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**THE ANALYSIS OF THE EFFECT OF POLY(LACTIC ACID) AND FILLED  
POLY(LACTIC ACID) CRYSTALLINE STRUCTURE ON THE TECHNICAL  
PROPERTIES**

**PHD THESIS BOOKLET**

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## **1. Introduction**

Since the second part of the 20th century the plastic industry has started to grow and it has been producing more and more raw materials with better quality, which have been appearing in many technical fields. Because these synthetic polymers are based on crude oil, and their widespread distribution, we might think that the plastics industry uses a large amount of crude oil, but it is only 7% of the world production, all the other parts are spent on energy production. According to Plastics Europe's 2017 report the plastic production was 355 million tonnes and due to the finite amount of oil stocks and strict environmental regulations the industry had to look for new resources for plastic production. So the renewable based biodegradable polymers got more and more attention in the polymer industry and research.

These biopolymers could solve a number of problems such as recycling or environmental pollution, because these types of polymers under appropriate conditions (water, temperature, microorganisms) are decomposed into carbon dioxide, humus and water. It is important to mention that biopolymers could be processed with conventional thermoplastic technologies (injection molding, extrusion, etc.) but their wide application is not typical yet.

Poly(lactic acid) is one of the most promising biopolymer, which has good tensile strength (50-60 MPa) and modulus (2-3 GPa) compared to the conventional oil based technical polymers. Unfortunately PLA has some disadvantages such as the rigid behaviour and the low heat resistance (55°C). For this reason, its application has not been extended to technical areas it has only been involved mostly in the packaging industry, while conventional oil based plastics are still the main raw materials in the field of technical applications. There are several possible ways to modify PLA to get better properties, such as the modification of crystallinity and crystal structure, the usage of various nucleating agents and fillers or making biocomposites with cellulose based fibers.

The aim of my dissertation is to analyse the connections between the crystalline structure and the mechanical and thermal properties of neat and filled PLA.

## **2. Summary of the literature, objectives of the dissertation**

Poly(lactic acid) was known at the beginning of the 20th century, but it got attention in the 2000s. Numerous literature (articles, books) focus on PLA due to its outstanding mechanical properties among the biopolymers, which placed the PLA in the center of many researches. The research results showed that the heat deflection temperature and toughness of PLA should be improved for technical applications, which in most cases the researcher tried to achieve by some kind of fiber reinforcement.

One of the most important properties of PLA is its crystallinity and the crystalline structures what are produced during the processing of PLA. In the literature several articles can be found about the crystallization of a selected PLA type under different conditions. However, these articles only discussed the different crystal structure, what were formed during different crystallization processes, and did not make connections between the crystalline structure of PLA and its mechanical and thermal properties. Therefore, our information is incomplete about mechanical (strength, modulus, impact strength, creep) and thermal (heat deflection) properties during different crystallization conditions.

An other important properties of each PLA type is its D-lactide content, which also has an effect on the main properties of PLA. By increasing the D-lactide content the maximum crystallinity, that can be obtained and the crystal melting temperature are decreased. Above around 10% D-lactide the specimen remains amorphous. Furthermore, it is important to mention the slow crystallization of PLA, because some type of PLAs reach low crystallinity even at 5°C/min cooling rate. This disadvantage can be effectively counteracted by using different nucleating agents. Generally, in the scientific articles only one type of PLA is used, so it is difficult to compare the mechanical, thermo-mechanical and thermal properties of the PLAs produced in the same conditions but with different D-lactide content.

One of the main disadvantage of PLA is its low toughness ( $\sim 2-3$  kJ/m<sup>2</sup> notched Charpy impact strength) which makes it difficult to use in technical applications. It can be a good alternative solution, that PLA can be mixed with natural rubber. The basic properties of PLA/NR blends can be found in the available literature, but these mainly focus on the increased impact strength, and less information can be found about the other properties. At the same time these articles did not mention the effect of NR on the crystalline structure, and the combined effect of NR and the presence of different crystalline structures on the mechanical and thermal properties.

Another possible way to modify the strength, impact strength, heat deflection temperature and other properties of PLA is to produce fiber reinforced composites. Natural fiber reinforcement increases the strength, modulus, impact strength, and it could be preserve the biodegradability of PLA composite. There are many literature results about the properties of different cellulose based fiber (hemp, cotton, jute kenaf, etc.) reinforced PLA composites. These results showed that the most important factor is the fibre-matrix adhesion. In some cases the fiber reinforcement had negative effect and the strength of the composite did not reach the strength of PLA. In many research number of surface treatments have been tested, among them alkaline and silane versions gave the best result. The disadvantages of surface treatments are that they are toxic, and the application time is long. In the field of biocomposites, most of them were made by film stacking and injection molding was used only in few cases. Only one article mentioned the long fiber granulates, but the researchers extruded

these granulates again before the injection molding, which caused fiber break. Furthermore the cross effect between the fibers and the crystalline structure has not been analysed.

In addition to mechanical and thermal properties it is necessary to know the long-term (creep) properties of PLA for use in technical applications. In the literature there is less information about the long-term behaviour of PLA.

Based on the literature review, I set out the following objectives:

- The analysis of the effect of crystallinity and different crystalline structures on the mechanical, thermal properties, under different crystallization conditions
- The investigation of D-lactide content of PLA in terms of heat treatment, mechanical and thermal properties
- Examination of the effectiveness of different nucleating agents on the crystallization of PLA with different D-lactide content.
- Increasing the toughness of PLA by using renewable resource based materials such as natural rubber and cellulose fibers.

### **3. Materials and methods**

#### **3.1. Materials**

For the experiments three different PLA grades were chosen from Natureworks which were Ingeo 3100HP, 3001D and 3052D, which contained 0.5%; 1.4% and 4% D-lactide respectively. As a crystalline nucleating agent an aromatic phosphonate (Ecopromote, Nissan Chemicals Industries Ltd., Japan), a potassium dimethyl 5-sulfisophthalate (LAK301, Takemoto Oil & Fat Co. Ltd., Japan) and orotic acid were used. For the PLA/natural rubber blends SVR CV60 type natural rubber (Variachem, Hungary) was used. For the composites regenerated cellulose fibre (Viscord Bohemia Super 2, Glanzstoff Bohemia, Czech Republic) was used as a reinforcement.

#### **3.2. Processing methods**

The specimens were made by injection molding on an Arburg Allrounder 370S-290 type machine. The melt temperature and the mold temperature were 190°C and 25°C. The injection molding parameters were the following: injection volume: 44 cm<sup>3</sup>, switchover point: 12 cm<sup>3</sup>, injection rate: 50 cm<sup>3</sup>/s, holding pressure: 600 bar, holding time: 20 s, residual cooling time: 40 s. In the case of composite injection molding also 170, 210 and 230 °C were used as melt temperature.

The samples with nucleating agents were made by an internal mixer for the differential scanning calorimetry. The used mixing temperature was 190°C and the mixing time was 5 minutes.

The poly(lactic acid)/natural rubber blends were made by extrusion and internal mixing technology. 190°C was chosen for processing temperature for both technology, while the screw speed was 20 rpm for the extrusion and the internal mixing parameters were 50 rpm and 5 minutes

The cellulose fibre reinforced poly(lactic acid) preforms were made by extrusion coating with a special coating die. the extrusion temperature was 190°C while the die temperature was 250°C.

### 3.3. Testing methods

#### 3.3.1. Determination of moisture content

During the moisture loss measurement the i put the samples in a vented oven at 80°C 100°C and 120°C. I calculated the moisture loss by using the mass measurement of the samples time by time. According to the (1) the moisture loss is:

$$n_{le} = \frac{m_{sze} - m_{sz}(t)}{m_{sze}} \cdot 100 [\%], \quad (1)$$

where  $n_{le}$  [%] is the moisture loss,  $m_{sze}$  [g] is the mass of the sample before the drying,  $m_{sz}(t)$  [g] is the mass of the sample during the drying at given time.

#### 3.3.2. Melt flow index (MFI)

To characterise the melt flow index of different PLA samples a Ceast 7027 type melt flow tester were used. The used temperature and load were 210°C and 2.16 kg respectively. Also 1 minute preheat was used.

#### 3.3.3. Tensile test

Tensile testing was performed by right of MSZ EN ISO 527-1:2012 standard. Zwick Z020 universal tensile testing machine was used equipped with a type Zwick BZ 020/TN2S force measuring cell For the tensile 1A type dumbbell specimens were injection molded. Test speed was 5 mm/min, the initial distance between grips was 110 mm. Measurements were performed at room temperature. From the force-extension curves tensile strength, tensile modulus, and strain at break were calculated.

### **3.3.4. Flexural test**

Flexural test was performed by right of MSZ EN ISO 178:2011 standard. Zwick Z020 universal tensile testing machine was used equipped with a type Zwick BZ 020/TN2S force measuring cell. For the bending test 4 mm thick, 10 mm wide specimens were injection molded. Test speed was 5 mm/min, the length of span between supports was 64 mm. Measurements were performed at room temperature. From the force-extension curves flexural strength, flexural modulus were calculated.

### **3.3.5. Charpy impact test**

Charpy impact test was performed by right of MSZ EN ISO 179:2010 standard. For the test notched specimens, were used with 4x8 mm area and the length of span between supports was 62 mm. 2 J hammer was used with an initial angle of 150°, thus the impact energy was 2 J. Measurements were performed at room temperature. From the absorbed energy notched Charpy type impact strength was calculated.

### **3.3.6. Creep test**

Creep tests were made according to the PhD work of Péter Bakonyi, PhD. The easurements were carried out in a tensioning mode at a room temperature (25°C) in a force controlled mode on a Zwick Z005 type universal testing machine. For the measurements I used standard 1A type injection molded specimens. Each measurement were carried out at different load levels (5, 7.5, 10, 12.5, 15, 20, 25, 30, 35, 40, 50, 60, 65, 70, 75, 80, 85, 90, 95% of maximum breaking force) for one hour. Short-time creep curves shifted along the logarithmic time axis using the principle of the load level and time superposition to determine the master curves for the selected load levels of each sample.

### **3.3.7. Scanning electron microscopy (SEM)**

The SEM observations were made using a Jeol JSM-6380LA type scanning electron microscope. The samples were coated with Au by using a Jeol JFC-1200 gold coating equipment to avoid electrostatic charging during the measurements. 15 kV of accelerator voltage and a magnification of 50, 100, 200, 500 were used.

### **3.3.8. Polarized light microscopy (PLM)**

Polarized optical microscopic images of heat-treated samples were made with a Keyence-VHX-6000 microscope equipped with a VHX-Z100R objective and polarized lenses.

### **3.3.9. Heat deflection temperature (HDT)**

The HDT Type B measurement was carried out according to the MSZ EN ISO 75: 2004 standard on a Ceast HV3 6911 instrument. For the measurements I used standard 4x10 mm cross section and 80 mm long injection molded specimens. The support distance was 64 mm and the applied load was 0.45 MPa. The test specimens were placed in a silicone oil bath and measured the temperature at which the bending of the specimen reached 0,34 mm during the three-point bending. The heating rate was 2°C/min during the measurement.

### **3.3.10. Differential scanning calorimetry (DSC)**

DSC measurements were made with a TA Instruments Q2000 type machine. The sample size was between 3-6 mg. Different isotherm (80-140°C) and heat-cool-heat measurements were carried out. During the isotherm measurement the heating rate was 50°C/min, and in the heat-cool-heat analysis it was 5°C/min.

### **3.3.11. Dynamic mechanical analysis (DMA)**

DMA measurements were performed on a TA Instruments Q800 type equipment. The specimen had a cross section 4x10 mm, the span between the support was 35 mm. The measurement were done in 0-180°C range and dual cantilever setup was used with 20 µm amplitude and 1 Hz frequency. The heating up rate was 2°C/min.

### **3.3.12. Small angle X-ray scattering (SAXS)**

The SAXS measurements were made at Institute of Materials and Environmental Chemistry, (Research Centre for Natural Sciences of Hungarian Academy of Sciences) with a unique SAXS equipment of Biological Nanochemistry Research Group called „Credo” The equipment uses a Xenocs Genix3D X-ray source (Cu K $\alpha$  0.1542 nm) and a Dectris Pilatus 300K type detector. Samples with a size 7x7x1.2 mm were used for the measurements.

### **3.3.13. Wide angle X-ray diffraction (WAXD)**

The WAXD measurements were made in the SZIKKTI Laboratory, Materials Research and Testing Laboratory for Silicate Industry Ltd. with a Philips model PW 3710 based PW 1050 Bragg-Brentano parafocusing goniometer using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). For the WAXD measurements 15x35 mm area, 2 mm thick samples were cut off from the injection moulded flat specimens. The angle between the diffraction plane and the X-ray was varied in 5-35° range.

### 3.3.14. Gel permeation chromatography (GPC)

The tests were carried out at the University of Oxford, by using a Agilent PL-GPC 50 System GPC / SEC. The PLA samples were dissolved in chloroform (30 mg / ml). For the measurement, 4 GPC columns were used (3 PL-Gel Mixed C (5  $\mu\text{m}$ ) and 1 PL-Gel Mixed E (3  $\mu\text{m}$ )). The measurement was carried out at 30°C at a chloroform flow rate of 1 ml/min.

### 3.3.15. Determination of fibre content by density measurement

I used density measurement and the rule of mixture to determine the fiber content of the composite specimens. During the density measurements I measured the weight of the specimen in air and in ethyl alcohol and the density of the specimen can be calculated by knowing the density of the ethyl alcohol. In terms of densities, the fiber content can be estimated based on the rule of mixture.

## 4. Conclusion

Nowadays, due to the sustainable development and strict environmental regulations the renewable based and biodegradable polymers got more attention. These biopolymers may provide a solution if the crude oil, which is the raw material of the conventional plastics will be used in the future. Another advantage for biopolymers is that some of their types are biodegradable, so products made from them can be degraded in the compost under controlled conditions. However, in addition their beneficial properties their prices limit the applications of biopolymers even if some type have good mechanical and other properties compared to the petrol based polymers.

Poly(lactic acid) (PLA) is one of the most promising biopolymer with high tensile strength (50-60 MPa) and high modulus (2-3 GPa), however it has low heat deflection temperature and PLA is rigid. From the literature many informations could be obtained about the properties and modification of PLA. The most important fields are: the crystalline structure of PLA, modifying PLA with toughening additives, nucleating agents and natural fibers. However the effect of the different crystalline structures on the main properties of PLA has not been studied in detail. On the basis of this my aim was to analyze the effects of PLA's crystal structure on its properties.

For the PLA, the key factors are its crystalline fraction and its crystal structure. It can be found in the literature that which crystalline modification of PLA occurs under certain crystallization conditions. Of these, the crystalline modalities  $\alpha'$  and  $\alpha$  formed during the melting production technologies were relevant. During my research I produced PLA samples with different crystallinity and crystalline structures using the cold-crystallization following the injection molding. During my work, I pointed out that for a PLA, a crystallinity limit, under which the HDT type B heat deflection of the product is determined by its glass transition temperature, and above that the heat deflection

temperature is between the glass transition temperature and crystal melting temperature. Based on the DSC, DMA, PLM, small and wide X-ray diffraction studies, the explanation is that PLA sample with crystallinity below this limit loses its dimensionally stability over  $T_g$  due to the amorphous phase enters into the rubbery state. A PLA sample with crystallinity above the this limit has an improvement in its HDT type B heat deflection due to the increased crystallinity, the ordering of  $\alpha'$  crystals to  $\alpha$  and the increased lamellae size.

The D-lactide content of PLA is an other determining factor. Based on the results of the literature, this mainly affects the thermal properties, including the rate of crystallization, crystal melting and cold-crystallization. During my work I studied three PLA with a D-lactide content of 0,5%, 1,4% and 4% but these had the same molecular weight and molecular weight distribution. In the case of injection molded specimens, there was no significant difference between the strength, modulus and impact strength values. PLA with the smallest D-lactide content proved to be the best in the long-term studies (creep) due to thr higher crystalline fraction. The crystalline ratio was 3.2% at 4% D-lactide content and 21.2% at 0.5% D-lactide.

As in the previous studies, I analyzed the effect of heat treatment on the formed crystal structure and other properties as a function of D-lactide content after the injection molding cold-crystallization. During my research DSC, PLM, X-ray diffraction and mechanical studies were performed on various D-lactide-containing PLAs. I found that by increasing the D-lactide content to 4%, the available crystallinity is 10% less, but the strength and modulus are the same. Small differences are observed in the crystalline particle size and long period, where a significant difference is found in the case of 4% D-lactide content. Furthermore, in the polarization lighth microscopy images up to 110 ° C, the spherulite size is greater for the PLA with the largest D-lactide content than for the other two PLAs with a smaller D-lactide content. As a result a PLA with 0,5% D-lactide content and annealed between 80-110°C has a higher crystalline ratio (~50%) and the crystal structure still in the less ordered  $\alpha'$  form. Due to this the speciemens has higher impact resistance, and the Charpy impact strength increased by six times (12 kJ/m<sup>2</sup>) compared to the non-annealed reference PLA.

PLA crystallization is also an important field which affected by the D-lactide content and the applied cooling rate during the melt processing technologies. Based on the literature data and my own measurements, I found that for some type of PLA have a few percent crystalline fraction after cooled from melt with a cooling rate of 5 °C/min. In the chase of injection moldig and extrusint the cooling rates are higher tha n 5°C/min so the researcher tried to find effective nucleating agents which helps the crystallization of PLA. By collecting the nucleating agents from the literature I characterized them by using the crystallization peak temperature and crystallization half time. I made samples with three different nucleating agents with differend efficency by using PLAs with 0.5%; 1.5% and 4 % D-

lactide content. The DSC results showed no significant improvement in the crystallization peak temperature and crystallization half time over 0.5 wt% amount of nucleating agent. In addition, it can be concluded that the growth of D-lactide content from 0.5% to 4% also decreases the efficiency of nucleating agents. The crystallization temperature decreasing linearly, and the crystallisation half time increasing with increasing D-lactide content.

The wider application of PLA is restricted by its rigid behaviour so one of my goals was to modify the PLA toughness while I kept the biodegradability of PLA. The best solution for my purpose was the use of natural rubber. In addition of different quantities and processing technologies, I analyzed the effect of NR on the PLA. According to the results the blend with 5 wt% NR was found to be the optimal in terms of increased impact strength and tensile strength loss. The critical point of the PLA/NR blends is the size of the distributed NR droplets in the PLA matrix, which was found to be smaller in the case of internal mixing also at higher NR filling rates. An other important result is that natural rubber promotes the crystallization of PLA. Based on the Impact test results of unfilled and annealed PLA samples I also annealed the PLA/NR blends. Because of the presence of natural rubber (0-20 wt%) and the crystal structure of PLA, which developed during the annealing have a positive cross effect on the impact properties. The examination is the presence of natural rubber helps forming the less ordered  $\alpha'$  crystal structure which is more suitable for the impact loads and moreover during the fracture the crack, which goes along the border of the spherulites also has to go through the more ductile rubber particles. As a result, the blend which contains 5 wt% natural rubber and annealed at 100°C has a notched Charpy impact strength of 37,3 kJ/m<sup>2</sup>, which is higher than the unfilled and annealed (12 kJ/m<sup>2</sup>) and the filled and not-annealed (3,5 kJ/m<sup>2</sup>) references.

Another possible modification option for PLA is the use of cellulose-based fibres to produce biocomposites. In the case of natural fiber reinforced PLA composites the most widely used production technology is the film-stacking method. In the literature the most common choice for this technology is the fact that with this process higher fibre content can be achieved compared to injection molding. During my experiment I made continuous cellulose fiber reinforced preform with extrusion coating, which can be directly injection molded. By using 30 wt% of regenerated cellulose fiber the strength, the impact strength and the heat deflection temperature of the injection molded biocomposites increased by 33%, 60% and 40% respectively compared to neat PLA.

## 5. Theses

### 1. thesis

I prove that in the case of injection molded poly(lactid acid) products, independently from the D-lactide content there is a crystallinity limit, under which the HDT type B heat deflection of the product is determined by its glass transition temperature, and above that the heat deflection temperature is between the glass transition temperature and crystal melting temperature. The explanation is that PLA sample with crystallinity below this limit loses its dimensionally stability over  $T_g$  due to the amorphous phase enters into the rubbery state. A PLA sample with crystallinity above the this limit has an improvement in its HDT type B heat deflection due to the increased crystallinity, the ordering of  $\alpha'$  crystals to  $\alpha$  and the increased lamellae size. My statement proved with differential scanning calorimetry, dynamic mechanical analysis, small- and wide angle X-ray diffraction and heat deflection measurements, by using injection molded and annealed (at 80-140°C) PLAs with a D-lactide content of 0,5%, 1,4% and 4%.

### 2. thesis

I revealed the connection between the annealed (at 80-140°C) PLA crystalline structure and its mechanical properties (strength, modulus, impact strength, heat deflection and long-term properties). In the case of heat treatment at a temperature of 80-110 ° C, the resulting small lamellae size (~ 20nm) as well as the crystalline particle size and the less ordered  $\alpha'$  crystalline form, cause that the heat treated polylactic acid exceed the values of the reference polylactic acid. At 120 ° C, the formation of the more ordered  $\alpha$  crystal form and the larger lamellae size (~ 24 nm) reduces the strength and impact strength, but causes further growth in heat deflection and modulus. My statement proved with differential scanning calorimetry, small- and wide angle X-ray diffraction, heat deflection and Charpy impact measurements, by using injection molded and annealed (at 80-140°C) PLAs with a D-lactide content of 0,5%, 1,4% and 4%.

### 3. thesis

I proved that the D-lactide content has influence on the formed crystalline modifications during the heat treatment. With decreasing D-lactide content the ordering of  $\alpha'$  crystals shift to higher temperatures and the maximum crystallinity increases by 20%. As a result a PLA with 0,5% D-lactide content and annealed between 80-110°C has a higher crystalline ratio (~50%) and the crystal structure still in the less ordered  $\alpha'$  form. Due to this the specimen has higher impact resistance, and the Charpy impact strength increased by six times (12 kJ/m<sup>2</sup>) compared to the non-annealed reference PLA. My statement proved with differential scanning calorimetry, small- and wide angle X-ray

diffraction and Charpy impact measurements, by using injection molded and annealed (at 80-140°C) PLAs with a D-lactide content of 0,5%, 1,4% and 4%.

#### 4. thesis

In the case of nucleated PLA I demonstrated that with the increase of D-lactide content, the effect of the nucleating agents on the crystallization temperature is linearly reduced in the 0,5-4% D-lactide range. My statement was based on the differential scanning calorimetry results of PLA with 0,5%, 1,4% and 4% D-lactide content and filled with 0.5%, 1% and 2% nucleating agents with different efficiency.

#### 5. thesis

I prove that the presence of natural rubber (0-20 wt%) and the crystal structure of PLA, which developed during the annealing have a positive crosseffect on the impact properties. The examination is the the presence of natural rubber helps forming the less ordered  $\alpha'$  crystal structure which is more suitable for the impact loads and moreover during the fracture the crack, which goes along the border of the spherulites also has to go through the more ductile rubber particles. As a result, the blend which contains 5 wt% natural rubber and annealed at 100°C has a notched Charpy impact strength of 37,3 kJ/m<sup>2</sup>, which is higher than the unfilled and annealed (12 kJ/m<sup>2</sup>) and the filled and not-annealed (3,5 kJ/m<sup>2</sup>) references. My statement proved with differential scanning calorimetry, small- and wide angle X-ray diffraction and Charpy impact measurements, by using injection molded and annealed (at 80-140°C) PLAs with a D-lactide content of 0,5%, and filled with 0-20 wt% natural rubber with a Mooney viscosity (ML1+4, 100°C) of 60.

#### 6. thesis

I developed the continuous extrusion technology for long regenerated cellulose fiber reinforced PLA preforms for direct injection molding of long fiber reinforced PLA biocomposites. By using 30 wt% of regenerated cellulose fiber the strength, the impact strength and the heat deflection temperature increased by 33%, 60% and 40% respectively compared to neat PLA.

## 6. List of own publications

- 1 Tábi T., **Hajba S.** Kovács J. G.: *Effect of crystalline forms ( $\alpha'$  and  $\alpha$ ) of poly(lactic acid) on its mechanical, thermo-mechanical, heat deflection temperature and creep properties.* European Polymer Journal, **82**, 232-243 (2016).
- 2 Tábi T., Kovács N.K., Sajó I.E., Czigány T., **Hajba S.**, Kovács J.G.: *Comparison of thermal, mechanical and thermomechanical properties of poly(lactic acid) injection-*

*molded into epoxy-based Rapid prototyped (Polyjet) and conventional steel mold. Journal of Thermal Analysis and Calorimetry, 123, 1, 349-361 (2016).*

- 3 Tábi T., **Hajba S.**, Wacha A. F.: *Effect of D-lactide content of Poly(lactic acid) on its mechanical, thermo-mechanical, heat deflection temperature and creep properties.* Benyújtva
- 4 **Hajba S.**, Tábi T.: *Gócképzők hatása a politejsav tulajdonságaira.* Polimerek, elfogadva.
- 5 **Hajba S.**, Tábi T.: *Politejsav szívósságának növelése növényi kaucsuk segítségével.* Polimerek, **2**, 238-242 (2016).
- 6 **Hajba S.** Tábi T.: *Poly(lactide Acid)/Natural rubber blends.* Matetial Science Forum, 885, 298-302 (2017).
- 7 **Hajba S.**, Czigány T. Tábi T.: *Development of cellulose-reinforced Poly(Lactide Acid) (PLA) for engineering applications.* Materials Science Forum, 812 59-64, (2015).
- 8 **Hajba S.**, Tábi T., Bakonyi P.: *Fröccsöntési paraméterek hatása a hosszú cellulóz szállal erősített politejsav kompozitokra.* OGÉT 2016: XXIV. Nemzetközi Gépészeti Találkozó, konferencia kiadvány, 175-178, (2016).
- 9 Tábi T., Bakonyi P., **Hajba S.**, Herrera-Franco P. J., Czigány T., Kovács J. G.: *Creep behaviour of injection moulded Poly(Lactic Acid) reinforced with basalt fibres.* Journal of Reinforced Plastics and Composites, 35, 1600-1610 (2016).