Molar mass determination of polylactic acid alternatives by capillary viscometry method

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Abstract. The molar mass of polymers is a basic property that defines the appropriate processing method and the field of application of polymers. Therefore, the measurement of molar weights is a crucial point of polymer synthesis. In absence of modern but expensive equipment a rheology-based method can be used to define the molar mass with reliable result. By evaluation of molar mass, the entire polymerization can be monitored and controlled.

During my experiments polylactic acid alternatives (PLLA, PDLA, PDLLA) have been synthesized by direct polycondensation methods. According to the relevant literature, by this method and with the adequate setup of its parameters 10⁴-10⁵ g·mol⁻¹ molar mass can be reached. The two most important parameters are the process time and temperature that strongly effects on the value of molar mass of polymer. In this work standard polycondensation method has been used to produce the mentioned polylactic acid alternatives then the molar masses of polylactic acid polymers were calculated by followed the correlation of Mark – Houwink relation.

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

1. Introduction

Huge volume of polymers has been used in the food industry as primary or secondary packaging material. The most frequently used polymer is the polyethylene-terephthalate. According to the new endeavor of environmental friendly approach of future packaging materials, a new alternatives forced to be used which can fulfill the food (sweet) industrial specific requirements.

Table 1. Physical and chemical parameters of the PLA and PET foils [1]

| Properties                        | PDLA  | PLLA  | PDLLA        | PET               |
|-----------------------------------|-------|-------|--------------|-------------------|
| Crystalline structure             | Crystalline | Semi crystalline | Amorphous          | Amorphous and semi-crystalline |
| Melting temperature (Tm)/ °C      | 180   | 180   | variable     | 260               |
| Glass transition temperature (Tg)/ °C | 50-60 | 50-60 | variable     | 67-81              |
| Half-life in 37°C normal saline   | 4-6 month | 4-6 month   | 2-3 month   | 700 year         |
| Elongation at break/ (%)          | 20-30 | 20-30 | variable     | 14-19             |
| Breaking strength/ (g/d)          | 4-5   | 5-6   | variable     | 5-9               |

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The scoped area is the field of chocolate manufacturers where the plastic materials are used as thermo/vacuum formed blisters and trays. The polyactic acid as PLLA, PDLA and PDLLA is that sort of material which can be optimal substitute for PET.

Two main polymerization processes as direct polycondensation and ring opening methods can be applied to produce PLA.

\[
\begin{align*}
\text{CH}_3\text{COOH} & \quad \xrightarrow{\text{Dehydration}} \quad \text{HOOC-CH}_2\text{OH} + \text{H}_2\text{O} \\
\text{HOOC-CH}_2\text{OH} & \quad \xrightarrow{\text{Dehydration}} \quad \text{HOOC-CH}_2\text{OH} + \text{H}_2\text{O} \\
\text{HOOC-CH}_2\text{OH} & \quad \xrightarrow{\text{Depolymerization}} \quad \text{HOOC-CH}_2\text{OH} \\
\text{HOOC-CH}_2\text{OH} & \quad \xrightarrow{\text{Ring opening}} \quad \text{HOOC-CH}_2\text{OH}
\end{align*}
\]

**Figure 1.** Direct polycondensation of Polylactic acid [2]

The polycondensation method is the simpler but more time-consuming process compared to the ring-opening polymerization alternative. Other advantage of this mod, less chemical additives need to be used which let the polymer be more safe as direct contact packaging for foodstuff.

**Figure 2.** Ring opening polymerisation of Polylactic acid [3]

In my work the polycondensation process has been used to produce PLLA, PDLA and PDLLA. To monitoring the efficiency of the method, the molecular mass of periodically taken samples were determined by capillary viscometry method.

2. Experimental

2.1. Material and methods

The L and D lactic acid raw materials have been ordered from Musashino Chemical Laboratory Ltd. The purity of raw materials was > 90%. The stereochemical purity of materials was > 99%. Catalysator material was chosen as Stannous- Octoate (C_{16}H_{30}O_4Sn) that was ensured by University Of Miskolc [4]. In case of standard polycondensation HEIDOLPH Laborota 400 efficient with joined Vacuubrand ME 1C type vacuum pump were used ensured by KISANALITIKA Kft.
To determine the molar masses of polymers capillary viscometry method was applied. To create the polymer solutions chloroform (CHCl₃) was used with 99% purity. For measurement of flow times of solvent and polymer solutions Ubbelohde capillary viscometer was used [5].

All synthetized polymers have been analyzed by Fourier-transform infrared spectroscopy (FTIR) and Differential scanning calorimetry (DSC). During the FTIR analysis BRUKER Tensor 27, in case of DSC measures DSC131 Evo equipment was used with dT/dt = 10°C min⁻¹ heating/cooling rate.

2.2. PLA polymerization by direct polycondensation

The reaction was conducted in 500 ml one necked flask reactor mounted to manually adjustable HEIDOLPH laborota equipment in line with water-cooling condenser and vacuum pump. The lactic acid 400 ml added to the reactor flask. In case of heterogeneous mix, the ratio of L and D lactic acids was chosen as 50/50%. At the beginning of polymerization the temperature was gradually increased to 120°C in 60 minutes then kept the temperature on the same level for 60 minutes. The reaction mixture was stirred continuously. After the pre-polymerization phase 1 wt% stannous-octoate (C₁₆H₃₀O₄Sn) as catalyst was added to the reactor and the pressure of the system was reduced and fixed at 100 mbar. The temperature was varied from 160-200°C, and the reaction time was varied from 48-72 hours. [6]

2.3 Fourier-transform infrared spectroscopy analysis of polylactic acid samples

To make it verified the produced materials are polylactic acid polymers, FTIR spectroscopy were used.

Figure 3. HEIDOLPH Laborota 400 efficient with Vacuubrand ME 1C vacuum pump and Ubbelohde capillary viscometer

Figure 4. FTIR spectra of PDLA and PLLA synthetized by standard polycondensation
Each polymer samples were analyzed by FTIR. The results of the measurements were compared to the library PLA standard. Based on the equality of results of measured samples and library standard, all analyzed polymers were found as polylactic acid [7].

2.4 DSC analysis of polylactic acid samples
During the function analysis, the PLLA and PDLA which was polymerized by standard polycondensation and the PLLA that was produced by microwave initiated polycondensation were tested on DSC131 evo machine as well.

Table 2. DSC measurement data of analysis of PLLA, PDLA and PDLLA produced by standard polycondensation

| Material Type                  | PLLA | PDLA | PDLLA |
|-------------------------------|------|------|-------|
| Heating/Cooling ratio (°C/min) | 10   | 10   | 10    |
| Heat Range (°C)               | -10 - 200 | -10 - 200 | 0 – 200 |
| Heat Ramp                     | Linear | Linear | Linear |
| Glass transition temperature (°C) | 43,7 | 41,4 | 33,7 |

According to the relevant literature the glass transition temperature of polylactic acid is range of 40 – 70 °C. The actual glass transition temperature highly depends on the structure of the synthetized material. Beside the crystal content/ratio of polymer, the length of polymer chain – the molar mass – has a significant impact on the $T_g$ too [8]. The glass transition temperatures were defined (Table 2.) based on the results of DSC analyzations.

Figure 5. DSC result of PDLLA synthetized by standard polycondensation

The most important result of DSC analysis is that, the crystallization and the de-crystallization phases are missing in case of PDLLA (synthetized by standard polycondensation) this outcome has been investigated by X-ray diffraction (XRD) method in a joined work.
2.5 Definition of molar mass of PLA samples by capillary viscometry method.
In absence of expensive analytical equipment an indirect rheology-based method can be used with reliable result. The basis of this method is the measurement of polymer solution viscosity that is highly depends on the concentration and the length of polymer chains (ie. molar mass) [9]. Therefore, in the first step polymer solutions were created for all synthetized materials with different 0.5%, 0.5%, 1% and 2% concentrations. During this process chloroform with 99% purity was used as solvent. In the second step the flow times of pure solvent and the polymer solutions were measured on room temperature at 25°C with using of Ubbelohde capillary viscometer and a simple stopwatch. Based on the records the relative viscosity (\(\eta_{\text{rel}}\)), the specific viscosity (\(\eta_{\text{sp}}\)) and the reduced specific viscosity (\(\eta_{\text{red}}\)) could be defined by the following equations [10].

\[
\eta_{\text{rel}} = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}}
\]
\[
\eta_{\text{sp}} = \eta_{\text{rel}} - 1
\]
\[
\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{C} = \left(\frac{\eta_{\text{rel}} - 1}{C}\right)
\]
\[
[\eta] = \left(\frac{\eta_{\text{sp}}}{C}\right)_{c \to 0}
\]

Table 3. Average flow-times and viscosities of PLLA produced by standard polycondensation

| Type of solution | Concentration % | \(C_p\) g·mol\(^{-1}\) | Average flow time \(\bar{X}\) (s) | Viscosities |
|-----------------|-----------------|------------------------|-------------------------------|-------------|
| PLLA            | 2               | 0,02                   | 16,69                         | 1,35        |
|                 | 1               | 0,01                   | 14,20                         | 1,14        |
| PLLA            | 0,5             | 0,005                  | 13,39                         | 1,07        |
|                 | 0,2             | 0,002                  | 12,87                         | 1,02        |
|                 | C \to 0         | \(C_p \to 0\)          | -                             | -           |

Using the data of reduced specific viscosities (\(\eta_{\text{red}}\)) of different concentrations the intrinsic viscosities could be graphically determined. [11]

![Figure 6. Graphical determination of intrinsic viscosity of PLLA sample](image-url)
Based on the reduced viscosities the intrinsic viscosities could be graphically determined then the molar mass of produced polymers could be calculated by following the Mark-Houwink relations [12]:

\[ [\eta] = K M^a \]  \hspace{1cm} (5.)

\[ M = \frac{a [\eta]}{K} \]  \hspace{1cm} (6.)

The “K” and “a” constants are specific material depend parameters. As we had no possibility to define them previously, other similar parameters were used in the calculations as K=0,0066 and \( a = 0,67 \) [13].

**Table 4. Molar masses of polymers defined by capillary viscometry method**

| Type of polymer | Polymerization process time (h) | \( \bar{M} \) (g·mol\(^{-1}\)) |
|-----------------|-------------------------------|-------------------------------|
| PLLA           | 72                            | \( 6,97 \times 10^4 \)         |
| PDLA           | 48                            | \( 1,88 \times 10^4 \)         |
| PDLLA          | 100                           | \( 3,6 \times 10^4 \)         |

3. **Results**

PLLA, PDLA and PDLLA polymers were synthetized by standard polycondensation method with success. The entire process has been divided for two phases as pre-polymerisation and main polycondensation. The produced materials were analysed by FTIR method and identified as polylactic acid. The glass transition temperatures were defined by DSC analysis and mostly found them in the literary range of PLA. In case of PDLLA its \( T_g \) was out of this range as the initial mixture contained L and D lactics in ratio of 50/50% and this almost equal volume of the components made the whole polymerization process more difficult to evolve appropriate chain length. This problem could be observed on the result of XRD analysis as the structure of polymerized material is simply amorphous without any crystal parts. This result is very important as materials with different crystalline and morphological compositions have different chemical and physical parameters [14].

The definition of molar mass by capillary viscometry method completed with Mark-Houwink relations is an appropriate approach. Although this method is simple and cost efficient, many parameters need to be well controlled to make the result accurate and reliable. Time consuming process because numerous flow-time measurement need to be done in order to make the scatter of average flow time reduced, because if the scatter is high then the distorted average would lead to false result of finally calculated molar mass.

4. **Conclusion**

The standard polycondensation can be used to synthetize polylactic acids. In case of definition of molar mass of each synthetized polymer the capillary viscometry method can be successfully applied but during the analysis all parameters need to be accurately adjusted and well controlled and handled carefully. The calculation of molar mass based on the basic data production of capillary viscometry method followed by the calculations of Mark-Houwink relations can provides reliable results so it could be successfully applied during this work.

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