# EFFECT OF SPINNING AND DRAWING CONDITIONS ON STRUCTURE PARAMETERS AND MECHANICAL PROPERTIES OF PLA FIBRES

**Z. Tomčíková, Š. Krivoš, D. Rerková and K. Holcová**

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

***Abstract:*** *The biodegradable polymer, polylactic acid (PLA), is becoming more and more popular with manufacturers and traders in an effort to save our planet from plastic contamination. Pure or modified PLA is used in a variety of industrial areas, including fibres. Depending on the stereochemistry of the main chain, PLA can be partially crystalline or completely amorphous, from which its processing properties and method of use also depend. In this work the PLA of Luminy LX175 type was used. This PLA is a high viscosity, low flow, amorphous and transparent PLA resin suitable for film extrusion, thermoforming and also for fibres spinning. The influence of spinning temperature, PLA melt dosing and drawing on the basic parameters of the supramolecular structure (birefringence, sound speed and crystallinity), fineness and basic mechanical properties of fibres (Young's modulus, tenacity and elongation at break) were studied. It was found that the above-studied parameters have a significant effect on the evaluated properties of fibres.*

***Keywords:*** *PLA fibres, supermolecular structure, mechanical properties.*

## 1 INTRODUCTION

The development of the bioplastics industry has changed dramatically since the early 1990s. The latest generation is moving towards durable bioplastics with a high content of biological materials. The main goal is to replace "fossil carbon" with "renewable carbon", a holistic strategy to mitigate climate change by minimizing the product's impact on the environment during its life cycle. Durable bioplastics are in demand for multiple long-term uses in the automotive, food biomedical but also textile industries. The preference for "renewable carbon" over "fossil carbon" stems from the very awareness of our need to reduce the consumption of non-renewable resources and greenhouse gas emissions [1, 2]. The current pandemic situation also supports the growing global demand for personal protective equipment such as masks, gloves, gowns and bottled hand sanitiser, leading to the accumulation of solid polymer waste [3-5]. The search for materials with similar technical plastics that come from renewable sources is becoming a reality in the 21$^{st}$ century. Although there are already several bio-based technical plastics available on the market, the aim is to take advantage of the price competitiveness and unique properties of polylactic acid (PLA). PLA offers unique properties of biodegradability, biocompatibility, thermoplastic processability and ecological safety [6-8].

PLA was discovered in the 1920s by Wallace Carothers the scientist who invented nylon, but at this time never had been successfully commercialized on a large scale. PLA is aliphatic polyester, due to the ester bonds that link the monomeric units generally producing a lactic acid synthesis that can be produced from renewable sources such as corn, starch, sugar or other biomass [9, 10]. It is high-potential biodegradable thermoplastic polyester due to its unique physical properties, making it useful in a variety of applications, including surgical and medical applications, fibres, films and packaging. PLA is naturally degraded by an in situ hydrolysis mechanism: water molecules break the ester bonds that form the polymer backbone. PLA serves as an alternative to certain petroleum-based plastics in commercial applications. At present, there is a comparable price on the market to commonly available plastics such as polypropylene [2, 6].

PLA fibres are produced using lactic acid as a starting material, which comes from the fermentation of various sources of natural sugars. PLA fibres are used to provide low moisture absorption and high rise by capillary for sports and performance clothing and products. They have a high resistance to ultraviolet light, which is beneficial for outdoor use of furniture and furnishings. In addition to coming from renewable sources every year, PLA fibres are easily melted and offer production benefits that lead to greater consumer choice [11, 5].

The paper presents the results of a study of the PLA, type Luminy LX175, specifically the influence of spinning temperature, PLA melt dosing and drawing on the supermolecular structure parameters and basic mechanical properties of prepared fibres.

## 2 EXPERIMENTAL AND METHODS

### *2.1 Materials*

Polylactic acid LX175 (PLA) produced by Total Corbion PLA B.V with MFI = 12.8 g/10 min (210°C/2.16 kg) was used.

### *2.2 Fibre preparation*

The samples of PLA fibres were prepared using the classical discontinuous process of spinning and drawing. The laboratory discontinuous line had an extruder with a diameter of 32 mm, with a discontinuous one-step drawing process. PLA biopolymer has been dried before spinning for 4 hours at 85°C. The fibres were prepared at two spinning temperatures of 210°C and 220°C with a final spinning process speed of 1500 m/min. Subsequently, the fibres were drawn to a drawing ratio of $\lambda$=1.4, 1.6 and maximum drawing ratio $\lambda_{max,}$, at a drawing temperature of 100°C and a final drawing process speed of 100 m/min. Two 25 holes spinning nozzles were used for spinning, with a diameter of nozzle hole 0.26 mm. The two different dosage amounts of polymer melt 34.7 g/min and 22.5 g/min during spinning were used. Under the above conditions, samples of PLA fibres 1-16, which are listed in Table 1, were prepared.

**Table 1** The samples of PLA fibres prepared from biopolymer Luminy LX175

| Sample No. | Dosage of polymer melt [g/min/nozzle] | Temperature [°C] | Drawing ratio λ |
|---|---|---|---|
| 1 | 34.7 | 210 | undrawn |
| 2 | 34.7 | 210 | 1.4 |
| 3 | 34.7 | 210 | 1.6 |
| 4 | 34.7 | 210 | 1.68 |
| 5 | 34.7 | 220 | undrawn |
| 6 | 34.7 | 220 | 1.4 |
| 7 | 34.7 | 220 | 1.6 |
| 8 | 34.7 | 220 | 1.88 |
| 9 | 22.5 | 210 | undrawn |
| 10 | 22.5 | 210 | 1.4 |
| 11 | 22.5 | 210 | 1.6 |
| 12 | 22.5 | 210 | 1.66 |
| 13 | 22.5 | 220 | undrawn |
| 14 | 22.5 | 220 | 1.4 |
| 15 | 22.5 | 220 | 1.6 |
| 16 | 22.5 | 220 | 1.88 |

### *2.3 Methods used*

*Melt Mass-Flow Rate (MFR) of PLA* was evaluated using a capillary rheoviscosimeter Dynisco Kayness according to EN ISO 1133-1 under conditions: a temperature: 210°C, a load of 2.16 kg, a detention time of 5 min, nozzle diameter of 2.095 mm, a nozzle length of 8.00 mm, shear stress of 19.5 kPa. The sample has been dried before measurement 4 hours at 85°C.

*Birefringence*

The orientation of macromolecular chains in fibre expresses the level of anisotropy of the oriented polymer system (fibre). The total orientation of prepared modified PLA fibres was evaluated using polarization microscope DNP 714BI. The refractive indexes of light in the fibre axis ($n_{//}$) and in the perpendicular direction of fibre ($n_{\perp}$) were determined. From the difference of refractive indexes of light, the fibre birefringence ($\Delta n$) was calculated.

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

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

$$\beta = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m,0}} \cdot 100\ \% \qquad (1)$$

where: $\Delta H_{m,0}$ is the melting enthalpy of a 100% crystalline PLA (93.6 kJ.kg$^{-1}$) [12].

*Mechanical properties* were measured using Instron 3345 equipment (USA) with a gauge length of 250 mm and clamping rate of 250 mm.min$^{-1}$. An average of at least 10 individual measurements was used for each fibre. The mechanical characteristics (tenacity at the break, elongation at break and Young's modulus) were determined according to EN ISO 2062 and fineness according to the STN EN ISO 2060.

## 3 RESULTS AND DISCUSSION

The spinning of the studied type PLA biopolymer Luminy LX175 on two 25 holes spinning nozzles at a dosage of PLA melts 34.7 g/min per nozzle was at both spinning temperatures 210°C and 220°C at the standard level. Also, the spinning processes with dosing PLA melt 22.5 g/min per nozzle were satisfactory at both temperatures without interrupting the flow of the polymer stream under the nozzle.

**Table 2** Supermolecular structure parameters of PLA fibres

| Sample No. | Dosing and spinning temperature | Birefringence $\Delta n.10^3$ | $Vk_{\Delta n}$ [%] | Sound speed *c* [km/s] | $Vk_c$ [%] | Crystallinity $\beta$ |
|---|---|---|---|---|---|---|
| 1 | 34.7 g/min 210°C | 8.19 | 2.66 | 1.66 | 2.41 | 0.143 |
| 2 | | 17.91 | 2.98 | 1.81 | 2.34 | 0.265 |
| 3 | | 19.83 | 2.11 | 1.95 | 2.31 | 0.298 |
| 4 | | 24.41 | 1.94 | 2.05 | 2.53 | 0.314 |
| 5 | 34.7 g/min 220°C | 6.52 | 2.08 | 1.62 | 1.93 | 0.129 |
| 6 | | 13.78 | 3.17 | 1.75 | 2.04 | 0.249 |
| 7 | | 19.02 | 3.00 | 1,84 | 1.91 | 0.264 |
| 8 | | 23.57 | 1.34 | 1.94 | 2.61 | 0.304 |
| 9 | 22.5 g/min 210°C | 7.78 | 2.74 | 1.70 | 1.92 | 0.160 |
| 10 | | 16.41 | 2.70 | 1.94 | 2.71 | 0.301 |
| 11 | | 22.08 | 1.99 | 2.00 | 2.66 | 0.314 |
| 12 | | 22.35 | 2.04 | 2.08 | 1.97 | 0.347 |
| 13 | 22.5 g/min 220°C | 5.59 | 2.91 | 1.59 | 1.97 | 0.131 |
| 14 | | 13.14 | 3.09 | 1.79 | 2.08 | 0.231 |
| 15 | | 17.22 | 3.45 | 1.86 | 2.28 | 0.250 |
| 16 | | 22.18 | 3.18 | 1.97 | 2.15 | 0.264 |

The drawing of the fibres to a drawing ratio of 1.4 and 1.6 was reliable, without break, at both higher and lower dosing of the melt during spinning. A drawing to the maximum drawing ratio, only samples spun at 220°C showed a standard level. The samples spun at 210°C showed deterioration, with occasional fibre break during unidirectional deformation (drawing).

First, the structure of PLA fibres prepared from biopolymer Luminy LX 175 was studied. The results of supermolecular structure parameters are listed in Table 2. The change of spinning temperature, i.e. increasing the temperature from 210°C to 220°C, affects the supermolecular structure parameters. The effect of the spinning temperature of the PLA biopolymer on the supermolecular structure parameters was compared under the same dosing of PLA melt per nozzle. It was found that increasing the temperature from 210°C to 220°C reduces all structure parameters of undrawn fibres (Table 2).

For fibres 1-8 with a melt dosage of 34.7 g/min/nozzle, the total average orientation of macromolecular chains (birefringence) decreases by 20%, while for fibres 9-16 with a melt dosage of 22.5 g/min/nozzle there is a decrease of 28%. The decrease in the orientation of macromolecular chains in surface areas (sound speed) in the spinning field at the spinning speed of 1500 m/min did not exceed 10% in both cases of PLA melt dosing during spinning. At the same time, with increasing spinning temperature, a decrease of crystallinity at 10% in fibres 1-8 with a melt dosage of 34.7 g/min/nozzle and at 18% in fibres 9-16 with a melt dosage of 22.5 g/min/nozzle was observed. As the drawing ratio increases, the parameters of the supermolecular structure increase proportionally, as we can see in Table 2. The effect of different PLA melt dosing on the parameters of the supermolecular structure at the same temperatures was not clearly evident in the fibres. Slight deviations were noted, but in most cases they did not exceed 10%.

The spinning temperature also affects the process of uniaxial deformation of the fibres - drawing. A higher maximum drawing ratio ($\lambda_{max}$=1.88) was achieved for fibres prepared at a spinning temperature of 220°C, independent of the PLA melt dosing, which is due to the higher mobility of macromolecular chains and their segments at higher temperatures.

The reduction of the PLA melt dosing from 34.7 g/min per nozzle to 22.5 g/min per nozzle was most significantly reflected in the change in overall fibre fineness, which was reduced by 33% (Figure 1). The defined parameters of super-molecular structure undrawn and drawn PLA fibres affected their mechanical properties (Figures 1b, 2a and 2b).

The decrease in crystallinity due to the higher spinning temperature (220°C, Table 2) results in an increase in the elongation of the PLA fibres compared to the fibres obtained at the spinning temperature of 210°C, compared at the same drawing ratios (Figure 1b). At the same time as the drawing ratio increases, the elongation of the fibres decreases. With a lower melt dosage of 22.5 g/min per nozzle and a higher spinning temperature of 220°C, the fibres with the highest elongation were obtained.

The tenacity of the fibres depends on several factors. The first significant effect on increasing fibre tenacity at break has a drawing ratio, as seen in Figure 1. The highest tenacity of 2.7 cN/dtex was achieved at fibre prepared at a lower spinning temperature, with lower dosing, at the maximum drawing ratio.

The second significant effect on fibre tenacity has the spinning temperature. It can be seen in Figure 2a that the tenacities at the maximum drawing ratio and 210°C are comparable and higher

compared to the tenacities at 220°C and $\lambda_{max}$, even though the higher drawing ratio was obtained with fibres prepared at higher spinning temperatures (Table 2). The different of the PLA melt dosing on the fibre tenacity at the spinning temperature of 210°C did not manifest itself. A reduction in the tenacity of more than 16% was found for fibres prepared at 220°C with a melt dosing of 22.5 g/min per nozzle, except for the fibre at a drawing ratio of 1.4.

Young's modulus increases as the drawing ratio accretion. It is related to the increment in crystallinity in the fibres with a rising drawing ratio (Table 2).

The effect of the different spinning temperatures was manifested especially at drawing ratios 1.4 and 1.6, as can be seen in Figure 2b. By increasing the spinning temperature, the Young's modulus decreased by 16% at a dosing of 34.7 g/min per nozzle and by 26% at a dosing of 22.5 g/min per nozzle.

It follows from the above that, as in the parameters of the supermolecular structure, the most significant changes occur in fibres with a dosage of 22.5 g/min per nozzle due to the spinning temperature.

The obtained values of the basic mechanical properties are in good correlation with determined values of their supermolecular structure parameters.

## 4 CONCLUSION

From the spinning processes (spinning speed of 1500 m/min) and drawing (drawing ratios $\lambda$=1.4, 1.6 and $\lambda_{max}$) it follows, that processes are stable, only at maximum drawing ratios some occasional fibre breaks were occurred.

The dependencies of influence of spinning temperature, dosing of PLA melt per nozzle and uniaxial deformation (drawing) to the supermolecular structure parameters and basic mechanical properties were evaluated.

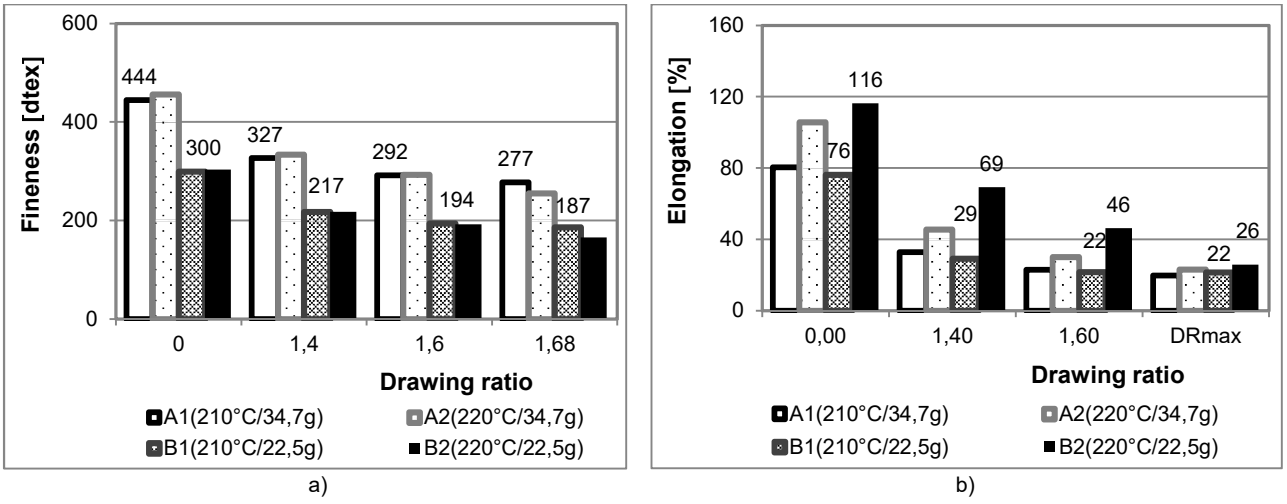


**Figure 1** Dependencies of fineness and elongation at the break on drawing ratio of PLA fibres

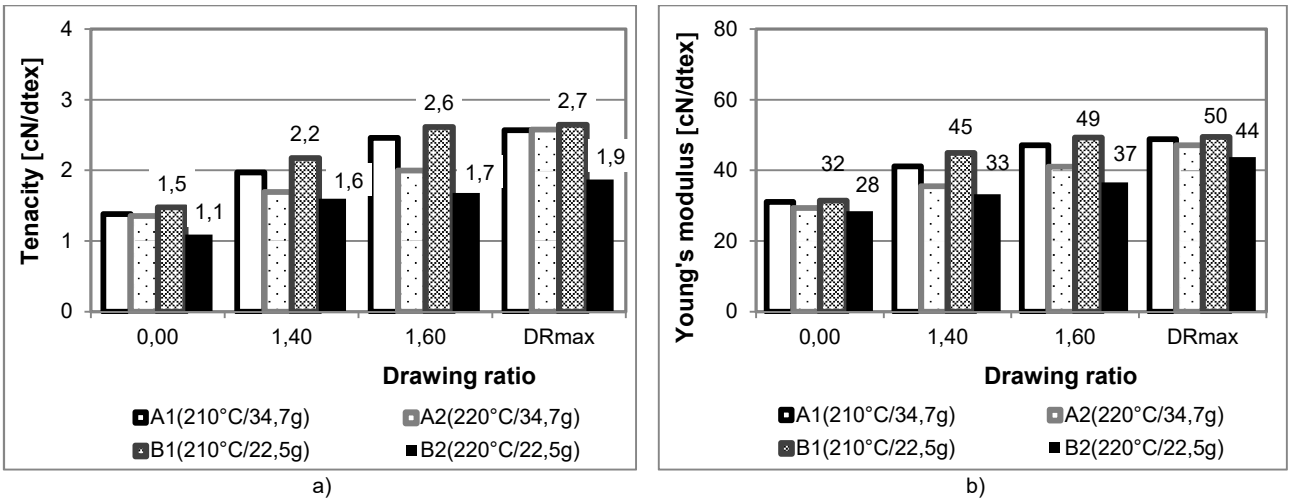


**Figure 2** Dependencies of tenacity at break and Young's modulus on drawing ratio of PLA fibres

It was found that in the spinning field at spinning temperature of 220°C a lower total orientation of macromolecular chains had occurred, which resulted to lower tenacity fibres in comparison with PLA fibres at 210°C. At the same time, lower crystallinity had occurred in PLA fibres prepared at 220°C, resulting in lower Young's modulus and higher elongation of fibres. Fibres with a lower dose of 22.5 g/min/nozzle show more significant changes in the parameters of the supramolecular structure due to temperature than fibres with a higher melt dose of 34.7 g/min/nozzle, but the impact of PLA melt dosing per nozzle on the supermolecular structure and mechanical properties of fibres is not obvious. The reduction of the melt dosage from 34.7 g/min/nozzle to 22.5 g/min/nozzle had the most significant effect on the change in the overall fineness of the fibres.

It was also found that process of uniaxial deformation has significant influence on studied properties of PLA fibres. The highest maximum drawing ratio at uniaxial deformation was reached for fibres prepared at a spinning temperature of 220°C. Nevertheless, the tenacities at a spinning temperature of 210°C were comparable and higher at the maximum drawing ratio compared to the tenacities obtained at the maximum drawing ratio at 220°C. As the drawing ratio increased, all structural parameters increased. By comparing the structure of drawing fibres at the same drawing ratios ($\lambda$=1.4 and 1.6), it was found that the increase in the crystallinity due to the increase in the spinning temperature. The decrease of the orientation of macromolecules chains in the direction of fibre axis of fibre (birefringence) as well as the orientation of macromolecules chains in the surface layers of fibre (sound speed) occurs mainly by increasing the spinning temperature from 210°C to 220°C.

The tenacity of drawing fibres increases in the same order at the same drawing ratios: 220°C/22.5 g/min < 220°C/34.7 g/min < 210°C/34.7 g/min < 210°C/22.5 g/min. Reciprocally to the tenacity, the elongation of the fibres decreases.

From the achieved structural and mechanical properties of the fibres was found, that the best suitable spinning process from PLA Luminy LX175 is the spinning temperature of 210°C, dosing of PLA melt per nozzle 22.5 g/min.

***ACKNOWLEDGEMENT:*** *This work was supported by the Slovak Research and Development Agency under the contracts No. APVV-18-0187 and No. APVV-17-0078.*

## 5 REFERENCES

1 Ibarra V.G., Sendón R., de Quirós A.R.B.: Antimicrobial food packaging based on biodegradable materials, chapter 29 in: Antimicrobial Food Packaging, 2016, pp. 363-384, https://doi.org/10.1016/B978-0-12-800723-5.00029-2

2 Nagarajan V., Mohanty A.K., Misra M.: Perspective on polylactic acid (PLA) based sustainable materials for durable applications: focus on toughness and heat resistance, ACS Sustainable Chemistry & Engineering 4(6), 2016, pp. 2899-2916, https://doi.org/10.1021/acssuschemeng.6b00321

3 European Environment Agency: Plastics, the circular economy and Europe's environment - A priority for action, Report No 18, 2020, pp. 1-76, ISBN: 978-92-9480-312-2, ISSN: 1977-8449, doi: 10.2800/5847

4 Shanmugam V., Babu K, Garrison TF, et al: Potential natural polymer-based nanofibres for the development of facemasks in countering viral outbreaks, Journal of Applied Polymer Science 138(17), 2021; pp. 1-19, https://doi.org/10.1002/app.50658

5 Gumel A.M., Suffian M, Annuar M., Heidelberg T.: Current application of controlled degradation processes in polymer modification and functionalization, Wiley Periodicals, Inc. Journal of Applied Polymer Science 129(6), 2013, pp. 3079-3088, doi: 10.1002/APP.39006

6 Carrasco F., Pages P., Gamez-Perez J., Santana O.O., Maspoch M.L.: Processing of poly(lactic acid): Characterization of chemical structure, thermal stability and mechanical properties, Polymer Degradation & Stability 95, 2010, pp. 116-125, doi: 10.1016/j.polymdegradstab.2009.11.045

7 Farah S., Anderson D.G., Langer R.: Physical and mechanical properties of PLA, and their functions in widespread applications – A comprehensive review, Advanced Drug Delivery Reviews 107, 2016, pp. 367-392, http://dx.doi.org/10.1016/j.addr.2016.06.012

8 Dreier J., Castellón S.M., Bonten Ch.: Bio-foams made of modified polylactide, bioplastics Magazine 16(01), 2021, pp. 32-33, ISSN 1862-5258

9 Gupta B., Revagade N., Hilborn J.: Poly(lactic acid) fiber: An overview, Proress in Polymer Science 37, 2007, pp. 455-482, doi: 10.1016/j.progpolymsci.2007.01.005

10 Ilyas R.A., Sapuan S.M., Harussani M.M., Hakimi M.Y.A.Y., Haziq M.Z.M., et.al.: Polylactic acid (PLA) biocomposite: processing, additive manufacturing and advanced applications, Polymers 13, 2021, 1326 pp. 1-34, https://doi.org/10.3390/polym13081326

11 Casalini T., Rossi F., Castrovinci A., Perale G.: A perspective on polylactic acid-based polymers use for nanoparticles synthesis and applications, Frontiers in Bioengineering and Biotechnology 7, 2019, Article 259, pp. 1-16, doi: 10.3389/fbioe.2019.00259

12 Cayuela D. et al.: 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, pp. 48-53, Dubrovnik, Croatia, October 3-6, 2010