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DOI: https://doi.org/10.51573/Andes.PPS39.SS.DBC.1

December 2024

View Online

Export Citation

Modelling Hydrolytic, Thermal, and Mechanical Degradation of PLA During Single-Screw Extrusion

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Abstract: Since melt processing causes degradation of poly(lactic acid) or PLA, it is crucial to understand the effect of extrusion conditions on the molecular weight reduction. Kinetic models found in literature are promising tools to describe hydrolytic, thermal, and mechanical degradation during extrusion. In order to use these models, extrusion parameters (that are equipment dependent) should be translated into the four fundamental parameters that determine degradation: moisture content in PLA, residence time, shear stress history and temperature history. This work presents a methodology to use numerical simulations to translate extrusion parameters into fundamental parameters. The results show that numerical simulations can be used successfully to describe the extrusion process based on residence time, shear stress history, and temperature history.

Keywords: Extrusion, PLA, Numerical Simulation, Process-Induced Degradation

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DOI: https://doi.org/10.51573/Andes.PPS39.SS.DBC.1

Introduction

The sensitivity of the ester bonds in poly(lactic acid) or PLA is a major concern in processing biopolyesters. The potential presence of moisture in the granules combined with high shear stresses and temperatures during the melt processing can lead to a significant molecular weight reduction due to hydrolytic, thermal, and mechanical degradation [1-3]. Previous research has presented a kinetic degradation model to successfully predict the decrease of viscosity (and thus molecular weight) over time by studying the effect of processing temperature and moisture content in the granules using a rheometer [4]. Extending the kinetic degradation model to estimate degradation during single-screw extrusion implies differences in two aspects. First, mechanical degradation should be included in addition to hydrolytic and thermal degradation. Second, since the processing temperature and shear stress inside the barrel vary throughout the extrusion process, the temperature history and shear stress history as a function of time need to be understood. Degradation of PLA is expressed in terms of four fundamental parameters (moisture content in the granules, processing temperature, shear stress, and residence time), while extruding PLA requires a set of processing parameters (e.g., screw rotation speed, die and screw geometry, and processing temperature build-up in different heating zones). The combined processing parameters determine the total residence time, shear stress history, and temperature history, thus the essential data required to apply the aforementioned kinetic degradation model on extrusion [4]. The goal of this paper is to translate extrusion parameters to fundamental parameters using numerical simulations, enabling a description of the extrusion process in a universally applicable (equipment-independent) manner. This approach allows other researchers or companies to compare data, even if another extruder, die or screw geometry is used.

Materials and Method

PLA 2500HP Ingeo™ (supplied by NatureWorks) is selected as the material of interest. This PLA grade is characterized by a high molecular weight ($\overline{Mn}$ 65 kDa, $\overline{Mw}$ 124 kDa) and a D-isomer content of less than 0.5%. To remove moisture from the PLA granules, the material is dried in a Moretto Mini Dryer D4 for a minimum of 24h at 80°C.

A COLLIN single-screw extruder with a diameter D of 30 mm and an L/D ratio of 28 was used. The extruder is equipped with five pressure and temperature transducers along the barrel and can be used in combination with FECON software, that enables monitoring the stability of the extrusion process and capturing data. The screw geometry and locations of the pressure and temperature transducers are presented in Figure 1. Behind the barrel, the die section starts as seen in Figure 2. The die section consists of a coupling piece (inner diameter 25.6 mm, length 102 mm) and a round capillary die (diameter either 2, 3, or 4 mm, length 30 mm) or open (no capillary die).

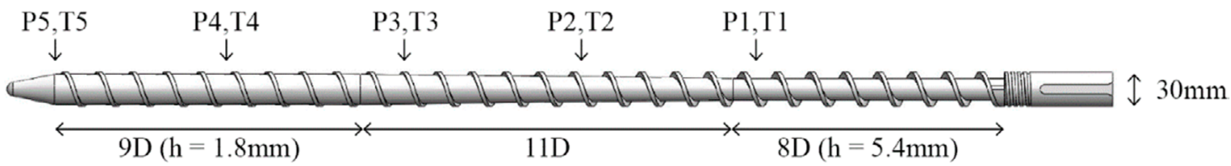

Figure 1. Screw geometry and locations of five pressure and temperature transducers.

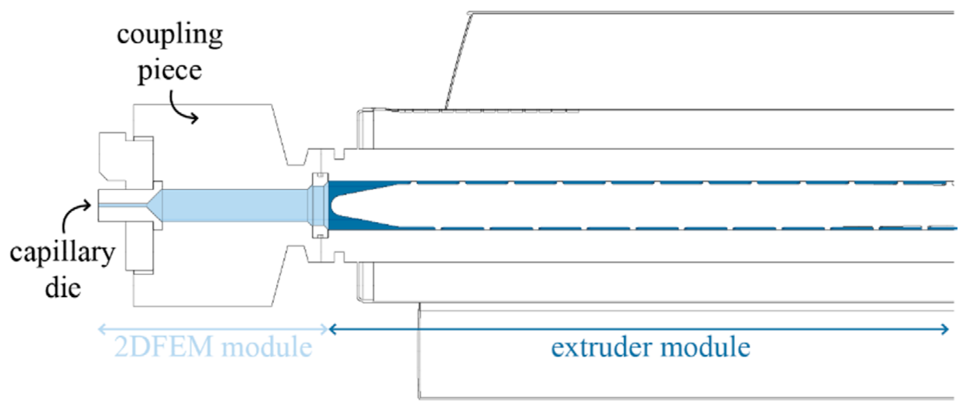

Figure 2. Use of an *extruder module* for screw section and a *2DFEM module* for die section in VEL.

Twelve extrusion experiments are performed, as shown in Table 1. In each experiment, one variable is changed compared to the reference set of parameters (210°C, 30 rpm and a capillary die with a diameter of 4 mm). During each experiment, the pressure is measured at the five locations along the extruder, as reported in Figure 3. The highest pressure, measured at location 3 (P3), is reported in Table 1, together with the measured mass flow rate (MFR) in each experiment.

Table 1. Processing combinations and results for P3 (pressure at location 3) and MFR (mass flow rate).

Name	Processing parameters			Experiment		Simulation		Difference	
[-]	T [°C]	n [rpm]	die [-]	P3 [MPa]	MFR [kg/h]	P3 [MPa]	MFR [kg/h]	ΔP3 [%]	ΔMFR [%]
190°C	190	30	4 mm	22.7	4.08	23.3	4.19	-2.78	-2.74
200°C	200	30	4 mm	21.1	4.01	20.0	4.26	5.65	-6.05
210°C	210	30	4 mm	18.2	4.17	18.3	4.42	-0.37	-5.76
220°C	220	30	4 mm	16.6	4.15	15.7	4.54	6.19	-8.62
230°C	230	30	4 mm	14.2	4.25	13.5	4.68	5.36	-9.26
20rpm	210	20	4 mm	13.7	2.70	14.1	2.96	-3.07	-8.67
25rpm	210	25	4 mm	17.8	3.56	16.2	3.69	9.98	-3.45

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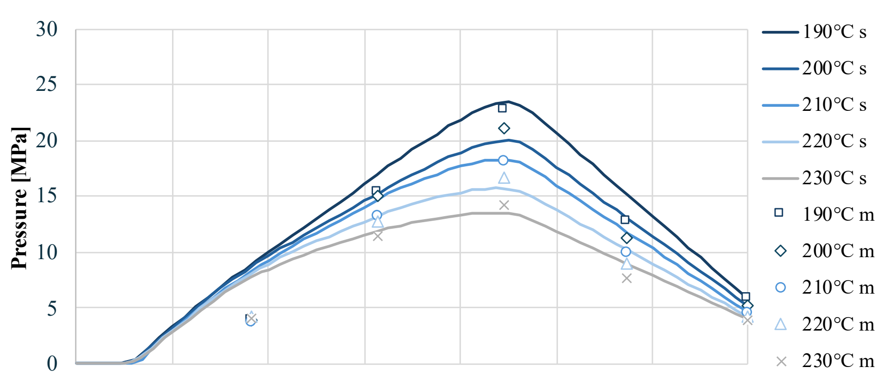
Name [-]	Processing parameters			Experiment		Simulation		Difference	
	T [°C]	n [rpm]	die [-]	P3 [MPa]	MFR [kg/h]	P3 [MPa]	MFR [kg/h]	ΔP3 [%]	ΔMFR [%]
30rpm	210	30	4 mm	18.2	4.17	18.3	4.42	-0.37	-5.76
35rpm	210	35	4 mm	21.3	4.87	20.4	5.16	4.53	-5.74
40rpm	210	40	4 mm	23.5	5.54	22.3	5.90	5.43	-6.05
open	210	30	open	18.6	4.24	17.7	4.53	4.94	-6.42
4 mm	210	30	4 mm	18.2	4.17	18.3	4.42	-0.37	-5.76
3 mm	210	30	3 mm	21.2	3.97	19.5	4.21	8.86	-5.80
2 mm	210	30	2 mm	22.2	3.64	22.3	3.90	-0.22	-6.72

The extrusion combinations named *210°C, 30 rpm* and *4 mm* refer to the same measurement and are repeated in Table 1 for better comparison with other data. The mentioned temperature (e.g., 210°C) is the set temperature of the last of seven heater bands on the extruder (30–170–190–210–210-210-210°C). The actual, measured temperature is 10°C higher for all processing combinations due to shear heating.

The simulations are performed in a Virtual Extrusion Laboratory (VEL) developed by Compuplast. Two modules in VEL are used: *extruder module* to model the process from hopper until the end of the screw, and *2DFEM module* to model the process in the die, as shown in the geometry (Figure 2). The used screw geometry and measured material properties are presented in Figure 1 and Table 2. The Carreau model is used to describe the rheological properties of the PLA melt (equation 1):

$$\eta(\gamma, T) = \frac{A * f(T)}{[1 + (r * \gamma * f(T))^a]^{\frac{1-n}{a}}} \qquad 1)$$



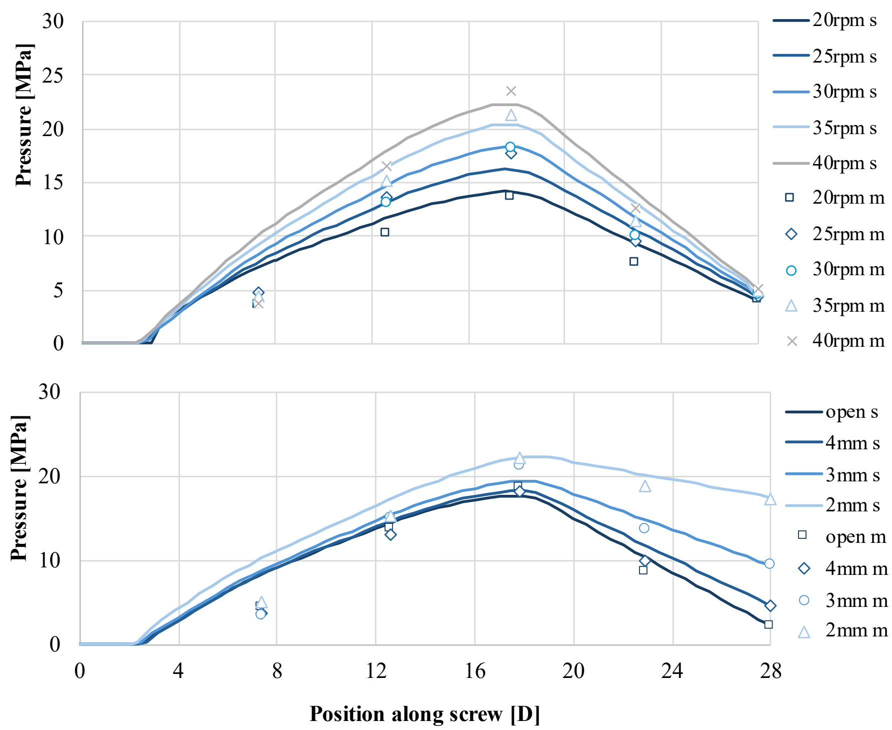


Figure 3. Measured (m) and simulated (s) pressure evolution throughout the extruder.

Table 2. Measured material properties used for simulations.

ρ_{solid} [kg/m³]	ρ_{melt} [kg/m³]	ρ_{bulk} [kg/m³]	$T_{freezing}$ [°C]	T_{melt} [°C]	Cp_{solid} [J/kg/°C]	Cp_{melt} [J/kg/°C]	ΔH_f [J/kg]	k [W/mK]
1240	992	790	143.5	173	1682	2258	40780	0.16

With zero shear viscosity *A* (1795.28 Pa.s), constant *r* (0.004611), constant *a* (0.65161), constant *n* (0.1) and $f(T) = e^{-b\,(T-Tr)}$ with temperature dependency parameter *b* (0.03836 1/°C), and reference temperature *Tr* (210°C). The same extrusion combinations (Table 1) are simulated and compared with P3 and MFR of the experimental results (Figure 3) to check the quality of the simulation results. The percentage deviations of P3 and MFR are calculated and reported in Table 1.

Results and Discussion

As the relative deviations between experimental and simulation results are less than 10% for P3 and MFR (Table 1), it can be concluded that the simulation is able to correctly describe the actual experiments. Thereby, the simulation output of VEL can be used to extract information about the residence time of the material inside the extruder, temperature throughout the extrusion process, and shear stress throughout the extrusion process.

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Results residence time

The residence time of the material starts when the material exceeds the melting temperature of 173°C. This point was selected as in this work the authors assumed that process-induced degradation occurs in the melt state. Figure 4 presents the residence time of the material inside the feeding, compression, and metering zone of the screw, and the die section of the extrusion line. The temperature of the material exceeds 173°C around position 6D (slightly different for each experiment) while the feeding zone has a length of 8D. Therefore, the reported residence time in the feeding zone in Figure 4 is around 25% of the total feeding zone residence time that is calculated in VEL. It is assumed that no process-induced degradation occurs in the first 75% of the feeding zone, since the granules are in a solid state. To estimate the residence time in the die section, the volume of the die section and the measured MFR are used. The residence time results indicate that the residence time is longer at a lower processing temperature, a lower screw rotation speed, and when a smaller die is used, which was expected.

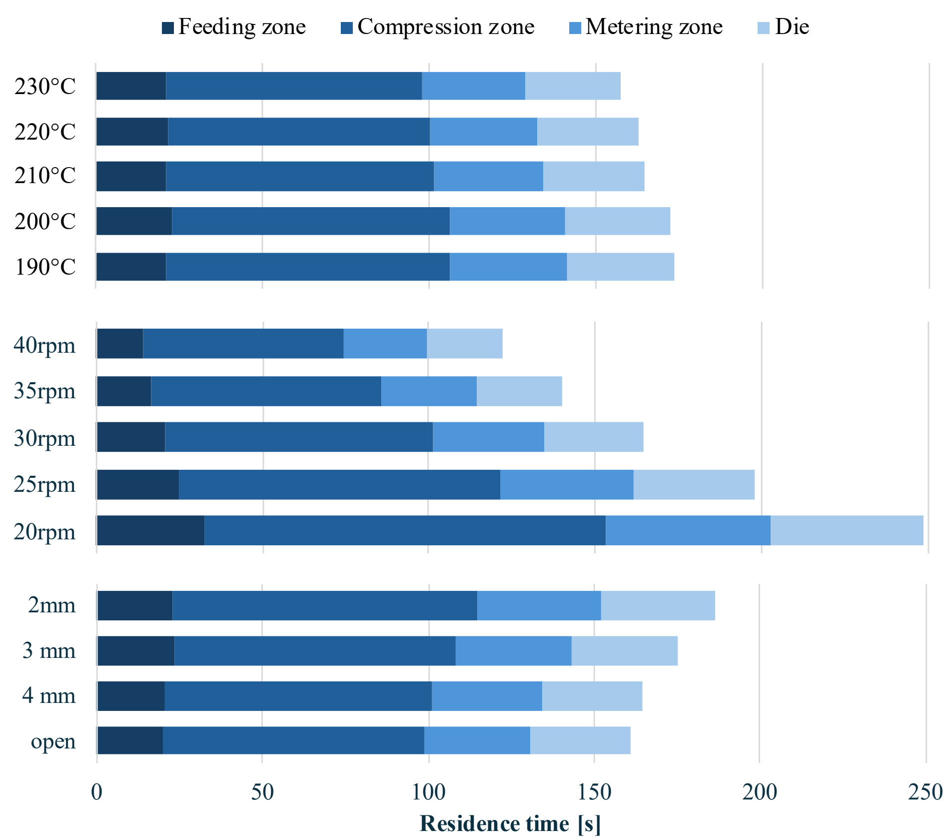

Figure 4. Residence time in each zone for the different extrusion combinations.

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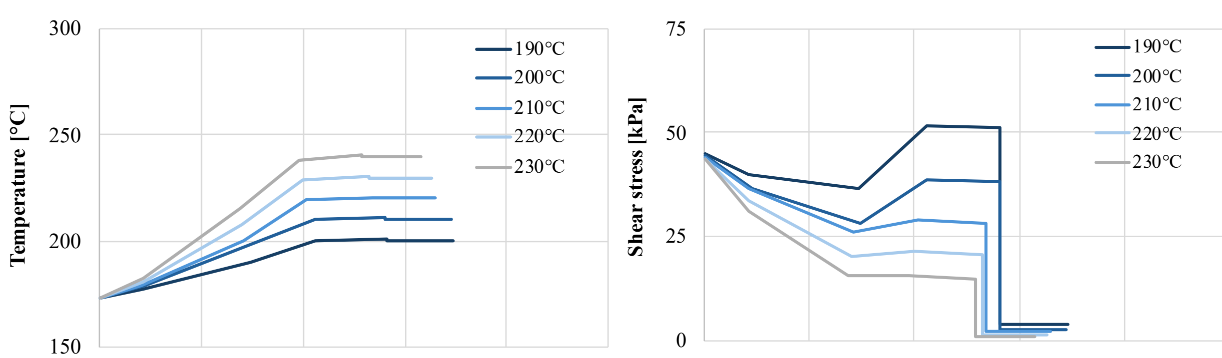
Results Temperature History

During extrusion, the temperature of the melt varies along its screw position, caused by the heating or cooling of the barrel and the shear heating energy dissipation. The material temperature along the screw is calculated at each location as an average value over the screw channel cross-section. The common output in VEL is temperature as a function of position along the screw (expressed in D), which is therefore linked to the extrusion geometry and inevitably equipment-dependent. In this work, the desired output is the temperature as a function of time, which makes the results equipment-independent. The residence time data is known at five positions along the extruder, as seen in the previous section: start of the degradation when the temperature exceeds 173°C (t = 0s), end of feeding zone 8D, end of compression zone 19D, end of the metering zone 28D, and end of the die section. Due to the changing channel depth in the compression zone, a sixth location at 13.5D is defined. The residence time inside the compression zone is divided proportionally to the volume of the channel in this section that is 62% between 8-13.5D and 38% between 13.5D-19D. This allows us to express the bulk temperature throughout the process as a function of time, presented in Figure 5. The temperature evolution occurs as expected: an increase in temperature occurs more rapidly at a higher processing temperature and a faster screw rotation speed, particularly when a larger die diameter is used, after which the temperature stabilizes.

Results Shear Stress History

Similar to the bulk temperature, shear stress as a function of position along the extruder (in D) should be translated into the shear stress as a function of time. The same six locations are used as described in the previous section. The reported shear stress at the six locations is the weighted average shear stress across the screw section (Figure 5). A higher shear stress is obtained at a lower processing temperature and a higher screw rotation speed. When comparing the effect of the die diameter, it can be concluded that the shear stress is not significantly affected. This range of dies mainly affects the residence time of the material, but the effect on the shear stress is less pronounced, due to the short residence time of the material in the capillary die.



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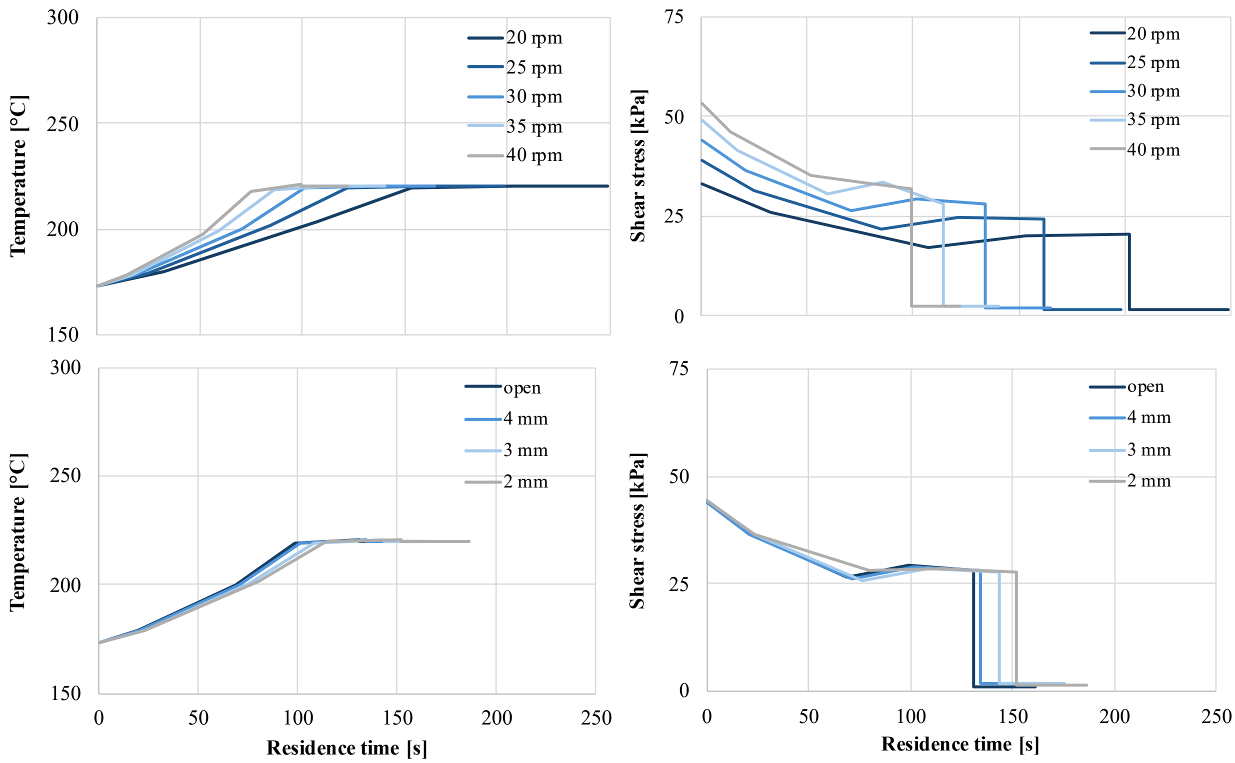

Figure 5. Plots of bulk temperature and shear stress against residence time.

Conclusion

The goal of this work is to translate extrusion parameters to fundamental parameters using numerical simulations. The results indicate that numerical simulations in VEL enable reconstruction of the temperature history, shear stress history, and residence time of the molten PLA inside the extruder. The method, combining experimental results with numerical simulations, can be used to describe the extrusion process in a way that is universally applicable (equipment-independent). This means that the results are no longer linked to the screw geometry, processing parameters, and die selection, enabling comparison of results with other researchers or processors working with PLA or other types of polyesters.

Outlook

The translation step from processing to fundamental variables is a critical step to prepare data for further use in a kinetic degradation model. In future work, this translated data is the basis for predicting thermal and mechanical degradation during processing with a kinetic model. A next step will be to perform extrusion experiments and simulations with PLA that contains moisture, in order to also investigate hydrolytic degradation.

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Acknowledgments

This study was supported by the Research Foundation – Flanders (FWO), grant number 1S16122.

References

1. A. A. Cuadri and J.E. Martin-Alfonso, "Thermal, thermo-oxidative and thermomechanical degradation of PLA: A comparative study based on rheological, chemical and thermal properties", *Polymer Degradation and Stability*, vol. 150, pp. 37-45, 2018.
2. G. Gorrasi and R. Pantani, "Hydrolysis and biodegradation of poly(lactic acid)", *Advances in Polymer Science*, vol. 279, pp. 119-151, 2018.
3. I. Velghe, B. Buffel, V. Vandeginste, W. Thielemans and F. Desplentere, "Review on the Degradation of Poly(lactic acid) during Melt Processing", *Polymers*, vol. 15, 2023.
4. V. Sperzanza, A. De Meo and R. Pantani, "Thermal and hydrolytic degradation kinetics of PLA in the molten state", *Polymer Degradation and Stability,* vol. 100, pp. 37-41, 2014.

DOI: https://doi.org/10.51573/Andes.PPS39.SS.DBC.1