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Properties of polylactide, obtained from lactic acid in the process of lactic fermentation of lactose in whey post production (waste)

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ABSTRACT

Purpose: This publication provides a description of RDC Glokor's own research into the effectiveness of the lactic fermentation process of lactose, lactic acid concentration and polylactide (PLA) production by ring-opening polymerization obtained from the condensation of two molecules of lactic acid. Furthermore, this publication sets out to determine potential applications of the PLA as a commercial material with a selection of thermal properties.

Design/methodology/approach: In the described research works, a lactic fermentation process was used in which lactose is converted to lactic acid with the participation of Lactic Acid Bacteria. Polylactide was obtained indirectly by Ring Opening Polymerization and by direct polymerization, straight from lactic acid, omitting the intermediate stages. Next, the obtained lactide and polylactide were examined by spectroscopic methods (IR, NMR) to determine their purity. Thermal methods (TG, DSC) to determine thermoplastic properties, i.e. softening point, decomposition temperature and glass transition temperature.

Findings: Obtained from waste whey, PLA and its copolymers are excellent biodegradable polymers that have the potential to be used in medicine as resorbable surgical strands, biopolymers for implant production, as well as in many industries including for the production of biodegradable bottles and disposable packaging, 3D printer cartridges.

Research limitations/implications: The research on lactic acid and lactide polymerization described in this article is still a new issue that requires further research to optimize PLA processes with industry-specific thermoplastic and physicochemical properties.

Originality/value: In the basic waste processing of milk, there is a large volume of whey sour, which is ecologically dangerous for waste treating. Due to the high content of lactose (up to 6%) this waste can be used as a raw material in the lactic fermentation process in which lactose is converted to lactic acid with the participation of lactic acid bacteria. Lactic acid can be concentrated and subjected to a dehydration process to lactide, which in the final stage is subjected to the process of ring-opening polymerization in order to produce biodegradable polylactide. The described process of carrying out the lactose contained in PLA whey is an innovative way to obtain a biodegradable usable polymer, which can be used to replace plastics such as polypropylene and polyethylene.

Keywords: Lactic acid, DSC, TG, Polymerization, Polylactide, PLA

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PROPERTIES

1. Introduction

Whey, as a waste product during cheese production, is a mixture of many valuable ingredients: lactose, proteins, fats, calcium, and phosphorus, organic acids and vitamins. At the same time, it is a volatile liquid, as it quickly breaks down due to presence of microflora.

Depending on the technological method of production of cheese and dairy products, dairy companies produce three types of whey: rennet (so-called sweet), acidic (acidic) and mixed.

The rennet whey is produced in the production of ripening cheeses and the acid in the production of cottage cheese. Whey differ in chemical composition and physicochemical properties. Whey acid (pH 3.8-4.6) is characterized by higher lactic acid (up to 0.7%) and lower protein content than rennet (pH 5.2-6.7) [1,2]. Annual production of whey in Poland ranges from 2.5 to 3.5 million m^3, which accounts for 65-90% of waste leaving production [3].

2. The processing of lactose to lactic acid

The high lactose content of lactose (up to 6%) in whey gives an economic basis to secrete it in pure form as a dietary supplement or animal feed.

However, after deproteinization and degreasing whey, it seems economical to use purified whey in a lactic fermentation process where lactose is converted to lactic acid with the participation of Lactic Acid Bacteria (LAB) [4,5].

$$C_{12}H_{22}O_{11} + H_2O = 4CH_3CHOHCOOH$$

Production of lactic acid in the process of lactic fermentation involving LAB has an advantage in comparison with chemical synthesis, which with the appropriate choice of strain of bacteria, a specified isomer of lactic acid can be obtained [6].

Lactic acid bacteria are different in: nutritional requirements, the type of metabolites produced, the culture medium reaction, and the culture temperature.

During the studies the optimum use of thermophilic species (increase in temperature: 37-45°C) belonging to relative anaerobes was found.

Apart from LAB, of all the starter cultures utilised in the dairy processing industry, the most common are Lactobacillus strains (l. helveticus, l. delbrueckii SSP. bulgaricus) which prefer the environment with a pH 5.5-5.8. During the growth of LAB and fermentation, the pH of the substrate is reduced as a result of the accumulation of lactic acid [7-10].

One of the factors of selectivity when choosing appropriate strains is the form of producing lactic acid. Individual species of LAB synthesized this in three forms: spring end types D (-), right-pointing L (+), and occasionally in the form of a mixture of racemic.

Lactic acid obtained industrially in the way of chemical synthesis is produced only in the form of a racemic mixture and it is useless to produce tactical polylactide (PLA) with the relevant properties of Thermo-plastic to be able to use the polymer in medicine for example in: surgical thread, implants etc.

The optical purity of lactic acid is also important for the proper conduct of the process in the PLA polymerization [11,12].

Strains which have the ability to synthesize lactic acid in the form of L (+), are particularly valuable as there is a definite need for products derived from this isomer. The undoubted advantages of LAB in the production of lactic acid isomers have made them applicable in the industrial synthesis of these compounds [13,14].

3. Receiving PLA

Polylactide is received indirectly during ring-opening polymerization (ROP – Ring Opening Polymerization) and also as a result of direct polymerization straight from lactic acid, omitting transitional stages [15] (Fig. 1).

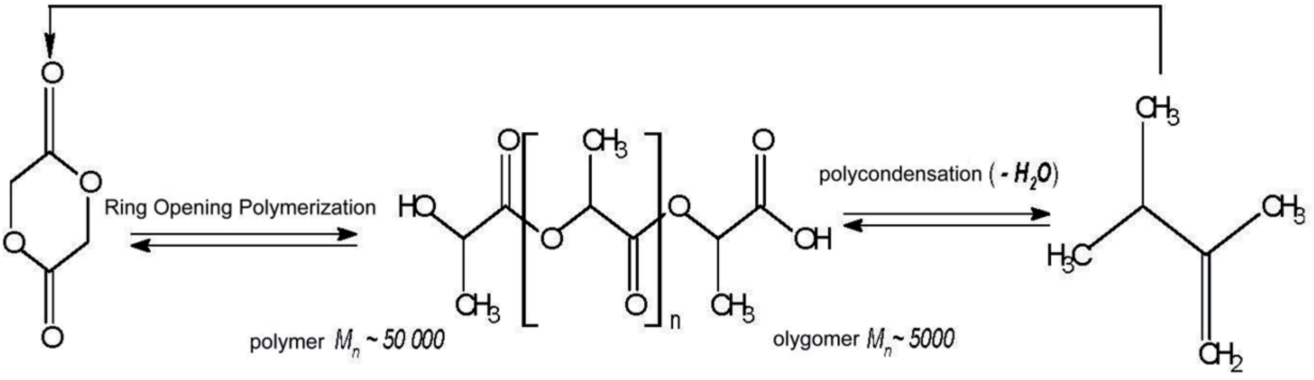

Fig. 1. Reaction scheme of receiving PLA

During intermediary polymerization, PLA is derived from the great particle mass, it is a two-step method which primarily involves the synthesis of lactide, which are cyclic diesters of lactic acid.

Lactide synthesis was first described by Pelouze in 1845 [16]. At the moment ROP is the most commonly used method in the industry, requiring several stages of lactide purification. Processes of lactide purification and preparation contribute to an increase in PLA price in relation to synthetic polymers. Ring-opening polymerization can be carried out in different forms: solution, bulk, melt and suspension.

The reaction mechanism of this polymerization may be cationic, anionic, coordination or radical [17,18].

The PLA obtained by polycondensation has a lower molecular weight, reduced mechanical properties and therefore has a limited applicability.

Direct lactic acid polycondensation allows for low and medium molecular weights (Mw) to 20,000 Da. Kokugan and his co-workers performed a non-catalytic polycondensation reaction under vacuum conditions and at a temperature 200°C, leading the process for 89 hours to obtain a polymer with a molecular weight of 90,000 Da, with a PLA yield of 52-75% [19,20].

The Lei and Moon teams used a binary catalyst-activator system in their studies to obtain the L-PLA isomer.

A catalyst uses stannous chloride dihydrate and succinic anhydride or metal alkoxides, e.g. aluminium, titanium, yttrium, germanium or p-toluenesulfonic acid as the tin catalyst activator.

The addition of p-toluenesulfonic acid enables the increase of the L-PLA performance up to 80% and Mw from 40,000 to 500,000 after 5-15 h reaction under vacuum at a temperature of 180°C [21-23].

By indirect polymerization (lactic acid - lactide - PLA) polymers with a higher molecular weight (Mw) up to 50,000 and incomparably better mechanical properties-higher glass transition temperature and melting are obtained.

The literature shows a variety of chemical compounds used as lactide ring-opening initiators which are based on metals such as lead, zinc, iron, aluminium, yttrium, bismuth, copper, calcium forming associations of comprehensive, alkoxides, acetates [24-32].

In the literature, glass transition temperature Tg, melting point (softening) Tm, and decomposition temperature Tz, for PLA ranged between Tb: 50-90°C, Tm: 140-180°C, Tz: above 260°C, for the lactide melting point Tt: 55-80°C [33-36].

3.1. Research process

Within the framework of the project, the operational programme innovative economy 2007-2013 implemented by the Research and Development Centre GLOKOR an attempt was made to develop an industrial waste processing installation with the dairy industry while obtaining biodegradable biopolymers.

Within the framework of the project the innovative economy operational programme 2007-2013 implemented by the RDC GLOKOR attempted to develop industrial waste processing installation with the dairy industry while obtaining biodegradable biopolymers.

Research was carried out in stages:

- The first stage – receiving in the process of lactic fermentation, lactic acid from lactose in whey acid. To research lactic fermentation bacteria is applied:

Lactobacillus delbrueckii, Lactobacillus acidophilus, Lactobacillus plantarum, Lactobacillus casei or Lactobacilus fermentum. Strains of lactic acid bacteria came from the collection of the Institute of Immunology and experimental therapy PAN in Wrocław. Lactic acid bacteria were transferred to a liquid culture fermentation reactor with a smooth breeding ground. At each stage of the process of lactic fermentation the lactose content was determined in a modified Bertrand method and the acidity by the potentiometry method.

In the final stage of the research process of lactic fermentation selected, the strain Lactobacillus delbrueckii achieved the highest concentration of lactic acid in the range 3.5-5% depending on the types of whey.

- The second stage – obtained by lactic fermentation, lactic acid was purified from fermentation broth (filtration, deproteinization) and then concentrated in the membrane process. In the process, is achieved acid concentration at the level of 45-60%.
- The third stage – obtained lactic acid at a concentration up to 60% applying dehydration by distillation and after dehydration lactide was obtained.
- The fourth stage – the obtained lactide was transferred to polyactide using zinc-based organometallic catalysts (Tin chloride dihydrate) and zirconium (zirconium IV acetylacetonate).

  At this stage the research work was conducted to obtain an optimal catalytic system and optimal polymerization reaction conditions.
- The fifth stage – physicochemical studies of the obtained lactide and PLA, e.g. IR spectroscopy, DSC differential scanning calorimetry, TG thermo-gravimetry, 1H i 13C NMR spectroscopy.

4. Obtained results

4.1. Study of the solubility of the PLA

The solubility of poly (lactic acid) tested in solvents of different polarity (dielectric constant).

The prepared weight of 200 mg was dissolved in 1 ml of solvent. The following solvents were tested: acetonitrile (ε = 37.5), acetone (ε = 20.7), cyclohexanone (ε = 15), tetrahydrofuran (ε = 7.6), chloroform (ε = 4.8), benzene (ε = 2.3). In all solvents used, PLA shows complete solubility at room temperature.

Solvent tests were performed to select the solvent to prepare solutions for determining molecular weight and specific rotation.

4.2. Molecular weight and hardness of PLA

The viscosity of the average molecular weight $\overline{M_V}$ was determined by the relationship between viscosity and molecular weight as described by Mark-Houwinka (or Kuhna-Marka-Houwinka-Sakurady) equation:

$$[\eta] = KM^{\alpha} \tag{1}$$

where: K and α are constants for a given pair of polymer-solvent at a given temperature.

The research was conducted in two solutions: benzene and chloroform, using Ubbelohde'a viscosimeter with temperature stabilization in a water bath (25°C).

Uses a fixed K and α for the temperature of 25°C in accordance with the literature [37-40]:

benzene: K – 2.27 $x10^3cm^3g^{-1}$, α – 0.75

chloroform: K – 6.6 $x10^3cm^3g^{-1}$, α – 0.67

For polydisperse samples, the average molecular weight determined by the viscosimetric method has an intermediate value between the number average molecular weight $\overline{M_n}$ and weight average molecular weight $\overline{M_W}$. Viscosity average molecular weight = when α = 1.

Obtained molecular weights:

$\overline{M_V}$ (benzene) = 89.800

$\overline{M_V}$ (chloroform) = 91.100

4.3. Optical rotation (proper) PLA

The Carl Zeiss Jenna circular polarimeter was used as the solvent, chloroform was used as the solvent and the specific rotation was calculated by the following formula.

Measured using polarimeter pie Carl Zeiss Jenna, chloroform was used as a solvent and appropriate rotation was calculated from the formula:

$$[\alpha]_{589}^{20} = \frac{\alpha \cdot 100}{l \cdot c} \; \frac{deg \cdot ml}{g \cdot dm} \tag{2}$$

where: *c* – PLA concentration in g/100 ml chloroform, *l* – optical length of solution in decimeters

Average value of correct PLA rotation was obtained from numbers of tests, which is equal to:

$$[\alpha]_{589}^{20} = -158.5 \; \frac{deg \cdot ml}{g \cdot dm} \tag{3}$$

The value obtained is approximate to the values achieved by other researchers [41].

4.4. Biodegradability study of PLA

A sample of 5 g PLA was placed in 50 ml of water in a closed flask and placed in oven at 36°C. Total decomposition (dissolution) of sample was obtained after 8 weeks.

4.5. NMR spectroscopy for lactide and PLA

Particles structure, purity of PLA and lactide obtained were confirmed by carry out research in NMR spectroscopy type Avator 400 MHz from Bruker company. As a solvent, deuterochloroformu was used.

In the ^{1}H NMR spectrum we observed two dominant peaks at: 1.6 ppm derived from CH_3 groups and 5.4 ppm derived from CH groups (Fig. 2).

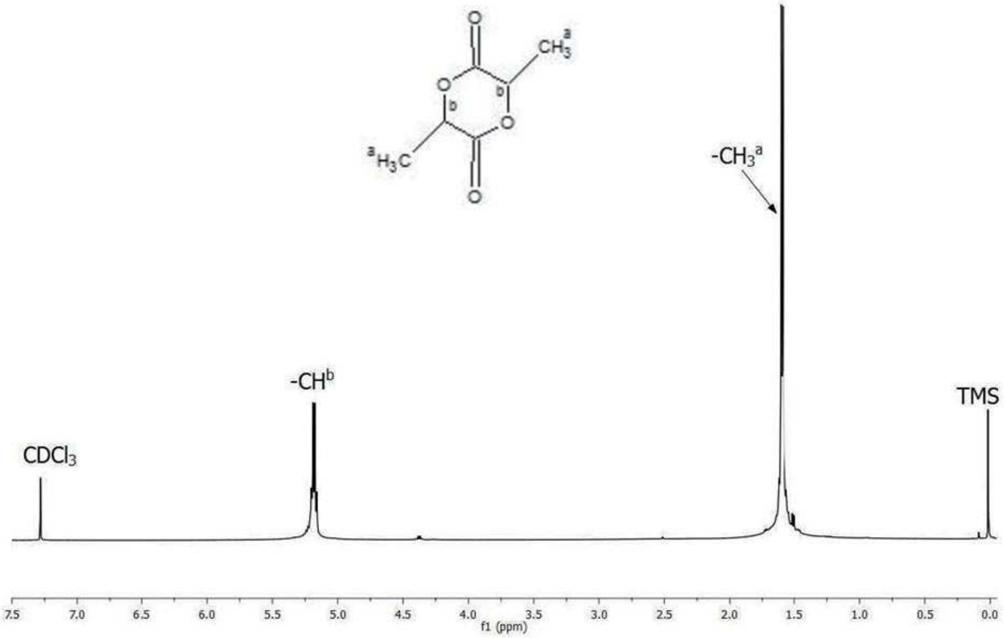

Fig. 2. ^{1}H NMR spectra for lactide

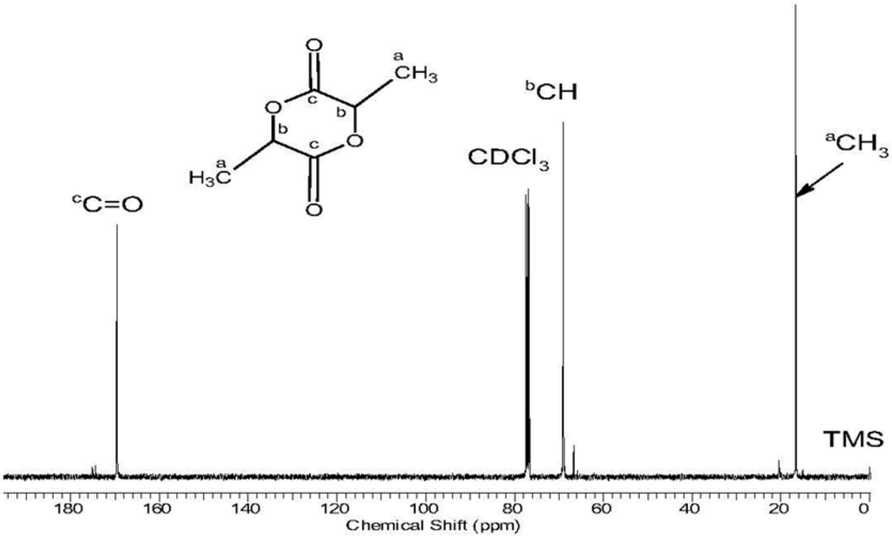

Fig. 3. ^{13}C NMR spectra for lactide

In the ^{13}C NMR spectrum we observed three dominant peaks at: 18 ppm derived from CH_3 groups, 68 ppm derived from CH groups and 170 ppm derived from the carbonyl group (Fig. 3).

In the ^{1}H NMR spectrum we observed four dominant peaks at: 1.5 ppm and 1.7 ppm derived from CH_3 groups, 4.4 ppm and 5.2 ppm derived from CH groups (Fig. 4).

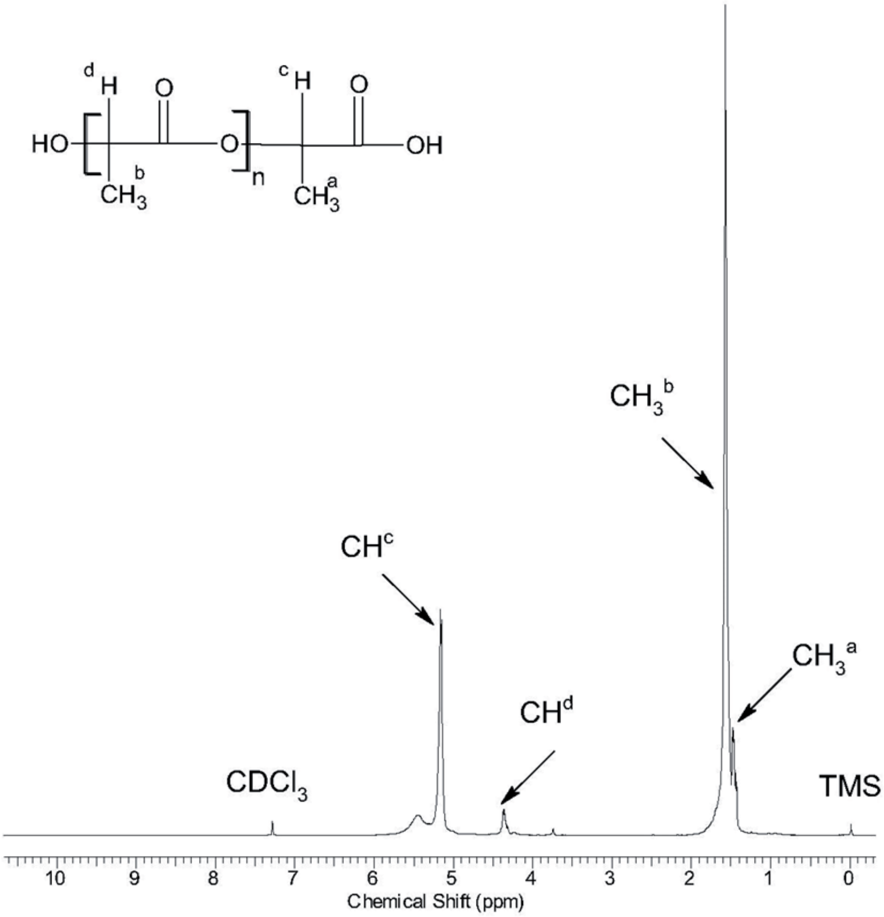

Fig. 4. ^{1}H NMR spectra for PLA

In the ^{13}C NMR spectrum we observed six dominant peaks at: 18 ppm and 20 ppm derived from CH_3 groups, 68 ppm and 70 ppm derived from CH groups and 170 ppm and 175 ppm derived from the carbonyl group (Fig. 5).

4.6. IR spectroscopy for lactide

Characteristic functional groups for lactide were confirmed using IR spectroscopy in the FT-IR SpectrumOne spectrometer. made by PerkinElmer company. The analysis was done by the KBr pellet method.

Bandes characteristic for lactide on the IR spectrum (Fig. 6):

- 2998-2948 cm^{-1} – symmetrical and unsymmetrical oscillations -CH originating from the group -CH_3 and -CH;
- 1760 cm^{-1} – stretching vibrations characteristic for the group -C = 0,
- 1458 and 1387 cm^{-1} – symmetrical and unbalanced oscillations -CH originating from the group -CH_3 and -CH,
- 1214 cm^{-1} – asymmetric vibration C-O-C,
- 1094 cm^{-1} – symmetrical oscillations C-O-C.

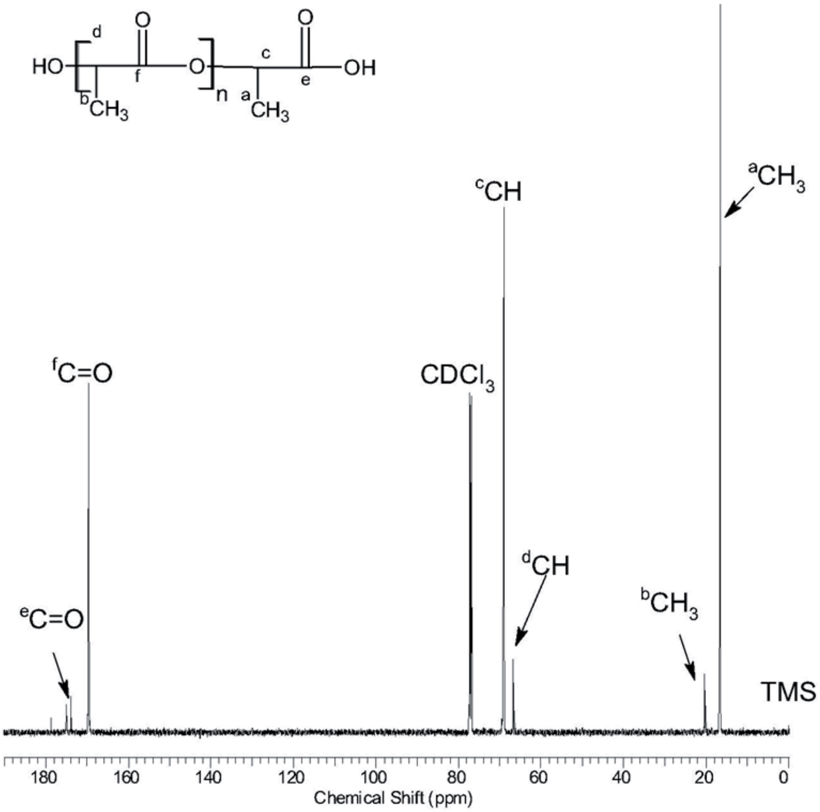

Fig. 5. ^{13}C NMR spectra for PLA

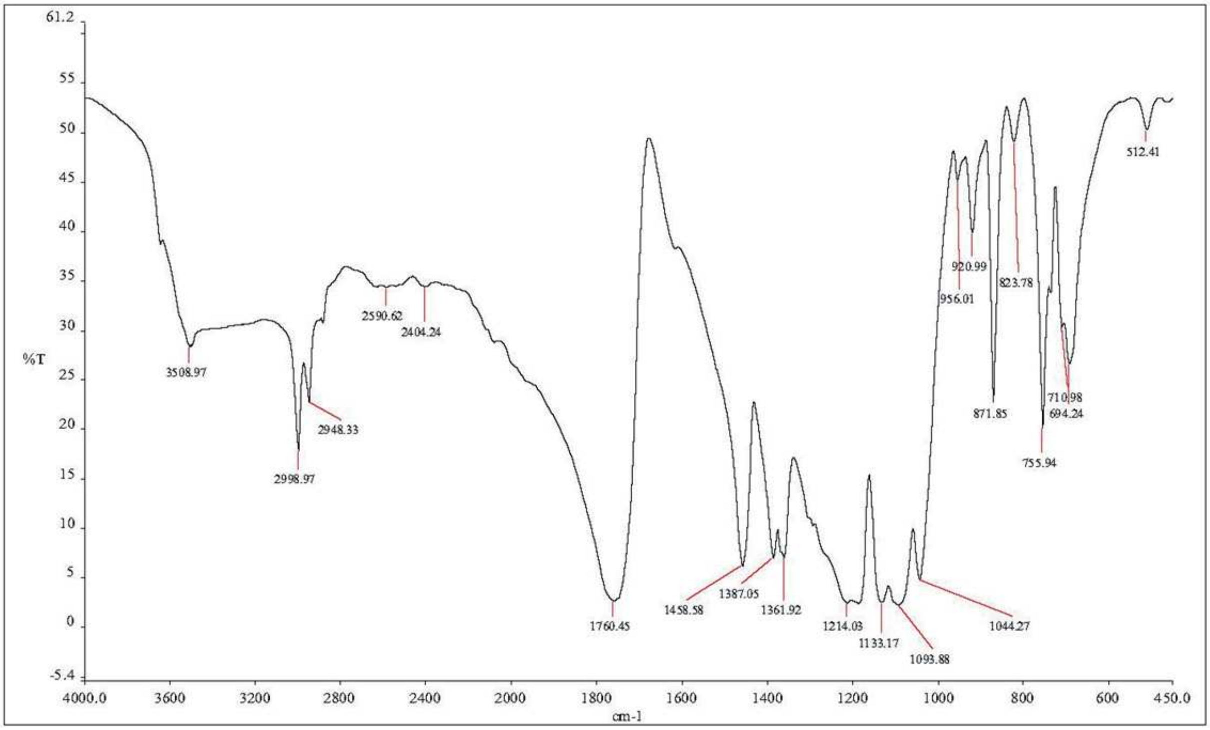

Fig. 6. IR spectra for lactide

4.7. Determination of thermal parameters of lactide and PLA using DSC and TG method

Thermal parameters such as the glass transition temperature, softening temperature and decomposition temperature were determined in the apparatus: Differential Scanning Calorimeter Pyris 1 and Thermogravimeter Pyris 1, made by PerkinElmer company.

Studies in both techniques were carried out under nitrogen atmosphere.

During research were used 5 mg samples. Each of samples were analysis by TG and DSC methods (heated at 10°C/min, and for DSC cooling at 20°C/min).

TG and DTG decomposition curve for lactide, DSC curve for lactide, TG and DTG decomposition curve for PLA and DSC curve for PLA are shown in Figures 7-10 respectively.

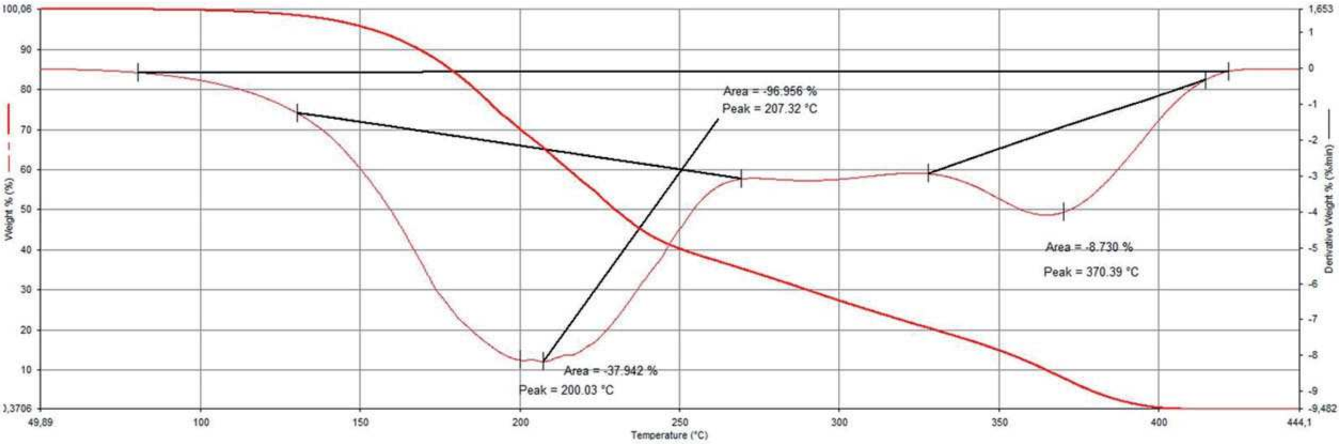

Fig. 7. TG and DTG decomposition curve for lactide. Temperature at 5% weight loss: Td5 = 150°C. The temperature at which the first maximum of 37.9% of the mass loss occurs: Tmax1 = 200°C. Temperature at which the total maximum of 99% weight loss (total thermal decomposition): Tmax2 = 400°C

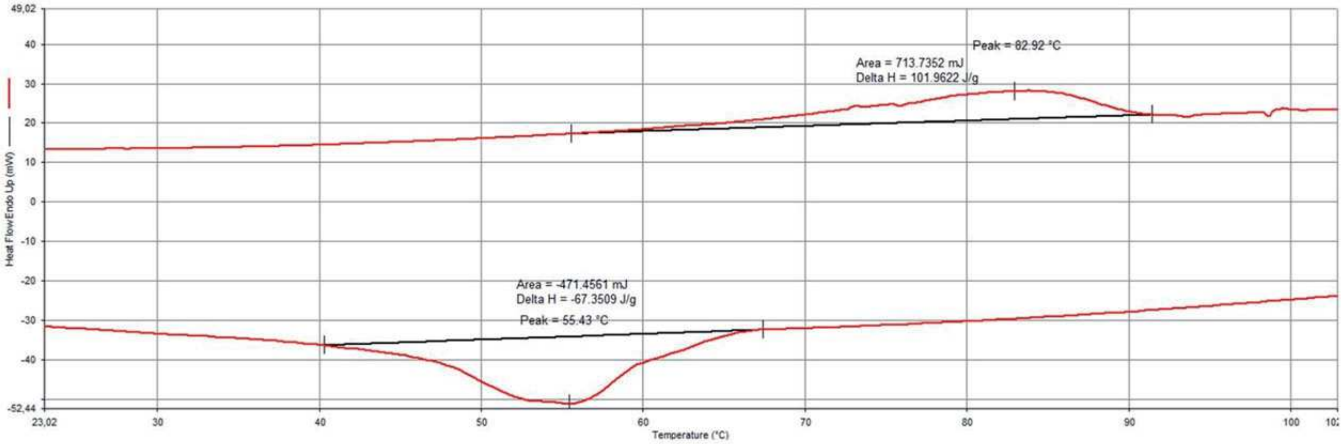

Fig. 8. DSC curve for lactide. DSC analysis determined the lactide melting temperature: 82.9°C and the lactide solidification temperature: 55.4°C

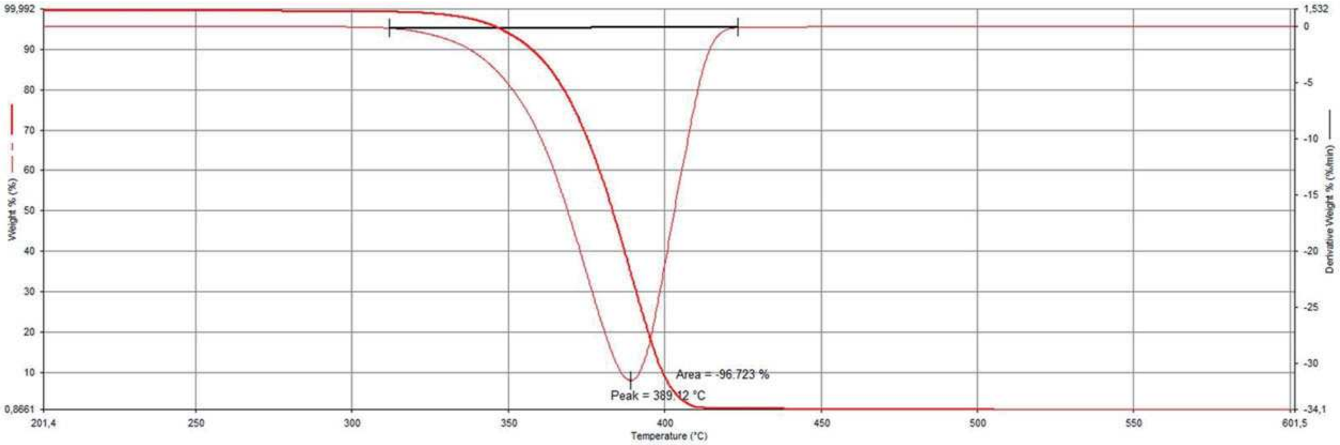

Fig. 9. TG and DTG decomposition curve for PLA. Temperature at 5% weight loss: Td5 = 350°C. Temperature at which a maximum of 99% weight loss (total thermal decomposition): Tmax = 430°C

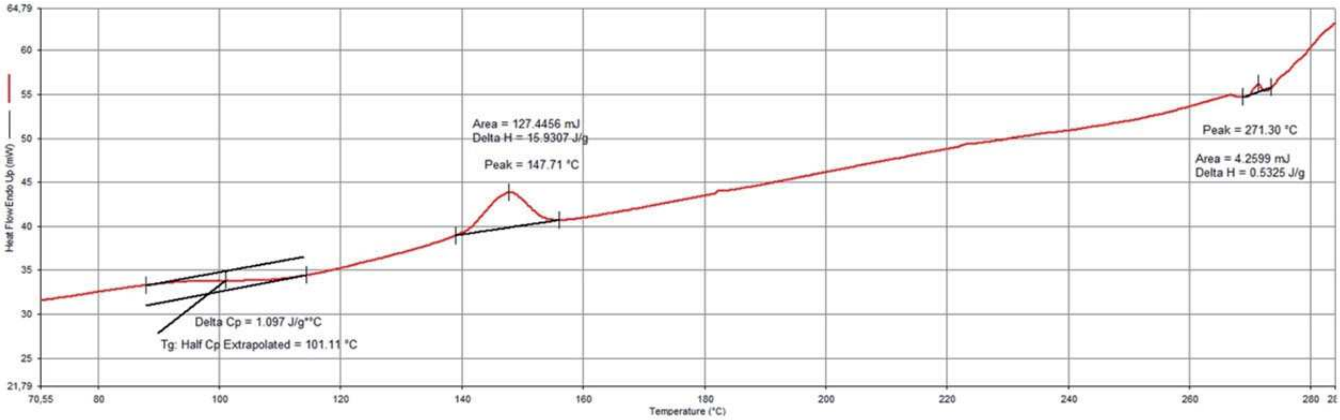

Fig. 10. DSC curve for PLA

As a result of the DSC analysis, a glass transition temperature was determined – of Tg = 101°C, melt temperature (flow) Tm = 147.7°C and initial decomposition temperature about 272°C. A value of Tg is greater than 100°C and indicates that the resulting polymer has a high molecular weight over 60,000.

5. Conclusions

In this paper we present an economically viable possibility of using a waste whey, on the basis of which a polylactide was produced.

The results obtained for the PLA received by transformation: lactose-lactic acid-lactide-PLA indicate that the resulting polymer has good thermoplastic properties: high softening temperature, very high decomposition temperature.

The obtained polymer purity and its physicochemical properties allow to be compared it to the industrial-synthetically obtained PLA.

Obtained from waste whey, PLA and its copolymers are excellent biodegradable polymers that have the potential to be used in medicine as resorbable surgical strands, biopolymers for implant production, as well as in many industries including for the production of biodegradable bottles and disposable packaging, 3D printer cartridges.

It is estimated that the PLA will be replaced in the coming years due to the non-biodegradability of polyolefins (PE, PP) and other polymers from non-renewable raw materials (e.g. PET, PMMA). As a result, global PLA production is on an upward trend.

The research on lactic acid and lactide polymerization described in this article is still a new issue that requires further research to optimize PLA processes with industry-specific thermoplastic and physicochemical properties.

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