THE INFLUENCE OF THE INJECTION MOULDING PROCESS ON CHANGES IN SELECTED PHYSIOCHEMICAL AND MECHANICAL PROPERTIES OF POLYACTIDE (PLA)

Marek Jałbrzykowski, Łukasz Minarowski
Izabela Krucińska
Lucyna Herczyńska, Grzegorz Markiewicz

S u m m a r y

Purpose: The aim of this paper was to assess the influence of parameters of the injection moulding process on changes in selected physiochemical properties and performance of parts made from PLA.

Materials/Methods: 6201D trade polylactide by NatureWorks was used for the tests. Before the tests, the plastic was dried according to the manufacturer's recommendations, and then injected by means of a Borche BS60 injection moulding machine. The process of injection was carried out at excessively high or excessively low process parameters. The obtained samples were subjected to tensile testing; then, their physiochemical properties were assessed by means of DSC, TGA and GPC.

Results: The obtained test results indicate that parameters of the injection moulding process have an impact on the characteristics of parts made from PTA, such as: tensile strength, molecular mass, the degree of crystallinity, and time of degradation.

Conclusions: The influence of the parameters of the injection moulding process on the changes of, among others, molecular mass, the degree of crystallinity and mechanical properties of PLA were observed. The obtained research results show that there exists a relationship between the parameters of the injection moulding process and molecular mass, the degree of crystallinity, and mechanical properties of parts made from polylactide. Considering that a change in molecular mass has an impact on the rate of PLA degradation, it is possible to control time of degradation, through the control of parameters of the injection moulding process.

Keywords: polylactide, performance, molecular mass, degree of crystallinity, decomposition time

Wpływ parametrów procesu wtryskiwania na właściwości fizyczne, chemiczne i mechaniczne polilaktydu (PLA)

S t r e s z c z e n i e

W pracy przedstawiono wyniki badań wpływu parametrów procesu wtryskiwania na właściwości fizyczne, chemiczne i mechaniczne wyrobów z PLA. W badaniach stosowano handlowy polilaktyd 6201D firmy NatureWorks. Materiał był suszony zgodnie z zaleceniami producenta. Proces wtryskiwania wykonano za pomocą wtryskarki Borche BS60. Zrealizowany był dla jego dopuszczalnych maksymalnych

Address: Prof. Izabela KRUCIŃSKA, Lucyna HERCZYŃSKA, PhD Eng., Łódź University of Technology, 116 Żeromskiego Str., 90-924 Łódź, Marek JAŁBRZYKOWSKI, PhD Eng., Grzegorz MARKIEWICZ, MSc Eng., Białystok University of Technology, Wiejska 45C, 15-351 Białystok, Łukasz MINAROWSKI, PhD, Medical University of Białystok, 1 Jana Kilińskiego Str., 15-089 Białystok

i minimalnych parametrów Dla wytworzonego materiału określono właściwości mechaniczne w próbie statycznej rozciągania oraz właściwości fizyczne i chemiczne metodami DSC, TGA i GPC. Analiza uzyskanych wyników badań wskazuje na wpływ parametrów procesu wtryskiwania na: wytrzymałość na rozciąganie, masę cząsteczkową, stopień krystaliczności, temperaturę rozpadu. Ustalono stopień korelacji pomiędzy parametrami procesu wtryskiwania a masą cząsteczkową, stopniem krystalizacji oraz właściwościami mechanicznymi wyrobów. Stwierdzono, że zmiana masy cząsteczkowej ma wpływ na kinetykę rozpadu polilaktydu PLA. Istnieje więc możliwość kontrolowanego sterowania czasem rozpadu PLA, poprzez sterowanie parametrami procesu wtryskiwania.

Słowa kluczowe: polilaktyd, właściwości użytkowe, masa cząsteczkowa, stopień krystaliczności, czas rozpadu

1. Introduction

Poly(lactic acid), also known as polylactide (PLA), is currently one of the most popular bioabsorbable polymers. PLA is produced from plant-based materials (e.g. maize, sugar beets) and constitutes a viable alternative to materials of petrochemical origin. However, it is characterized by lower strength properties, in comparison with technical plastics, which forces researchers and entrepreneurs to look for means of their improvement [1-3]. This state of affairs is exacerbated by the fact that the strength parameters are further lowered during the process of degradation [4]. The characteristics described in literature as insufficient are, among others [5]: strength properties, heat deflection temperature, resilience, barrier properties, sensitivity to humidity, fast physical aging, or brittleness. For these reasons, the technological usefulness of PLA becomes problematic, which is mainly connected with its generally low mechanical characteristics. Popular directions of research aimed at the search for a better general performance of polylactide include, for instance, the possibility for obtaining fibrous composites on a PLA base, or polymer blends containing it [5]. Currently, it is known that it is possible to control the properties of PLA through changes of the conditions of its processing [6, 7]. Polylactide, as a thermoplastic polymer, can be successfully used for injection moulding. It is highly likely that a properly performed injection moulding process may radically change the physiochemical and mechanical properties of PLA. For example, due to the long crystallization time of pure PLLA, the main ingredient of commercial polylactide plastics, the injection moulded parts are almost completely amorphous (short cooling time). Parts characterized by a predominantly amorphous structure have worse mechanical properties than parts made from crystalline PLA [8, 9]. For instance [8, 9], the tensile strength of an amorphous material is approx. 30 – 53 MPa, whereas it is approx. 50 to 70 MPa for a crystalline material. The values of resilience for notched samples are approx. 1.9 – 2.6 kJ/m^2 and approx. 3.2 – 7.0 kJ/m^2 for amorphous and crystalline material, respectively. The values of resilience for samples without notches are approx. 13.5 – 19.5 kJ/m^2, and approx. 18 – 35 kJ/m^2 for amorphous and crystalline material, respectively. The situation is similar in the case of molecular mass. Table 1 compiles literature data, which clearly show that the higher molecular mass of the

polymer, the better the general mechanical properties of the part (unfortunately, this is not true for all the characteristics).

Table 1. Some physical and mechanical properties of selected bioresorbable polymers [10]

Characteristics	Properties					
	Physical		Mechanical			
Polymer name (molecular mass)	Glass transition point, °C	Melting point °C	Tensile strength MPa	Modulus of elasticity in tension MPa	Modulus of elasticity in bending MPa	Elongation at break %
L-PLA (50.000)	54	170	28	1200	1400	6.0
L-PLA (100,000)	58	159	50	2700	3000	3.3
D,L-PLA (20,000)	50	-	-	-	-	-
D,L-PLA (107,000)	51	-	29	1900	1950	6.0
D,L-PLA (550,000)	53	-	35	2400	2350	5.0

In this context, a question arises whether it were possible to control PLA performance by means of appropriately selected parameters of the injection moulding process. Indeed, it is possible to increase the cooling time in order to obtain a greater proportion of crystalline structure. Moreover, an attempt can be made to obtain a higher molecular mass through appropriate structure packing. At the same time, a question arises whether the change will have a visible and cost-effective impact on the end properties of the product, provided that a modified PLA structure is obtained by means of processing parameters.

2. Materials and methods

Trade pellets made from polylactide 6201D by NatureWorks (Table 2) were used for the tests. Before the injection moulding process, the plastic was dried for 3 h in a SHINI SHD-T drier in a temperature of 60°C. After drying, the pellets were fed into the hopper of a Borche BS60 injection moulding machine and subjected to the process of injection, which was performed at various times, packing pressures and injection pressures. These particular parameters were selected due to their being among the most important parameters that impact the performance of injection moulded parts. Other adjustable parameters such as, for example, temperatures on cylinder zones, mould temperature, or back pressure, were constant.

Table 2. Selected physiochemical properties of PLA 6201D (manufacturer's information)

Physical properties	PLA 6201D	ASTM norm
Density, g/cm^3	1.24	D792
Relative viscosity	3.1	D792
MI, g/10 min, 210°C	15-30	D1238
Liquid state density, g/cm^3, 230°C	1.08	D792
Melting point, °C	160-170	D3418
Glass transition point, °C	55-60	D3417

Table 3. Example values of the controlled parameters of the injection moulding process

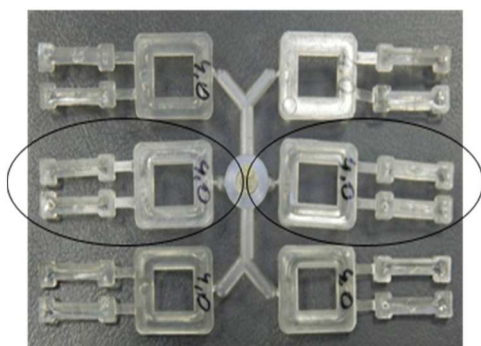| Sample	Parameters			
	Injection pressure MPa	Injection rate %	Packing pressure MPa	Packing time s
A	7	60	4	5
B	7	60	4	0.5
C	7	60	1	0.5
D	6	60	5	0.5
E	10	60	10	5
F	7	100	10	5
G	7	40	14	5
H	7	50	14	5
I	7	60	5	5
J	7	60	4	2

Table 3 shows an example sequence of parameters at which the further tested parts were manufactured.

After manufacturing the samples (Fig. 1a) by means of an injection moulding machine, an assessment of their selected physiochemical and mechanical properties was commenced. The samples were first subjected to the static tensile test with the use of a Zwick/Roell Z010 universal testing machine (Fig. 1b) pursuant to DIN EN ISO 527-1 and DIN EN ISO 527-2. The dimensions of the samples taken for the tests were 30 x 6 x 4 mm (length x width x thickness).

After the strength tests, the samples were subjected to DSC tests, at a measurement range of $50 + 300$°C and a heating rate of 5°C/min. Afterwards, tests of the molecular mass of the polylactide were performed with the use of the GPC method. A Waters 2695 gel chromatograph equipped with a viscometric and refractometric detector was used for the measurements. A single PLgel MIXED-C column with a length of 30 cm and a diameter of 7.5 mm, filled with polystyrene gel with a grain size of 5μm, was used. The eluent used for the tests was dichloromethane (CH_2Cl_2) for HPLC chromatography. The flow rate was 0.8 mL min^{-1}. The test was carried out at a constant column temperature of 30°C. The reference polymer samples aa well as those tested before measurement were

filtered through 1 μm pore size glass filters. The system was calibrated based on polystyrene standards. The dn/dc value for a PLA system in CH_2Cl_2, i.e. 0.035 mg mL^{-1}, was used. TriSEC software by Viscotek, dedicated to the calculation of average molecular masses by means of the conventional calibration method with the use of polystyrene standards with molecular masses between 418 and 1090000, was used for computer-based collection and elaboration of data.

a)   b)

Fig.1. View of: a) an example moulding (the ellipses mark the elements from which samples for the strength tests were taken), b) the Zwick/Roell Z010 universal testing machine

3. Results and discussion

Figure 2 shows selected results of the tests of mechanical properties. The presented data pertain to the impact of packing pressure on changes in tensile strength. The presented graph shows that tensile strength increases together with packing time. Obviously, the relationship is not strictly linear, but an increasing trend is clearly visible. The 95% confidence interval is marked with the dashed line. The presented data corroborate the beneficial influence of packing pressure on tensile strength of injection moulded parts made from PLA. Of course, it must be remembered that only a small batch of samples was manufactured for the purpose of this study, in specific constant conditions, hence it is difficult to say whether the tendencies would continue if the study was expanded or if disturbances were introduced into the process. Nonetheless, a beneficial impact of process parameters on the analysed mechanical property was obtained in this particular case.
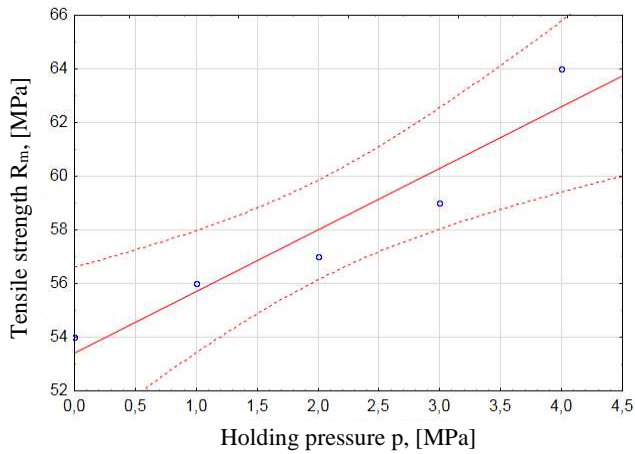
Fig. 2. The impact of packing time on tensile strength
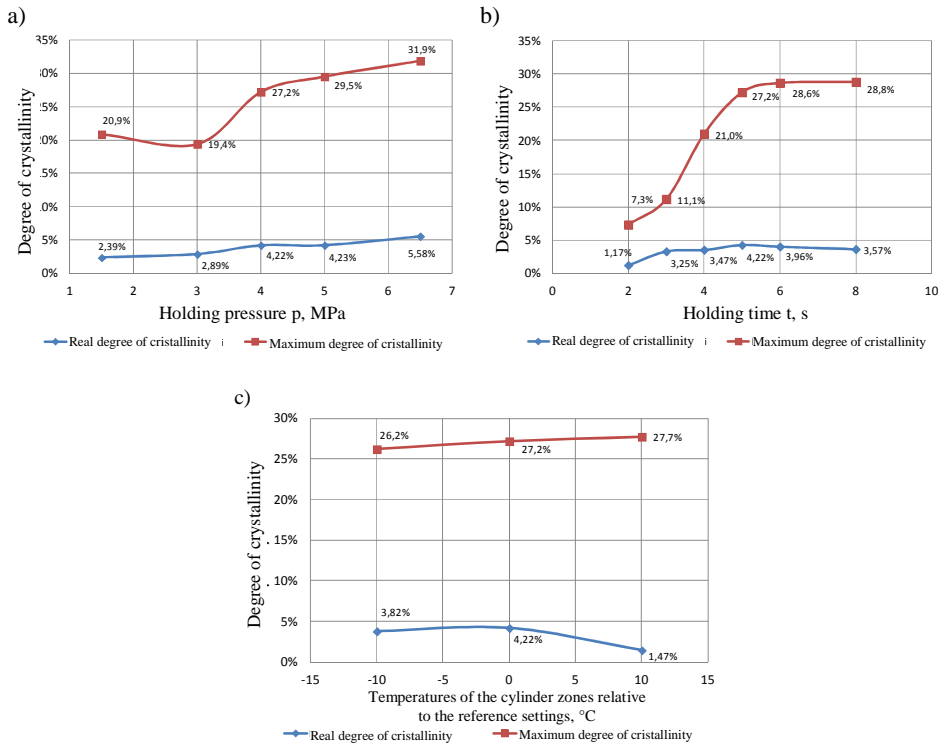of injection moulded PLA parts

a)

b)

c)

Fig. 3. The influence of: a) packing/holding pressure, b) packing/holding time, c) temperature
on cylinder zones – on changes in the degree of crystallinity of PLA structure

Figure 3 illustrates selected results of the tests of the degree of crystallinity of the prepared samples. It should be reiterated at this point that polylactide processing, especially injection moulding-based, results in obtaining an almost amorphous polymer structure. This is the consequence of the rapid cooling of plasticized mass. The process of polylactide crystallization requires a time of approx. 10-20 minutes [11]. This, however, is impossible to attain in the case of manufacture of goods with the use of traditional moulding methods, including injection moulding, with cycle times measured in seconds. The factor that determines such a short cycle time is obviously productivity. Yet, an increase in the degree of crystallinity can be obtained without the need to extend cooling time, e.g. by changing the temperature of liquid alloy, or other process parameters such as packing time and pressure, among others. Fig. 3 illustrates the assessment of the influence of selected settings of the injection moulding process on changes in the degree of crystallinity of polylactide. The values of real and maximum degrees of crystallinity were calculated (on the basis of thermograms obtained in DSC tests) using the following equations:

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_{m(100\%)}} \qquad X_c^M = \frac{\Delta H_m}{\Delta H_{m(100\%)}}$$

where: X_c – real degree of crystallinity, X_c^M – maximum degree of crystallinity, ΔH_m – measured enthalpy of fusion of the sample, ΔH_c – tested cold crystallization enthalpy of the sample, $\Delta H_{m(100\%)}$ – enthalpy of entirely crystalline fusion of PLA – value assumed 93 J/g.

As can be seen, packing pressure (Fig. 3a), packing time (Fig. 3b), and temperature of liquid alloy (Fig. 3c) have an impact on changes in the degree of real crystallinity. Although these changes are in the order of several percent, they are not inconsequential for the other characteristics of the material. The data presented in Fig. 4 show that an increase of the degree of crystallinity by approx. 5% resulted in an approx. 10% increase in tensile strength. It can also be noticed that a higher degree of crystallinity has an impact on a totally different behaviour of the material during tension testing as well as greater elongation at break.

Table 4 summarizes the results of TGA tests for the prepared samples. In the tests, special attention was paid to temperature at the start of degradation T_p, temperature at the end of degradation T_k, and temperature of the most intense loss in mass T_{max}. These temperatures were determined based on a theory known in literature [12-14] concerning changes in the values of the aforementioned temperatures as a result of plastics processing and their correlation with molecular mass. Processing results in the appearance of new fractions characterized by a different, lower or higher, molecular mass, which originate from partial decomposition and radical recombination of chains. In addition, the theory states

that a reduction in the molecular mass of a polymer is correlated with a decrease in temperature at the start of degradation (and vice versa); at the same time, an increase in temperature of the most intense loss in mass and temperature at the end of degradation may indicate an increase in molecular mass. The appearance of lighter fractions, characterized by a lower temperature at the start of degradation T_p as well as heavier fractions, characterized by a higher temperature at the end of degradation T_k, may indicate mechanochemical action of processing, as a consequence of chain scission and regrouping, separation of side-chains, or radical recombination of polymers [14]. As a result, structures with a smaller or greater molecular mass are obtained.
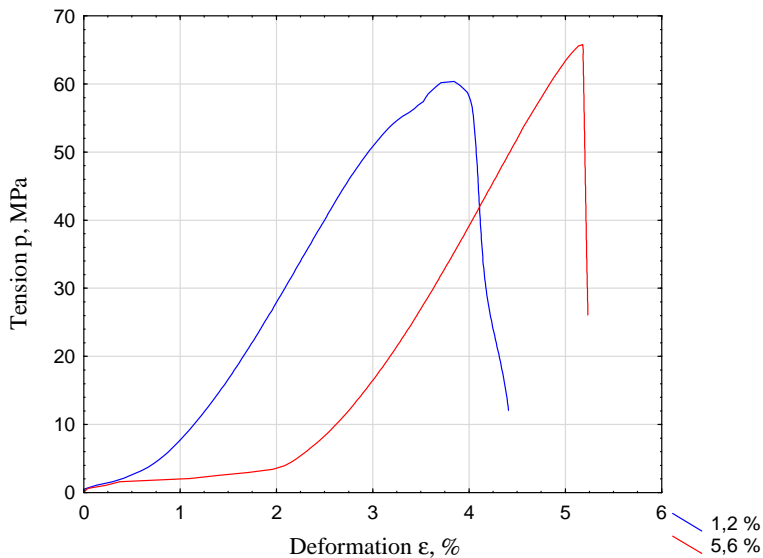

Fig. 4. The impact of the degree of crystallinity on mechanical properties of PLA

Following the theory, as well as the data in table 4, it can be concluded that an increase in packing time (samples A, J, B), packing pressure (samples B, C), and injection rate (samples H, G) results in an increase in the molecular mass of PLA. Obviously, further studies should be performed that would determine the exact changes in molecular mass values resulting from control of the parameters and whether this has a significant impact on the level of PLA performance.

Table 5 below presents the data pertaining to the assessment of the molecular mass of PLA samples. It should be added that the data presented in the table concern only selected cases.

Table 4. The impact of parameters of the injection moulding process on changes in the ranges of temperature of degradation

Sample	Parameters				Temperature of degradation		
	Injection pressure MPa	Injection rate %	Packing pressure MPa	Packing time s	T_p °C	T_k °C	T_{max} °C
A	7	60	4	5	322.88	373.93	362.36
J	7	60	4	2	323.95	370.96	359.50
B	7	60	4	0,5	318.60	365.38	355.68
H	7	50	14	5	324.18	369.39	358.07
G	7	40	14	5	321.47	369.55	358.85
I	7	60	5	5	312.65	369.30	357.14
A	7	60	4	5	322.88	373.93	362.36
B	7	60	4	0,5	318.60	365.38	355.68
C	7	60	1	0,5	314.18	365.39	352.18

Table 5. Results of measurements of molecular mass of selected PLA samples

Parameter/ Charac- teristic Sample	Injection pressure MPa	Injection rate %	Packing pressure MPa	Packing time s	Average molecular mass (numerically) M_n	Average molecular mass (by mass) M_w
C	7	60	1	0.5	104300	189200
J	7	60	4	2	126400	212200
I	7	60	5	5	111500	188500
E	10	60	10	5	108700	185800

Before commencing the tests, the samples were first prepared at optimum parameters of the injection moulding process (injection pressure 7MPa, injection rate 60%, packing pressure 5 MPa, packing time 4 s). Then, samples were prepared at excessively high parameters (sample E), excessively low parameters (sample C), in addition to samples intermediate between the excessively low and optimal state (sample J), and between the optimal and the excessively high state (sample I). The presented data show that the smallest molecular mass was obtained in the case of the sample produced at excessively low injection parameters. The highest molecular mass was obtained at optimal and close to normal injection parameters. At excessively high injection parameters, on the other hand, a reduction of the molecular mass of PLA samples could be observed. The obtained results show that molecular mass of PLA, as well as its other performance properties, can be controlled by means of targeted changes of injection parameters. Change of molecular mass of PLA at the stage of its processing may be extremely significant in the case of biomedical applications. As is widely known, the time of degradation of PLA depends on its molecular

mass, among other factors, i.e. the greater the mass, the longer the time of degradation, as well as its general performance. This may be applied in the production of bioabsorbable inserts, implants, stents, etc. This is also important from the technological point of view as with a single material at their disposal, the manufacturer is able to produce, for instance, implants with varied times of absorption. Apart from molecular mass itself, mechanical properties of PLA can also be improved by means of control of injection parameters.

4. Conclusion

Considering the obtained test results and their analysis, the following final conclusions have been formulated:

1. An impact of the described injection parameters on changes of selected physiochemical and mechanical properties of PLA samples was discovered.

2. The following can be listed among the features that are correlated with parameters of the injection moulding process, among others: the degree of crystallinity, tensile strength, elongation at break, or molecular mass.

3. As for the degree of crystallinity, it can be said that increased packing time and pressure and lowered alloy temperature has an impact on the increase of the degree of crystallinity. A higher degree of crystallinity, in turn, results in better mechanical properties of the polymer.

4. As for molecular mass and temperatures at the start T_p and at the end of degradation T_k, it can be said that an increase in packing time, packing pressure, or injection rate has an impact on T_p and T_k range differences and the increase of molecular mass. The higher the molecular mass the longer the tie of degradation of the polymer.

5. By consciously controlling the injection parameters, including outside the ranges of optimal values, mechanical properties of parts made from PLA as well as its time of degradation, can be changed. This may be extremely significant in the context of improving its mechanical properties as injection parameters can be used as an additional method, in addition to the currently used fillers. At the same time, its time of degradation and the higher time when mechanical properties remain at a higher level can be influenced in the same manner. This fact is extremely important as far as the diverse needs of biomedical applications in this area are concerned.

References

[1] Z. FOLTYNOWICZ, P. JAKUBIAK: Poli(kwas mlekowy) – biodegradowalny polimer otrzymywany z surowców roślinnych. *Polimery*, **47**(2002)11-12, 769.

[2] S. POŁOWIŃSKI, R. JANTAS, J. SZUMILEWICZ, D. STAWSKI, L. HER-CZYŃSKA, Z. DRACZYŃSKI: Modification of PLA fibres with bioacceptable hydrophilic polymers. *Fibres & Textiles in Eastern Europe*, **90**(2012)1, 78-85.

[3] E. MAZGAJCZYK, P. SZYMCZYK, E. CHLEBUS: Zastosowanie technologii Rep-Rap do wytwarzania funkcjonalnych struktur z PLA. *Aktualne Problemy Biomechaniki*, **8**(2014), 109-114.

[4] J. CHŁOPEK, A. MORAWSKA-CHOCHÓŁ, B. SZARANIEC, M. ZIĄBKA, M. El FRAY: Ocena wpływu warunków in vitro na właściwości mechaniczne polimerów resorbowalnych o różnym czasie resorpcji. *Engineering of Biomaterials*, (2008)81-84, 25-28.

[5] M. JAŁBRZYKOWSKI, I. KRUCIŃSKA, J.R. DĄBROWSKI: Tests of selected mechanical properties of PLA-PLA type composites. *Composites Theory Pract.*, (2016)2, 84-89.

[6] J. REN: Biodegradable Poly(Lactic Acid): Synthesis, modification, processing and applications. Springer, Berlin 2010.

[7] M. JAŁBRZYKOWSKI, S. OBIDZIŃSKI, Ł. MINAROWSKI: Wpływ wybranych parametrów procesu wtryskiwania na wytrzymałość na rozciąganie detali z polilaktydu starzonych w środowisku płynu Sorensena. *Przemysł Chemiczny*, **96**(2017)9, 1869-1872.

[8] G. PEREGO, G.D. CELLA, C. BASTIOLI: Effect of molecular weight and crystallinity on poly(lactic acid) mechanical properties. *Journal of Applied Polymer Science*, **59**(1996)1, 37-43.

[9] G. TÁBI, I.E. SAJÓ, F. SZABÓ: Crystalline structure of annealed polylactic acid and its relation to processing. *eXPRESS Polymer Letters*, 4(2010)10, 659-668.

[10] B.D. RATNER, A.S. HOFFMAN, F.J. SCHOEN, J.E. LEMONS: Biomaterials science: An Introduction to materials in medicine. Academic Press, California 1996.

[11] A. SOTERGARD, M. STOLT: Properties of lactic acid based polymers and their correlation with composition. *Progress in Polymer Science*, **27**(2002), 1123-1163.

[12] F. CARRASCO, J. GÁMEZ-PÉREZ, O.O. SANTANA, M.L. MASPICH, Processing of poly(lacticacid)/ organomontmorillonite nanocomposites: microstructure, thermal stability and kinetics of the thermal decomposition. *Chemical Engineering Journal*, **178**(2011), 451-460.

[13] R. Al-ITRY, K. LAMNAWAR, A. MAAZOUZ: Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy, *Polymer Degradation and Stability*, **97**(2012), 1898-1914.

[14] B. KRÓLIKOWSKI: Wpływ rozwiązania konstrukcyjnego ślimaków w wytłaczarce dwuślimakowej współbieżnej na wybrane właściwości otrzymywanych mieszanin polimerowych. Cz. 2, Monografie – Politechnika Lubelska, Przetwórstwo Tworzyw polimerowych, aspekty technologiczne i nowe trendy, Lublin 2016, 9-33.