THE INFLUENCE OF FLUORESCENT PIGMENT ON STRUCTURE AND MECHANICAL PROPERTIES OF MODIFIED PP AND PLA FIBRES

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Abstract: *The objective of this study was to prepare modified fibers from two types of polymer, polypropylene (PP) and polylactide (PLA). Fibers were modified by fluorescent pigment. Fluorescent pigments cause color change of material after illumination by UV light with a short time of luminescence decay. Their application into fibers can be served as one from solutions how to protect of original products. The influence of uniaxial deformation on the supermolecular structure and basic mechanical properties of modified fibres was investigated as well as colour performance of mentioned pigment in fibers under day light (D65) and after illumination with UV lamp. Supermolecular structure parameters as birefringence, sound velocity in fibres and crystallinity were studied and compared between PP and PLA modified fibres. Also, basic mechanical properties as fineness, Young´s modulus, tenacity at break and elongation at break of undrawn and drawn modified fibres prepared by discontinuous technological process were evaluated and compared. The obtained experimental results concerning supermolecular structure and mechanical characteristics of both types of modified fibres were compared with of their non-modified undrawn and drawn fibres prepared under the same technological conditions.*

Keywords: *modified PP fibres, modified PLA fibres, fluorescent pigment, structure, mechanical properties.*

1 INTRODUCTION

The market of the world textile industry in the year 2016 has exceeded the threshold of 100 million tons although the world fiber market has a continued slowing of growth in the 4th consecutive year. Man-made fibres (MMF) grew 2.0% while natural fibers remained unchanged. The main countries of manufactures fibres are China, India and the USA [1].

Polypropylene (PP) is one of the most widely used thermoplastic materials on petroleum base, because has good mechanical properties, easy processing and low price [2, 3]. It can be used in a wide variety of applications, for example: textiles, automotive components, packaging, stationery, plastic parts and reusable containers of various types, laboratory equipment and other [4-6]. The increasing concerns about our ecological system have results a lot of research activity in the area of bio-based plastics. At present, one of the most promising fully biodegradable polymers is polylactide (PLA) [7] which attract of various markets e.g. textile, packaging and automotive industries, as an eco-alternative to traditional petroleum-based commodity polymers. Although PLA exhibits high strength and stiffness, on the other side has the inherent brittleness [8-10].

In recent years much attention is focused on originality products protection [11, 12] because there are a huge number of counterfeits in all industry areas. It is practically impossible to distinguish original products from the fakes. One of the cost acceptable solutions is an application of fluorescent pigments which have short time of luminescence decay [13]. Fluorescent pigments belong to the group photoluminescent materials where the excitation is caused by light. Photoluminescent materials exist as organic and inorganic ones as solid materials and liquid as well [14, 15]. Fluorescence of individual samples can be detected by dint of fluorophores. Fluorophore is a compound capable to absorb light of certain wavelength and successively emits the light with longer wavelength.

The objective of this study was to prepare two types of fibers with the different polymer matrix (PP and PLA) modified by fluorescent pigment and to compare their properties. The undrawn and drawn modified fibres by discontinuous technological process were prepared. The influence of uniaxial deformation and pigment content on the supermolecular structure and basic mechanical properties was investigated and compared between two types modified fibers. Subsequently different colour performance of fluorescent pigment in fibers under day light (D65) and after illumination with UV lamp was studied. Obtained results of both types of fibres modified with fluorescent pigment were compared with fibers without pigment content prepared under the same technological conditions.

2 EXPERIMENTAL AND METHODS

2.1 Materials

Isotactic polypropylene (PP) produced by Slovnaft (Slovakia) with MFI = 27.6 g/10 min (230°C/2.16 kg), Polylactide acid (PLA) produced by NatureWorks®LLC (USA) with MFI = 22.8 g/10 min (210°C/2.16 kg) and special organic fluorescent pigment of Radiant Color Company were used. PP masterbatch (pigment content of 2.0 wt.%, MFI = 20.9 g/10 min (230°C/2.16 kg), Filter index = 84 $MPa.kg^{-1}$) and PLA masterbatch (pigment content of 2.0 wt.%, MFI = 33.6 g/10 min (210°C/2.16 kg), Filter index $<$ 50 $MPa.kg^{-1}$) developed by Research Institute for Man-Made Fibres, a. s. Svit were used during fibres preparation process.

2.2 Fibre preparation

The modified PP fibres with content of pigment 0.01; 0.05; 0.1; 0.15; 0.2 and 0.3% were prepared from mechanical mixture of PP granulated polymer and PP masterbatch using the classical discontinuous process of spinning and drawing. The laboratory discontinuous line has an extruder with diameter of D = 32.0 mm, with a discontinuous one-step drawing process. The constant processing conditions - spinning temperature of 220°C, spinning die plate of 2x25 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.

The modified PLA fibres with the same content of pigment as polypropylene fibres were prepared from mechanical mixture of PLA granulated polymer and PLA masterbatch using the same process of spinning and drawing as had the above mentioned modified PP fibres. In this case the constant processing conditions - spinning temperature of 210°C, spinning die plate of 2x25 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 80°C and final drawing process speed of 100 $m.min^{-1}$ were used.

2.3 Methods used

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 modified PP and 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 below:

$$\Delta n = n_{\parallel} - n_{\perp} \tag{1}$$

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 fibres and may be evaluated using various methods. In this work, a Perkin Elmer DSC 4 device was used for the evaluation of the thermal properties of non-modified and modified PP and PLA fibres. The non-isothermal process of analysis was performed. All samples of PP fibres were heated in temperature range from 60 to 260°C and PLA fibres in temperature range from 60 to 200°C at a rate of 10°$C.min^{-1}$ under a nitrogen flow. From melting endotherm of 1st heating of PP fibres the melting enthalpy *(ΔHm)* was determined. This value was used for the calculation of crystallinity β in PP fibres using Equation 2:

$$\beta = \frac{\Delta H_m}{\Delta H_{m,0}} \cdot 100\% \tag{2}$$

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

The crystallinity β of PLA fibres was calculated according to the following Equation 3 [16]:

$$\beta = \frac{\Delta H_m - \Delta H_c}{\Delta H_{m,0}} \cdot 100\% \tag{3}$$

where ΔH_m is the measured melting enthalpy of PLA fibres, ΔH_c is the cold crystallization enthalpy of PLA fibres obtained during heating scan and $\Delta H_{m,0}$ is the melting enthalpy of a 100% crystalline PLA (93.6 $kJ.kg^{-1}$) [17].

Mechanical properties of fibres

The mechanical properties of non-modified and modified PP and PLA fibres using Instron 3343 equipment were measured in accordance with the STN EN ISO 2062:2010 and fineness was measured in accordance with the STN EN ISO 2060:1998.

3 RESULTS AND DISCUSSION

From the processes of spinning (spinning speed of 1500 m.min^{-1}) and drawing (drawing ratio λ = 2.0) of the studied modified systems of PP and PLA it follows that both systems (PP/fluorescent pigment and PLA/fluorescent pigment) are fibre forming and processes are stable in the whole range of concentration of fluorescent pigment (0.01 – 0.30 wt.%). The stability of these processes was comparable with spinning and drawing of non-modified PP and PLA fibres.

First, the supermolecular structure parameters of modified PP and PLA fibres were evaluated. The obtained results (Figures 1 and 2) show the effect of uniaxial deformation and various fluorescent pigment content on the supermolecular structure parameters of undrawn and drawn modified PP and PLA fibres.

Evaluation of supermolecular structure of undrawn fibres shows that PP fibres have a much more higher total average orientation of macromolecular chains (birefringence, Figure 1a) and a little bit higher orientation of macromolecular chains in surface areas (sound velocity, Figure 1b) in the spinning field at spinning speed of 1500 m.min^{-1} when compared to PLA fibres. At the same time, during the spinning, a higher crystallization of PLA matrix of undrawn fibres has been occurred in comparison with PP undrawn fibres (crystallinity, Figure 2). The influence of fluorescent pigment content on the orientation of macromolecular chains and crystallinity of PP and PLA matrices of undrawn modified fibres is insignificant. In the process of uniaxial deformation at drawing ratio λ=2.0, when compared to undrawn fibres, there is a significant increase both of the total average orientation of macromolecular chains in the direction of the fibre axis (birefringence) and of the orientation of macromolecular chains in surface areas (sound velocity), as well as to the increase of crystallinity for both PP and PLA drawn fibres.

The orientation of macromolecular chains in drawn PP fibres is higher than in PLA drawn fibres, and the crystallinity of PLA drawn fibres is significantly higher than the crystallinity of PP drawn fibres. Insignificant influence of fluorescent pigment content on orientation of macromolecular chains and crystallinity of PP drawn fibres was observed. In case of PLA drawn fibres the influence of increased fluorescent pigment content resulted in the increase of macromolecular chains total average orientation in the direction of fibre axis (Figure 1a) and slight decrease in their crystallinity (Figure 2). This can be the result of plasticizing effect of organic fluorescent pigment on PLA matrix in drawn fibre. It follows from the above that the process of uniaxial deformation has significant influence on the formation of supermolecular structure of the final form of drawn modified PP and PLA fibres. The influence of fluorescent pigment content in range 0.01 – 0.30 wt.% was not significant.

Secondly, the mechanical properties of modified PP and PLA fibres were evaluated. Figures 3 and 4 show the effect of uniaxial deformation and fluorescent pigment content on the basic mechanical properties of undrawn and drawn modified PP and PLA fibres.

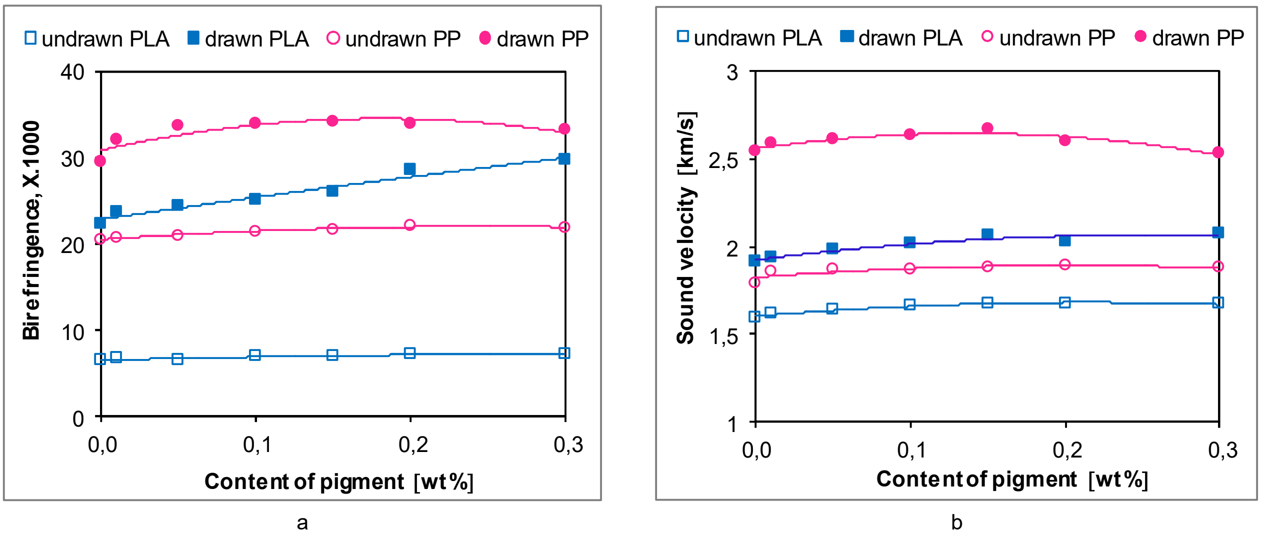


Figure 1 Dependence of birefringence (a) and sound velocity (b) of undrawn and drawn modified PP and PLA fibres on fluorescent pigment content

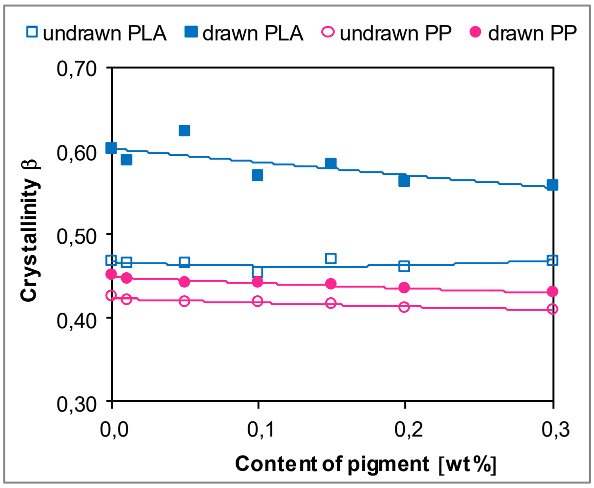
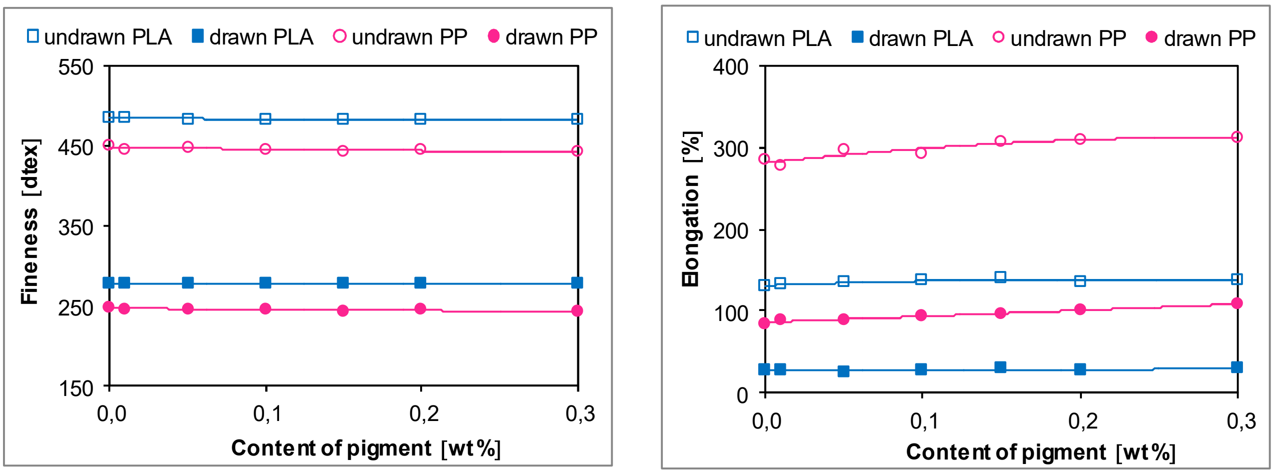


Figure 2 Dependence of crystallinity β of undrawn and drawn modified PP and PLA fibres on fluorescent pigment content



a b

Figure 3 Dependence of fineness (a) and elongation at break (b) of undrawn and drawn modified PP and PLA fibres on fluorescent pigment content

It was found that the content of fluorescent pigment 0.01 – 0.30 wt.% in the fibre mass does not affect the fineness of undrawn and drawn modified PP and PLA fibres (Figure 3a). Different fineness of PP and PLA fibres result from different of density of PP and PLA fibres polymer matrix.

The defined parameters of supermolecular structure of undrawn and drawn modified PP and PLA fibres affected their mechanical properties. From the determined of mechanical properties of undrawn fibres prepared at a spinning speed of 1500 m.min^{-1} follows that the tenacity of PP fibres is higher (max 62%) in comparison with the tenacity of PLA fibres (Figure 4a). This is a result of the both much higher total average orientation of macromolecular chains (birefringence, Figure 1a) and higher orientation of macromolecular chains in surface areas (sound velocity, Figure 1b) of undrawn PP fibres in comparison with undrawn PLA fibres. At the same time, the Young's modulus of undrawn PLA fibres is significantly higher (Figure 4b) and elongation is significantly lower (Figure 3b) in comparison with undrawn PP fibres. This is related to higher crystallinity of undrawn PLA fibres compared to undrawn PP fibres (Figure 2). The effect of fluorescent pigment content of 0.01 – 0.30 wt.% on all evaluated mechanical properties of undrawn PP and PLA fibres is not significant as well as its effect on supermolecular structure of these fibres.

The process of uniaxial deformation at drawing ratio λ=2.0 significantly increases the tenacity (Figure 4a) and Young's modulus (Figure 4b) of drawn PP and PLA fibres in comparison with undrawn fibres. This results from substantial increased total average orientation of macromolecular chains in the direction of axis of drawn fibres (birefringence, Figure 1a), substantial increased orientation of macromolecular chains in surface areas of drawn fibres (sound velocity, Figure 1b), as well as increased crystallinity of drawn fibres (crystallinity, Figure 2).

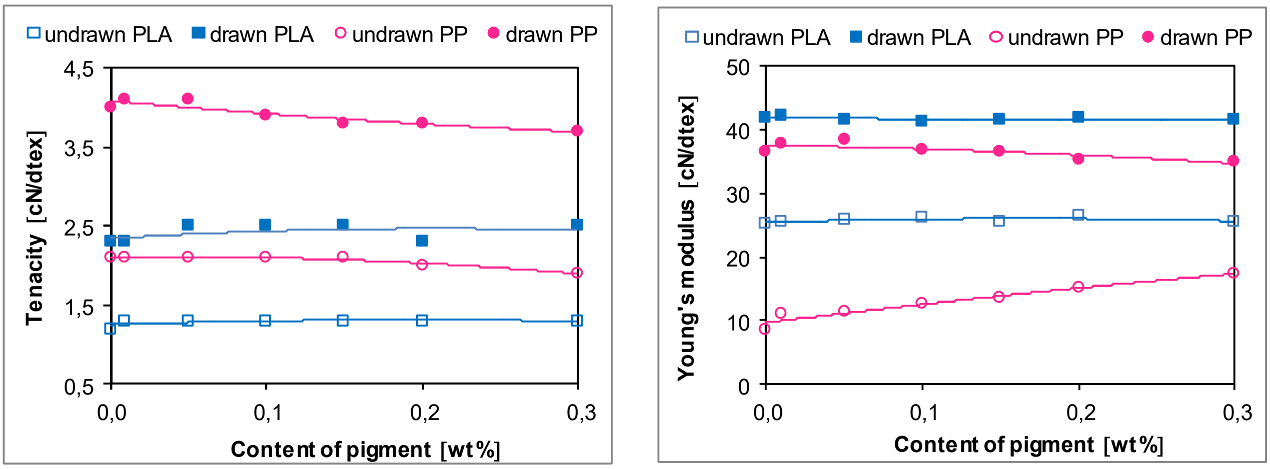


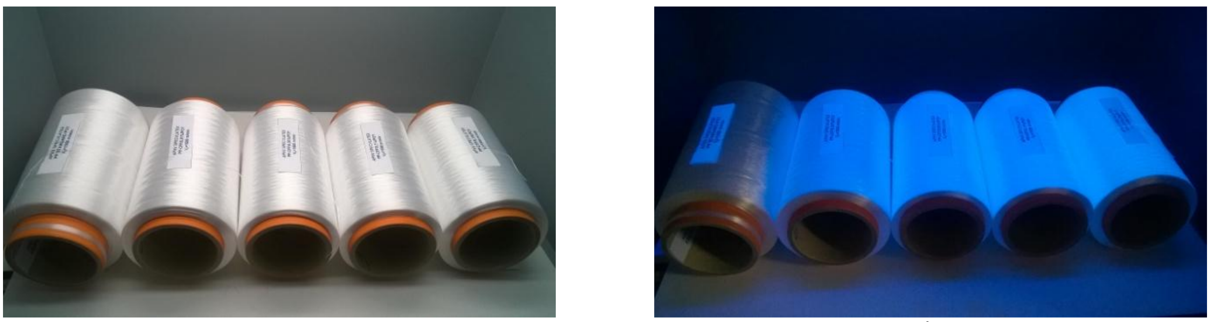
Figure 4 Dependence of tenacity at break (a) and Young's modulus (b) of undrawn and drawn modified PP and PLA fibres on fluorescent pigment content

At the same time, the tenacity of drawn PP fibres is prominently higher than the tenacity of drawn PLA fibres (Figure 4a). This results from significantly higher total average orientation of macromolecular chains (birefringence, Figure 1a) and higher orientation of macromolecular chains in surface areas (sound velocity, Figure 1b) of drawn PP fibres. The finally, the Young's modulus of drawn PLA fibres is higher (Figure 4b) and elongation is lower (Figure 3b) when compared to drawn PP fibres. It is affected by prominently higher crystallinity of drawn PLA fibres in comparison with drawn PP fibres (Figure 2). The significant influence of fluorescent pigment content of 0.01 – 0.30 wt.% on all evaluated mechanical properties was not proved, nor was its influence on supermolecular structure of drawn fibers.

The obtained values of the basic mechanical properties of undrawn and drawn modified PP and PLA fibres are in good correlation with determined values of their supermolecular structure parameters.

The last evaluated parameter was color performance of modified PP and PLA fibres investigated under UV lamp. Figures 5 and 6 show the effect of the fluorescent pigment content on color performance of modified PP and PLA fibres.

Figures 5a and 6a clearly show that under the daylight (D65) all prepared modified PP and PLA fibers are white. Under the UV lamp only non-modified PP and PLA standard fibres (Figure 5b and Figure 6b) are not shiny while the modified PP and PLA fibres with fluorescent pigment shine blue. The color intensity rises with increased content of fluorescent pigment in modified PP and PLA fibres. It can be seen that even the lowest pigment content 0.01 wt.% (samples 2 from left to right in figures 5b and 6b) of evaluated fluorescent pigment provides clearly visible color change under UV lamp.



a b

Figure 5 The influence of fluorescent pigment with content 0.01; 0.05, 0.10 and 0.30 wt.% on the color performance of modified PP fibres in comparison with non-modified PP fibre (on the left) under daylight D65 (a) and under UV lamp (b)

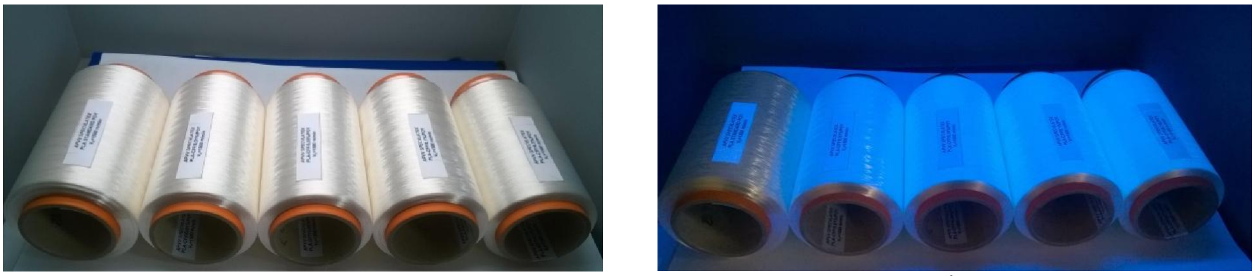


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Figure 6 The influence of fluorescent pigment with content 0.01; 0.05, 0.10 and 0.30 wt.% on the color performance of modified PLA fibres in comparison with non-modified PLA fibre (on the left) under daylight D65 (a) and under UV lamp (b)

4 CONCLUSION

Processes of spinning (spinning speed of 1500 $m.min^{-1}$) and drawing (drawing ratio $\lambda = 2.0$) of the studied systems - PP/fluorescent pigment and PLA/fluorescent pigment have showed that their stability is comparable with the stability of processes of non-modified PP and PLA fibres. The both systems were fibre forming and processes were stable in the whole concentration range of fluorescent pigment (0.01 – 0.30 wt.%). The technological conditions for stable spinning and drawing of modified PP and PLA fibres were found. The basic dependencies of the influence of uniaxial deformation and fluorescent pigment content on the supermolecular structure parameters, basic mechanical properties and color performance under UV lamp of modified PP and PLA fibres were evaluated.

It was found that in the spinning field there occurs a higher total orientation of macromolecular chains in PP matrix of modified fibres, which resulted in higher tenacity of undrawn PP fibres in comparison with undrawn PLA fibres. At the same time, higher crystallinity occurs in the PLA matrix of modified fibres, resulting in higher Young's modulus and lower elongation of undrawn PLA fibres in comparison with undrawn PP fibres. The influence of fluorescent pigment content on supermolecular structure and mechanical properties of undrawn PP and PLA fibres is not significant.

It was also found that the process of uniaxial deformation of undrawn fibres has significant influence on supermolecular structure and mechanical properties of the final form of drawn modified PP and PLA fibres. By drawing, a significant increase in total orientation of macromolecular chains in the direction of fibre axis and the increase in crystallinity of drawn PP and PLA fibres is achieved, while the tenacity of drawn PP fibres is significantly higher than the tenacity of drawn PLA fibres. This is influenced by significantly higher total orientation of macromolecular chains in the direction of fibre axis. At the same time, the Young's modulus of drawn PLA fibres is higher and the elongation is significantly lower when compared to drawn PP fibres, which is related to their significantly higher crystallinity than that of drawn PP fibres. The influence of the fluorescent pigment content on supermolecular structure and evaluated mechanical properties of drawn PP and PLA fibres was not significant.

An important result is also the finding that the color performance under UV light is visible even at lowest fluorescence pigment content (0.01 wt.%) in both modified PP and PLA fibres.

Based on the results obtained, it can be stated that the evaluated fluorescent pigment has no negative impact on technological stability of preparation of modified PP and PLA fibres; it does not significantly influence their supermolecular structure and mechanical properties, and is coloristically effective under UV lamp at even low concentrations. Therefore, it can be used as a tool for protection of original PP and PLA textile products.

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5 REFERENCES

1. An.: Fiber production surpassed 100 million tons in 2016, Chemical Fibers International 67(2), 2017, p. 68
2. Gahleitner M., Paulik Ch.: Chapter 11 – Polypropylene and Other Polyolefins, In Book: Brydson's Plastics Materials (Eighth Edition), 2017, pp. 279-309, ISBN: 978-0-323-35824-8
3. Panaitescua D.M., Nicolaea C.A., Vulugaa Z., Vitelarub C., Sanporeanc C.G., Zahariad C.,Floreaa D., Vasilievicia G.: Cover image influence of hemp fibers with modified surface on polypropylene composites, Journal of Industrial and Engineering Chemistry 37, 2016, pp. 137-146
4. Manek V., Gudiyawar M.Y.: Thermal and flame-resistance behavior of polypropylene fabrics, Chemical Fibers Int. 65(3), 2015, pp. 177-179
5. Niebel V., Gloy Y.S., Gries T.: Polyolefin melt adhesion fibers and yarns and implementation into textile applications, Man-Made Fiber Year Book 2015, 65, 2015, pp. 47-48

6. Kazmi S.M.R., Jayaraman K., Das R.: Single-step manufacturing of curved polypropylene composites using a unique sheet consolidation method, Journal of Materials Processing Technology 237, 2016, pp. 96-112
7. Avérous L.: Polylactic Acid: Chapter 21 – Synthesis, Properties and Applications, In Book: Monomers, Polymers and Composites from Renewable Resources, 2008, pp. 433-450, ISBN: 978-0-08-045316-3
8. Liu H., Zhang J.: Research progress in toughening modification of poly(lactic acid), J. Polym. Sci., Part B – Polym. Phys. 49(15), 2011, pp. 1051-1083
9. Tan K.L., Lim S.K., CHan J.H., Low CH.Y.: Overview of poly(lactic acid) production with oil palm biomass as potentional feedstock, International Journal of Engineering and Applied Sciences 5(4), 2014, pp. 1-10
10. An: Improve transparency and performance of PLA, bioplastics Magazine 11(06), 2016, p. 31
11. Rossier R., Hersch R.D.: Hiding patterns with daylight fluorescent inks, 19th Color and Imaging Conference, 2011, pp. 223-228
12. Hersch R.D., Donzé P., Chosson S.: Color Images Visible under UV Light, ACM Trans. Graphics, Proc. ACM SIGGRAPH, 2007, 26(3), 75:1-75:9
13. Bamfield P.: Chromic phenomena, Technological Applications of colour chemistry, The Royal Society of Chemistry, Cambrige, 2001
14. Jarraya N.A., Khemakhem K., Turki-Guermazi H., Abid S., Saffon N., Fery-Forgues S.: Solid-state fluorescence properties of small iminocoumarin derivatives and their analogues in the coumarin series, Dyes and Pigments 132, 2016, pp. 177-184
15. Davidson M.V. (1998, July 20) Fluorescence microscopy, Retrieved 12, February 2009, from Molecular Expressions Optical Microscopy, Primer: http://microscope.fsu.edu/primer/techniques/fluorescene/fluorhome.html
16. Drieskens M., Peeters R., Mullens J., Franco D., Lemstra P.J., Hristova-Bogaerds D.G.: Structure Versus Properties Relationship of Poly(lactic acid). I. Effect of Crystallinity on Barrier Properties, J. Polym. Sci. Part B – Polym. Phys. 47(22), 2009, pp. 2247-2258
17. Cayuela D., Montero L.A., Manich A.M.: Variation of microstructure of textured and fixed polylactide fibres with the texturing conditions, In: Book of Proceedings of the 5th International Textile, Clothing & Design Conference, Magic World of Textiles, Dubrovnik, Croatia, October 3-6., 2010, pp. 48-53