Impact of temperature and particle size on polylactic acid anaerobic biodegradability

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Abstract: The growing concern about plastic pollution and the environmental impact of these materials has fostered interest in bioplastics. This study evaluated the biodegradability of polylactic acid (PLA), the most widely used bioplastic, using biomethane potential (BMP) tests. Experiments explored the impact of temperature (i.e., mesophilic (35 ºC) and thermophilic (55 ºC)) at four different particle sizes, ranging from 125 to 4000 µm. Destructive samples were used to study the structural characteristics of crushed PLA along the degradation by means of infrared spectrophotometry (FTIR-ATR) and differential scanning calorimetry (DSC). These techniques allowed evaluating what occurred in the PLA structure during the anaerobic digestion process.

PLA samples from Smart Materials 3D (SMARTFIL®PLA) were tested: pellet without pretreatment (> 4000 µm), flattened (> 2000 µm), crushed (> 1500 µm), and powder (125 - 750 µm). Flattened particles were obtained by pressing pellets with a hydraulic press, while crushed and powder PLA were obtained by using a commercial blender (Bosch MMB6382M) with titanium blades. The blender operated in cycles with time breaks to prevent overheating. Ice was used to cool and avoid PLA melting and recrystallization (García-Depraect et al. 2021). Mesophilic and thermophilic inoculum were obtained from a pilot-plant anaerobic digester (5 m^3) at a wastewater treatment plant in Navarra, Spain, which treated a mixture of biomass from trickling filters and activated sludge from surrounding wastewater treatment plants.

Biochemical methane potential (BMP) tests were carried out in accordance with the guidelines of Holliger et al. (2021), utilizing 250 mL Wheaton® serum bottles under both mesophilic (35 °C) and thermophilic (55 °C) conditions. Each bottle contained 160 mL of inoculum and the required amount of PLA to achieve a 1:1 inoculum-to-substrate ratio on VS-basis. BMP results were validated through a positive control test involving microcrystalline cellulose. The gas density (GD) method was employed to measure mass loss and biogas volume during the biodegradation process (Justesen et al., 2019). Additionally, three extra bottles per condition were used to monitor the degradation of crushed PLA, employing infrared spectrophotometry (FTIR-ATR) and differential scanning calorimetry (DSC).

The experimental results revealed notable differences in the biodegradability of PLA under mesophilic and thermophilic conditions, depending on particle size. Figure 1 depicts specific methane production over 450 days, highlighting distinct behaviors in PLA degradation between the temperature conditions and particle size. Mesophilic conditions exhibited a prolonged lag phase (~100 days) and slower degradation kinetics, which lead to an incomplete conversion into methane within a period of 450 days. In contrast, thermophilic conditions showed a shorter lag phase (~10 days) and higher degradation rates, proving to be more effective in PLA degradation. Moreover, particle size significantly influenced biodegradation kinetics at both temperatures, with smaller PLA particles degrading faster.

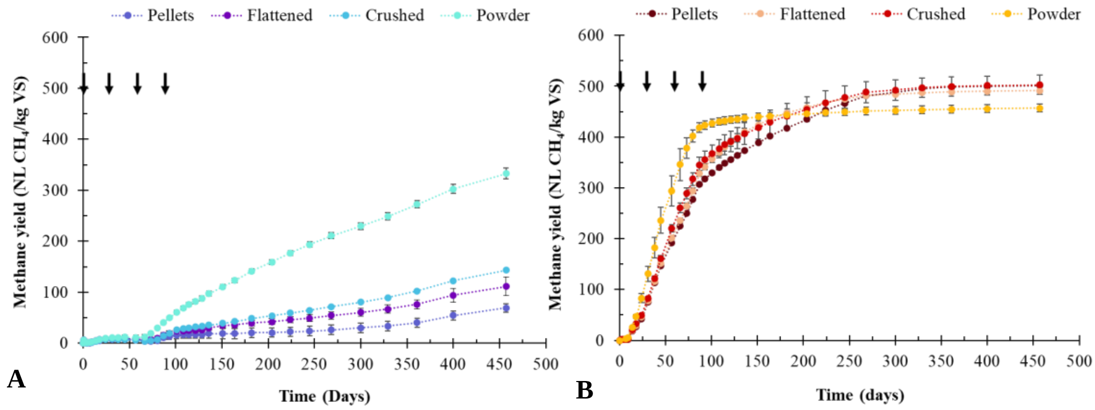

Fig. 1. Mean cumulative methane production in mesophilic (35 ºC, **A**) and thermophilic (55 ºC, **B**) conditions. Error bars represent the standard deviation of the replicates. Arrows indicate the time at which the sampling for the visual, IR and DSC analyses was performed.

Figure 2 illustrates that mesophilic samples show no significant spectral changes after 90 days of degradation. Peak intensity varies based on the sample thickness and roughness, which is in turn influenced by PLA degradation. For thermophilic samples there were significant changes in the peaks around 1750 cm^{-1}, where a single peak splits into two, and a new peak emerges around 1600 cm^{-1} with increasing degradation time. In contrast, mesophilic samples initially exhibit C=O (1600 cm^{-1}) bond formation, which decreases over time.

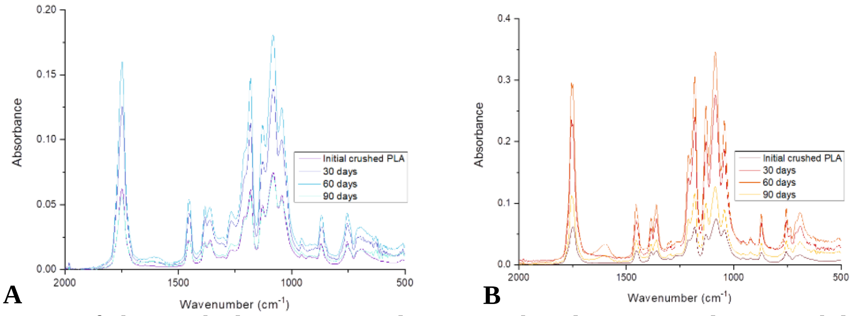

Figure 2. IR spectra of the crushed PLA exposed to anaerobic digestion under mesophilic (35 ºC, **A**) and thermophilic (55 ºC, **B**) conditions.

DSC results show that with increasing degradation time, the glass transition temperature (T_g) of PLA decreases, indicating a reduction in its crystalline structure (Table 1). The crystallinity percentage decreases over time during anaerobic degradation, with thermophilic conditions significantly impacting PLA's crystalline structure compared to mesophilic conditions. In the first 60 days of thermophilic conditions, there is an initial increase in crystallinity (up to 42%), possibly due to an annealing process close to PLA's T_g. However, for longer durations, crystallinity decreases to 2.2% and 0.7%, likely due to an enzymatic process by microorganisms. Mesophilic conditions show a similar trend, albeit less pronounced, with no significant changes during the first 30 days. The decrease in crystallinity and mass in PLA reactors corresponds to higher biogas production.

In conclusion, this study demonstrates that thermophilic conditions are more effective in degrading PLA than mesophilic conditions, with a significant reduction in the polymer's crystallinity and T_g under these conditions. A correlation was observed between the decrease in crystallinity and higher methane production.

Table 1. The DSC results for PLA thermal properties.

Sample	Time	T_g	ΔH_{cc}		ΔH_m		Crystallinity
	Days	ºC	J·g^{-1}	ºC peak	J·g^{-1}	ºC peak	%
Initial	0	60.50	25.58	117.40	-25.36	153.58	27.07
Mesophilic	30	62.41	26.41	115.28	-25.45	152.42	27.16
	60	57.84	16.43	120.65	-17.54	153.64	18.72
	90	57.24	11.50	121.63	-13.57	153.38	14.48
Thermophilic	30	49.70	38.10	100.01	-39.36	149.56	42.01
	60	48.75	1.20	117.23	-2.02	132.66	2.16
	90	45.82	-	-	-0.62	131.23	0.66

***Tg is the glass transition temperature, ΔH_{cc} is the cold crystallization enthalpy, ΔH_m is the melting enthalpy and the percentage of crystallization χ(%) of PLA.

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