



Determination of thermal properties of polylactide

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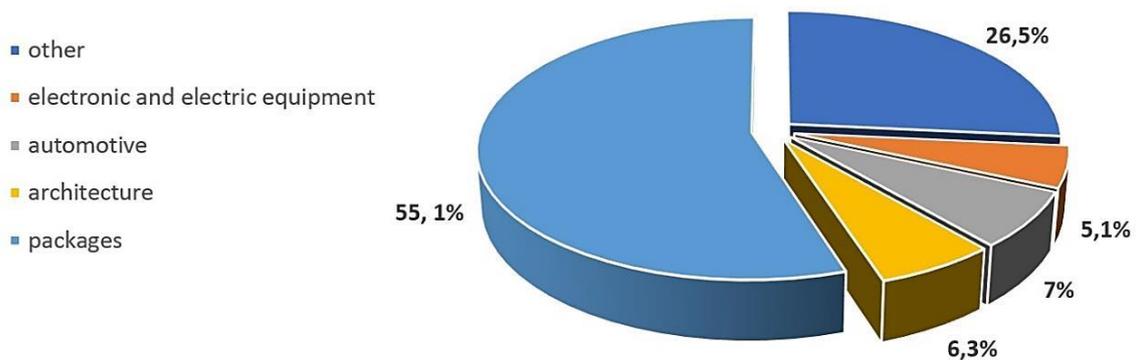
ABSTRACT

The article contains information related to a material that is polylactide, also known as polylactic acid. The results of study presented in the article are related to the PLA moldings made with the use of the 65 - 160 C1 injection molding machine. The publication presents the results of thermal analysis obtained by using differential scanning calorimetry (DSC), thanks to which the thermal properties of polylactide were determined. The results that have been presented relate to the moldings obtained with different parameters of the injection molding process, while parameters such as the temperature of mold or injection molding are being changed during the process. Conducted examinations are aimed to determine the thermal properties.

Keywords: polylactide, DSC, PLA, polymer, polylactic acid

1. INTRODUCTION

Plastic is a very broad group of materials used in various fields and industries (Fig. 1). These materials contain synthetic polymers that naturally do not exist in nature, or polymers that are modified using, for example, thermal stabilizers, UV stabilizers and many others [1].



Together 145 thousands ton

Figure 1. A division of the use of plastics in the industry [2].

Plastics have a very broad division into various types and groups. Examples include:

1. Biodegradable and biodegradable plastics [3,7].
2. Fluoropolymers.
3. Styrene polymers.
4. Polyolefins.
5. Polycarbonates.
6. Epoxy and polyester resins.

All groups of polymers are divided into thermoplastics and thermosetting ones. Thermoplastics have the ability to be further processed by melting and other used methods. On the other hand, thermosetting plastics when hardened do not soften during heating – they are called duroplasts. Examples from each group are [4]:

✓ Thermoplastics:

1. ABS - acrylonitrile - butadiene - styrene.
2. PC - polycarbonate.
3. PET - polyethylene terephthalate.
4. PS - polystyrene.
5. PVC - polyvinyl chloride.

✓ Thermosetting:

1. EP - epoxies.
2. PUR - polyurethanes.
3. UP - polyester resins.

Plastics are increasingly being used in medicine, biomedical engineering and all derivatives of these fields. Biomaterials, in other words biomedical materials, are a group of materials from which devices and elements that will have a direct contact with human body

can be produced. Among plastics considered as biomedical materials, they can be distinguished as follows with an example of usage [5]:

1. Si - surgical gloves
2. PA, PP, PVAL, PUR - Surgical thread
3. PMMA - contact lenses
4. PC, Si - surgical instruments
5. PLA - dental implants.

Poly lactide (PLA) is a material obtained by lactide ring opening during polymerisation process or by a second method by polycondensation of lactic acid. PLA belongs to the group of aliphatic polyesters. This material is obtained from natural resources such as e.g. sweetcorn or sugar beets. It is fully biodegradable, which is its significant advantage. It has properties similar to PS (polystyrene) but the modification process gives an opportunity to obtain properties similar to PP (polypropylene) or PE (polyethylene). The PLA has found a wide application in, among others [6,8-10]:

1. biomedical engineering
2. 3D printing
3. Food packaging
4. Fiber production

2. MATERIALS AND METHODS

The aim of the research was to determine the thermal properties of poly lactide (PLA) by differential scanning calorimetry (DSC). The subject of study was type 1A molding with the dimensions shown on figure (Fig. 2.) made of PLA plastic. The injection molding process was conducted on a type 65-160 C1 injection molding machine. The samples of the moldings were taken from the core of the moldings. Moldings were made with different injection parameters so it was possible to compare the influence of parameter changes on the properties of the obtained products. All parameters are correlated in the table (Table 1).

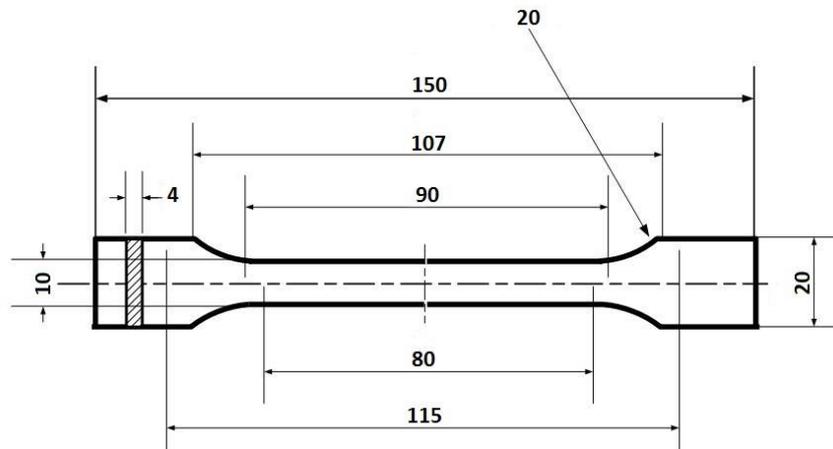


Figure 2. Dimensions of moldings.

Table 1. A list of injection parameters.

Serial number	Injection temperature	Mold temperature	Injection pressure	Clamping time	Injection speed	Injection time
3	205 °C	20 °C	90 MPa	12 s	50 mm/s	0.67 s
4	195 °C	20 °C	90 MPa	12 s	50 mm/s	0.67 s
9	195 °C	20 °C	90 MPa	25 s	30 mm/s	0.67 s
10	195 °C	20 °C	90 MPa	12 s	30 mm/s	0.92 s

The sample series numbers were matched to the needs of this article. Parameters that were changed were injection temperature, clamping time, injection speed and injection time. Differential scanning calorimetry (DSC) was performed with the use of a Netzsch DSC 214 Polymor calorimeter. A following characteristic was adopted for the study: H-C-H, heating-cooling-heating. The process started at 20 °C, heating was running at speed 10 K/min to reach 200 °C, while at the time of reaching the set temperature, a constant temperature was kept for 120 s. After completion of the isotherm, the cooling process was performed at speed 10 K/min to reach 50 °C, at which point another isotherm occurred for 120 s.

3. RESULTS

The results were presented in the form of thermograms in the graphs below (Figs. 3 - 10.). Presented thermographs show the results of DSC measurement in the first and second heating of the sample to 200 °C. Figures (Figs. 3 - 6) present the results for the first heating.

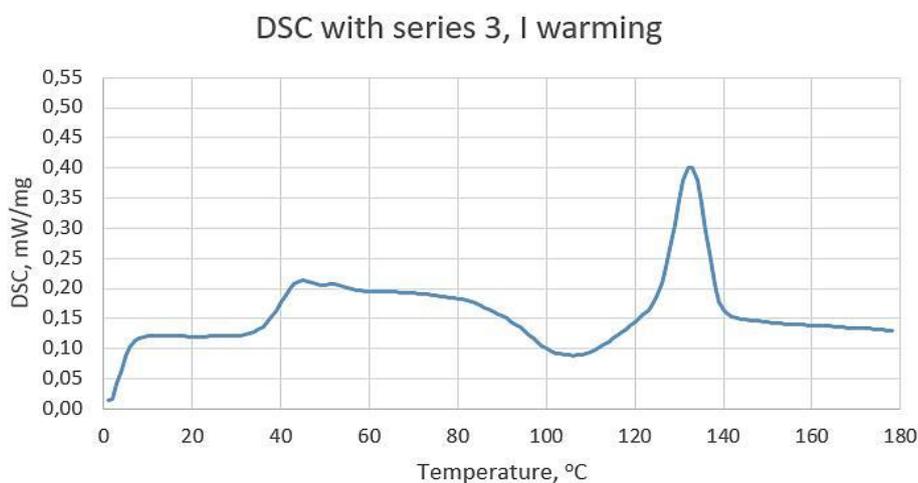


Figure 3. A graph for sample no. 3.

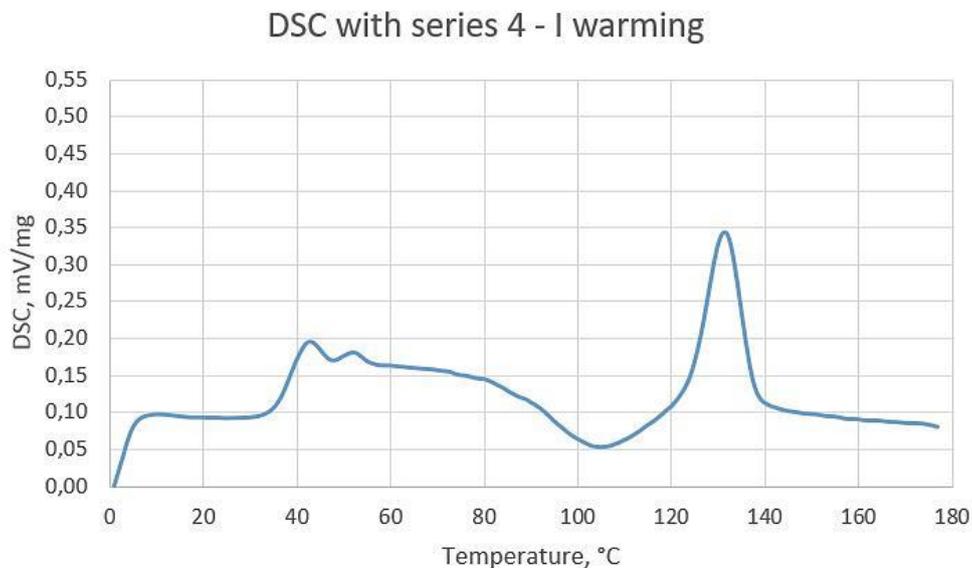


Figure 4. A graph for sample no. 4.

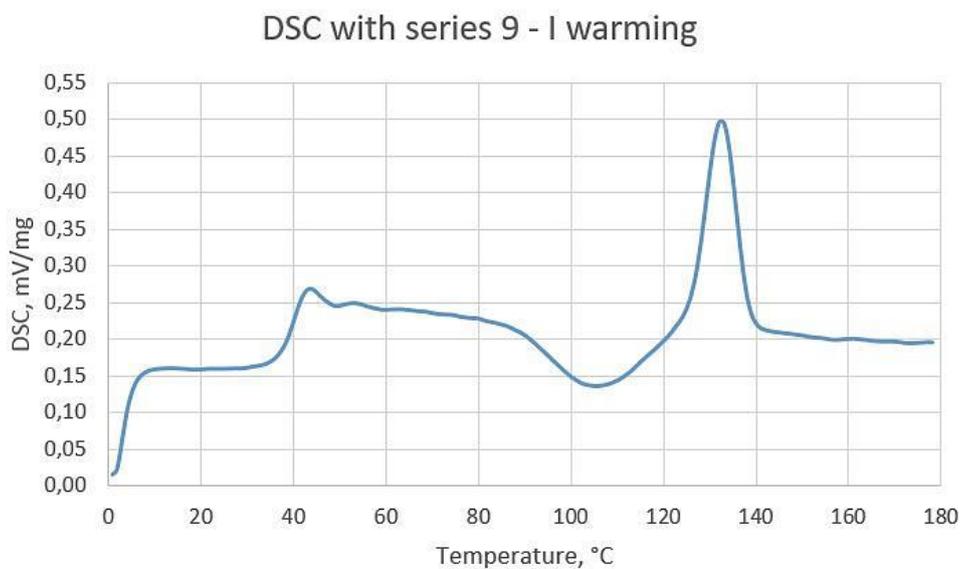


Figure 5. A graph for sample no. 9.

In the case of obtained results for samples with the parameters as in the table (Table 1), the highest melting enthalpy has sample no. 9 with a value of 18.39 J/g, while the smallest enthalpy has the sample no. 10, which value is 11.81 J/g. The other two samples have similar values (Table 2). As a result of measurements, the initial and final melting temperature of the crystalline phase was obtained. The sample no. 4 shows the highest temperature range, the

initial temperature equals 142 °C and the final temperature equals 157.7 °C. The smallest temperature range shows the sample no. 9, in this case 143.1 °C is the beginning of the melting phase and 156.8 °C the end of the melting phase. Another set value when considering DSC testing is the range of temperatures in which transition from the vitreous phase to the high energy phase is performed. In this case, the sample with the highest temperature range is no. 10, in which the initial phase started at 55.8 °C, ended at 63.9 °C, while the lowest temperature range is observed in the context of the sample no. 9 – temperature range is 56.7-60.6 °C. When considering sample no. 3, the beginning of transition from the vitreous phase began at the lowest temperature of 54.6 °C. All characteristic DSC parameters for the first heating are listed in the table (Table 2).

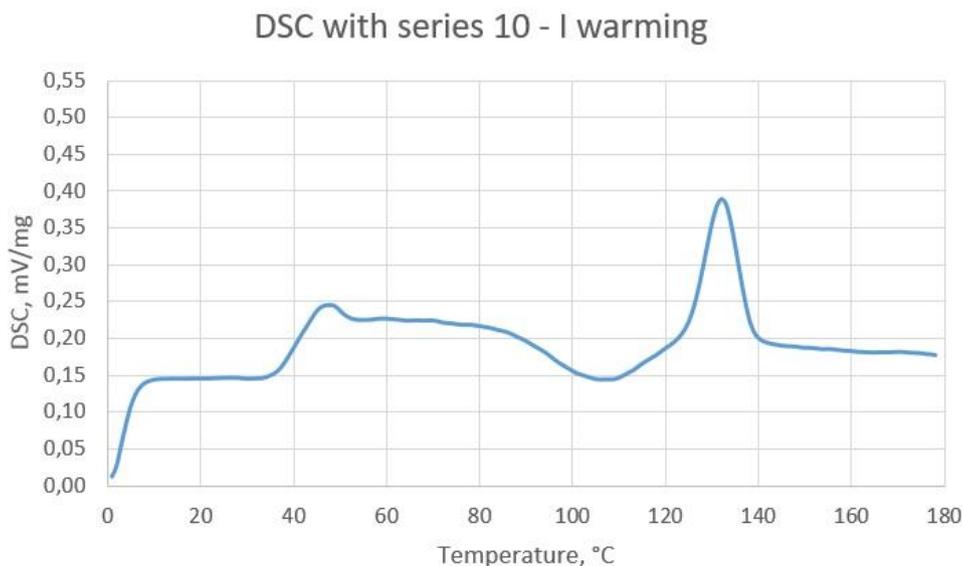


Figure 6. A graph for sample no. 10.

Table 2. A list of obtained values for the first heating.

Name of the sample	Area [J/g]	Complex Peak [°C]		Glass Transition [°C]	
		Onset	End	Onset	End
3	17.15	142.5	157.5	54.6	60.9
4	17.57	142.0	157.7	55.5	60.5
9	18.39	143.1	156.8	56.7	60.6
10	11.81	142.6	157.1	55.8	63.9

Following graphs (Figs. 7-10) present thermographs obtained by second heating for samples 3, 4, 9, 10.

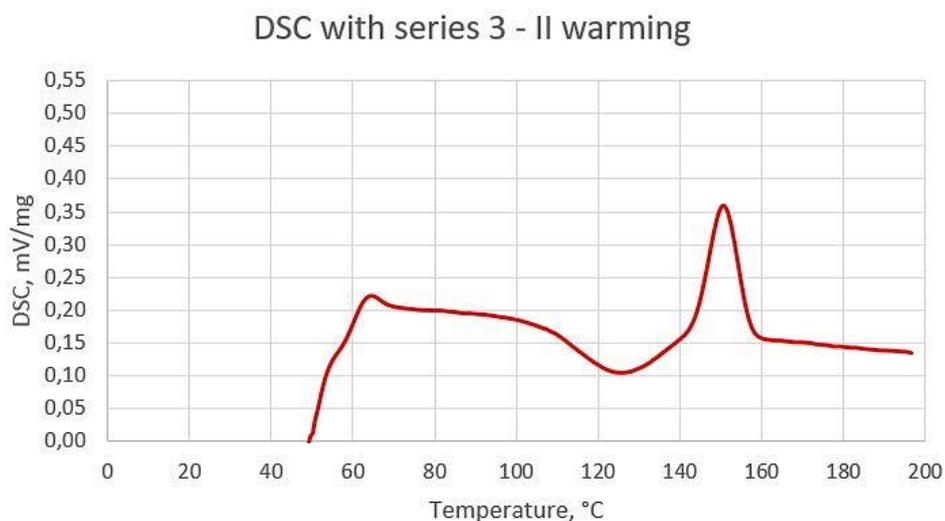


Figure 7. A graph for sample no. 3.

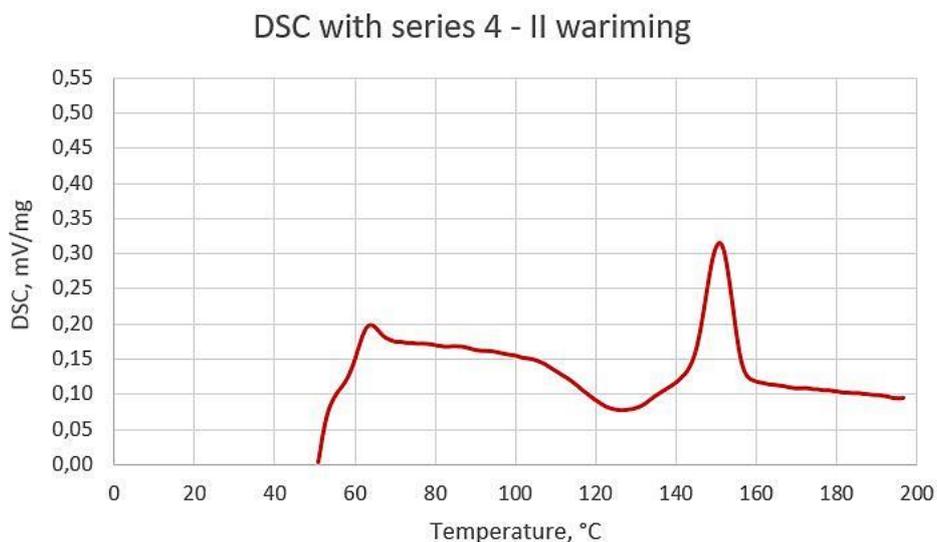


Figure 8. A graph for sample no. 4.

The results obtained during the second heating of PLA samples are slightly different from the first ones. The melting enthalpy decreased in each sample. The greatest decrease occurred in sample no. 4 from 17.57 J/g to 11.85 J/g, enthalpy difference is 5.72 J/g. In sample no. 10 the melting enthalpy has the smallest value which equals 8.99 J/g. In the case of the initial and final melting temperatures of the crystalline phase in two samples no. 4 and no. 10 the initial temperature has risen, but in the case of the final temperature in the three samples a drop in value is observed, one sample, no. 3, remained at the same level of 157.5 °C.

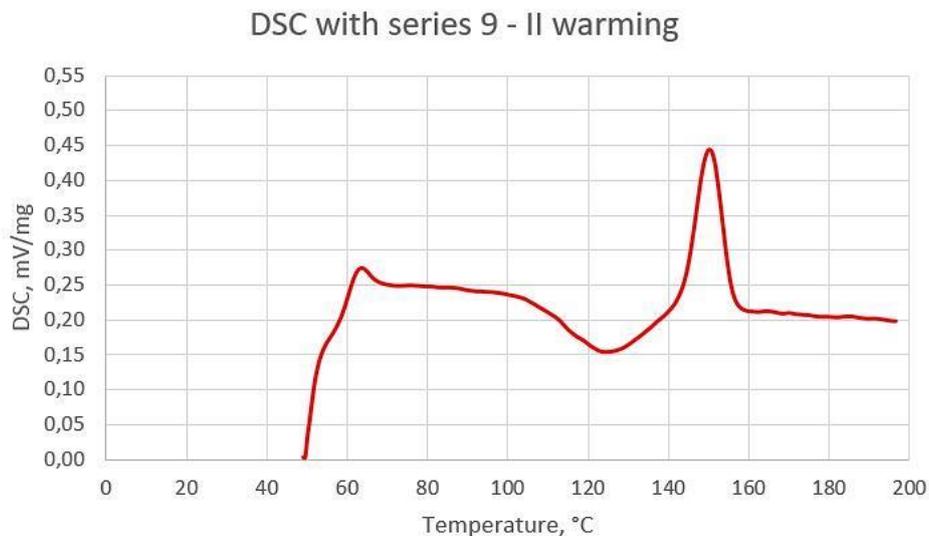


Figure 9. A graph for sample no. 9.

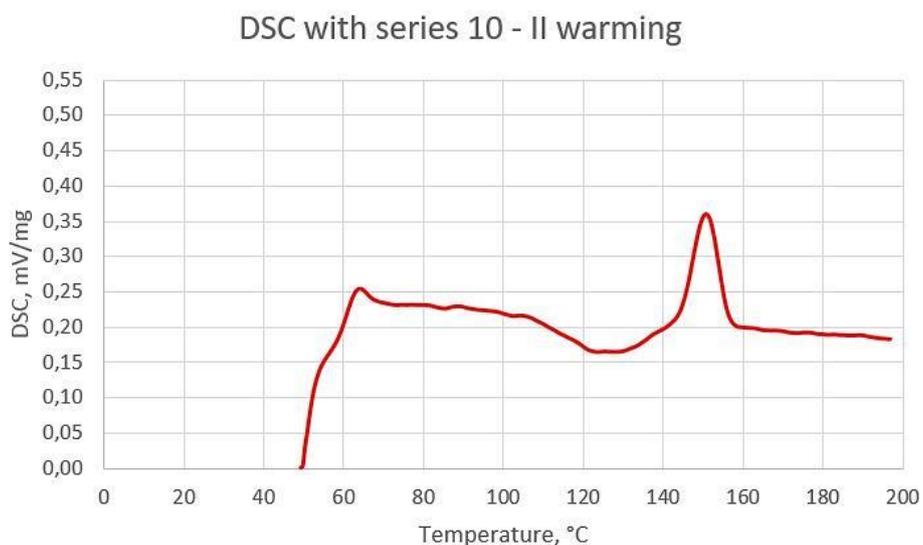


Figure 10. A graph for sample no. 10.

However, the value of the temperature drop was not greater than 0.9 °C which was recorded when considering the sample no. 4 with a temperature of 157.7 °C to 156.8 °C.

The results show the transition of temperatures from the vitreous to the elastic phase, the initial temperatures obtained by the samples all increased. Sample no. 3 has reached the highest growth value of 3.5 °C from 54.6 °C to 58.1 °C but it was still the lowest initial temperature, samples no. 4 and no. 10 are characterized by the highest one. The initial

temperature for both has reached 58,7 °C. The obtained final temperatures in three samples increased their value, sample no. 4 showed the greatest increase from 60.5 °C to 62.7 °C, while the sample no. 10 showed a decrease in temperature from 63,9 °C to 63 °C. The characteristic parameters with obtained values are presented in the table (Table 3).

Table 3. A list of obtained values for the second heating.

Name of the sample	Area [J/g]	Complex Peak [°C]		Glass Transition [°C]	
		Onset	End	Onset	End
3	13.44	142.4	157.5	58.1	62.4
4	11.85	143.5	156.8	58.7	62.7
9	14.21	142.9	156.3	58.5	62.3
10	8.99	143.5	156.4	58.7	63.0

4. CONCLUSIONS

According to the research conducted on PLA samples, it shows that the processing parameters, in this case the injection temperature, the clamping time, the injection speed and the injection time have the greatest impact on the enthalpy of melting. In the case of complex peak and glass transition the values obtained are slightly different, but the differences are not substantial. On the basis of the results it can be stated that what has the greatest influence on the difference in properties is the injection time, but only for the results of enthalpy. When it comes to other results, the values are similar to the rest of the samples. DSC results show that the initial melting point of the crystalline phase is between 142.0 °C and 143.5 °C, while the melting point of the crystalline phase is in the range of 156.3 °C to 157.7 °C.

The presented results relate to the first and the second heating of a test sample. Results on the temperature at which the transition takes place from the vitreous phase to the highly elastic phase for the first heating, the initial temperature is within the range of 54.6 °C to 56.7 °C, while for the second heating, this temperature is slightly higher and ranges from 58.1 °C to 58.7 °C. In the case of temperatures that close the transition from one phase to the other, the temperature distribution is as follows: for the first measurement the value is in the range of 60.5 °C to 63.9 °C, while for the second one it is from 58.1 °C to 63.0 °C. The study allowed to determine the thermal properties of the polylactide that was obtained at different injection parameters.

This research helped to determine which factor has the greatest influence on used molds. Further studies will allow to extend obtained results by different variable parameters of the injection process. Additionally, further studies will also be carried out to determine the mechanical properties of PLA.

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