Molar mass determination of microwave initiated polycondensation produced PLLA by capillary viscometry method

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Abstract. The microwave initiated polycondensation is a new approach for polylactic acid production. The time need of this process is quite less compared to the standard polycondensation process, but the progress and improvement of the molar mass is the most important basic factor. In my earlier work the standard polycondensation has already been investigated, so to be able to compare both methods PLLA has been produced by microwave initiated polycondensation too. The measurement of molar weights is a crucial point of polymer synthesis. According to my earlier work a rheology-based method was used again to define the molar masses during the polymerization process and make the comparison reliable. During my experiments PLLA has been synthesized by microwave initiated polycondensation method. According to the relevant literature, by standard polycondensation 10⁴-10⁵ g·mol⁻¹ molar mass can be reached, so the main question was that how long should be the microwave process run to result the same level of molar mass. During the experiments PLLA samples have been taken according to a special time plan, then solved in chloroform prepared samples with different concentrations for further analysis. To measure the flow-times Ubbelohde capillary viscometer was applied at this time too. Based on the data of viscometry measurements the intrinsic viscosities have been graphically defined then the molar masses of polylactic acid polymers were calculated according to the correlation of Mark – Houwink relation.

Keywords: capillary viscometry, solution rheology, PLLA, PDLA, PDLLA

1. Introduction

The polylactic acid as PLLA, PDLA and PDLLA is that sort of material which can be optimal substitute for PET which is widely used in the food industrial segment as primary or secondary packaging material. The new challenges that forced to use more environmental friendly packagings getting stronger, therefore the importance of bio-sourced and biodegradable materials which also fulfills the specific requirements of the scoped industrial segment is significant.

Literarily two main polymerization method as direct polycondensation which is relatively simple but time-consuming process, and the ring opening method known and applied to produce PLA [1].
The new polymerization approach is the microwave initiated polycondensation that is able to reduce the process time significantly. In this work the microwave initiated polycondensation process has been used to produce PLLA then compared to the standard thermally initiated polycondensation. To monitoring the efficiency of this method, the molecular masses of periodically were determined by capillary viscometry method.

2. Experimental

2.1. Material and methods

The L lactic acid has been sourced from Musashino Chemical Laboratory Ltd. The purity of raw material was > 90% with appropriate stereochemical purity (> 99%). Stannous octoate was chosen as catalysator which was provided by University Of Miskolc [3]. During the microwave initiated polymerization LG MB-3822G equipment with 700W nominal performance was applied. During the determination of molar masses of polymer samples capillary viscometry method was applied. Polymer solutions were prepared for viscometry measurements. The solvent was chloroform (CHCl₃) with 99% purity [4]. The flow time measurements of solvent and polymer solutions was carried out on Ubbelohde capillary viscometer [5].

The microwave initiated polycondensation produced polymers were analyzed by Fourier-transform infrared spectroscopy (FTIR) and Differential scanning calorimetry (DSC). For FTIR analysis BRUKER Tensor 27, in case of DSC measurement DSC131 Evo equipment was used. The heating/cooling ramp was dT/dt = 10°C min⁻¹.

2.2 PLA polymerization by microwave initiated polycondensation

The microwave (MW) irradiation provide further advantages compared to the conventional heating. Over the reduced process time, the increased efficiency and balanced/uniformed heating are those opportunities which made this method widely utilized [6]. In case of microwave initiated polycondensation 160 ml lactic acid was added to a glass pot. The power output of microwave equipment was set to 700W on 2450 Mhz. After 20 minutes 1 wt% catalysator stannous-octoate was added to the reaction mixture. During the polycondensation samples were taken at reaction time 2,5; 5; 7; 9; 12 and 14 hours.

2.3 Fourier-transform infrared spectroscopy analysis of polylactic acid samples

FTIR spectroscopy were used to investigate the molecular structure of produced polymer and prove that the resulted product is PLA.
The resulted FTIR spectrum of produced PLA were compared to the library PLA standard. According to the observed equality of sample spectrum and the basic library standard, it is found the produced material is polylactic acid [7].

2.4 DSC analysis of polylactic acid samples
During the function analysis the PLLA was also tested on DSC131 evo machine.

### Table 1. DSC measurement data of analysis of microwave initiated polycondensation produced PLLA foils

| Material Type                      | PLLA microwave initiated |
|-----------------------------------|--------------------------|
| Heating/Cooling ratio (°C/min)    | 10                       |
| Heat Range (°C)                   | -10 – 200                |
| Heat Ramp                         | Linear                   |
| Glass transition temperature (°C) | 46.16                    |

**Figure 2.** FTIR spectrum of PLLA synthetized by microwave initiated polycondensation

**Figure 3.** DSC result of PLLA synthetized by microwave initiated polycondensation
The relevant literature is indicating the glass transition temperature for polylactic acid is in range of 40 – 70 °C. In case of produced PLLA the \( T_g \) is found at 46 °C which is the lower field of the approval range. Obviously, the temperature of glass transition section depends on more factors. Over the structure of the synthetized material the crystal content/ratio of polymer is also quite important, as well the length of polymer chain does significant impact on the \( T_g \) [8].

Interesting result of DSC analysis is that, the crystallization and de-crystallization phases are missing in case of PLLA that was synthetized by microwave initiated polycondensation.

In order to verify this outcome, the relevant samples were analysed by X-ray diffraction (XRD) method.

2.5 X-ray diffraction (XRD) analysis of PDLLA (produced by standard polycondensation) and microwave initiated polycondensation produced PLLA.

![Figure 4. XRD results of microwave initiated polycondensation produced PLLA, and standard polycondensation synthetized PDLLA](image)

The typical PLA diffractograms are showing peaks at \( \theta = 16.8° \) and 19.5° as crystalline part of the material. The results of measurements proved that the structures of relevant polymers are amorphous without any crystal parts. This result is quite interesting mainly in case of PLLA that is produced from only the L-lactate therefore the structure of the material is appropriate to build crystals [8]. The further analyzation of this matter is going to be discussed in separated work.

2.6 Definition of molar mass of PLA samples by capillary viscometry method.

The measurement of polymer solutions’ viscosity is the base of this method that gives basic data to the further calculations. The flow time of the polymer solution highly depends on the concentration and the length of polymer chains that refers to the molar mass. This connection of viscosity and molar mass is the basic of this method. During the measurement, polymer solutions were created with different 0.5%, 0.5%, 1% and 2% concentrations in the first phase. To create the solutions, the polymer samples have been solved in chloroform with 99% purity. In the next phase the flow times of pure solvent and the polymer solutions were measured at room temperature (25°C). During this step Ubbelohde capillary viscometer and a simple stopwatch were used. The relative viscosity (\( \eta_{rel} \)), the specific viscosity (\( \eta_{sp} \)) and the reduced specific viscosity (\( \eta_{rod} \)) were defined by relevant calculations [9].
Table 2. Average flow-times and viscosities of PLLA produced by microwave initiated polycondensation

| Type of solution | Concentration % | \( C_p \) g·ml\(^{-1} \) | Average flow time \( \bar{K} \) (s) | Viscosities
|------------------|-----------------|-----------------|------------------|------------------|
| PLLA             | 2               | 0,02            | -                | \( \eta_{rel} \) | \( \eta_{spec} \) | \( \eta_{red} \) ml·g\(^{-1} \) |
|                  | 1               | 0,01            | 13,94            | 1,13             | 0,13             | 13,27          |
|                  | 0,5             | 0,005           | 13,08            | 1,06             | 0,06             | 12,56          |
|                  | 0,2             | 0,002           | 12,60            | 1,02             | 0,02             | 11,73          |
|                  | C → 0           | \( C_p \) → 0   | -                | -                | -                | 11,46          |

Figure 5. Graphical determination of intrinsic viscosity of PLLA sample

The intrinsic viscosities could be graphically determined based on the calculated reduced specific viscosities [10] then the molar masses of polymer samples were computed with following the Mark-Houwink relations [11]:

\[
[\eta] = KM^a \tag{1}
\]

\[
M = \frac{\sqrt{K}}{a} \tag{2}
\]

As it was also indicated in the joined article, the “K” and “a” constants are specific material depend parameters. As we had no possibility to define them with specific measurements previously, other similar parameters were used in the calculations as \( K=0,0066 \) and \( a = 0,67 \) sourced from reliable literature [12].

Table 3. Molar masses of standard and microwave initiated polycondensation produced PLLA polymers

| Type of polymer                  | Polymerization process time (h) | Average molar mass \( M_v \) (g·mol\(^{-1} \)) |
|----------------------------------|---------------------------------|-----------------------------------------------|
| PLLA standard polycondensation   | 72                              | \( 6,97 \times 10^4 \)                         |
| PLLA microwave initiated         | 14                              | \( 6,84 \times 10^4 \)                         |
Table 4. Change of molar mass of microwave initiated PLLA in function of process time

| Type of polymerization | Process time (h) | M_v (g·mol⁻¹) |
|------------------------|------------------|---------------|
| Microwave initiated polycondensation of PLLA | 2.5 | 1,37·10⁴ |
|                        | 5                | 1,84·10⁴ |
|                        | 7                | 2,50·10⁴ |
|                        | 9                | 3,73·10⁴ |
|                        | 12               | 4,18·10⁴ |
|                        | 14               | 6,84·10⁴ |

Based on the results, it is proven that the microwave initiated polymerization could be successfully applied to produce PLLA with almost the same molar mass that we experienced in case of standard polycondensation produced PLLA. As it highlighted in the Table 8., the total process time to produce PLLA with almost the same molar mass with microwave initiated polycondensation is significantly lower than in case of standard polycondensation.

3. Results
The microwave initiated polycondensation as a new method have been successfully applied to produce polylactic acid polymer. The produced material has been identified as PLLA by FTIR method. With the DSC analysis the glass transition temperature of PLLA was determined. The result meets with the literary range of PLA. During the DSC analysis an interesting event was experienced. Even if this material built from pure L-lactices and the molar mass of produced PLLA is adequate for crystallization, any crystallization and de-crystallisation could be observed. Same issue was found at the result of XRD analysis as the structure of polymerized material is simply amorphous without any crystal parts that resulting different morphological chemical and physical parameters [13].

The molar mass of PLLA could be determined by capillary viscometry method completed with Mark-Houwink relations. The result of this common/merged methods is reliable but very sensitive for the accurate handling and controlling of the parameters. Although cost efficient process but due to the numerous flow-time measurements it is quite time-consuming procedure.

4. Conclusion
The microwave initiated polycondensation is a potential technique to synthetize polylactic acid. The reaction time of microwave initiated polycondensation is less compared to the standard thermal initiated one because with 1/5 process time almost the same molar mass could be reached. Although the glass transition temperature is corresponding to the literary range of PLA and the PLLA easily builds material structure with crystalline parts, the amorphous structure of PLA polymer was observed. Further experiments and analysis are going to be done to understand the background mechanism of this issue.

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