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10TH International Conference on Sustainable Energy and Environmental Protection:

Materials

(June 27TH - 30TH, 2017, Bled, Slovenia)

(Conference Proceedings)

Editors:
Emeritus Prof. dr. Jurij Krope
Prof. dr. Abdul Ghani Olabi
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Prof. dr. Stanislav Božičnik

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10TH INTERNATIONAL CONFERENCE ON SUSTAINABLE ENERGY AND ENVIRONMENTAL PROTECTION (JUNE 27TH – 30TH, 2017, BLED, SLOVENIA), MATERIALS
J. Krope, A.Ghani Olabi, D. Goričanec & S. Božičnik

Energy Efficient Poly(Lactide) Obtaining by Microwave Synthesis

IVAN RISTIĆ, MILOVAN JOTANOVIĆ, TAMARA ERCEG, LJUBIŠA NIKOLIĆ, SUZANA CAKIĆ, VLADAN MIĆIĆ & STEFAN PAVLOVIĆ

Abstract The world is faced with the consequences of drastic reduction in fossil fuel reserves, because of their widespread use, not only as an energy source, but also as a feedstock for monomers obtaining. In order to solve this problem, the scientific community has focused on finding the new ways to exploit renewable resources and optimize the process of polymer materials production. The aim is to obtain applicable polymer whose complete life cycle is put in ecological framework. Poly(lactide) (PLA) meets these requirements as biodegradable polyester whose monomer is derived from plant feedstock containing carbohydrates. Different methods can be applied for PLA synthesis, but from the point of energy saving, as well as environmental protection, the microwave synthesis of PLA is the best solution. The use of microwaves enables homogenous heating of reaction mixture, lower consumption of organic solvent and drastic reduction in polymerization time, obtaining, in the same time, high molecular weight polymers.

Keywords: • poly(lactide) • microwave synthesis • energy efficiency • bandgap engineering • 3D •

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1 Introduction

From the 19th century fossil fuels have been the primary energy source and the source for production of polymer materials. Excessive exploitation of fossil fuels has resulted in drastic reduction of their reserves as well as in economical and environmental pollution issues. Synergism of these factors has initiated the development and implementation the principles of the concept of energy saving. The concept of energy saving has several items including replacing fossil fuels by alternative energy resources and the use of renewable raw materials as feedstock for polymer synthesis. The interest in sustainable product was the driving force for the development of methods for obtaining, modifying and applying of biopolymers. Complete life cycle of such materials is fit into environmental framework, starting from their preparation to the final application and disposal. Biopolymers are biodegradable polymers extracted from the biomass or synthesized from the monomers obtained from the renewable resources. Natural resource origin and biodegradability of biopolymers make them more suitable for obtaining and using in comparison with conventional plastic. Those materials can be appropriate replacement for polymers derived from fossil fuels if they possess certain functional properties. Poly(lactide) (PLA) meets these requirements as biodegradable polyester whose monomer is derived from the plant feedstock containing carbohydrates. The main building block of PLA is lactic acid (2-hydroxypropanoic acid), that can be obtained either by fermentation of carbohydrates or chemical synthesis, but fermentation is the most common procedure for lactic acid obtaining [1, 2]. Waste products of the food industry and agriculture, rich in carbohydrates, can be used for the preparation of lactic acid by fermentation, which not only decreases the cost of polymer manufacture, but also solves the problem of waste disposal.

PLA is also important because of its biocompatibility; subjected to hydrolysis it gives a lactic acid that can be metabolised in human body as well as in natural environment.

Two optically active enantiomers of lactic acid (L and D) can give three forms of cyclic diester of lactic acid: L-lactide, D-lactide and D,L-lactide. Poly(lactic acid) is obtained by polymerization of lactic acid and the poly(lactide) is the product of polymerisation of lactide [2]. Depending on the ratio of enantiomers, it is possible to obtain PLA polymers with different properties [3].

Direct polycondensation of lactic acid gives only the low molecular weight polymer – poly (lactic acid). It is equilibrium reaction, with water as by-product, that should be removed during the synthesis, in order to get higher conversions. Removing of water during the synthesis as well as using a coupling agent to obtain higher molecular weights makes this process longer, more complicated and more expensive. For the preparation of high molecular weight polymer, cyclic lactide is used as monomer for the ring opening polymerisation (ROP) [4] (Figure 1). This process can be carried out via cationic, anionic and non-ionic insertion mechanism [2]. ROP process demands high purity of the monomer, specific catalyst and solvent. Depending on methods, it requires high temperature, high pressure or vacuum. Cationic polymerization is efficiently initiated by

trifluoromethanesulfonic acid (as a catalyst) in organic solvent such as dichlormethane [5]. The reaction takes place for at least four hours. Various metallic alkoxides are employed as initiator in anionic ROP polymerization of lactide in some organic solvent as reaction medium [6]. Tin (II) 2-ethylhexanoate $SnOct_2$ is one of the commonly used catalyst for the synthesis of poly(lactide). Two mechanisms are suggested for synthesis of PLA initiated by this catalyst. The first proposed mechanism is an activated monomer mechanism in which the monomer coordinate with $SnOct_2$ [7]. In the second proposed mechanism $SnOct_2$ reacts with compounds containing OH groups giving an initiator such as tin (II) alkoxide or hydroxide. Chain growth is achieved via inserting a monomer [8]. Therefore, different mechanisms are proposed for polymerization of lactide in solution. These traditional methods of synthesis require large consumption of energy, time and reagents. Polymerization in organic solvent takes place from 4 to 50 hours depending on applied mechanism, temperature, catalyst and solvent. The applied temperature ranges from 40 to even 280 °C. Long polymerization time and high temperature require significant quantities of energy.

Difficulties that occur during the traditional methods of PLA synthesis can be overcome using a microwave heating. This procedure simplifies and accelerates the reaction of polymerization of lactide that lasts only 5-30 minutes. Sensitivity of the reaction to impurities and moisture from the air is significantly reduced due to the fact that the reaction takes place very quickly, so there is no need for recrystallization of monomers or carrying out of reaction under the vacuum [2, 9]. Homogenous heating of the whole reaction mixture and high transfer energy per unit of time result in faster polymerization rate [9, 10]. Microwave synthesis allows obtaining a high molecular weight polymer in a short time in improved yield [9].

This paper gives a comparison of traditional and microwave method of PLA synthesis, emphasising the aspects of saving energy and resources accomplished by using a synthesis in microwave reactor.

2 Results and Discussion

The group of authors compared the parameters of different method for synthesis of PLA as well as properties of obtained polymers. They carried out synthesis in vacuum sealed vessels, synthesis in high pressure reactor, in dichlormethane and in microwave reactor [3, 9]. Synthesis in vacuum sealed vessels has taken 110-150 minutes, in high pressure reactor 4-8 hours, as well as in solution. Microwave synthesis has been lasted just for 0.17-0.5 hours. The consequence is reduced energy consumption fallowed by improved yield. Poly(lactide) samples synthesized in microwave reactor have high molecular weights, higher than ones synthesized by traditional methods [9].

Lactide absorbs the microwaves, so the temperature increases rapidly in the first 200 s (Figure 2). Exothermic effect of the polymerization reaction additionally leads to the temperature increasing.

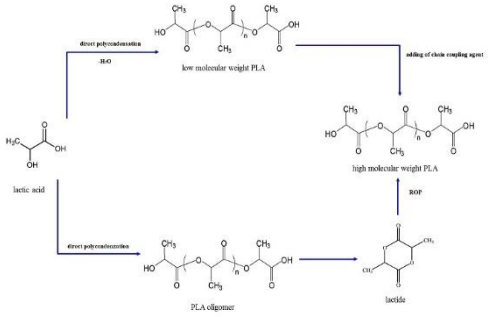

Figure 1. Synthesis of PLA via direct polycondenzation and via ROP method.

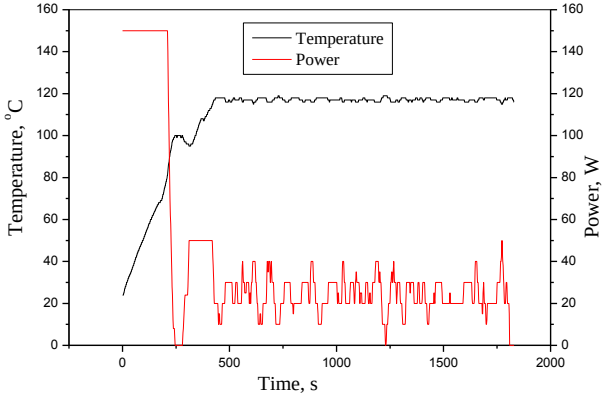

Figure 2. Temperature and microwave radiation power dependence on reaction time.

Loop on the upward curve comes from the presence of polymer and monomer in the reaction mixture, which have different abilities to absorb microwaves. Monomer shows greater ability to absorb microwaves than synthesized polymer. Between 8 and 9 minutes, temperature maintained on the same value of about 120 °C. This implies that conversion of monomer into polymer is almost complete. After reaching the value of 120 °C, temperature does not change.

Therefore, overheating does not occur during the microwave synthesis as it occurs during the bulk polymeriziaton in vacuum sealed vessels. The applied power of 150 W at the beginning of reaction is reduced on 0 W after reaching the temperature value of 100 °C. Power of 40 W in pulses applied in the continuation of the reaction is enough for the maintaining the constant temperature.

The molecular structure of polymer synthesized by microwave polymerization was confirmed by FTIR analyses (Figures 3 and 4). Broad peak at 3465.22 cm^{-1} is due to the

O-H stretching. Weak peak at 2995.56, indicates the presence of C-H stretching and peaks at 2879.76 and 2831.19 cm^{-1} indicate the presence of C-CH_3 bond. CH_2 bending vibrations are confirmed by weak peak at 1453.55 cm^{-1}. Sharp peak at 1757.55 cm^{-1} implies the C=O stretching vibrations. In lactide FTIR spectrum (Figure 3), this peak is appeared at 1770.44 cm^{-1}. In FTIR spectrum of lactide C-O-C stretching vibrations are detected at 1267.28 and 1099,83 cm^{-1}(Figure 3). The asymmetrical valence vibrations of C–O–C of the aliphatic chain were shifted at 1188.76 cm^{-1} and symmetrical valence vibrations of C–O–C at 1090.69 cm^{-1} (Figure 4).

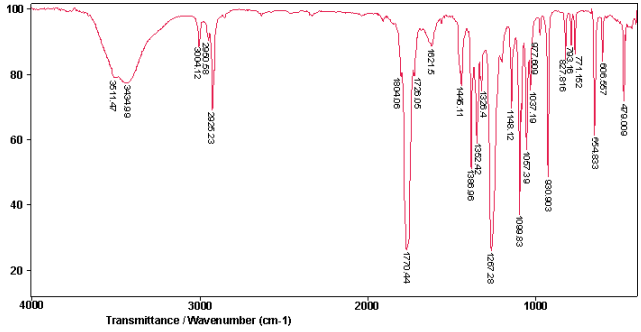

Figure 3. FTIR spectrum of monomer lactide.

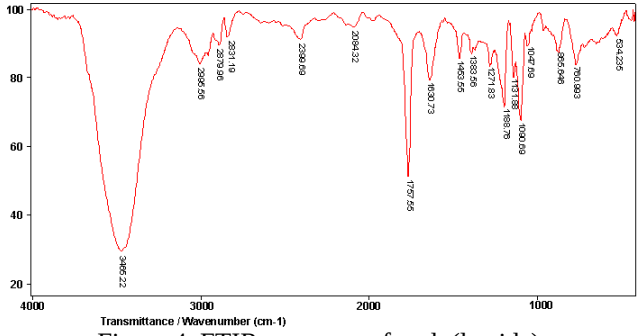

Figure 4. FTIR spectrum of poly(lactide).

Thermal properties of prepared poly(lactide) samples were investigated by differential scanning calorimetry (DSC). The comparative DSC curves are given in the Figure 5. The sample synthesized by traditional method has glass transition temperature (Tg) at 40.32 °C. Crystallization and melting behaviour was not observed. Endothermic and the exothermic peaks at DSC curve for PLA synthesized by microwave polymerization indicate presence of ordered structure. At temperature of 89.49 °C there is a maximum of the exothermic peak corresponding to the "cold" crystallisation of the amorphous region. Melting point is occurred at 135.45 °C, as minimum of endothermic peak. Based on the size of the area of endothermic and exothermic peaks, it can be estimated that enthalpy of crystallisation has higher absolute value than enthalpy of melting, because the melting

corresponding to initial crystalline fraction and newly crystalline regions developed by "cold" crystallisation.

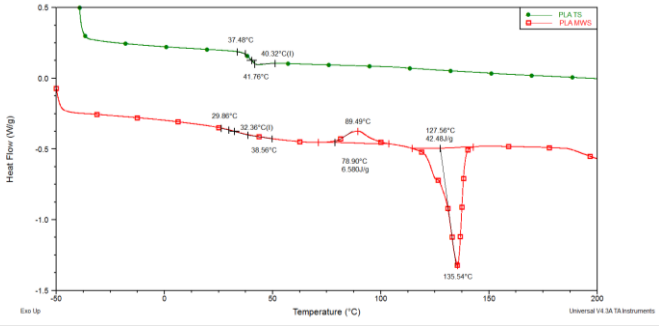

Figure 5. DSC curves for polymer synthesized by traditional method (PLA TS) and by microwave (PLA MW).

3 Conclusions

Reduced reserves of fossil fuels and problems with non-degradable waste have faced scientific community with necessity for investigation of renewable feedstock for production of polymer materials as well as development energy efficient process for their obtaining. Considering the process of obtaining and functional properties of poly(lactide), it was emerged as the great solution. Therefore, in accordance with the concept of energy saving, microwave synthesis of this polymer has been developed. Microwave synthesis gives high molar weight PLA with quite regular structure in improved yield. Shorter polymerization time and reduced consumption of energy and resources accompanied with desired properties of polymer, make microwave synthesis applicable to contemporary requirements.

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