Thermophilic anaerobic biodegradation of commercial polylactic acid products

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Abstract: The environmental impact of fossil-based plastics has increased interest in biodegradable alternatives based on polylactic acid (PLA). This study investigates the anaerobic degradation of six commercial disposable PLA-based products under thermophilic conditions. Experiments explore the degradation process over time, including kinetic and product characterisation. Advanced analytical techniques, e.g., Fourier transform infrared (FTIR-ATR) were used to monitor changes in chemical composition, while differential scanning calorimetry (DSC) was used to track the thermal properties of PLA, allowing for a comparison of the impact of bioconversion on biodegradation.

The single-use PLA-based products were selected from commercially available products that comply with EN 13432. Six different products from different industrial manufacturers were selected for the study, including lunch box (Ecoologic), spoon (Bepulp), dish (Dopla Green), cup lid (MonoUso), shot glass (MonoUso) and plastic cup (Gold Plast). The products were manually cut into squares of around 1x1 cm to ensure an homogeneous particle size. The inoculum was collected from a pilot-scale (5 m^3) thermophilic anaerobic digester located in a municipal wastewater treatment plant in Navarra (Spain). The anaerobic digesters treat a mixture of biomass from tricking filters from the wastewater treatment plant (WWTP).

Biochemical methane potential (BMP) tests were carried out in 250 mL Wheaton® serum bottles following the guidelines of Holliger et al. (2021) under thermophilic (55 ± 1 °C) conditions. Each bottle contained 160 mL of inoculum and the amount of PLA needed to reach an inoculum-to-substrate ratio (ISR) of 1 in VS basis. BMP results were validated through a positive control test involving microcrystalline cellulose. The gas density method (GD-BMP) was employed to measure mass loss and biogas volume during the biodegradation process (Justesen et al., 2019). To monitor the biodegradation of the PLA products without disturbing the methane measurements, three additional serum bottles were set up for each product at 55 °C, which were operated in parallel and stopped after 30, 60 and 90 days.

The experimental results revealed that all PLA-based products showed similar methane production yields around 507 L CH_4 kg^{-1} VS, with a nearly complete biodegradation after 385 days (Figure 1). The products showed a slow degradation rate, with an average kinetic constant of 0.008 d^{-1}. Despite full biodegradability, estimated degradation at full-scale digesters at a 30-day hydraulic retention time is expected to be under 20 % due to the low hydrolysis rates, limiting anaerobic digestion as an end-of-life process for these PLA products.

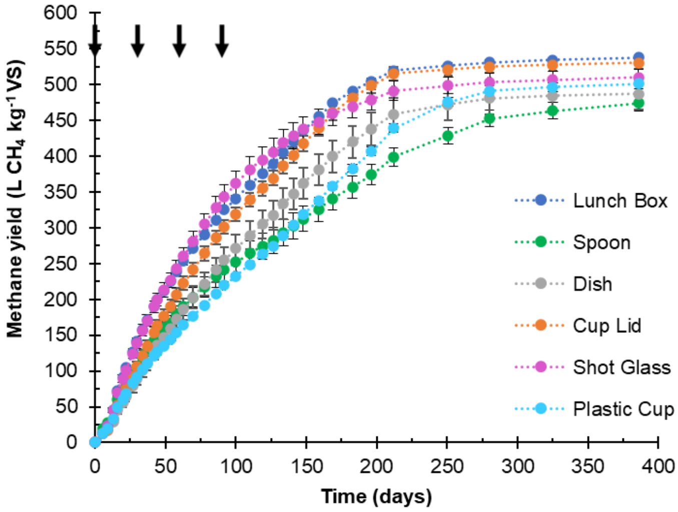

Figure. 1. Curves of specific methane production for the thermophilic tests with the different PLA-based products. The error bars represent the standard deviations of the replicates. Arrows (↓) indicate sampling events for the visual, IR and DSC analyses.

The collected PLA fragments after 30, 60, and 90 days of biodegradation, showed a similar IR response regardless of the test duration, but shifts in intensity occurred, such as an increase in peaks at around 1200 cm^{-1}, possibly indicating higher crystallinity or new C-O vibrations. A second peak at about 750 cm^{-1} also appears, possibly related to newly formed C-H or C=C bonds. Finally, a band at 1585-1600 cm^{-1} indicates a residual microbial biofilm on the PLA surface. Degradation of the products by visual inspection showed that all products exhibited changes in colour and fragmentation after 30 days, which were even more pronounced after 60 and 90 days.

The DSC analyses revealed that most PLA-based products initially exhibited a glass transition temperature (T_g) comparable to pure PLA (approx. 50–60 °C), although differences in T_g may be due to molecular weight and crystallinity (Table 1). Samples such as the lunch box and cup lid were practically amorphous, whereas the spoon, dish, shot glass, and plastic cup showed semi-crystalline behaviour. Under thermophilic conditions near or above the T_g of PLA (55 °C), crystallinity could increase; however, polymer chain breakage during degradation could also decrease crystallinity. The degree of crystallinity of the starting material was assessed to determine the initial state of each material (Table 1). Since the subsequent anaerobic degradation occurred at or near the T_g temperature, all materials eventually reached their maximum degree of crystallinity. Therefore, no significant differences were found among the materials.

Table 1. Initial thermal properties and degree of crystallinity (χ) of the PLA-based products.

Sample	T_g [ºC]	T_{cc} [ºC]	ΔH_{cc} [$J\cdot g^{-1}$]	T_m [ºC]	ΔH_m [$J\cdot g^{-1}$]	χ [%]
Lunch Box	58.1	131.7	7.11	156.65	8.27	1.25
Spoon	-	69.8	13.61	124.99	17.70	18.76
Dish	49.9	124.4	8.50	146.20	10.30	11.08
Cup Lid	58.8	116.3	17.51	148.00	18.62	1.19
Shot Glass	46.2	106.7	38.80	138.80	39.70	42.69
Plastic cup	58.7	114.5	26.44	148.30	27.57	29.65

*The glass transition temperature (T_g), cold crystallization (T_{cc}) and melting (T_m) temperatures. ΔH_{cc} is the cold crystallization enthalpy, ΔH_m is the melting enthalpy and the percentage of crystallinity χ (%) of PLA.

Two different patterns were observed in the changes in melting temperature (T_m) during the degradation process: the spoon, dish, and shot glass showed a slight increase in T_m after 30 days (indicating recrystallisation), followed by a decrease after 60 and 90 days. Meanwhile, the lunch box, cup lid and plastic cup showed a continuous T_m reduction, likely due to polymer chain scission and lower molecular weight. Overall, these shifts confirm that the PLA products degrade under anaerobic conditions.

In conclusion, all products showed similar methane production values around 507 L CH_4 kg^{-1} VS, with an estimated 100 % biodegradability after 385 days. The degradation is well characterised by first-order kinetics, with hydrolysis constants averaging 0.008 d^{-1}. This low degradation rate limits the industrial applicability of anaerobic digestion as an end-of-life process for these PLA products, since the estimated degradation at full-scale was below 20 %. Despite variations in crystallinity and discrepancies in the thermogravimetric analyses, these had no influence on the degradation extent or the degradation rate.

References

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