SYNTHESIS OF BIODEGRADABLE POLYMER. THE POLYMERIZATION OF LACTIC ACID WITH MICROWAVE RADIATION

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Abstract

During the last decade, most of the countries have introduced regulations to the plastic materials in order to increase its biodegradability and reduce the build-up in the environment.

This work was done by a group of undergraduate students. The goal was to find new products and technology producing biodegradable polymers and final prototypes has to be presented. Constant supervision was given during all the semester to accomplish the goals.

Lactic acid obtained from natural sources was reacted with the use of microwave radiation, to get a biodegradable polymer. Changing the time and the temperature of the polymerization different polymers were obtained. The properties of the final polymers were from extremely soft, ideal to be uses as glue, to a very hard, to produce solid objects.

Keywords: Polymerization, lactic acid, biodegradable polymer, microwave.

1 INTRODUCTION

Environmental issues and the increases of global demand for energy, chemicals and materials, for a growing global population, has significantly increases the interest in develop low environmental impact technologies based on renewable raw material. The use of food crops for chemicals, and biofuels can reduce the food available for the humans and animals. The new developments, integrate several strategies based on sustainable process, like the use of by-products or wastes.

There are non-product flows of raw materials whose economic value are less that the cost of collection and recovery for use; therefore discarded as waste. Waste produced by consumers and food processing companies can be used to obtain valuable chemicals. One way of increasing the value of the by-products is transforming them into high value products. Agro industrial residues as sugar cane bagasse, coffee husk and pulp, wheat, rice bran, corn etc., contains products that can be transformed biotechnological into a raw material for producing biodegradable end products.

1.1 Biomass

1.1.1 Cellulose and Starch.

The biomass consists mainly of lignin and cellulose. Cellulose is abundantly available and is present in

all the plants, is a natural polymer consisting of glucose units. Its annual production is estimated at $2x10^9$ tons. [1] Today fossil fuels such as coal, oil and natural gas are the main source of fuels and polymers, with the growing demand of energy and diminishing reserves of these non-renewable resources, the supply will be reduced in the near future. The U.S. Department of Energy has a study that in 20 years 20% of the transportation fuel and 25% of chemicals will be produced from biomass.

Cellulose is the major constituent of the plants, trees are 30-40% cellulose, cotton is more than 90%.

Structurally, cellulose is a polysaccharide composed of D-glucose units joined by. β(1,4) glycosidic linkages The average range of glucose units are between 7000 to 12 000.

Hydrolysis of all the glucosidic bonds of cellulose yields D-glucose. Starch is also a polysaccharide made of glucose, however unlike cellulose the glycosidic linkages are α. This small change of

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stereochemistry between cellulose and starch creates a large difference in their shape and properties, for instance starch is soluble in water, cellulose is not.

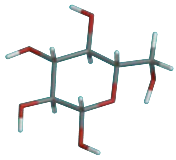

Fig 1 glucose

Starch consists of two types of molecules, amylose (normally 20-30%) and amylopectin (normally 70-80%). Both consist of polymers of α-D-glucose units in the 4C1 conformation. In amylose these are linked (1--4), with the ring oxygen atoms all on the same side, whereas in amylopectin about one residue in every twenty or so is also linked (1--6) forming branch-points. The relative proportions of amylose to amylopectin and (1--6) branch-points both depend on the source of the starch, for example, amylomaizes contain over 50% amylose whereas 'waxy' maize has almost none (~3%)[2]

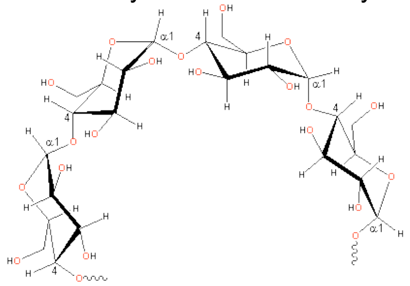

Fig2 Amylose

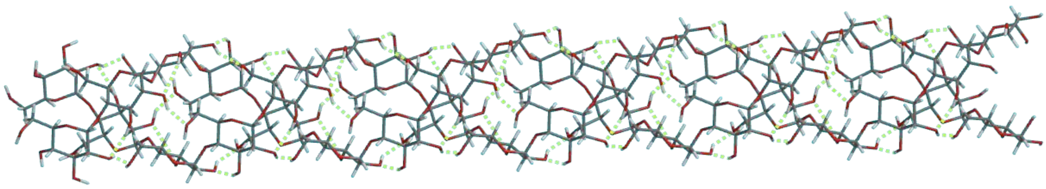

Fig 3 Amylose double helix

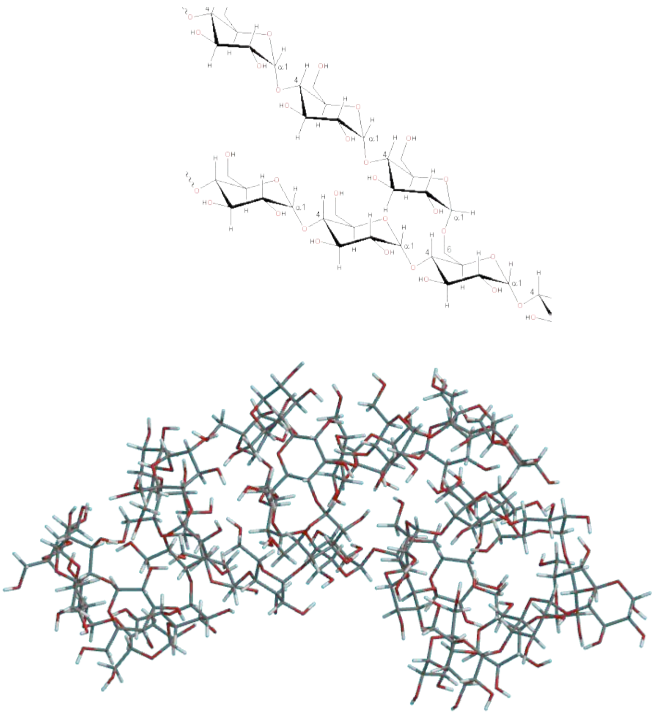

Fig 4 Amilopectine

Cellulose is an insoluble molecule consisting of between 2000 - 14000 residues with some preparations being somewhat shorter. It forms crystals (cellulose Iα) where intra-molecular (O3-HO5' and O6H-O2') and intra-strand (O6-HO3') hydrogen bonds holds the network flat allowing the more hydrophobic ribbon faces to stack. Weak C6-HO2' hydrogen bonds may also make some contribution to the crystal stability. [3]

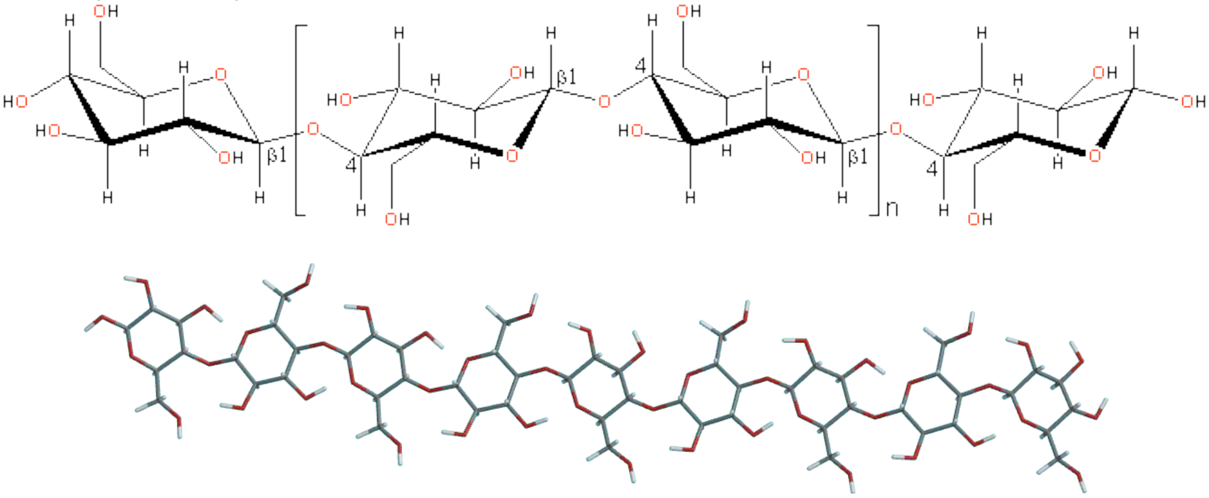

Fig 5 Cellulose

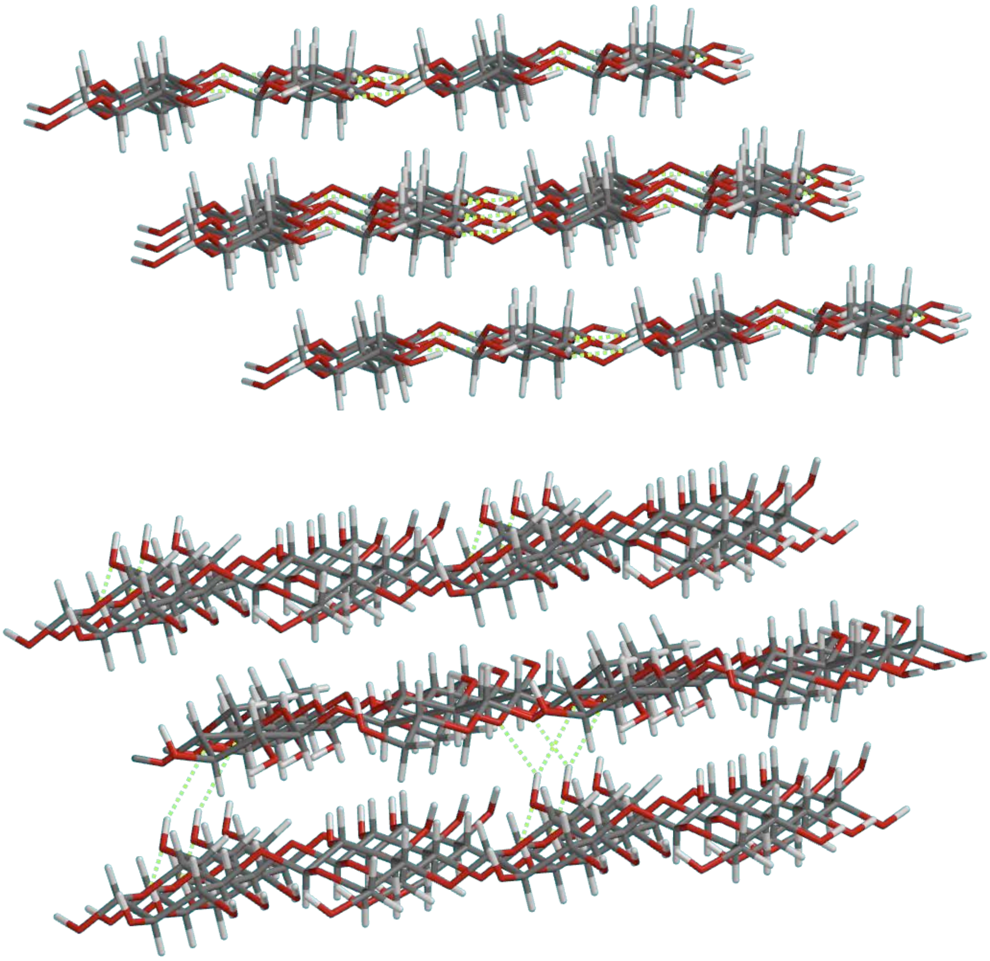

Fig 6 Cellulose Stacks

1.1.2 Lactic Acid

Lactic acid was first discovered in sour milk by Scheele in 1780, who initially considered it a milk component. In 1857, however, Pasteur discovered that it was not a milk component, but a fermentation metabolite generated by certain microorganisms [4]. Lactic acid can be produced by either microbial fermentation or chemical synthesis. Although racemic DL-lactic acid is always produced by chemical synthesis from petrochemical resources, an optically pure L(+)- or D(–)-lactic acid can be obtained by microbial fermentation of renewable resources when the appropriate microorganism that can produce only one of the isomers is selected [5].

Lactic acid could be potentially used for the manufacturing of large-volume oxygenated chemicals, such as propylene glycol, propylene oxide, propylene glycol, acrylic acid, and acrylate esters, and other chemical intermediates such as lactate ester plasticizers.[6]

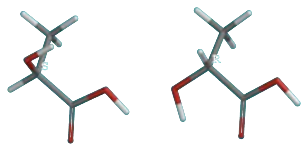

Fig7 Lactic acid S, R .

One of the large markets for lactic acid is the production of Polylactic acid PLA . Currently there are 25 companies at 30 sites across the world producing PLA. Global production capacity currently stands at around 180,000 tonnes per year, of which US-based NatureWorks accounts for 140,000 tonnes.[7].

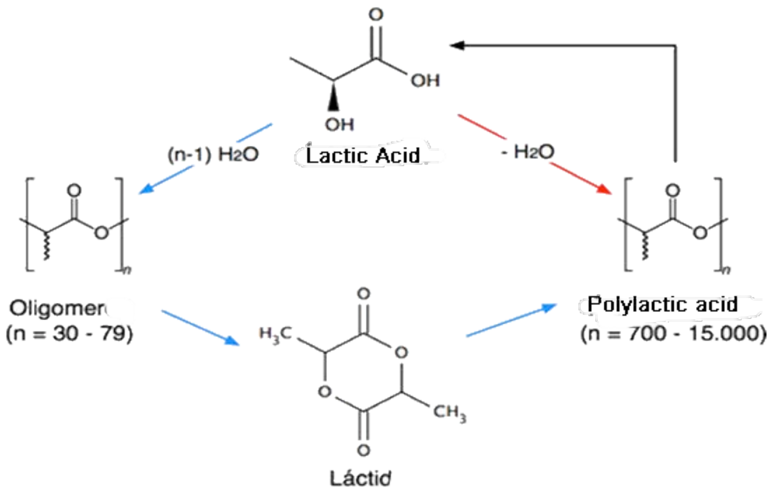

Fig 8 Production of Polylactic Acid (PLA)

2 PROJECT

2.1 Problem

The polymers derived from petrochemicals have become a real pollution problem. The degradation of the waste can take up to 100 years [8]. The use of a biodegradable polymer for consumer is ideal for the preservation of the environment.

Microwave heating has attracted a great deal of attention for its potential as a polymerization force instead of conventional heating. Microwave technology has been introduced to synthesize PLA of high molecular weight via direct melt polycondensation DMP since 2001.[9-19]

In this project the use of a solution of lactic acid was the starting material to produce PLA. The objective was to find the influence of the temperature, catalyst and time of reaction in the polymerization of Lactic acid

The indiscriminate use of plastics from oil and environmental pollution they generate has stimulated research to develop new materials and production methods that allow synthesizing biodegradable polymers with the same properties of petrochemical plastics, but having a shortest degradation period.

One of the most attractive polymers to accomplish this purpose is polylactic acid (PLA), which is a precursor molecule which thermoplastic biopolymer is lactic acid. The PLA has mechanical properties similar to petrochemicals, and polymers can be synthesized from raw materials derived from renewable bio resources such as corn or sugar cane, which can be good alternatives to replace fossil fuels.

In this project, we studied the synthesis of polylactic acid in a reactor of microwave radiation, which significantly reduced the reaction time, obtaining high yields of biodegradable PLA polymer with appropriate specifications and properties for use in different applications. The independent variables were time and measure the temperature of polymerization. The response variables were dependent or the yield (percent conversion) and the biodegradable polymer properties obtained. Both experimentation and product evaluation is performed at the Department of Graduate School of Chemistry of UNAM

2.2 Project Justification

The indiscriminate use of plastics from oil and environmental pollution they generate has stimulated research to develop new materials and production methods that allow synthesizing biodegradable polymers with the same properties of petrochemical plastics, but having a shorter degradation time. One of the most attractive polymers for this purpose is polylactic acid (PLA), which is a thermoplastic biopolymer precursor molecule which is lactic acid. Due to their biodegradability, biocompatibility and barrier properties, this biopolymer has many applications, such as biomedical materials among others, as it has an unusually wide range of properties, from the amorphous to the crystalline state; characteristics that can be achieved by manipulating the mixture's D isomers (-) and L (), molecular weights and copolymers.

PLA has mechanical properties similar to the petrochemical polymers, except for a low elongation. However, this property can be tuned during polymerization. It can be as hard as acrylic or as soft as polyethylene, polystyrene rigid or flexible elastomer. It can also be formulated to provide a variety of resistances. PLA resins can be subjected to sterilization with gamma rays and is stable when exposed to ultraviolet rays. The polylactic acid has other attractive properties such as smoothness, scratch resistance and wear, and can be synthesized from raw materials derived from renewable bio resources such as corn or sugar cane, which can be good alternatives to replace to fossil resources.

Furthermore, the use of microwave radiation reactor for the polymerization of lactic acid significantly reduces the reaction time of 30 hours, in conventional conditions at 120 ° C, at about 110 min. to 165 ° C, and therefore, the energy used for their preparation.

2.3 Project Objectives

• Get the biodegradable polymer: polylactic acid from the poly condensation of lactic acid, used as a heating medium the microwave radiation.

• Determine the time and the temperature most suitable for the polymerization of lactic acid in the microwave reactor, enabling the best performance of the biopolymer and the most suitable properties.

• Determining the biodegradable polymer yield nuclear magnetic resonance.

• Determine the purity of the biodegradable polymer thus obtained from the melting properties and decomposition by differential thermal testing.

2.4 Use of microwave to obtain the polymer

Microwave radiation has become a energy source increasingly used in organic chemistry, especially in the synthesis of polymers, where the conversion time decreases significantly due to it is possible to raise the reaction temperature, and the microwave effect. The use of microwaves allows in the polymerization reactions an homogeneous heating, the reaction rate increases, decreases conversion time and leads to goods yields and higher purity products.

Polylactic acid (PLA) is a biodegradable polymer of superior transparency, and excellent mechanical properties can be synthesized from lactic acid from natural raw materials such as corn and sugar cane. At present, the PLA is industrially produced by ring-opening polymerization of L-lactide, a cyclic dimer of lactic acid, which has to be synthesized in the process, which increases production costs. Furthermore, the direct poly condensation of lactic acid leads to lower molecular weight products (1000 g / mol) as a result of an unfavorable equilibrium constant and low reaction rate.

There have been many attempts to obtain a polylactic acid high molecular weight by direct poly condensation of lactic acid or its oligomers. However, these processes require many stages with high-energy consumptions, and the reaction time can be prolonged to several hours or even days. Due to this chemical industry demand for more efficient processes of polymerization in a single step, involving low energy consumption and where reaction times are significantly reduced.

Recent research has used microwave radiation for the synthesis of polylactic acid by the direct poly condensation of lactic acid, with a significant decrease in reaction time of the polymerization product and obtaining a much higher molecular weight, up to 10 000 g / mol.

In order to obtain the polylactic acid with a high molecular weight from the lactic acid, in one step, it is necessary to separate continuously the water formed during the polymerization process and using a catalyst which accelerates the reaction, such as hydrated tin chloride (II) ($SnCl_2\ 2H_2O$) or 2-ethylhexanoate, tin (II) ($C_{16}H_{30}O_4Sn$) which have given excellent results, but one of the problems that might arise during polymerization are trans esterification side reactions that can affect the optical purity of the product.

3 EXPERIMENTAL PROCEDURE

3.1 Set up

In order to answer the questions raised in the problem statement, meet project objectives and test this hypothesis, we developed a research design that included experimental and primarily quantitative:

A . Get the biodegradable polymer: polylactic acid from the poly condensation of lactic acid, using as a heating medium Reactor microwave radiation, particular:

B. The time and temperature most suitable for the polymerization of lactic acid.

C. gets the yield of polylactic acid by Nuclear Magnetic Resonance.

D. Determine the properties of melting point and decomposition.

. Experiments were carried out in the Laboratory of Organic Chemistry Division of Graduate Studies, Faculty of Chemistry, UNAM,

3.2 Description of the procedure.

The first tests for obtaining lactic acid biopolymer were to determine the most appropriate operating conditions in terms of temperature and reaction time, also polymerization at normal pressure and vacuum. For such purposes were carried out the following procedure:

a.- 10 ml of lactic acid in 85% aqueous solution were measured and was transferred to a ball flask with ground glass joints. Three drops of 2-ethylhexanoate catalyst tin (II) ($C_{16}H_{30}O_4Sn$) were added (Fig, 9)

b.- The operating conditions were programmed into a computer connected to the reactor; temperature and reaction time in the microwave reactor.The operating power was 75 w. The equipment was controlled by a softwawe from a laptop. (Fig10)

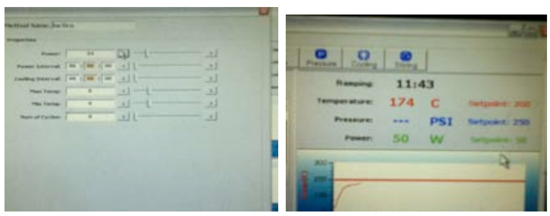

Fig 9

Fig 10

c.- A coolant was adapted to the flask to condense water vapors obtained during the reaction. A measuring cylinder was placed at the coolant outlet to determine the amount of extracted water. (Fig. 11). Temperature and reaction time were monitored, and distilled water was measured in the process.

When the right amount of water distilled the flask was connected to a vacuum system in order to fully dehydrate the polymer obtained.

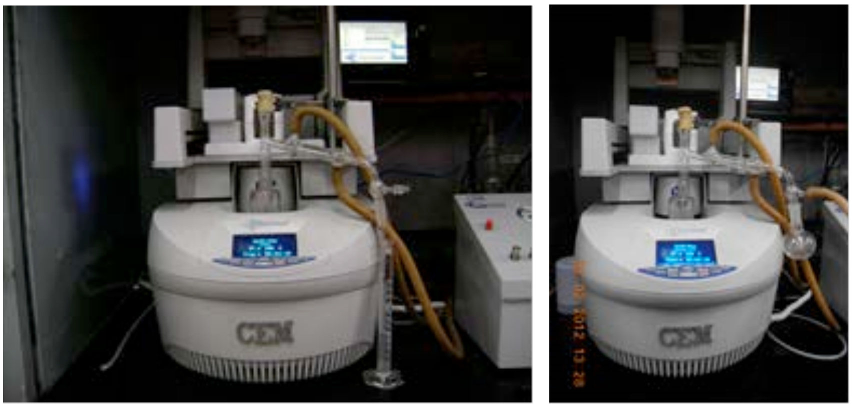

Fig 11

3.3 Specification of the equipment.

CEM microwave reactor brand, model Discover Explorer Hybrid, up to 200 watts of power.

Vacuum Pump Mastercool brand 1.5 HP, 3450 rpm 110/60 Hz, max vacuum 25 microns.

4 RESULTS

The following table shows the first experimental tests carried out at different conditions of temperature and reaction times. In these initial, tests did not separate the product water. (table 1)

Lactic acid(ml)	Cat. (drops)	Temperature (°C)	Time (hr.: min)
10	2	200	1:30
10	3	200	1:30
10	2	185	1:00
10	2	200	1:30
10	2	200	1:00
10	2	175	1:30
10	2	180	1:30
10	2	185	1:30
10	2	185	1:30

Table 1

Products obtained Fig 12

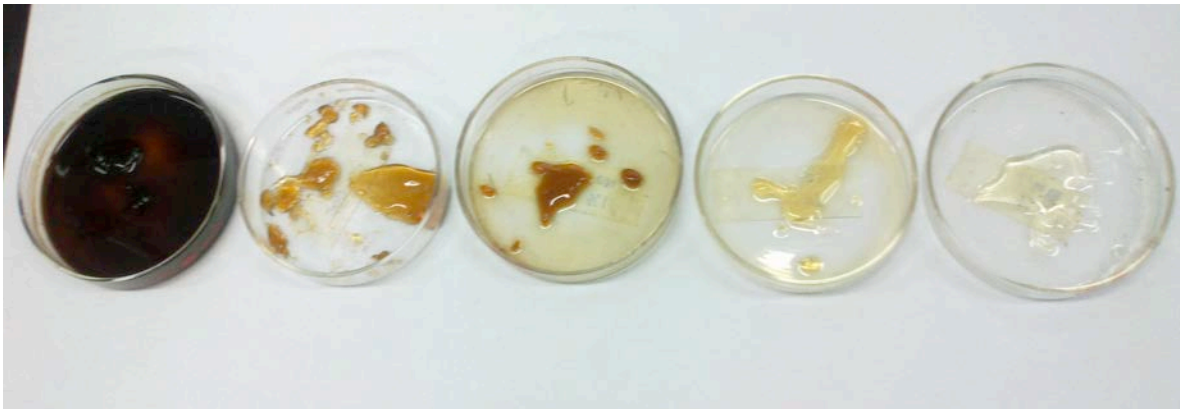

Fig13

Products obtained as films Fig 13

Fig 13

Casting of the polymer Fig 14

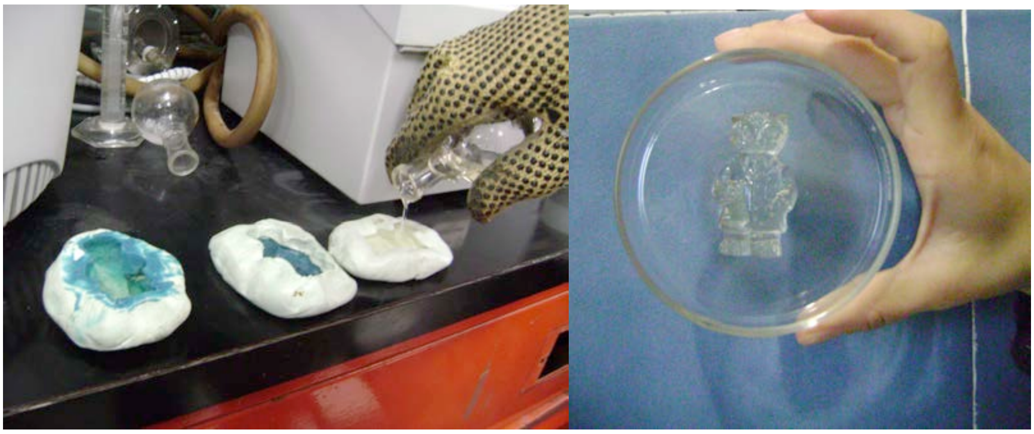

Fig 14

Figure 15 is the nuclear magnetic resonance spectrum of the sample of polylactic acid obtained. Traces are observed dimer of lactic acid and other radical (A and B). Considering the area under the curve of the polymer conversion was approximately 93%

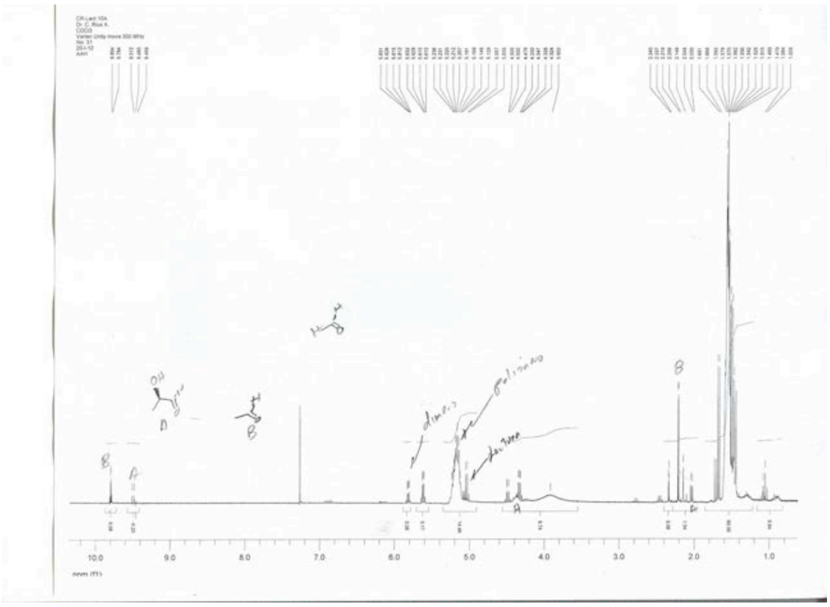

Fig 15

Using DTF the melting point of polylactic acid was determined and the degradation temperature. The melting temperature of the product was 187.41 ° C, which is within the range of commercial polymer. The degradation temperature is 305.09 ° C, according to these results it is considered that the molecular weight of the product is in the range of 6000 g / mol (Fig. 16)

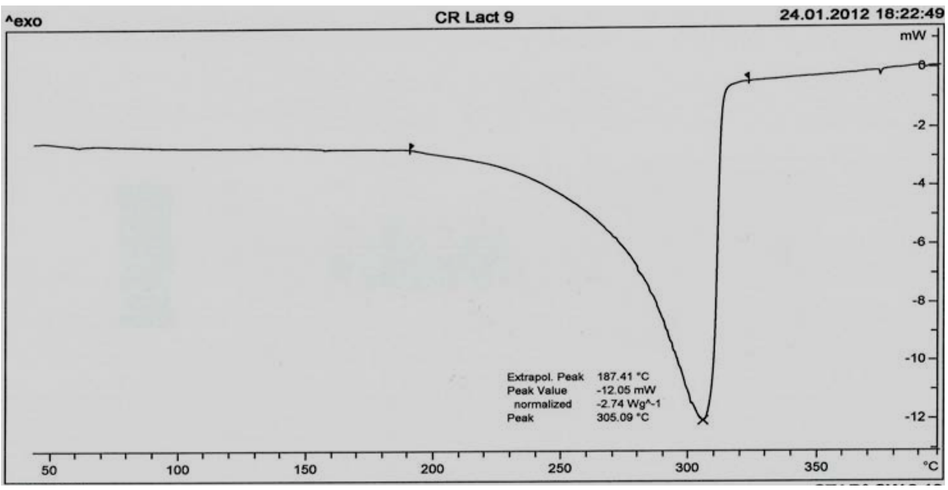

Fig 16

5 CONCLUSIONS

With the condensation of lactic acid a biodegradable polymer is obtained: polylactic acid, using as a heating medium microwave radiation. The reaction time for the polymerization of lactic acid using a microwave reactor is significantly less than that used in the conventional process. the biodegradable polymer: polylactic acid with in obtained with a purity of at least 90% and yields achieved are superior to 80% The biodegradable polymer obtained (PLA) comply with the standard specifications and properties suitable for use in manufacturing comercial products.

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REFERENCES

[1] Sasaki, M.; Adschiri, T.; Arai, K. Production of Cellulose II from Native Cellulose by Near- and Supercritical Water Solubilization. J. Agric. Food Chem. 2003, 51, 5376.

[2] N. Singh, J. Singh, L. Kaur, N. Singh Sodhi and B. Singh Gill, Morphological, thermal and rheological properties of starches from different botanical sources, *Food Chem*. 81 (2003) 219-231

[3] B. Lindman, G. Karlström and L. Stigsson, On the mechanism of dissolution of cellulose*, J. Mol. Liquids*156 (2010) 76-81

[4] H. Benninga: A History of Lactic Acid Making*, Kluwer Academic Publishers*, Dordrecht, Netherlands (1990) pp. 1–61.

[5] K. Hofvendahl, B. Hahn-Hägerdal, Factors affecting the fermentative lactic acid production from renewable resources,*Enzyme Microb. Technol.* 26 (2000) 87–107.

[6] Datta R, Henry M (2006) Lactic acid: recent advances in products, processes and technologies—a review. *J Chem Technol Biotechnol* 81:1119–1129

[7] http://www.innovativeindustry.net/types-of-bioplastic

[8] Aizenshtein. E.M. (2006) World production and consumption of polyester fibers and threats. **Fibre Chemistry**. (38) 3. 264-271

[9] Kéki S. (2001) Fast Microwave-Mediated Bulk Polycondensation of d,l-Lactic Acid. *Macromolecular Rapid Communications* 22, 1063–1065

[10] Hirao K. (2010), Alcoholysis of Poly(L-lactic acid) under microwave irradiation *Polymer Degradation and Stability* 95 925-928

[11] Hoogenboom R.; Schubert U.S. (2007), Microwave-Assisted Polymer Synthesis: Recent Developments in a Rapidly Expanding Field of Research. *Macromolecular Rapid Communications*. 28 368-386

[12] Liu L.J. (2001), Microwave-assisted Polymerization of D, L-Lactide with Stannous Octanoate as Catalyst Chinese Chemical Letters 12 (8), 663–664

[13] Marques D.A.S. (2010) Poly(lactic acid) Synthesis in Solution Polymerization *Macromolecular Rapid Communication* 296, 63–71

[14] Nagahata R. (2007) Microwave-Assisted Single-Step Synthesis of Poly(lactic acid) by Direct Polycondensation of Lactic Acid *Macromolecular Rapid Communications* 28, 437–442

[15] Nakamura T. (2010) In-situ measurement of microwave absorption properties at 2.45 GHz for the polycondensation of lactic acid *Polymer* 51 329–333

[16] Nikolic L. (2010) Novel Microwave-Assisted Synthesis of Poly(D,L-lactide): The Influence of Monomer/Initiator Molar Ratio on the Product Properties *Sensors Journal* 10, 5063-5073

[17] Pandey A. (2008) Synthesis of polylactic acid–polyglycolic acid blends using microwave radiation. Journal of the Mechanical Behavior of Biomedical Materials 1 227–233

[18] Zhang C. (2007), Microwave-Assisted Synthesis of PLLA-PEG-PLLA Triblock Copolymers. *Macromolecular Rapid Communications*. 28, 422-427

[19] Zhang Y.M. (2007), Microwave Irradiation: A Novel Method for Rapid Synthesis of D,L-Lactide, *Macromolecular Rapid Communications*. 28, 417–421.