

FIBRES FROM BIODEGRADABLE POLYMERS AND ADDITIVES FOR TEXTILE APPLICATIONS

Anna Ujhelyiová¹, Kristína Baníková¹, Jozef Ryba², Roderik Plavec¹, Veronika Hrabovská¹ and Marcela Hricová¹

¹Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Natural and Synthetic Polymers, Department of Plastics, Rubber and Fibres, Radlinského 9, 812 37 Bratislava, Slovak Republic

²Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Natural and Synthetic Polymers, Department of Polymer Processing, Krškanská 21, 949 05 Nitra, Slovak Republic
anna.ujhelyiova@stuba.sk

Abstract: Poly-(lactic acid) (PLA) is a biodegradable polymer from renewable resources produced as potential alternative to the synthetic polymers. One of the alternative applications is a preparation of PLA fibres. The PLA fibres prepared by classical spinning technology do not have good mechanical properties, especially elongation at the break. The prepared PLA fibres are very brittle with bad processability. The modification of the PLA fibres with plasticisers and additives/nanoadditives is one of the perspective ways for improvement of processability of the PLA fibres and increasing of multi-functional properties of these fibres. This work focuses on the preparation of fibres from various types of PLA modified with nucleating agent talc. The effect of content of various PLAs and additives on rheological properties of blends was evaluated. The thermal, mechanical and thermo-mechanical properties of prepared fibres from PLAs and modifiers were monitored.

Keywords: poly-(lactic acid) fibres, talc, rheological behaviour, viscosity, mechanical and thermal properties.

1 INTRODUCTION

Today, the use of polymeric materials is an essential part of human life. The products made from them are used in various fields. Increase of their consumption also brings the increasing waste at the end of their life/consumption cycle. This increases the global problem of waste accumulation that due to pollution of nature, oceans and other ecological areas. At the same time, there is a reduction of the fossil resources from which synthetic polymers are produced, too. One of the solutions of this problem is alternative to the synthetic polymers which are biodegradable polymers, primarily from renewable raw materials.

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 biodegradability, the possibility of extending the lifecycle of plastic products has emerged [1].

Poly-(lactic acid) (PLA) is 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. Stereoisomers affect the properties of the polymer itself, its processing conditions, and the properties of the end product.

Therefore, the processing by spinning and melt drawing is complicated. The preparation of monofilaments and multifilaments as well as non-woven textile structures is feasible in several ways, the processing conditions which are reflected in different properties of the fibres obtained [2, 3]. PLA is a unique polymer, which in many ways behaves like polyethylene terephthalate (PET) but also has many similarities to polypropylene (PP) [4].

This work focuses on the preparation of fibres from various types of PLA modified with nucleating agent. The effect of content of various PLAs and additives on rheological properties of blends was obtained. The thermal, mechanical and thermo-mechanical properties of prepared fibres from PLAs and modifiers were monitored.

2 MATERIALS AND METHODS

2.1 Materials

Poly-(lactic acid) fibres

In this paper the virgin poly-(lactic acid) INGEO™ Biopolymer 6202D (PLA6) and INGEO™ Biopolymer 4043D (PLA4) polymers produced by NatureWorks LLC., USA and nucleating agent talc Plustalc H05 (M) with particle size 1.8 µm and specific surface 12 m².g⁻¹ producer by Mondo Minerals were used for the preparation of PLA6/PLA4 or PLA6/PLA4/M fibres. The various types of PLA and/or nucleation agent were mechanically mixed and spinning using

a laboratory line with single screw extruder having ratio screw of L/D=32, a spinning nozzle of 35 holes with diameter 0.3 mm, at the spinning temperature of 190°C and final spinning process speed of 250 m.min⁻¹. The undrawn fibres were drawn on the drawing ratio $\lambda=2.5$ at drawing temperature of 100°C.

The characterization of prepared PLA4/PLA6 and PLA4/PLA6/M fibres is in the Table 1.

2.2 Characterization methods

Rheological properties

Measurement of the rheological properties was evaluated by the capillary rheometer Gottfert RG20 at defined temperature 190°C. There was capillary with circle diameter with L/D = 30/1 in the range of shear rates from 360 to 9000 s⁻¹. On the basis of various rate of shifting of piston and measurement of pressure gradient there were generated uncorrected dependences of shear stress and viscosity on the shear rate for the evaluated blends for the determination of flow consistency index *K* and flow behaviour index *n* from Ostwald de Waele power (1):

$$\tau = K \cdot \dot{\gamma}^n \quad (1)$$

where: τ is shear stress and $\dot{\gamma}$ is shear rate.

All blends are materials with the Non-Newtonian behaviour therefore all measured rheological parameters were corrected using Rabinowitsch correction.

Supermolecular structure

Differential scanning calorimetric (DSC) measurement:

DSC 1/700 STAReSystem DSC 1/750 from Mettler Toledo was used for the evaluation of the thermal properties of pure and dyed PLA fibres. Non-isothermal analysis of prepared PLA4/PLA6 and PLA4/PLA6/M fibres was performed. A sample of original fibre was isothermally held for 3 minutes at the 30°C and next heated at a rate of 10°C.min⁻¹ from 30 to 190°C. All measurements were carried out in a nitrogen atmosphere. There was measured only 1st heating to the determined structure of prepared fibres during the spinning and drawing. From melting endotherms of 1st heating the glass temperature (*T_g*), enthalpy relaxation (ΔH_{ER}),

temperature (*T_{cc}*) and enthalpy (ΔH_{cc}) of cool crystallization, melting temperatures (*T_m*) and melting enthalpies (ΔH_m) were determined.

The sound speed in fibres:

The internal structure arrangement of PLA4/PLA6 and PLA4/PLA6/M fibres affects the sound speed in substances. Higher arrangement of super-molecular elements of structure gives the higher sound speed in fibre. It is used for the determination of the level of fibre anisotropy that characterises the super-molecular structure of observed fibres. The sound speed in fibres is given 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 PLA fibres dyed in mass was measured by Dynamic Modulus Tester PPMSR (USA).

Mechanical properties

The mechanical properties are represented by tenacity at the break, elongation at the break and Young's modulus. The mechanical properties (tenacity at the break σ , Young's modulus *E_Y* and elongation at the break ε) of PLA4/PLA6 and PLA4/PLA6/M fibres were analysed using Instron 3343 equipment (USA). Measuring conditions were the fibre length of 125 mm and the clamping rate of 200 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 the break) were determined in accordance with standard (Standard ISO 2062:1993).

Thermo-mechanical properties

Thermo-mechanical characteristics of PLA4/PLA6 and PLA4/PLA6/M fibres were measured by equipment Schimadzu TMA-50 (Japan). The deformation (extension *I₂* or shrinkage *I₁* [%]) and the temperature of first distortion of the fibres (*T*) were measured. The fibre was heated in the temperature range 30°C and 100°C, at the heating rate of 5°C.min⁻¹, fibre length 9.8 mm and at constant load; the dependence of the dimensional stability of fibre on the temperature was obtained from which the thermo-mechanical characteristics were determined.

Table 1 The characterization and fineness of the prepared PLA4/PLA6 and PLA4/PLA6/M fibres

PLA4/PLA6	C _{PLA4} [wt.%]	C _{PLA6} [wt.%]	T [tex]	PLA4/PLA6/M	C _{PLA4} [wt.%]	C _{PLA6} [wt.%]	C _M [wt.%]	T [tex]
10/90	10	90	85.6	30/70/0.25	30	70	0.25	103.6
20/80	20	80	87.1	30/70/0.5	30	70	0.50	86.8
30/70	30	70	106.3	30/70/0.75	30	70	0.75	85.6
40/60	40	60	83.1	30/70/1	30	70	1.00	79.3

3 RESULTS AND DISCUSSION

There were prepared two series of variously modified PLA fibres - PLA fibres with different contents of PLA4 and PLA6 and PLA fibres modified with various nucleation agent - talc content. Subsequently, the influence of PLA4 and nucleation agent on rheological, thermal, mechanical and thermo-mechanical properties of prepared fibres will be monitored (Tables 2-3, Figures 1-4).

Based on measurements of rheological properties, the higher PLA4 content decreases of the flow behaviour index n and increases the viscosities at two shear rates (1000 and 6000 s^{-1}) in comparison with the pure PLA6 that is the polymer produced for spinning process (Table 2). The higher talc content does not affect the flow behaviour of PLA4/PLA6/M (30/70/0-1) blends but the viscosity decreases significantly with the increasing of talc. The lower viscosity of PLA4/PLA6/M blends could provide their improved processability at the spinning and drawing and the preparation of fibres with the better structure and properties.

From the PLA4/PLA6 and PLA4/PLA6/M blends were prepared the fibres at the same conditions of spinning and drawing process. The observed properties – sound of speed, thermal parameter (glass temperature T_g , temperature T_{cc} and enthalpy ΔH_{cc} of cool crystallization, melting temperature T_m and melting enthalpy ΔH_m), mechanical (elongation at the break, tenacity at the break, Young's modulus) and thermo-mechanical (temperature of first distortion of the fibres, deformation - shrinkage or extension) was evaluated for the PLA4/PLA6 and PLA4/PLA6/M fibres with drawing ratio $\lambda=2.5$. For the PLA4/PLA6 (30/70 and 40/60) and PLA4/PLA6/M (30/70/0.25-1.00) fibres the drawing ratio $\lambda=2.5$ represents the maximal drawing ratio. The PLA4/PLA6 fibres with composition of 10/90 and 80/20 the drawing ratio $\lambda=2.5$ does not represent the maximal drawing ratio. It is possible to draw these fibres to the higher drawing ratio $\lambda=3.0$. The drawing ratio $\lambda=2.5$ was selected to compare properties of all prepared fibres.

The super-molecular structure of the prepared PLA4/PLA6 and PLA4/PLA6/M fibres was evaluated on the basis of the estimate of orientation by the sound of speed as well as of the thermal parameters - glass temperature, temperature and enthalpy of cool crystallization, melting temperature and enthalpy by DSC analysis (Table 3). The sound of speed of PLA4/PLA6 fibres was decreased with the increase of PLA4 content. But at same composition of PLA4/PLA6 (30/70) in PLA4/PLA6/M the sound of speed was increased after incorporation of nucleating agent compared with the sound of speed of PLA4/PLA6 (30/70) fibres. This may be the result of different crystallization ability of PLA in presence of the nucleating agent. The glass temperature for the all prepared PLA4/PLA6 and PLA4/PLA6/M fibres is more or less the same. The difference can be observed at the temperatures and enthalpies of cool crystallization and melting enthalpies of the prepared fibres. The temperatures and enthalpies of cool crystallization decrease with the increase of PLA4 content in PLA4/PLA6 fibres. In the PLA4/PLA6 fibres with the 30% PLA4 there were achieved the lowest temperature and highest enthalpy of cool crystallization. After addition of nucleating agent, the PLA crystallization process was changed. The single peak of cool crystallization with value of 98.9°C obtained for the PLA4/PLA6 fibre was divided into double peak of cool crystallization for the PLA4/PLA6/M fibres with the temperatures of about 77°C and 101°C. There was also observed the decrease of enthalpies of cool crystallization after the incorporation of nucleating agent that was reduced with the increase of content of nucleating agent (from 6 to 70%). Similarly, melting enthalpies of PLA4/PLA6 fibres were decreased with the increase of the PLA4 content. The addition of nucleating agent in the PLA4/PLA6/M fibres increased the melting enthalpies in comparison with the PLA4/PLA6 (30/70) fibre but the growth of content of nucleating agent did not cause a change in the melting enthalpies of PLA4/PLA6/M fibres.

Table 2 The rheological parameters (n , η) of the prepared PLA4/PLA6 and PLA4/PLA6/M fibres

PLA4/PLA6	n	η [Pa.s]		PLA4/PLA6/M	n	η [Pa.s]	
		$\dot{\gamma}=1000\text{ s}^{-1}$	$\dot{\gamma}=6000\text{ s}^{-1}$			$\dot{\gamma}=1000\text{ s}^{-1}$	$\dot{\gamma}=6000\text{ s}^{-1}$
0/100	0.33	405	68	30/70/0	0.28	534	89
10/90	0.29	413	69	30/70/0.25	0.27	449	75
20/80	0.29	414	69	30/70/0.5	0.28	437	73
30/70	0.28	431	72	30/70/0.75	0.29	446	74
40/60	0.26	477	79	30/70/1	0.30	439	73
100/0	0.24	534	89	-	-	-	-

Table 3 The sound of speed (C), glass temperature (T_g), temperature (T_{cc}) and enthalpy (ΔH_{cc}) of cool crystallization, melting temperature (T_m) and melting enthalpy (ΔH_m) of prepared PLA4/PLA6 and PLA4/PLA6/M fibres

PLA4/PLA6; PLA4/PLA6/M	C [m.s ⁻¹]	T_g [°C]	T_{cc} [°C]	ΔH_{cc} [J.g ⁻¹]	T_m [°C]	ΔH_m [J.g ⁻¹]
10/90	2246	63.1	104.9	14.7	164.4	31.8
20/80	2148	63.6	101.9	13.8	163.5	33.1
30/70	2067	62.6	98.9	17.4	161.8	26.3
40/60	2141	63.9	102.8	13.3	163.1	27.4
30/70/0.25	2264	62.9	76.9 100.6	16.1	162.6	30.2
30/70/0.5	2270	62.9	77.1 102.3	5.8	162.5	30.1
30/70/0.75	2191	63.1	76.8 100.8	12.2	162.4	30.6
30/70/1	2129	62.6	76.6 101.8	13.6	162.4	29.7

For the prepared PLA4/PLA6 and PLA4/PLA6/M fibres there were evaluated the mechanical properties like elongation at the break, tenacity at the break, Young's modulus in accordance with standard (Standard ISO 2062:1993) (Figures 1, 2). With the growth of PLA4 in the PLA4/PLA6 fibres the tenacity at the break and Young's modulus were reduced with the highest decrease for PLA4/PLA6 fibre with the PLA4 content of 30%. At the same the elongation at the break of PLA4/PLA6 fibres was decreased with the growth of PLA4 content. This is in conflict with the theory that expects that increase of tenacity and Young's modulus decreases elongation. This can be explained by the higher values of the elongation at the break.

The high values of the elongation at the break and the lower values of tenacity at the break and Young's modulus can show that the drawing process was not realised at the optimal preparation conditions.

At the evaluation of the mechanical properties (elongation at the break, tenacity at the break, Young's modulus) of PLA4/PLA6/M fibres with the content of 30% PLA4 and 0.25-1.00% nucleating agent it can be stated that elongation at the break decreases and tenacity at the break and Young's modulus increase. This may be the result higher orientation and crystallinity of PLA4/PLA6/M fibres in comparison with the PLA4/PLA6 fibres.

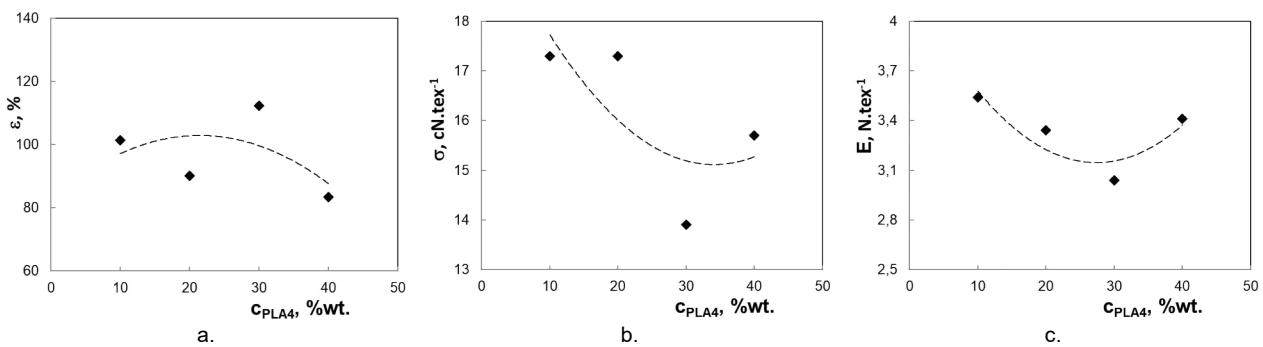


Figure 1 Dependencies of elongation at the break ε (a), tenacity at the break σ (b), Young's modulus E_γ (c) on the PLA4 content of PLA4/PLA6 fibres

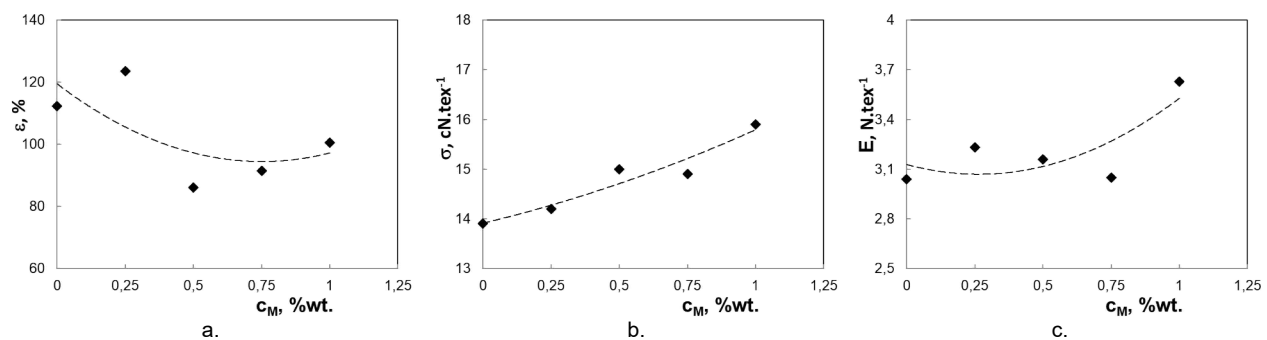


Figure 2 Dependencies of elongation at the break ε (a), tenacity at the break σ (b), Young's modulus E_γ (c) on the talc (M) content of PLA4/PLA6/M fibres

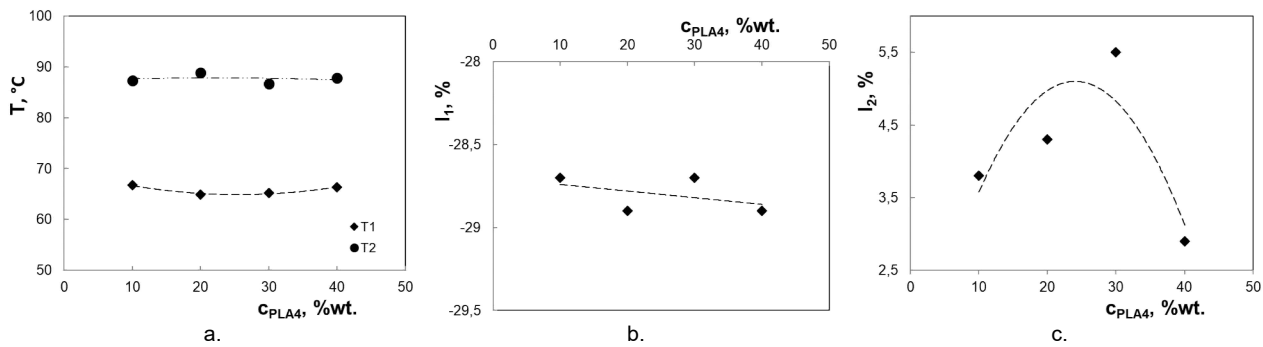


Figure 3 Dependencies of temperature of first distortion of the fibres T (a), deformation (shrinkage I_1 , b), deformation (extension I_2 , c) on the PLA4 content of PLA4/PLA6 fibres

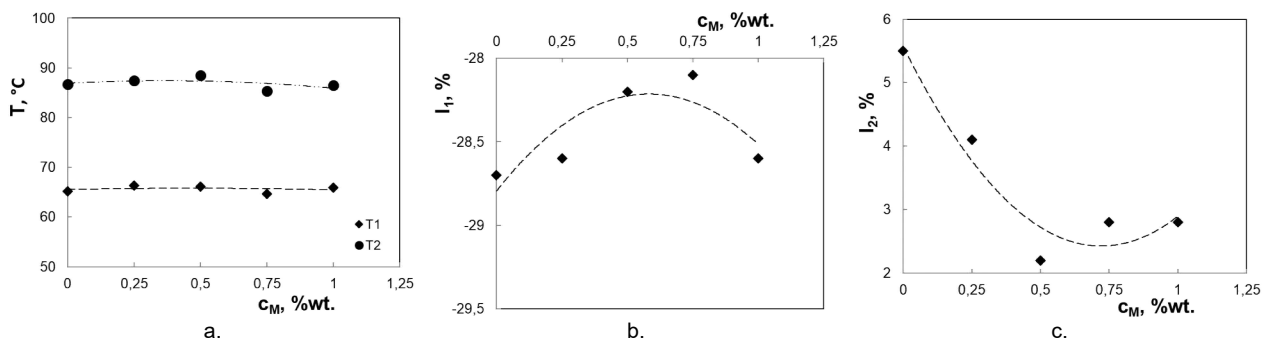


Figure 4 Dependencies of temperature of first distortion of the fibres T (a), deformation (shrinkage I_1 , b), deformation (extension I_2 , c) on the talc (M) content of PLA4/PLA6/M fibres

At the evaluation of thermo-mechanical properties (temperature of first distortion of the fibres, shrinkage/extension) there were observed the different behaviour of PLA4/PLA6 and PLA4/PLA6/M fibres (Figures 3, 4). The temperatures of shrinkage as well as temperatures of extension of all prepared PLA4/PLA6 and PLA4/PLA6/M fibres did not change in the full observed range of PLA4 (10-40%) and nucleating agent (0.25-1.00%) content. At the heating process of all prepared PLA4/PLA6 and PLA4/PLA6/M fibres temperature (about 65°C) it was observed as the first shrinkage at the temperature about 65-68°C and as the second extension at the temperature about 88-90°C. At the PLA4/PLA6 fibres the shrinkage was increased with the increase of PLA4 content. But the increase of nucleating agent content caused the reduction of shrinkage. This can be explained by the reinforcing effect of particles of nucleating agent at the lower temperatures. At the higher temperature during the heating process PLA4/PLA6 as well as PLA4/PLA6/M fibres were deformed. The extension of PLA4/PLA6 fibres rises with the increase of PLA4 to the 30% content. At the 40% PLA4 there were observed the reduction of extension of PLA4/PLA6 fibres. But the increase of content of nucleating agent induced the reduction of extension of PLA4/PLA6/M fibres. On the basis of obtained results from thermo-mechanical

properties it is possible to say that the PLA4 affects as the plasticizer in the PLA6 and the nucleating agent affects as the reinforcement in the PLA4/PLA6 systems for preparation of fibres.

4 CONCLUSION

The experimental work was focused on the preparation of fibres from various types of PLA and nucleating agent. There were prepared the PLA4/PLA6 and PLA4/PLA6/M fibres with the various content of PLA4 (10-40%) and various content of nucleating agent (0.25-1.00%). There was evaluated orientation, thermal, mechanical and thermo-mechanical properties. On the basis of obtained results following conclusions can be stated:

- the orientation of PLA4/PLA6 and PLA4/PLA6/M fibres was decreased with the increase of PLA4 content as well as with the increase of content of nucleating agent;
- the addition of nucleating agent changes the thermal behaviour - crystallization ability of PLA6 in PLA4/PLA6/M fibres in comparison with crystallization ability of PLA6 in the PLA4/PLA6 fibres;
- the tenacity at the break, elongation of the break and Young's modulus decrease with the increase of PLA4 content;

- the tenacity at the break and Young's modulus increase and elongation at the break decreases with the increase of content of nucleating content;
- on the basis of obtained thermo-mechanical properties it can be to say that the PLA4 behaves as plasticiser in PLA4/PLA6 fibres and nucleating agent behaves as reinforcement in the PLA4/PLA6/m fibres.

ACKNOWLEDGEMENT: *This work was supported by the Slovak Research and Development Agency under the contract No: APVV-17-0078.*

5 REFERENCES

1. Sin L.T.; Rahmat A.R., Rahman W.A.W.A.: Poly(lactic Acid); PLA Biopolymer Technology and Applications, Elsevier, Oxford, UK, 2013, ISBN: 978-1-4377-4459-0
2. Drumright E.R.; Gruber P.R., Henton D.E.: Poly(lactic Acid) Technology, *Advanced Materials* 12(23), 2000, pp. 1841-1846, [https://doi.org/10.1002/1521-4095\(200012\)12:23<1841::AID-ADMA1841>3.0.CO;2-E](https://doi.org/10.1002/1521-4095(200012)12:23<1841::AID-ADMA1841>3.0.CO;2-E)
3. Gupta V.B., Kothari V.K.: *Manufactured Fibre Technology*, 1st edition, Chapman and Hall, (eBook), 1997, 661 p., DOI 10.1007/978-94-011-5854-1
4. Avérous L.: Poly(lactic Acid): Synthesis, Properties and Applications, chapter 21 in *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Oxford, UK, 2008, pp. 433-450, ISBN: 978-0-08-045316-3