

THE EFFECT OF DRAWING TEMPERATURE ON THE MECHANICAL PROPERTIES OF PLA FIBRES

Marcela Hricova, Erika Obertova and Anna Ujhelyiova

Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Department of Plastics, Rubber and Fibres, Radlinskeho 9, 812 37 Bratislava, Slovak Republic
marcela.hricova@stuba.sk

Abstract: Poly(lactic acid) (PLA) is one of the possible usable polymers that have the assumption to replace synthetic materials. Fibres made from PLA still do not achieve the properties of fibres made from synthetic polymers, and therefore the effort is to modify the production process of PLA fibres by additions of various additives. The aim of this work was to prepare the biodegradable fibres from PLA and to evaluate the influence of the preparation conditions on their mechanical properties. The special additives were added to the polymer mass to achieve better processability as well as better mechanical properties (tenacity and elongation at break) of PLA fibres. All prepared fibres were drawn at maximum drawing ratio λ_{max} at the drawing temperature 80; 90; 100 and 105°C. The effect of additives and the drawing temperature on the mechanical properties of the prepared PLA fibres was evaluated and discussed.

Keywords: Poly(lactic acid), biodegradable fibres, additives, mechanical properties.

1 INTRODUCTION

People have been using polymers for thousands of years. In ancient times was used natural plant gum, later were using plant-derived polymers, and about since 1495 the natural rubber was known. The first synthetic polymer (Bakelite) was invented by Leo Hendrik Baekeland in 1907 [1]. The invention of catalytic polymerization has significantly contributed to the rapid development of polymer technology in the last decades of the 20th century. Because common polymers (PE, PP, PS, ...) are very cheap and have a wide range of uses, environment contamination with polymers has become a serious worldwide problem. Synthetic polymers take hundreds years to completely degrade to harmless soil components. This, together with the reduction of oil resources, is forcing to orient the research to field of renewable materials as well as biodegradable polymers.

The first step in solving the problems with plastic waste was mixtures of polymeric biomass, which had better degradability compared to conventional plastics. The second step is biodegradable polymers which can be divided into two categories 1) petroleum-derived and 2) microorganism-derived [2]. 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 [3]. Most biodegradable polymers are in the polyesters group. Poly(lactic acid) (PLA) is a biodegradable polymer, which has been

receiving a lot of attention lately. PLA is made from lactic acid. Monomer - lactic acid can be produced by fermentation or chemical synthesis from carbohydrates. Fermentation of carbohydrates from agricultural crops such as sugar cane, potato and corn is more preferred [4, 5]. Poly(lactic acid) (PLA) was discovered in the early 19th century by Pelouze. The first PLA companies began to emerge in the 1990s [1]. PLA is the first melt-processable natural-based fibre which can be derived from 100% renewable resources [5, 6]. The environmental benefit of PLA is determined by its applications. PLA can be processed using conventional processing technologies used for thermoplastic polymers. From PLA can be formed transparent foils, fibres, or bottles (by injection into bottle preforms), etc. PLA has also excellent organoleptic properties and it is excellent for contact with food and packaging applications [7]. As PLA is the largest produced biodegradable polymer in the world and attains a reasonable price, many food industries, particularly those involving single-use applications like food packaging, utilize PLA as a food packaging material. PLA is a suitable substitute for existing petrochemical polymers for the fabrication of cups, containers, and packaging. At the spinning of PLA, the conditions and the way in which this process is carried out are very important. PLA fibres have been manufactured using both solution-spinning and melt-spinning methods [8, 9]. During the spinning from melt, the degradation of such material is greater than during the spinning from solution, and the molecular weight decrease correlates with the decrease in strength. By using of processing technology from melt, the two types

of fibres (mono and multifilaments) can be produced. Fibres made from PLA do not achieve the properties of fibres made from synthetic polymers (PP, PA, PET), and therefore, there is the attempt to modify not only the production process of PLA fibres but also the polymer mass, for example by the addition of various additives like fillers, plasticizers, pigments, nucleation agents, etc [10, 3].

This work was focused on the preparation of polylactic acid (PLA) fibres and modified PLA fibres with content of various additives. The influence of processing conditions and additives on mechanical properties (tenacity and elongation at break) of prepared PLA fibres was evaluated.

2 EXPERIMENTAL PART

2.1 Materials used

These materials were used in the experimental work:

Polylactid acid (PLA)

Additive 1 (A)

Additive 2 with lower concentration (B1) and additive 2 with higher concentration (B2)

2.2 Fibres preparation

PLA concentrates with final concentration of additives were prepared using LabTech extruder with diameter 28 mm (L/D = 40) at 190°C. Before spinning, PLA granulates were dried in a laboratory oven for 3 hours at temperature 80°C. PLA fibres and modified PLA fibres were prepared using a laboratory spinning plant at temperature 190°C with the take-up speed 150 m.min⁻¹. Fibres were drawn using a laboratory drawing machine at maximal draw ratios λ_{max} at drawing temperatures 80; 90; 100 and 105°C. The list and composition of fibres are presented in Table 1.

2.3 Method used

The Instron (Type 3343) was used for the measurements of the mechanical properties (tenacity and elongation at break) of fibres (according to ISO 2062:1993), evaluated from 15 measurements. The initial length of fibres was 125 mm and the time of deformation was about 20 sec.

3 RESULTS AND DISCUSSION

PLA fibres and modified PLA fibres with content of additives were prepared. The influence of drawing temperature and additives on mechanical properties of PLA fibres was investigated. With regard to the high sensitivity of polylactic acid on thermal degradation, the effect of real-time aging (during 90 days) on mechanical properties of prepared fibres was evaluated.

As we can see from the measured values in Table 1 and from the graphical dependence on Figure 1a, the tenacity of undrawn PLA fibres without the additives has a decreasing tendency depending on the aging time. The highest value of tenacity was measured after 14 days from the preparation of the fibres. The tenacity of PLA/A fibres increases slightly with increasing number of days. PLA fibres with the content of additive B also show similar dependences. The highest values of the tenacity of the undrawn modified PLA fibres were reached 90 days after spinning of fibres. In general, all undrawn PLA fibres containing additives showed lower tenacity than pure PLA fibre.

The addition of additives to the mass of PLA fibres caused an increase of the elongation at break for all modified fibres compared to pure PLA fibre (Table 1 and Figure 1b). The fibres containing the additive A show the highest values of elongation at break. The addition of additive B slightly reduces the elongation of the undrawn fibres, but these values are still higher than for pure PLA fibres.

Elongation at break for undrawn pure PLA fibres reached the lowest value after 90 days and the highest value after 21 days from fibre preparation. In general, modified PLA fibres show a decrease in elongation at break with on dependence on aging time. The exception is the elongation value 21 days after preparation, which is higher and comparable to the value immediately after fibre preparation and occurs for all PLA fibres with content of additives. The lowest values of elongation at break for these fibres were measured 90 days after fibre preparation (Figure 1b).

Table 1 Tenacity σ and elongation at break ε of undrawn PLA fibres measured during 90 days from spinning

| No. | composition of fibres | σ [cN/tex] | | | | | ε [%] | | | | |
|-----|-----------------------|-------------------|------|------|------|------|-------------------|------|------|------|------|
| | | 1 d* | 14 d | 21 d | 60 d | 90 d | 1 d | 14 d | 21 d | 60 d | 90 d |
| 1 | PLA | 6.7 | 7.3 | 6.6 | 6.4 | 5.6 | 181 | 164 | 189 | 166 | 142 |
| 2 | PLA/A | 5.1 | 5.4 | 5.3 | 5.5 | 5.8 | 240 | 223 | 240 | 214 | 202 |
| 3 | PLA/A/B1 | 4.6 | 4.9 | 4.8 | 5.3 | 5.6 | 221 | 201 | 211 | 188 | 177 |
| 4 | PLA/A/B2 | 5.1 | 5.3 | 4.8 | 5.3 | 5.8 | 230 | 219 | 224 | 197 | 181 |

*d – the number of days from spinning when the mechanical properties of the PLA fibres were measured

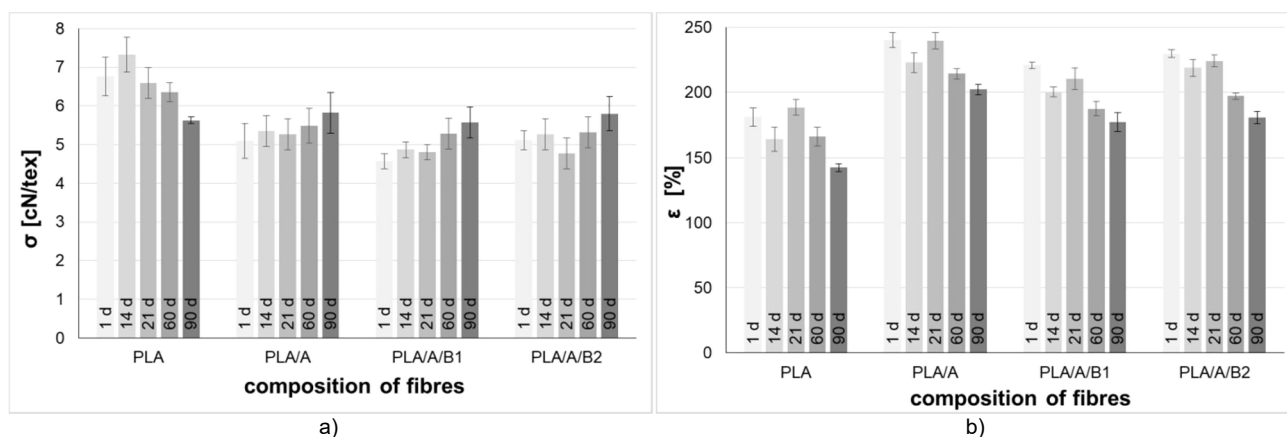


Figure 1 Tenacity (a) and elongation at break (b) of undrawn PLA and modified PLA fibres

Table 2 Tenacity σ and elongation at break ϵ of drawn PLA fibres measured during 90 days from spinning

| composition of fibres | drawing temperature [°C] | drawing ratio λ_{max} | σ [cN/tex] | | | | | ϵ [%] | | | | |
|-----------------------|--------------------------|-------------------------------|-------------------|------|------|------|------|----------------|------|------|------|------|
| | | | 1 d* | 14 d | 21 d | 60 d | 90 d | 1 d | 14 d | 21 d | 60 d | 90 d |
| PLA | 80 | 2.0 | 16.3 | 15.9 | 15.6 | 17.5 | 16.3 | 65 | 60 | 65 | 55 | 60 |
| PLA/A | | 2.7 | 15.0 | 17.1 | 16.9 | 17.2 | 17.0 | 60 | 71 | 53 | 52 | 71 |
| PLA/A/B1 | | 2.5 | 17.0 | 18.2 | 17.5 | 18.3 | 17.8 | 58 | 63 | 58 | 55 | 63 |
| PLA/A/B2 | | 2.6 | 18.0 | 19.9 | 17.8 | 18.9 | 18.1 | 52 | 57 | 61 | 47 | 50 |
| PLA | 90 | 2.4 | 21.1 | 20.0 | 21.4 | 22.2 | 23.3 | 64 | 41 | 41 | 37 | 44 |
| PLA/A | | 3.2 | 18.5 | 21.4 | 21.3 | 23.1 | 22.8 | 49 | 43 | 43 | 36 | 37 |
| PLA/A/B1 | | 3.0 | 18.4 | 22.9 | 20.3 | 21.5 | 22.1 | 45 | 44 | 47 | 41 | 39 |
| PLA/A/B2 | | 3.0 | 20.2 | 19.8 | 19.0 | 21.8 | 21.9 | 46 | 45 | 57 | 37 | 49 |
| PLA | 100 | 2.7 | 23.8 | 23.4 | 24.9 | 23.8 | 23.4 | 40 | 32 | 35 | 37 | 31 |
| PLA/A | | 3.5 | 23.1 | 24.1 | 23.1 | 25.2 | 23.7 | 36 | 35 | 42 | 38 | 31 |
| PLA/A/B1 | | 3.4 | 22.9 | 22.5 | 21.9 | 22.5 | 23.1 | 38 | 36 | 35 | 31 | 28 |
| PLA/A/B2 | | 3.5 | 20.2 | 23.4 | 22.9 | 24.4 | 25.9 | 33 | 38 | 38 | 32 | 37 |
| PLA | 105 | 3.0 | 25.4 | 25.2 | 25.8 | 25.4 | 26.4 | 32 | 26 | 26 | 26 | 26 |
| PLA/A | | 3.5 | 19.7 | 22.3 | 23.0 | 24.8 | 24.3 | 36 | 38 | 36 | 40 | 41 |
| PLA/A/B1 | | 3.6 | 20.5 | 24.8 | 24.4 | 23.6 | 25.7 | 35 | 33 | 32 | 31 | 29 |
| PLA/A/B2 | | 3.3 | 19.4 | 23.3 | 24.7 | 24.7 | 24.1 | 36 | 41 | 36 | 37 | 35 |

Pure PLA fibres as well as modified PLA fibres were drawn after spinning to the maximum drawing ratio at different temperatures in the range of 80-105°C. The influence of fibre composition as well as the conditions of their preparation, specifically drawing temperature, on the mechanical properties of PLA fibres was studied. At the same time, the effect of aging time on these fibres during three months after fibre preparation was monitored. The measured values of tenacity and elongation at break of drawn fibres are given in Table 2 and showed on Figures 2-5.

In the case of drawn PLA fibres, the influence of the drawing temperature dominates over the influence of the content of additives in the fibres. The effect of fibre's composition varies depending on the specific drawing temperature.

At the lowest drawing temperature 80°C, the effect of the fibre composition is clear, additives improve the tenacity of PLA fibres. The higher the additive content, the higher the fibres' tenacity (Figure 2).

At higher drawing temperatures (90-105°C) the unambiguous influence of the additives is lost and the tenacity values of pure as well as modified PLA fibres are similar within the measurement error (Figures 2a, 2b).

The drawing temperature is a very important factor influencing the mechanical properties of the drawn PLA fibres. From the graphical dependencies on the Figure 3, we can see that with increasing drawing temperature, the tenacity of the fibres increases. This is the case for pure PLA fibres as well as modified PLA fibres with additives.

The highest tenacity value of pure PLA fibres (26.4 cN/tex) was measured at drawing temperature of 105°C, 90 days after fibre preparation (Figure 3b).

The tenacity of PLA/A fibres reached the highest values at the drawing temperature of 100°C during the whole measurement period, while the largest increase in tenacity for PLA/A fibres was recorded 60 days after spinning (25.2 cN/tex).

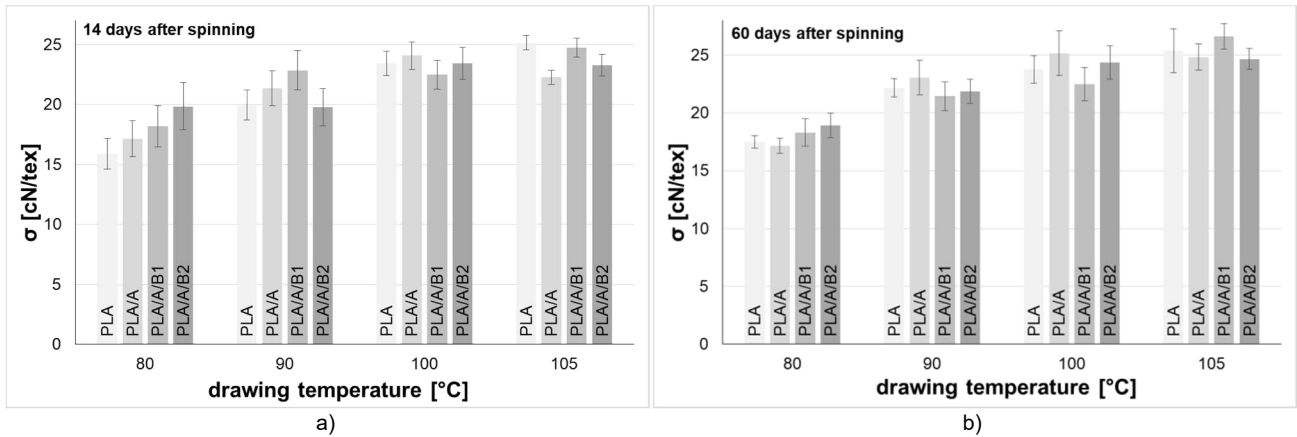


Figure 2 Tenacity of PLA and modified PLA fibres in dependence of various drawing temperature, measured a) 14 days and b) 60 days after spinning

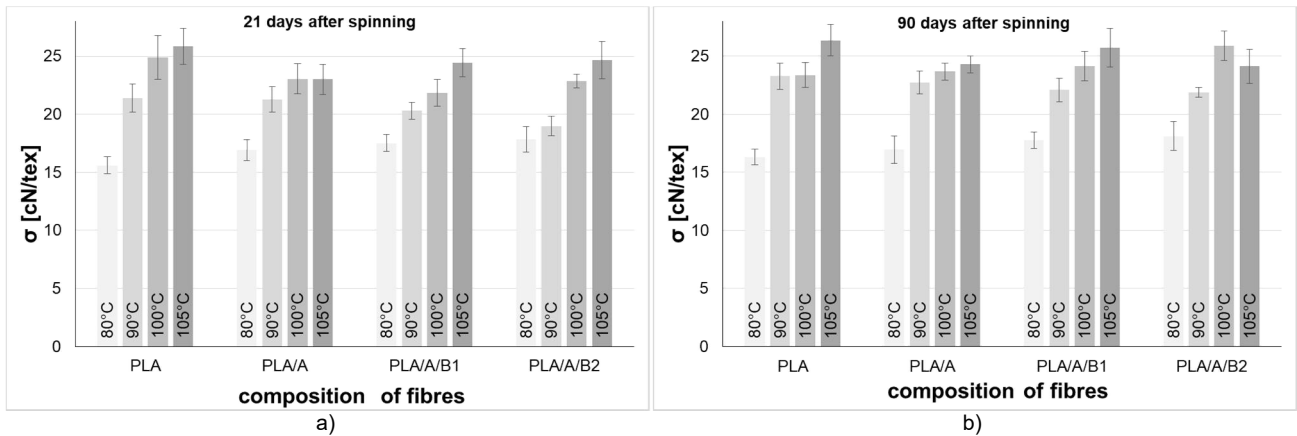


Figure 3 Tenacity in dependence of composition of PLA and modified PLA fibres, measured a) 21 days and b) 90 days after spinning

Fibres with a lower content of additive B generally show the best tenacity at drawing temperature of 105°C. The highest tenacity values were measured after 14 days (24.8 cN/tex) and 90 days (25.7 cN/tex) from fibre preparation. The tenacity of fibres with a higher concentration of additive B also increase with increasing drawing temperature and reach the highest value at 100°C after 90 days (25.9 cN/tex) and at 105°C after 21 days (24.7 cN/tex).

From the evaluation of these measurements, we cannot accurately determine one specific drawing temperature for all types of fibres, but based on the results, we can state that to achieve higher tenacity, PLA fibres must be drawn at a higher temperature 100-105°C.

During the whole period (1-90 days), when the mechanical properties of pure and modified PLA fibres were evaluated, no significant decrease in the tenacity of these fibres was recorded, even at any of the drawing temperatures.

The tenacity values practically did not change during the period of 90 days from the preparation of the fibres, or there was a slight increase. This suggests that no fibres degradation occurs over a period of 90 days. Likely, there is a gradual crystallization of the fibres, which results in an increase in the tenacity of the PLA fibres.

Elongation at break for pure PLA fibres as well as modified PLA fibres has a decreasing character depending on the drawing temperature (Table 2, Figure 4). At a drawing temperature of 80°C, all fibres, regardless of their composition, reach significantly higher values of elongation at break (47-71%) than at other drawing temperatures of 90°C (36-63%), 100°C (30-42%) and 105°C (26-41%). This shows to the fact that temperature of 80°C, in relation to the lowest achieved values of fibres' tenacity, is low and unsatisfactory for drawing of PLA fibres.

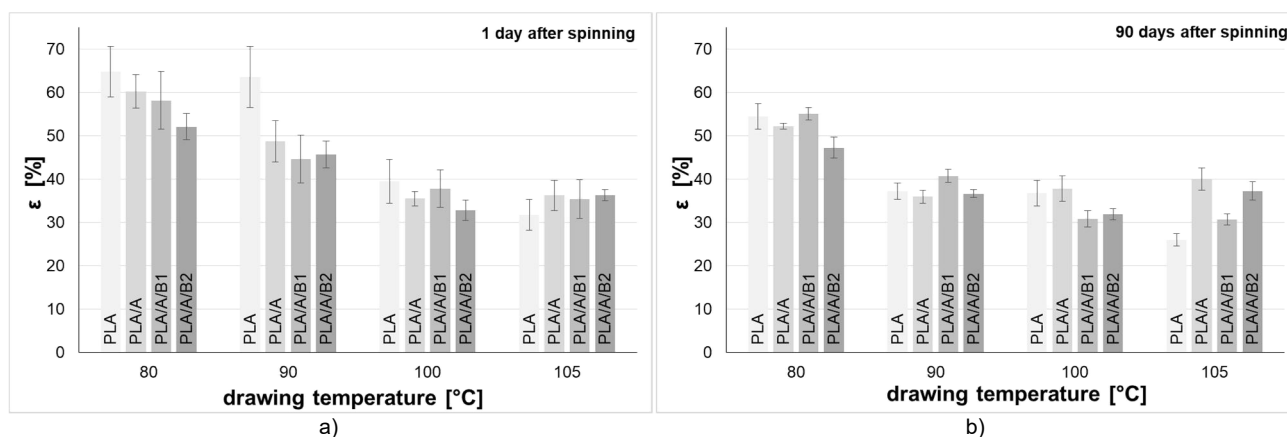


Figure 4 Elongation at break of PLA and modified PLA fibres in dependence of various drawing temperature, measured a) 1 day and b) 90 days after spinning

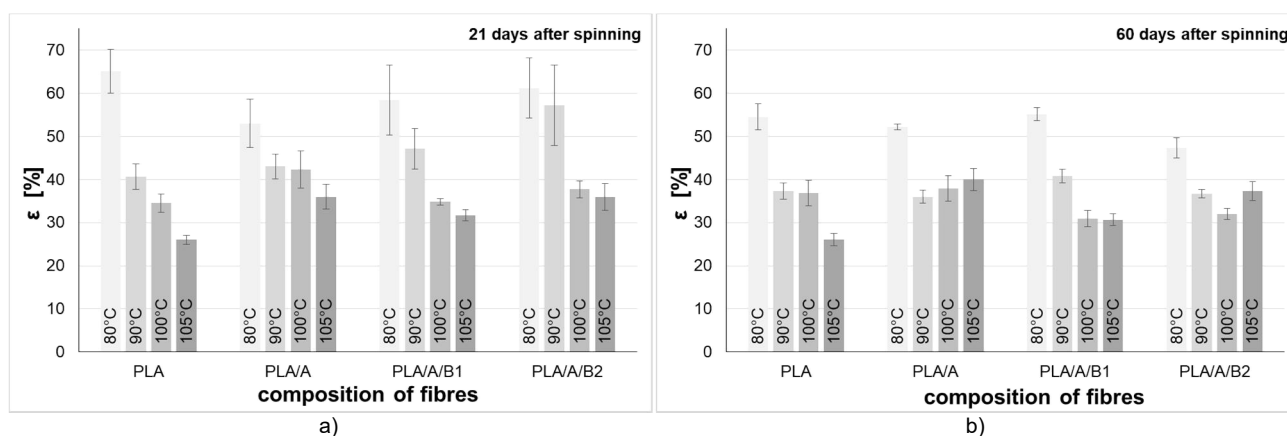


Figure 5 Elongation at break in dependence on composition of PLA and modified PLA fibres, measured a) 21 days and b) 60 days after spinning

The effect of the composition of individual types of PLA fibres is not clear. While at lower drawing temperatures of 80 and 90°C the difference in elongation values for individual fibres is more pronounced, at higher temperatures of 100 and 105°C it is lost and the elongation reaches similar values. This trend is especially visible in the first days after spinning (Figures 4a and 5a). After 60 days from the preparation of the fibres, their mechanical properties seem to have stabilized. There was a decrease in the elongation's values for the fibres drawn at 80 and 90°C, while the elongation's values for the PLA fibres drawn at 100 and 105°C remained at the same level (Figures 4b and 5b).

4 CONCLUSIONS

This work was focused on the preparation of polylactic acid fibres, which due to their properties could be a potential replacement for non-degradable petroleum-based polymers. The main goal of the experimental part was to observe and

evaluate the influence of fibre preparation conditions (drawing temperature) and the content of additives on the mechanical properties of PLA fibres. Based on the obtained data, the results can be formulated into the following conclusions:

- Pure PLA fibres and modified PLA fibres with content of additives were prepared and then drawn to a maximum drawing ratio at four different drawing temperatures of 80; 90; 100 and 105°C. The spinning and drawing of the fibres proceeded without any problems.
- In the case of undrawn fibres, the content of additives decreased the tenacity and increased the elongation at break of modified fibres in comparison with pure PLA fibres.
- The greater effect of drawing temperature than the effect of content of additives was found for drawn PLA fibres. The tenacity of drawn fibres increased with increasing of drawing temperature, in the case of pure PLA fibres as well as modified PLA fibres containing additives.

- No significant decrease in the tenacity of prepared PLA fibres was noticed (at any of the drawing temperatures) during the period (1-90 days), when the mechanical properties of pure and modified PLA fibres were evaluated,
- The elongation at break for pure PLA fibres as well as for modified PLA fibres has a decreasing character depending on the drawing temperature. A clear effect of the composition of individual types of PLA fibres and the concentration of additives on the elongation at break was not found.

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