

DETERMINATION OF THE VISCOSITY TEMPERATURE
COEFFICIENT (β) AND PSEUDOPLASTIC INDEX (n) OF
POLY(LACTID ACID) (PLA)

DETERMINACIÓN DEL COEFICIENTE DE TEMPERATURA DE VISCOSIDAD (β) Y
EL ÍNDICE DE PSEUDOPLASTICIDAD (n) DEL POLI(ÁCIDO LÁCTICO) (PLA)

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Abstract

Poly(lactic acid) (PLA) is one of the most important ecological thermoplastics due to its good mechanical properties. In light of this, investigations related to the effects of PLA processing parameters are important as they affect the final product performance. This work aimed to determine the viscosity-temperature coefficient (β) and pseudoplastic index (n) of PLA and estimate its degradation rate during processing using an internal mixer. The viscosity coefficient was determined applying different processing temperatures at the same rotors rotation rate, which allowed estimating $\beta = 0.048 \text{ }^{\circ}\text{C}^{-1}$. PLA's pseudoplastic index (n) under the tested conditions suggested a value of approximately 0.71. PLA's degradation rate was around 4% under rotor rate of 120 rpm and temperature of 190 $^{\circ}\text{C}$.

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Keywords: poly(lactic acid); viscosity coefficient; pseudoplastic index; internal mixer.

Resumen

El poli(ácido láctico) (PLA) es uno de los termoplásticos ecológicos más importantes en la actualidad, debido a sus buenas propiedades mecánicas. En vista de esto, las investigaciones sobre los efectos de los parámetros de procesamiento de PLA son importantes, ya que afectan el rendimiento final del producto. Este trabajo tuvo como objetivo determinar el coeficiente de sensibilidad de la viscosidad con la temperatura (β) y el índice de plasticidad (n) del PLA, así como estimar su tasa de degradación durante el procesamiento en un mezclador interno. Para el coeficiente de viscosidad del PLA se adoptaron diferentes temperaturas de procesamiento y la misma velocidad de rotación de los rotores, lo que permitió estimar $\beta = 0,048 \text{ }^{\circ}\text{C}^{-1}$. El índice de plasticidad (n) del PLA en las condiciones ensayadas sugirió un valor de aproximadamente 0,71. Se encontró que la tasa de degradación que sufrió el PLA fue de alrededor del 4 %, utilizando una rotación del rotor de 120 rpm y una temperatura de 190 $^{\circ}\text{C}$.

Palabras clave: poli(ácido láctico); coeficiente de viscosidad; índice de pseudoplasticidad; mezclador interno.

Introduction

Over the years, the plastic products consumption derived from commodity polymers has produced large amounts of waste, which have been accumulated and created environmental and social problems [1–3]. Non-biodegradable polymers contribute substantially to these problems, due to their high resistance to biological degradation and, consequently, taking years to be decomposed [4, 5]. In this respect, the industrial and academic communities seek to develop new ecological materials to increase sustainability and minimize the environmental impacts [6, 7]. Currently, polymers from renewable sources are increasingly

applied in industrial sectors [8–10]. Biodegradable biopolymers, especially polyhydroxybutyrate (PHB), poly(lactic acid) (PLA), and polycaprolactone (PCL), have drawn considerable attention due to their technological potential for product manufacturing [11–14]. PLA is the most promising biopolymer since its mechanical performance is similar to that of commercial polymers, such as polystyrene (PS) and poly(ethylene terephthalate) (PET) [15].

PLA is considered an ecological thermoplastic synthesized from lactic acid derived from renewable sources [16]. Regarding the mechanical properties, PLA has high mechanical strength and elastic modulus. It can be processed using conventional industrial equipment [17, 18]. PLA's applications include rigid packaging, thermoformed fruit and vegetable trays, biodegradable garbage bags, and capsules for release fertilizers and pesticides in the soil [19, 20]. Nevertheless, PLA has high brittleness, low impact strength, thermomechanical strength, and crystallization rate. Additionally, it is quite sensible to hydrolysis [21, 22]. These drawbacks limit its applications and compromise its processing and final performance. Therefore, generally, PLA is modified to tailor its properties and minimize its main disadvantages [23, 24]. The brittle character and low impact strength of PLA have been managed using impact modifiers [25, 26]. Alternatively, the thermomechanical strength of PLA has been improved through annealing [27]. Moreover, fast crystallization was reached using nucleating agent [28], favoring an early crystallization at higher temperature. PLA has been widely used to produce polymer blends and biocomposites, seeking new eco-friendly materials for practical applications [29–33]. In the literature, there is a scarcity of works on the processing conditions of molten PLA, aiming at determining experimental parameters for application in mathematical modeling. Operating conditions (e.g., temperature profile and rotational speed) need to be investigated to reduce the research gap in the literature, especially since PLA is a polymer under testing.

Processing parameters are factors that influence PLA's final product characteristics [34]. Therefore, searching for better properties and processability are always desired by the

manufacturing industry [35, 36]. Simulations to evaluate processing conditions can be carried out in the laboratory using an internal mixer, single screw, or twin-screw extruder. Internal mixers are widely used equipment in academic and industrial laboratories, which produce materials with different operating parameters and mixing intensity requirements [37, 38]. As a result, an internal mixer can provide essential polymer parameters and data for simulation in several mathematical models. The torque (Z), the temperature inside the processing chamber (T), and the rotors rotation rate (N) in the internal mixer are related to each other. This favors the application of mathematical models to determine experimental constants for polymers [39]. As a consequence, the literature [40, 41] has explored the determination of parameters related to poly(ethylene terephthalate)- PET and poly(caprolactone)- PCL processing in the molten state.

This work aimed to determine the coefficient that measures the temperature sensitivity of viscosity (β) and the pseudoplastic index (n) of PLA using a laboratory internal mixer.

Materials

Poly(lactic acid) (PLA) pellets with melt flow index of 6 g/10 min (ASTM D1238 - 210 °C/2.16 kg), density of 1.24 g/cm³, manufactured by Nature Works and distributed by 3D Lab (Brazil).

Methods

Before processing, the pellets were dried in a vacuum oven at 60°C for 24 hours. PLA was processed in a Thermo Fisher Scientific Haake Rheomix 3000 internal mixer, with roller rotors, under an air atmosphere for 15 min. The evaluation of the total mass (M_t) was performed using Equation 1

$$M_t = \rho \times f \times V_n \quad (1)$$

Where: ρ = density of neat PLA; f = fill factor of processing chamber; V_n = free volume of mixing chamber (310 cm³). The fill

factor used was $f = 0.7$ (70%), as recommended by the equipment manufacturer. Table 1 presents the applied processing parameters in the internal mixer chamber to determine the temperature coefficient of viscosity (β) and the pseudoplastic index (n) of neat PLA.

Material	Mass (g)	Temperature ($^{\circ}\text{C}$)	Rotor rate (rpm)
PLA	269	170	60
	269	190	60
	269	190	90
	269	190	120
	269	210	60

TABLE 1. *Processing parameters of neat PLA.*

Results and discussion

Figures 1(a) and 1(b) show the torque and temperature plots of PLA as a time function, respectively, acquired during mixing in the torque rheometer. As Figure 1(a) shows, PLA torque tends to decrease with increasing processing temperature, indicating an increment in fluidity. Generally, in the last processing stage (stable torque – 12 to 15 min) in an internal mixer with a constant rotor rate, torque (Z) is directly proportional to viscosity (η) [42]. Hence, the reduction in PLA torque can be attributed to a viscosity decrease with incremental temperature. Figure 1 (b) shows that the temperature was initially reduced (0 to 2 minutes) when the material was fed into the mixing chamber. Then, the temperature increased until reaching an approximately constant plateau. The temperature and torque plots as a time function practically remained constant in the time range from 12 to 15 minutes, a behavior that guarantees the results reliability [43]. Therefore, the temperature coefficient of viscosity (β) can be estimated with the results reported in Figure 1.

The temperature coefficient of viscosity (β) of PLA can be estimated with data acquired from the internal mixer. For this,

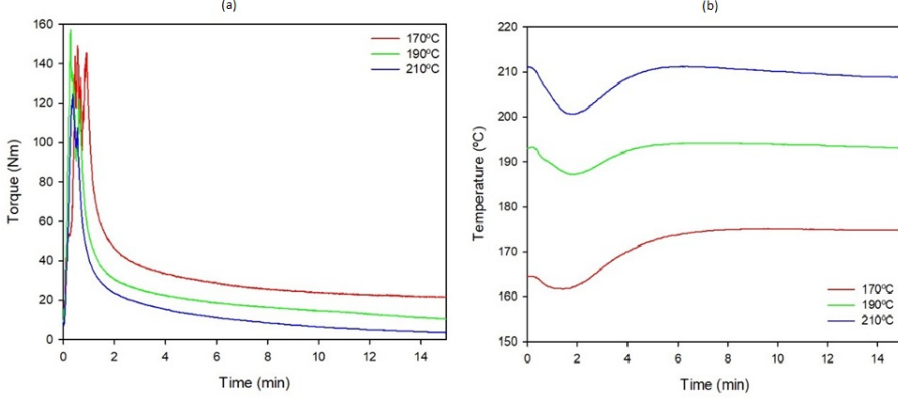


FIGURE 1. *Torque rheometry of PLA at different temperatures (170 °C, 190 °C, and 210 °C) and rotor rate of 60 rpm: (a) torque plots as a time function; (b) temperature plots as a time function.*

during experiments, different processing temperatures must be used with the rotors rotation rate kept constant [44], as seen in Figure 1. The adopted mathematical model is presented in Equation 2:

$$Z = ke^{-\beta(T-T_0)} \quad (2)$$

where: k is a constant; T is the experimental working temperature; T_0 is a reference temperature. However, in general, average values are adopted in a small stable time interval to minimize torque and temperature fluctuations in the final processing stage [45]. Therefore, the mathematical model becomes Equation 3:

$$\bar{Z} = ke^{-\beta(\bar{T}-T_0)} \quad (3)$$

or

$$\ln(\bar{Z}) = \ln(k) - \beta(\bar{T} - T_0)$$

The β coefficient can be determined by applying a linear regression of $\ln(\bar{Z})$ versus $(T-T_0)$. Figure 2 shows the plots of $\ln(\bar{Z})$ as function of $T-T_0$ for PLA, with temperatures (T) of 170 °C, 190 °C, and 210 °C, respectively. The reference temperature adopted was $T_0=180$ °C. It was observed that the experimental

points are close to the linear regression line (Figure 2), which resulted in a coefficient $\beta=0.048\text{ }^{\circ}\text{C}^{-1}$. This value represents a measure of viscosity sensitivity to PLA temperature and, therefore, this experimental data can be used in the aforementioned range (170-210 $^{\circ}\text{C}$).

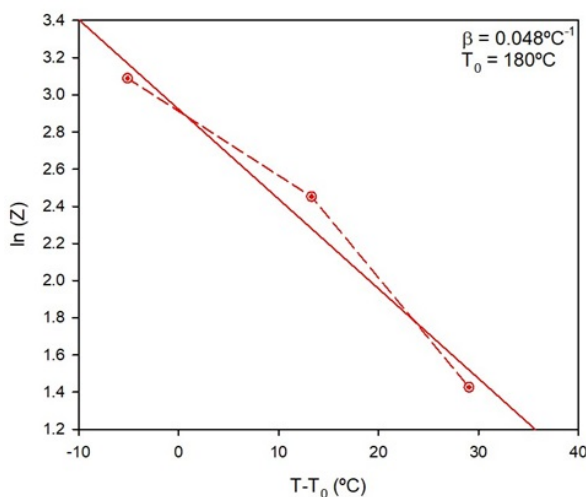


FIGURE 2. Log plots of average torque vs. the difference between the reference temperature and the temperature of the mixing chamber wall ($T-T_0$).

Figure 3 illustrates the torque and temperature plots as a time function using a constant temperature of 190 $^{\circ}\text{C}$ at different rotor speeds (60 rpm, 90 rpm, and 120 rpm). Figure 3 (a) evidences that the torque decreases inside the processing chamber as rotor speed increases. The average stabilized torque shows a continuous reduction in torque values, especially at 120 rpm. This indicates that PLA presents lower viscosity for higher rotor rates and suggests higher fluidity. Figure 3 (b) shows that, after 4 min, PLA processed at 60 rpm has higher stability among tested parameters. It was noted that the rates 90 rpm and 120 rpm severely increased the mixing chamber temperature after 2 min of processing. The increase in rotation rate imposed higher temperatures and shear on PLA, generating considerable energy dissipation by friction

[35]. However, PLA processed at 90 rpm and 120 rpm showed a maximum temperature peak in the mixing chamber that slowly and continuously decreased over time. When using 90 rpm and 120 rpm, there was no tendency to stabilize the temperature inside the chamber.

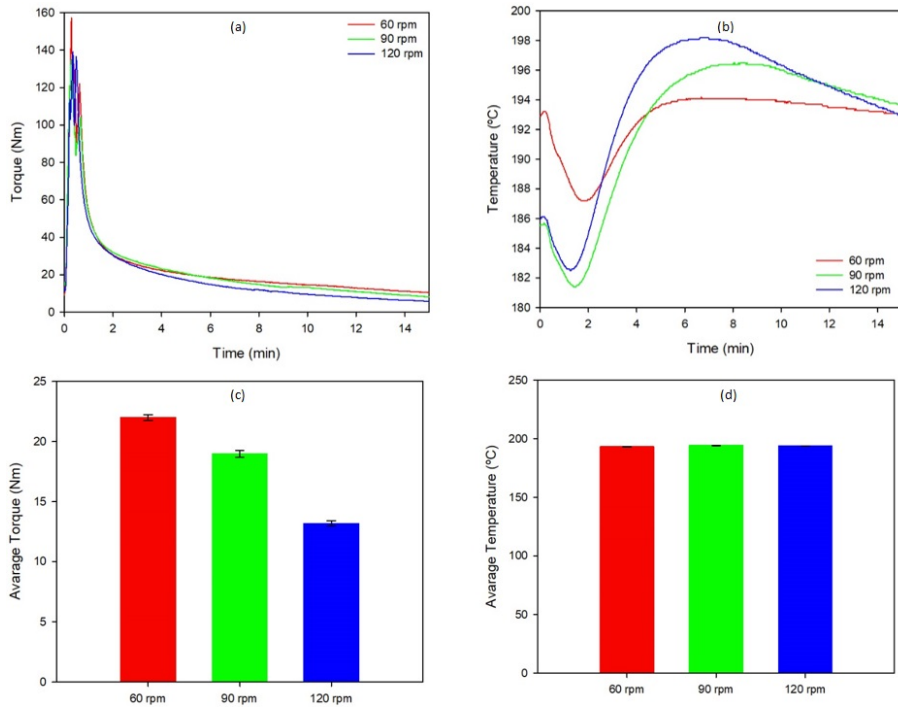


FIGURE 3. *Torque rheometry of PLA for different rotor rates at fixed temperature of 190 °C: (a) torque vs. time plots, (b) temperature vs. time plots, (c) average stabilized torque (12-15 min), and (d) average stabilized temperature (12-15 min).*

The pseudoplastic index (n) of PLA can be determined from experimental results acquired in the internal mixer. For n evaluation, the processing is carried out with different rotor rates and, at the same time, with a constant temperature in the chamber wall [46]. The present situation is different from the previous case. In this case, temperature $T(t)$ is a process variable, and rotor

rate (N) is an operating condition that can be kept constant at a chosen value. Therefore, the mathematical model that governs the situation is given by Equation 4:

$$Z^* = ke^{\beta(T-T_0)} = AN^n \quad (4)$$

where: Z^* is the adjusted torque; A is a constant and n is the pseudoplastic index. Similar to the viscosity coefficient (β), it is convenient to use average values in a short time range (12-15 min). This contributes to reduce torque and temperature fluctuations in the final processing stage, which results in Equation 5:

$$\overline{Z^*} = \overline{ke^{\beta(T-T_0)}} = AN^n \quad (5)$$

or

$$\ln(\overline{Z^*}) = \ln(A) + n\ln(N)$$

The application of a linear regression between $\ln(\overline{Z^*})$ versus $\ln(N)$ allows to determine the pseudoplastic index (n) of PLA. Furthermore, the coefficient $\beta = 0.048 \text{ } ^\circ\text{C}^{-1}$, determined earlier, is used to obtain the adjusted torque (Z^*). Figure 4 illustrates the logarithmic behavior of the adjusted torque versus rotor rate computed at constant temperature of $190 \text{ } ^\circ\text{C}$. It was observed that the pseudoplastic index of PLA was around 0.71 for the tested experimental conditions. Furthermore, it is worth mentioning that the pseudoplastic index obtained is valid only in the range of average shear rates.

Table 2 presents the following process parameters: the average temperature (\overline{T}), the average adjusted torque ($\overline{z^*}$), the relative reduction rate of the adjusted torque (R_Z), and the relative reduction rate of the weight-average molar mass (R_M).

The relative variation of adjusted torque at constant temperature ($190 \text{ } ^\circ\text{C}$) is a measure of PLA degradation rate:

$$R_Z = -\frac{1}{\overline{Z^*}} \frac{dZ^*}{dt}$$

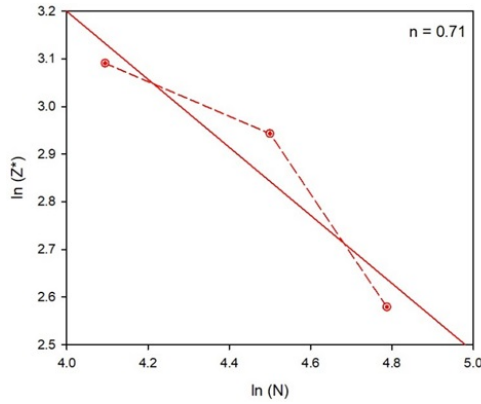


FIGURE 4. *Log plots of adjusted torque versus rotor rate at constant chamber wall temperature (190 °C).*

N (rpm)	\bar{T} (°C)	\bar{Z}^* (Nm)	$-R_Z$ (min ⁻¹)	$-R_M$ (min ⁻¹)
60	193.3 ± 0.02	22.0 ± 0.22	0.078	0.0244
90	194.3 ± 0.05	19.0 ± 0.29	0.119	0.0374
120	193.9 ± 0.08	13.2 ± 0.22	0.128	0.0401

TABLE 2. *Terminal processing parameters (12-15 min).*

where (\bar{Z}^*) is the average adjusted torque in the range Δt . If time is expressed in minutes, $100R_Z$ is the “% change in adjusted torque per minute of processing”.

The variation rate of the weight-average molar mass can be estimated by taking into account the dependence of viscosity on molar mass (M_W):

$$R_M = -\frac{1}{M_W} \frac{dM_W}{dt} = \frac{1}{2.5 + n} R_Z$$

If time is expressed in minutes, $100R_M$ is the “% change in weight-average molar mass per minute of processing”.

Table 2 shows that the increase in rotation rate did not significantly change the average temperature (\bar{T}) of the mixing chamber. However, the average torque was more sensitive to the rotation rate. There was a continuous reduction in torque with increasing rotor rate, suggesting lower PLA viscosity. Such behavior may be due to the thermomechanical degradation phenomenon of PLA during the 15 min of processing. Regarding the adjusted torque, it was found that the variation rate ($\frac{dZ^*}{dt}$) decreased for PLA by approximately 7.8%, 11.9%, and 12.8%, respectively, at rotor rates of 60 rpm, 90 rpm, and 120 rpm. It is suggested that prolonged PLA processing (high residence time) can promote deleterious effects on the molar mass. As seen in Table 2, the relative molar mass (R_M) reduction rate increased progressively for PLA, reaching approximately 4% at 120 rpm (12-15 min). Therefore, PLA processing for prolonged times can negatively affect the molar mass, which causes loss of mechanical properties. However, the degradation level of PLA under the tested conditions was low since the processing lasted 15 min. In this regard, for PLA processing by extrusion or injection, the degradation will be low since the residence time in the equipment will be shorter.

Conclusions

The temperature coefficient of viscosity (β) and pseudoplastic index (n) of PLA were determined by torque rheometry using a laboratory internal mixer. It was found that PLA torque tended to decrease upon increasing processing temperature, indicating an increase in fluidity. The estimated coefficient (β) for PLA was in the order of $0.048\text{ }^{\circ}\text{C}^{-1}$ and, consequently, this value can be used in the experiment range (170 - 210 $^{\circ}\text{C}$). In addition, PLA's pseudoplastic index was around 0.71, valid for average shear rates. The degradation rate of PLA is higher when using a higher shear rate, indicating thermomechanical sensitivity. However, even using a rotation rate in the order of 120 rpm, the degradation rate (around 4%) was not severe. The dependence of viscosity on temperature (parameter β) for PLA is relatively moderate. The presented results are valuable for the industrial sector since they help to control

PLA's processing parameters as well as to minimize the degradation effects.

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