medicine, electronics, construction and also automotive industries [3-6]. The simplicity of melt processing, unique property spectrum, renewable source of origin and of composting and recycling at the end of its useful life lead to growing interest in PLA. At the same time, polylactic acid is produced at the largest industrial scale of all biodegradable polymers (hundreds of thousand tons of PLA per year) [2].

Phenomena that involve energy absorption and subsequent light emission are generally classified as luminescence.

Depending on the method of excitation, there are several types of luminescence [7, 8]. Particularly interesting for fibres are photoluminescent pigments, which exist in organic and inorganic form [9-11]. The increasing interest in luminescent waveguides, applied as light concentrators, sensing elements, or decorative illuminating systems, is fostering efforts to further expand their functionality. By varying the concentration of luminophores can be tailored the overall color of yarn and fabric composition [12].

Smart textiles are defined as materials with responsiveness ability to an external stimulus such as light, electricity, chemicals, pH, solvent polarity and temperature [11]. In our work one from smart materials specifically PLA fibres were tried to prepare. Our fibres react to UV light as an effect of photoluminescent pigment content. As the first PLA masterbatch was prepared. The modified PLA fibres with protective photoluminescent pigment were prepared by the discontinuous process of spinning and drawing. The supermolecular structure and mechanical properties drawn modified PLA fibres were compared with drawn unmodified PLA fibre prepared under the same technological conditions. At the end, from modified and unmodified fibre the knitted fabric was prepared. The photoluminescent effect of the organic protective pigment was also observed in the knitted fabric.

2 EXPERIMENTAL AND METHODS

2.1 Materials

Poly lactide acid (PLA) produced by Total Corbion PLA B.V with MFI=8.9 g/10 min (210°C/2.16 kg) and organic protective photoluminescent pigment (OP) from Biesterfeld Company were used. PLA masterbatch with content 3.0 wt.% OP and MFI=10.91 g/10 min (210°C/2.16 kg) developed by Research Institute for Man-Made Fibres, a. s. Svit was used during fibres preparation process.

2.2 Preparation of PLA masterbatch

Before preparation of masterbatch the premix has been prepared. The premix consisted of a PLA carrier and organic protective photoluminescent pigment. The polymer and the pigment were milled and dried at 85°C for 4 hours before preparing of the premixes.

The PLA masterbatch was prepared on a Werner-Pfleiderer ZDSK 28 laboratory line with a twin-screw extruder (a screw diameter of 28 mm) and a vacuum zone. The preparation process of masterbatch had been carried out at a constant screws rotation speed 270 min⁻¹ and constant extrusion temperature of 210°C. The output was 3% masterbatch of OP.

2.3 Fibre preparation

The modified PLA/OP fibres, with organic protective photoluminescent pigment of a content from 0.1 and 0.3 wt.%, were prepared from mechanical mixture of PLA granulated polymer and PLA 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. The processing conditions were: the spinning temperature of 216°C, spinning die 25 holes with diameter 0.3 mm, final spinning process speed of 1500 m.min⁻¹, the drawing ratio $\lambda=1.5$, the drawing temperature of 80°C and final drawing process speed of 100 m.min⁻¹. The PLA fibre without OP under the same processing conditions was prepared for comparison.

2.4 Preparation of knitted fabric

From drawn unmodified PLA fibre and modified PLA/OP fibres the knitted fabrics of one meter length on a laboratory circular knitting machine were prepared. The principle of knitting was as follows: the needles move individually one after the other in the grooves of the cylinder, which rotates during work. The feet of the needles are gripped by a fixed lock, into the curved channel to which they fit. In this way, the needles move up and down, the supplied thread is caught by the needle head, forms an eyelet and threads them through the finished part of the knit.

2.5 Methods used

Application properties of PLA/OP masterbatch

The Melt Mass-Flow Rate (MFR), Melt Volume-Flow Rate (MVR) and viscosity (η) of PLA/OP masterbatch and PLA were measured on capillary rheoviscosimeter Dynisco Kayness using conditions: temperature of 210°C; load of 2.16 kg; detention time of 5 min; nozzle diameter of 2.095 mm; nozzle length of 8.00 mm and shear stress of 19.5 kPa. Samples have been dried before measurement for 4 hours at 85°C.

Thermal analysis of PLA/OP masterbatch

Evaluation of basic thermal properties of PLA/OP masterbatch was done by DSC technique using DSC-Q20 equipment from TA Instruments. In this procedure, the non-isothermal process of analysis was performed. PLA/OP masterbatch was heated at a rate of 16°C.min⁻¹ from 20 to 220°C, after tempering for 6 minutes the masterbatch was cooled again to a temperature of 20°C. All measurements were carried out in a nitrogen atmosphere. The masterbatch sample was not dried or treated by heat.

TGA analysis was performed using TGA-6 equipment from Perkin Elmer at isothermal temperatures 200°C, 240°C and 280°C. PLA/OP masterbatch was heated at the rate of 50°C.min⁻¹ from 25 to 50°C, the next was heating from 50°C to 200-280°C by rate 20°C/min with detaining time max. 20 min at the temperature required. All measurements were carried out in a nitrogen atmosphere.

By the same procedures, DSC and TGA analysis of the PLA polymer and the organic photoluminescent pigment were performed but OP by DSC technique was heated to a temperature 320°C. The DSC and TGA analysis were determined according to EN ISO 11 357-1: 2016 and EN ISO 11 358, respectively.

Orientation of fibre (the fibre's birefringence)

The orientation of macromolecular chains segments in fibre expresses the level of anisotropy of oriented polymer system (fibre). The total orientation of prepared modified PLA fibres was evaluated using a DNP 714BI polarization microscope, where the refractive indexes of light in the fibre axis (n_{\parallel}) 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:

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

The sound velocity in fibres

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).

Crystallinity of fibres

Crystallinity β represents the crystalline portion of fibre which may be evaluated using various methods. In this work DSC-Q20 apparatus from TA Instruments was used for the evaluation of thermal properties of unmodified PLA fibre and modified PLA fibres. The non-isothermal process of analysis was performed. All samples of PLA fibres were heated by rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ from 60 to 200°C under nitrogen flow. From melting endotherm of 1st heating of PLA fibres the melting enthalpy (ΔH_m) was determined. The crystallinity β of PLA fibres was calculated according to the following equation:

$$\beta = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m,0}} \cdot 100\% \quad (2)$$

where: ΔH_{cc} is the cold crystallization enthalpy of PLA fibres obtained during heating scan and $\Delta H_{m,0}$ is the melting enthalpy of 100% crystalline PLA ($93.6 \text{ kJ}\cdot\text{kg}^{-1}$) [13].

Mechanical properties of fibres

The basic mechanical characteristics (tenacity at break, and elongation at break) of unmodified PLA fibre and modified PLA fibres were measured using Instron 3345 equipment with a gauge length of 500 mm and clamping rate of 500 mm/min. An average of a least 10 individual measurements was used for each fibre. The mechanical characteristics and fineness were determined according to EN ISO 2062 and EN ISO 2060, respectively.

3 RESULTS AND DISCUSSION

For spinning and drawing technology research tests the masterbatch containing 3 wt.% OP was prepared. The illuminated PLA/OP masterbatch by daylight and under UV light is shown in Figure 1. It was shown, that PLA masterbatch has a photoluminescent effect under UV light.

The composition of PLA masterbatch and its application properties are given in Table 1 together with the PLA polymer used. By evaluating the application properties of the PLA/OP masterbatch (Table 1), it was found that the masterbatch of organic photoluminescent pigment has higher flow indexes and a reciprocal decrease in melt viscosity compared to the PLA polymer used. Values of application properties of PLA and PLA/OP masterbatch: MFR about 10 g/10 min and viscosity about 1000 Pa.s are suitable for achieving higher photoluminescent fibre tenacity.

Table 1 Application properties of PLA/OP masterbatch

| Sample | MFR [g/10 min] | MVR [cm/10 min] | CV _{MFR} [%] | η [Pa.s] | CV η [%] |
|-------------------------|----------------|-----------------|-----------------------|---------------|---------------|
| PLA | 8.90 | 8.04 | 6.6 | 1295.1 | 6.6 |
| 97 wt.% PLA / 3 wt.% OP | 10.91 | 9.96 | 12.80 | 1076.8 | 13.6 |

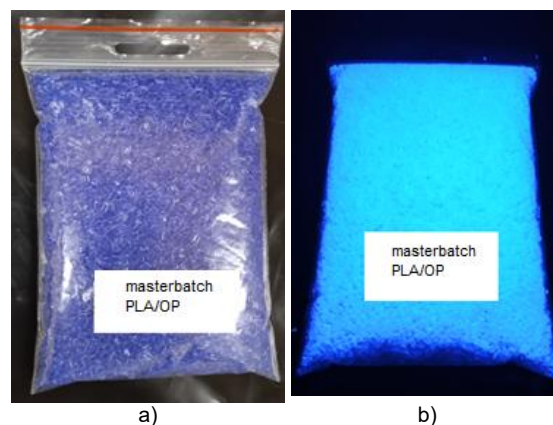


Figure 1 PLA/OP masterbatch with a content 0.30 wt.% of organic protective photoluminescent pigment illuminated by a) daylight D65 and b) UV lamp

The thermal properties of the PLA/OP masterbatch were evaluated by DSC thermal analysis where the following values were obtained: temperature of the cold crystallization - T_{cc} ; enthalpy of the cold crystallization - ΔH_{cc} ; melting temperature of the sample - T_m ; melting enthalpy of the sample - ΔH_m ; crystallinity - β ; crystallization temperature - T_c and crystallization enthalpy - ΔH_c . The results of PLA/OP masterbatch heating are given in Table 2 and results of PLA/OP masterbatch cooling are given in Table 3. Values of PLA and organic photoluminescent pigment are given in tables for comparison.

The measured melting temperatures of the PLA/OP masterbatch and the melting enthalpy values determined during the first and second heating (Table 2) correspond to the PLA polymer matrix and take into account the thermal history of the masterbatch. The relatively rapid cooling of the PLA/OP masterbatch melt and the presence of OP cause the cold crystallization of the sample, which was measured during the first heating. The difference between the first and second heating of the PLA/OP masterbatch is significant, because due to the defined heating and cooling, the cold crystallization completely disappears, the temperature and the melting enthalpy slightly decrease with the simultaneous increase of crystallinity from 0.221 to 0.451. The organic pigment which does not have a melting and crystallization temperature in the temperature range examined; may act as a nucleating agent in the PLA/OP masterbatch. As the melt cools after the first and second heats, the temperature and enthalpy of crystallization of the PLA/OP masterbatch decrease, as can be seen in Table 3.

Table 2 Results of DSC analysis (heating) of PLA, OP and PLA/OP masterbatch

| Sample | HEATING | Cold crystallization | | Melting of samples | | Crystallinity |
|--------------------|-------------------------|----------------------|--------------------------|---------------------|-------------------------|----------------|
| | Parameter | T _{cc} [°C] | ΔH _{cc} [kJ/kg] | T _m [°C] | ΔH _m [kJ/kg] | β |
| PLA/OP masterbatch | 1 st heating | 99.7 | 24.8 | 179.8 | 45.5 | 0.221 |
| | 2 nd heating | not determined | not determined | 178.5 | 42.2 | 0.451 |
| PLA | 1 st heating | not determined | not determined | 175.5 | 52.5 | 0.561 |
| | 2 nd heating | not determined | not determined | 172.2 | 5.1 | 0.054 |
| OP | 1 st heating | not determined | not determined | not determined | not determined | not determined |
| | 2 nd heating | not determined | not determined | not determined | not determined | not determined |

Table 3 Results of DSC analysis (cooling) of PLA, OP and PLA/OP masterbatch

| Sample | COOLING | Crystallization | |
|--------------------|-------------------------|---------------------|-------------------------|
| | Parameter | T _c [°C] | ΔH _c [kJ/kg] |
| PLA/OP masterbatch | 1 st cooling | 104.8 | 34.1 |
| | 2 nd cooling | 92.4 | 15.6 |
| PLA | 1 st cooling | not determined | not determined |
| | 2 nd cooling | not determined | not determined |
| OP | 1 st cooling | not determined | not determined |
| | 2 nd cooling | not determined | not determined |

Table 4 Results of TGA analysis of PLA, OP and PLA/OP masterbatch

| Heat load time [min] | Weight loss at isothermal temperatures [wt.%] | | | | | | | | |
|----------------------|---|-------|-------|-------|-------|-------|-------|-------|-------|
| | PLA/OP masterbatch | | | PLA | | | OP | | |
| | 200°C | 240°C | 280°C | 200°C | 240°C | 280°C | 200°C | 240°C | 280°C |
| 0 | 0.01 | 0.12 | 0.31 | 0.08 | 0.32 | 0.48 | 0.00 | 0.00 | 0.01 |
| 5 | 0.04 | 0.18 | 0.36 | 0.16 | 0.38 | 0.52 | 0.00 | 0.00 | 0.07 |
| 10 | 0.06 | 0.24 | 0.42 | 0.21 | 0.42 | 0.57 | 0.00 | 0.00 | 0.12 |
| 15 | 0.09 | 0.26 | 0.49 | 0.25 | 0.47 | 0.62 | 0.00 | 0.01 | 0.16 |
| 20 | 0.12 | 0.29 | 0.56 | 0.31 | 0.52 | 0.67 | 0.00 | 0.01 | 0.18 |

Table 5 Supermolecular structure parameters of drawn PLA fibre and PLA/OP fibres

| Content of OP [wt.%] | Δn.10 ³ | CV _{Δn} [%] | c [km/s] | CV _c [%] | β |
|----------------------|--------------------|----------------------|----------|---------------------|-------|
| - | 24.59 | 1.52 | 2.09 | 4.13 | 0.502 |
| 0.10 | 27.94 | 1.03 | 2.26 | 3.12 | 0.533 |
| 0.30 | 27.77 | 1.39 | 2.22 | 3.41 | 0.502 |

Table 6 Mechanical properties of drawn PLA fibre and PLA/OP fibres

| Content of OP [wt.%] | Fineness [dtex] | CV _F [%] | Tenacity [cN/dtex] | CV _T [%] | Elongation [%] | CV _E [%] |
|----------------------|-----------------|---------------------|--------------------|---------------------|----------------|---------------------|
| - | 147.4 | 0.6 | 2.97 | 4.9 | 18.5 | 5.2 |
| 0.10 | 147.6 | 0.5 | 3.06 | 2.4 | 19.8 | 4.7 |
| 0.30 | 147.3 | 1.6 | 3.01 | 1.8 | 21.0 | 4.6 |

TGA analysis of PLA/OP masterbatch, PLA granulate and OP in the temperature range of 200-280°C showed high thermal stability samples (Table 4). From the above, we can assume that in the working area of spinning 210°C, both – PLA/OP masterbatch and PLA polymer will have sufficient thermal stability.

From the mechanical mixture of PLA/OP masterbatch and from PLA granulate, PLA fibres containing 0.1 and 0.3 wt.% OP were prepared by spinning and discontinuous drawing to a drawing ratio of 1.5. For comparison, an unmodified PLA fibre was prepared in the same manner. From each type of fibre, the supermolecular structure and mechanical properties were evaluated (Tables 5

and 6). It is clear from Table 5 that due to the photoluminescent pigment, the orientation of the macromolecular chains segments (birefringence) increased slightly, up to 14% while the difference in the orientation of the macromolecular chains segments of the unmodified fibre and the modified fibres in the surface layers (sound velocity) as well as the crystallinity did not change significantly.

The basic mechanical properties of PLA/OP fibres compared to unmodified PLA fibre (Table 6) also did not change significantly. A positive finding is that the tenacity of PLA/OP fibres reaches a value above 3 cN/dtex.

As the OP content increases, the elongation increases moderately. It follows from the above that OP slightly affects the supermolecular structure and mechanical properties of the fibres and does not negatively influence studied properties.

The last evaluated parameter was color performance investigated under UV lamp of modified PLA fibres (Figure 2) and of the knitted fabric (Figure 3). From Figures 2 and 3 it can be clearly seen the color expression of the organic photoluminescent pigment under the UV lamp in modified PLA fibres and the knitted fabric. Both concentrations of OP 0.10 and 0.30 wt.% have the same color intensity under UV light when observed with the naked eye. The standard fibre does not shine and remains dark.



Figure 2 The influence of organic protective photoluminescent pigment with content 0.10 and 0.30 wt.% on the color performance of drawn PLA fibre under a UV lamp

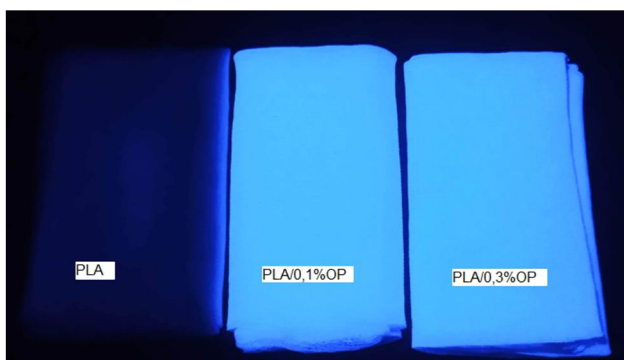


Figure 3 The influence of organic protective photoluminescent pigment with content 0.10 and 0.30 wt.% on the color performance of knitted fabric prepared from two drawn PLA fibres under a UV lamp

As can be seen from Figure 4a), during the formation of the sleeve from one fibre (with a total fineness of 147 dtex) the holes were formed and the loops were not uniform during knitting. Therefore two drawn PLA fibres were used, from which a sleeve with an even arrangement of loops was prepared (Figure 4b).

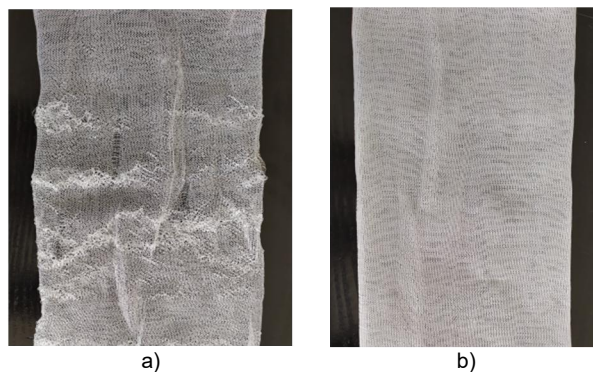


Figure 4 For comparison: the knitted fabric prepared from a) one drawn fibre and b) from two drawn fibres

4 CONCLUSION

- Preparation of PLA/OP masterbatch with a content 0.30 wt.% of organic protective photoluminescent pigment was smooth;
- The PLA/OP masterbatch has a satisfactory coloristic performance under UV light and suitable application properties therefore can be used in a mixture with PLA granulate for the preparation of modified PLA fibres;
- The PLA/OP masterbatch has high thermal stability up to 280°C;
- The studied polymer system: PLA/OP masterbatch and PLA granulated polymer is fibre-forming and the spinning process is stable for the studied concentrations of 0.1 and 0.3 wt.% of organic protective photoluminescent pigment;
- The significant effect of the organic protective photoluminescent pigment on the supramolecular structure and mechanical properties of PLA fibres with a total fineness of about 147.5 dtex has not been demonstrated;
- From each sample, a knitted fabric by combining two the same fibres was prepared;
- The masterbatch, fibres and knitted fabrics show strong blue-white radiation under a UV lamp, observable with the naked eye.

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