Research and application of PLA fibres

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Abstract. This work is focused on characterization of spinning process of PLA fibres. PLA polymer with high melting point was modified by two hydrolytic additives in amounts (0 and 1 wt. %). Fully drawn (FDY) PLA fibres were prepared by melt spinning technique in the company Chemosvit Fibrochem a. s. (Svit, Slovakia). Preparation of PLA fibres was done by two different processes of continuous and discontinuous type. Different drawing ratios, take-up speeds and spin finishes for optimal fibre properties were used. Physical and mechanical properties of prepared FDY fibres, such as elongation and tenacity were measured. Prepared PLA fibres with different hydrolytic additives were process able in manufacturing process and this material could be used for various textile and composite applications.

1. Introduction of PLA
In recent years, development of bioplastics, or biopolymers, became more popular not only due to motives of environmental but also strategic nature. In order to reduce the impact on environment, especially amount of CO2 released, part of the products obtained from agriculture, like cellulose, starch, wood etc., are used as raw materials for polymer production. Polylactic acid (PLA) is highly versatile, biodegradable, aliphatic polyester which can be derived from 100 % renewable resources, like corn and sugar beets. PLA proved itself to be a promising alternative for petroleum-based polymers as its properties are on a par with currently widely used polymers like polypropylene, polyethylene, polyvinyl chloride, and polysteresters, such as polyethylene terephthalate [1, 2].

The bypassing of fossil raw materials, in fact their substitution for plant-based raw materials, lowers the carbon footprint of PLA significantly. On the other hand the possibility of biodegradation of PLA to water, carbon dioxide and soil biomass represents the possibility of 100% closed life-cycle of products made of PLA. Polylactic acid can be produced using different routes. In general, three methods are usually used to produce PLA. First one is direct condensation polymerization, second method is azeotropic dehydration condensation and third method is ring-opening polymerization, where PLA is produced by formation of lactide monomer first and by help of catalyst then converted into final product [3].

The production of PLA consists of production of lactic acid and subsequent polycondensation, with water as a byproduct, to PLA via one of several possible processes. Since lactic acid is a chiral compound, the stereoregularity of resulting PLA depends on the isomer distribution of the lactic acid used, which in turn is given by the production route [4]. In general, most common fermentation
processes produce the L-lactic acid. Regarding the polymerization processes, the main nuisance is the removal of water, since the polycondensation (esterification) and hydrolysis are reversible reactions.

2. Polymerization of PLA

Lactic acid is the most widely occurring hydroxycarboxylic optical active acid that can be produced by fermentation or chemical synthesis. It can be prepared both by conversion of petrochemical feedstock, such as acetaldehyde, or more cheaply biotechnologically by fermentation of molasses or potato starch or dextrose from corn. Synthetic production of lactic acid yields a racemic mixture of D- and L- isomers, while the fermentation process usually gives exclusively L-lactic acid [5, 6]. The direct condensation of lactic acid to PLA is an equilibrium reaction and the difficulties removing water limit the achievable molecular weight [5]. To avoid water and hydrolysis lactic acid can be condensed to a cyclic dimmer called lactide, striped of water and used as a feedstock for ring opening polymerization (figure 1).

Despite its disadvantages the direct esterification process was developed by Mitsui Toatsu Chemicals: This process utilizes a high boiling solvent and azeotropic distillation to reduce the water content in the reaction mixture [7]. The resultant polymer is a low to intermediate molecular weight material, which can be used as is, or coupled with isocyanates, epoxides or peroxide to produce a range of molecular weights [6, 8]. However, the more advanced and preferred PLA polymerization process uses the lactide intermediate. Compounds of aluminum zinc, tin, lanthanides and metal alkoxides have been investigated as PLA polymerization catalysts. Depending on the catalyst system and reaction conditions, almost all conceivable mechanisms (cationic, anionic, coordination-insertion) have been proposed to explain the kinetics, side reactions, and nature of the end groups observed in lactide polymerizations. Cargill Dow LLC has developed a patented, low-cost continuous process utilizing lactide. The first step of this process is continuous condensation yielding low molecular weight pre-polymer followed by catalytic cyclization. The resulting lactide is purified by vacuum distillation and subsequently polymerized to high molecular weight PLA using tin(II)bis-2-ethylhexanoic acid (tin octoate) catalyst, utilizing an coordination-insertion mechanism [9]. The optimal reaction conditions are 180–210 °C and 100–1000 ppm of tin octoate catalyst (figure 2) [10].

The various grades of PLA differ in stereochemical purity, molecular weight, and additive packages. Besides the molecular weight and its distribution, the stereoregularity has a major impact on the physical properties of the resulting polymer: pure poly(L-lactic acid) is a highly crystalline polymer, while inclusion of high D-isomer content yields a fully amorphous polymer. PLA made from pure L-lactide, poly(L-lactide), has an equilibrium melting point of 207 °C and a glass transition temperature of about 60 °C, also a polymer containing 1:1 mixture of D- and L- isomers called stereocomplex PLA with higher melting points is known. The highest melt point of commercial PLA
grades is around 180 °C. The addition of stereodefects reduces the melting point, rate of crystallization, and extent of crystallization of the resulting polymer but has little effect on the glass transition temperature. Poly(L-lactic acid) with addition of circa 15 % of D-isomer is no longer crystallisable. Standard-grade PLA has high modulus and strength and is lacking in toughness. The toughness of PLA can be dramatically improved through orientation, blending, or copolymerization [11, 12].

![Diagram of process of preparing polylactic acid without solvent.](image)

**Figure 2.** Process of preparing polylactic acid without solvent.

### 3. Biobased self-functionalised self-reinforced composite materials based on PLA fibres

As we mentioned at the beginning of the theory the PLA is biobased and sustainable thermoplastic polymer with good technical and practical performance. Unfortunately, PLA use has some limitations for e.g. packaging applications, medical application and also in textile applications. PLA can be produced with controlled molecular configuration (crystallinity, molecular weight, amount of L- and D-lactic acid etc.) which gives PLA a range of mechanical properties and with range of thermal properties, including different melting points.

*Fibrochem a. s.* is an industrial partner of the European project *BIO4SELF*. The main idea is to prepare a new product biocomposite with high tenacity and high tough, that could be used in ordinary life and bring some more ecological aspect for materials using in automotive industries, electro technical industries and also textile industries (figure 3).

#### 3.1. Consortium of the project

*BIO4SELF* is industrial oriented consortium coexists of partners from universities that are responsible for research and testing part of PLA polymer, partners responsible for industrial extrusion part, also partners responsible for marketing and financial part and partners that can finally implement product to standard users in market. The all partners were divided into work package-WP each responsible for another part of project like prepare stabilized PLA grade, extrusion part of produce, preparing composites for measure and final application. Also this project has partners that ensure management above all project and connection at web or media area and conferences, too.
3.2. Preparation of PLA fibre with high $T_m$

As mentioned above is necessary to have a material that can be used as a reinforcement for the matrix for better parameters to prepare an appropriate product [13].

Fibrochem a. s., focus on optimization of processing conditions during extrusion for realizing a maximal modulus and prepare fibres that could be repeatable with good parameters and also convenient from financial part. First of all we had to find a PLA material that should be good quality, shouldn’t be a problem to get just any amount of material necessary for testing and also be in competitive price with another materials. Project partners chose PLA grades for high and low $T_m$. The first trials showed us that is necessary to decide some basic parameters that will be key in the process of extrusion. In the Fibrochem a. s., had two possibilities how to prepare fibres. Continues process that whole production was working in one machine or discontinues process that technology used 2 machines with different properties. Over trials we were also tried several spinning oils that should bring the best properties over the multifilament yarn.

3.3. Properties of hydrolyse stabilized PLA compound

One of the negative parts of using PLA material is his big property of taken a moisture from the area and with this ability is very hard to keep production in good stabilize process.

Due to this problem it was necessary to think about some good stabilization that could help stay this type of polymer in process able conditions. Our partner had to examine different additives like anti-hydrolysis agents and prepare good hydrolytically stabilized compound. The new stabilized polymer had to be tried how influenced the mechanical properties like modulus and tenacity of multifilament yarn.

After received this new modified PLA compound, we had to in the company Fibrochem a. s., ensure material ready for the process able condition so it was necessary to dry this material so before extrusion we dried PLA polymer in the automatic continual dryer that worked at absorption principal mechanism that not only air dry before to contact with product but also special process of dehumidify in special dry box. This mechanism secures really low concentration of residual moisture of material.
3.4. Industrial scale multifilament extrusion process of PLA with high $T_m$

3.4.1. Discontinuous process

In the discontinuous 2 step process, the extrusion of the filaments is performed first (figure 4), after which the yarn is drawn on the drawing machine. Work started with the selected high $T_m$ PLA grade.

![Diagram of multifilament extrusion process]

Figure 4. First step: extrusion process (a) and second step: drawing process (b).

The first trial was carried out on the laboratory spinning line and drawing of the yarn was performed on the industrial drawing machine. Only a small amount was produced to set the conditions for the industrial line. Drying of the pellets was done in the laboratory dryer. Because of the limited speed of the laboratory line, the maximum take-up speed was limited to 1800 m min$^{-1}$.

Table 1 summarizes the obtained results. As can be seen, fairly good mechanical properties were obtained with this first trial, showing us the capability of the PLA filament extrusion process.

| Sample | 1step | Fineness (dtex) | Tenacity (cN dtex$^{-1}$) | Elongation (%) | 2step | Fineness (dtex) | Tenacity (cN dtex$^{-1}$) | Elongation (%) |
|--------|-------|-----------------|---------------------------|---------------|-------|-----------------|---------------------------|---------------|
| 1      | Spinning process | 271.1 | 1.21 | 138.3 | Drawing process | 161.9 | 1.94 | 60.0 |
| 2      | 328.3 | 1.29 | 139.3 | 196.3 | 1.85 | 62.8 |
| 3      | 328.1 | 1.13 | 131.5 | 197.8 | 1.95 | 59.4 |

Table 2. Industrial discontinuous process and heat setting.

| Sample | 1step | Fineness (dtex) | Tenacity (cN dtex$^{-1}$) | Elongation (%) | 2step | Heat set | Fineness (dtex) | Tenacity (cN dtex$^{-1}$) | Elongation (%) |
|--------|-------|-----------------|---------------------------|---------------|-------|----------|-----------------|---------------------------|---------------|
| 4      | Spinning process | 705.1 | 1.87 | 81.7 | Drawing process | 2 hour | 411.1 | 2.85 | 28.7 |
|        |       |                |                           |               |       |          | 429.5 | 3.28 | 38.7 |
|        |       |                |                           |               |       |          | 197.8 | 2.50 | 49.9 |

As a next step, the process was upscaled using the industrial extrusion machine. The extruder temperature was set like in line with the conditions set by CTB at pilot scale. A high take-up speed was selected since this is optimal for the mechanical properties. A stable extrusion process was thus obtained. However, the second drawing step was more challenging because of fibre breaks. Yet, the obtained yarns had good mechanical properties, meaning a tenacity of 0.31 N tex$^{-1}$.

After the yarn production, the bobbins were heat set in an autoclave for 2 hours at using dry steam. This resulted in a decrease of the tenacity table 2.
Because of the promising results obtained with the 2 step process, it was decided to work on the optimization of processing conditions, both during the extrusion as well as during the drawing step. The winding speed during the POY extrusion was varied in between 1500–3000 m min\(^{-1}\). As expected, the highest tenacity of these POY filaments was obtained using the highest take-up speed. Next, the filaments were drawn on the drawing machine and also here the conditions were varied (table 3). The speed of the drawing machine was varied between 500–600 m min\(^{-1}\) with the suitable draw ratio. From the point of view of process ability, the samples marked with a star showed the best process ability. Several conditions resulted in tenacities above 0.3 N tex\(^{-1}\). The modulus of the filaments was measured at CTB. Based on all data, the conditions of sample “5/1” were selected as standard processing conditions for the discontinuous filament production process. With these conditions, yarns with a fineness of 400–500 dtex, a tenacity of 0.34 N tex\(^{-1}\).

Table 3. Industrial scale discontinuous process with different parameters.

| Sample  | 1step  | Take up speed (m min\(^{-1}\)) | Fineness (dtex) | Tenacity (cN dtex\(^{-1}\)) | Elongation (%) | 2step  | Speed of machine (m min\(^{-1}\)) | Fineness (dtex) | Tenacity (cN dtex\(^{-1}\)) | Elongation (%) |
|---------|--------|-------------------------------|----------------|-----------------------------|---------------|--------|-------------------------------|----------------|-----------------------------|---------------|
| 5/1     | Spinning process | 3000 | 785.1 | 3.39 | 93.10 | | | | | |
| 5/2     | Spinning process | 2000 | 762.0 | 1.37 | 112.20 | | 500 | 439.3 | 3.40 | 29.0 |
| 5/3     | Spinning process | 1500 | 761.0 | 1.10 | 182.60 | | 550 | 446.3 | 2.41 | 47.3 |

3.4.2. Continuous process

In the continuous process, the extrusion and drawing is performed in 1 step (figure 5). Also here work started with the high \(T_m\) PLA grade.

![Figure 5. One step process – spinning and drawing.](image)

Optimization of the process was done in two different test runs. The final speed was varied between 2000 and 3300 m min\(^{-1}\) and the draw ratio from 1.8 to 2.4 (tables 4 and 5). Increasing the draw ratio subsequently increases the tenacity. However, at the highest draw ratios, the process was less stable.
By decreasing the draw ratio and the temperature of the third godet, the production became stable. Also here some bobbins were used for heat setting at for 55 min, resulting in an increase of the modulus.

### Table 4. Industrial scale continuous process with different parameters: test run 1.

| Sample | 1 step | Draw ratio | ORV (rpm) | Fineness (dtex) | Tenacity (cN dtex⁻¹) | Elongation (%) |
|--------|--------|------------|-----------|-----------------|----------------------|----------------|
| 1      |        | 1.75       | 8.0       | 410.0           | 1.39                 | 48.6           |
| 2      |        | 1.75       | 8.0       | 408.0           | 1.47                 | 52.9           |
| 3      |        | 1.83       | 8.0       | 388.6           | 1.62                 | 40.7           |
| 4      |        | 1.92       | 8.0       | 371.9           | 1.76                 | 39.3           |
| 5      |        | 2.01       | 8.0       | 355.8           | 1.88                 | 40.6           |
| 6      |        | 2.08       | 8.0       | 346.6           | 1.93                 | 37.1           |
| 7      | Spinning process | 2.17       | 9.5       | 364.6           | 2.06                 | 37.7           |
| 8      |        | 2.25       | 9.5       | 377.6           | 1.97                 | 38.1           |
| 9      |        | 2.25       | 9.5       | 391.4           | 1.83                 | 31.6           |
| 10     |        | 2.25       | 9.5       | 342.5           | 2.04                 | 29.4           |
| 11     |        | 2.50       | 9.5       | 342.5           | 1.87                 | 29.3           |
| 12     |        | 2.49       | 10.5      | 379.2           | 1.71                 | 34.1           |
| 13     |        | 2.99       | 10.5      | 380.6           | 1.79                 | 26.2           |
| 14     |        | 2.85       | 10.5      | 384.0           | 1.93                 | 31.8           |

### Table 5. Industrial scale continuous process with different parameters: test run 2.

| Sample | Pressure on spinneret (bar) | Draw ratio | Fineness (dtex) | Tenacity (cN dtex⁻¹) | Elongation (%) |
|--------|----------------------------|------------|-----------------|----------------------|----------------|
| 15     | 21                         | 1.87       | 403.1           | 1.39                 | 48.6           |
| 16     | 21                         | 2.07       | 430.2           | 1.47                 | 52.9           |
| 17     | 21                         | 2.15       | not procesable  |                       |                |
| 18     | 21                         | 2.42       | not procesable  |                       |                |
| 19     | 21                         | 1.49       | 364.4           | 1.95                 | 48.1           |
| 20     | 21                         | 1.60       | 402.5           | 1.87                 | 36.9           |
| 21     | 21                         | 1.65       | not procesable  |                       |                |
| 22     | 21                         | 1.65       | 407.9           | 2.01                 | 39.4           |

Comparing the continuous and discontinuous process, better mechanical properties were obtained with the discontinuous process (a tenacity of 0.34 N tex⁻¹ for the discontinuous process compared to 0.20 N tex⁻¹ for the continuous process). However, a better process ability, being a more stable process, was obtained for the continuous process. Depending on the requirements for the end products, a selection will be made between both processes, also taking into account the costs.

### 3.4.3 Evaluation of different spinfinishes

Following the positive results of CTB with the different spinfinishes, they were also tested at industrial scale, using the continuous process. The goal of the test was to evaluate the overall process ability and the reached physical and mechanical properties. Four types of spinfinishes were next tested (at a concentration of 100 %): A, B, C, D.

Very good process ability was realized using these spinfinishes, with the best stability for the C-17-C, D. Also good mechanical properties were obtained with tenacity up to 0.28 N tex⁻¹ in the 1 step process (table 6).
Table 6. Spinfinish test – continuous process.

| Sample | Gear pump (rpm) | Fineness (dtex) | Tenacity (cN dtex⁻¹) | Elongation (%) |
|--------|-----------------|-----------------|----------------------|---------------|
| A      | 3               | 501.5           | 2.69                 | 26.31         |
| B      | 3               | 504.2           | 2.56                 | 28.82         |
| C      | 3               | 534.6           | 2.63                 | 30.69         |
| D      | 4               | 526.5           | 2.78                 | 31.86         |

4. Conclusion
The main idea of this project was to investigate if PLA material could be used for the composites in many fields of application. From the preliminary results we can say that this type of polymer that we decided to study has properties that should changed product that are using mostly nowadays.

Research of the possibility to extrude a material of PLA with high $T_m$ for reinforcement PLA composites shows up that could be process able in bigger production volume.

The direct conditions and work procedure to get FDY yarn for composites were more or less achieved by company Fibrochem a. s., responsible for this step of project. As best fineness we decided for 400 dtex and 100 filaments of raw PLA grade. The last result showed quiet good physical-mechanical properties in strength that was 2.6 cN dtex⁻¹ and elongation 24.4 %. From technological part as good choice we decided to use continuous process of extrusion that parameters were comparable with discontinuous process and we save one more technological step of whole process and also from time part it is better choice.

From financial view is still this type of composite expensive as a processed material but for the future potential to offer PLA yarn as good product for agro, geo, textile departments from especially environmental part.

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