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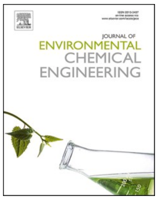

Assessment of methane production, disintegration, and biodegradation potential of bioplastic waste in anaerobic digestion systems

Giovanni Gadaleta[a], Sabino De Gisi[a,*], Caterina Picuno[b], Joern Heerenklage[b], Kerstin Kuchta[b], Andrea Sorrentino[c,*], Michele Notarnicola[a], Maria Oliviero[c]

[a] *Department of Civil, Environmental, Land, Building Engineering and Chemistry (DICATECh), Politecnico di Bari, Via E. Orabona n.4, 70125 Bari, Italy*
[b] *Hamburg University of Technology – Sustainable Resource and Waste Management, Blohmstraße 15, D-21079 Hamburg, Germany*
[c] *Institute for Polymers, Composites and Biomaterials (IPCB), National Research Council (CNR), P.le E. Fermi, 1, I-80055 Portici, Napoli, Italy*

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ABSTRACT

The suitability of bioplastics for treatment in anaerobic digestion and composting plants is not always clear despite their increasing popularity as an alternative to oil-based polymers. This study aims to estimate the anaerobic degradation of various combinations of bioplastics (cellulose acetate, polylactic acid (PLA) and polybutylene succinate (PBS)), filler (organic – gelatine – and inorganic) and plasticizer (triacetin) combinations, under conventional industrial digestion conditions. The investigation encompasses the evaluation of both physical (disintegration) and biological degradation processes, along with the modelling of their methane production utilizing various iterations of the Gompertz-type model. Results indicate that, during typical industrial residence time, cellulose-based bioplastics exhibit high methane yield (approximately 500 $NmlCH_4/gVS$) and near-complete degradation (both physical and biological), while PLA has minimal biodegradation (11%) and low methane yield (59 $NmlCH_4/gVS$). PBS-gelatine blends generate a significant amount of methane early in the digestion process (174 and 116 $NmlCH_4/gVS$ for flakes and pieces, respectively) but do not achieve full degradation. These findings suggest that the effectiveness of bioplastics degradation varies based on their composition, and further research is needed to optimize their treatment in common industrial facilities.

1. Introduction

Bioplastics are a range of commercial materials characterized by their source and biodegradability. In particular, they are defined as "bio-based" when derived from natural sources, whereas they can be considered “biodegradable” when common microorganisms are able to convert their polymeric structure into natural substances such as water, carbon dioxide, and compost [1]. Bioplastics can be defined compostable if they meet the EN 13432 standard, which requires a 90% biodegradability level within six months under controlled composting conditions [2]. Additionally, the disintegration residues must be less than 2 mm after three months of composting, and no ecotoxic effects should be observed on plant growth (agronomic test) [3]. Interestingly, the conditions required by the EN 13432, including residence time and temperature, are not coherent with the ones that actually occur in industrial plants [4]. For example, industrial anaerobic digestion typically does not exceed 30-day of retention time [5] while a thermophilic temperature during composting is maintained generally for 2–3 weeks [6]. Furthermore, the compostability standard only requires an evaluation of aerobic degradability, whereas there is no requirement to test the behavior under anaerobic conditions [7]. Inconsistencies of the conditions between standard tests and current treatment procedures result in incomplete bioplastic degradation during the actual composting and anaerobic treatments [8–10]. The presence of un-degraded bioplastics in digestate and/or compost necessitates expensive and complex procedures for the removal of not degraded fragments from the process outputs (especially with fragments < 2 mm) [11,12]. Since the amount of compostable bioplastics collected is continually increasing, this topic is gaining significant attention from both scientific and technological point of view. Compared to composting, there have been only few studies to evaluate the application of anaerobic digestion for bioplastics treatment [13,14]. Prior investigations, primarily conducted through batch testing, have indicated that it is necessary prolonged retention time (frequently exceeding 100 days) to achieve high degrees of bioplastics degradation [15]. Notably, while poly-hydroxy-alkanoates (PHA) exhibited a full degradation within approximately 10 days,

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* Corresponding authors.
E-mail addresses: sabino.degisi@poliba.it (S. De Gisi), andrea.sorrentino@cnr.it (A. Sorrentino).

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starch-based bioplastic and Polylactic Acid (PLA) materials displayed minimal degradation even after an extended period of 250 days [16]. Furthermore, both Cellulose-based films and PLA coffee capsules demonstrated degradation levels below 50% following anaerobic digestion at 55 °C, over a duration of 35 days [10]. Transitioning from batch testing to continuous or full-scale experiments have showed a further reduction in the degradation level achieved [17,18]. This is evident in the case of commercial carrier bags, which exhibited favorable degradability (>71%) in biochemical methane potential (BMP) tests, but showcased limited degradability (27%) in semi-continuous tests [7]. In the context of cellulose acetate, the degradation achieved through batch co-digestion with food waste (66%) [9] experienced notable reduction in both semi-continuous laboratory-scale studies [19] and in full-scale anaerobic digestion tests [20].

Anaerobic digestion holds particular significance in the realm of circular waste management, especially for processing organic waste [21]. Incorporating bioplastics into this context carries the potential to yield substantial methane production [22], enriching the anaerobic digestion process through the elevation of the substrate's C/N ratio [23]. Hence, it becomes imperative to discern the structural and compositional attributes of commercial bioplastics to ensure their compatibility [24]. Furthermore, bioplastics manufacturers typically employ a range of fillers and plasticizers to enhance various material properties [25]. On the other hand, it is important to recognize that their incorporation might influence the biodegradability and overall sustainability of bioplastics [26]. Previous studies have explored the effect of various fillers, such as nanoclay and graphite derived products, on the biodegradation rates of some bioplastics [27]. For instance, the introduction of nanoclay into polymers like PHB or poly(hydroxybutyrate-co-valerate) (PHBV) resulted in an augmented biodegradation in composting conditions [28]. This improvement was attributed to the increase of the surface area available for extracellular enzymes [29]. Conversely, Graphene Oxide, Carbon Nanotubes and Silver Nanoparticles exhibited counterproductive effects by impeding polymer biodegradation due to their cytotoxic towards a broad spectrum of microorganisms [30]. Therefore, careful analysis and optimization of such modifications become essential prerequisites for the effective advancement of bio-based materials [31].

The objective of this work is to assess methane yield and degradation patterns across various bioplastics during 32 days of anaerobic digestion (which represents a maximum hydraulic retention times in conventional AD plants treating organic solid waste). The assessment of bioplastics degradation is delineated into two phases: physical (disintegration) and biological degradation. To provide a comprehensive picture of the various types of bioplastics available in the market, the three most important polymer matrices (PLA, PBS, and Cellulose Acetate) were selected and combined with three different type of additives: an active filler for food packaging application, a plasticizer, and a biodegradation promoter (a gelatin protein). This experimental configuration enables the investigation of the interplay between bioplastics shape and the utilization of additives such as plasticizers and fillers. To enhance the comprehension of these bioplastics behaviour within the anaerobic digestion process, the acquired experimental data have been analyzed using a Gompertz-type mathematical model.

2. Materials and methods

2.1. Bioplastic samples

Anaerobic digestion tests were carried out on the following bioplastics samples.

2.1.1. PLA sample

A Polylactic Acid (PLA) in pellets with the trade name of 2002D was obtained from Natureworks LCC (Minnetonka, MN, USA). The D-LA enantiomer content is reported to be about 4%, whereas the molecular weight is characterized by Molecular number (M_n) = 115,000 and Molecular weight (M_w) = 215,000 [32]. The PLA pellets were firstly dried in a vacuum oven at 60 °C for 8 h and then extruded with a twin-screw extruder (Thermo Scientific EuroLab 16 XL) at 60 rpm and 180 °C to form a continuous, 150 μm thick, film samples (namely PLA). The effect of the processing conditions on the molecular weight, crystallization kinetics and the viscosity of the material were assessed in a previous work [33].

2.1.2. Cellulose acetate samples

Thermoplastic pellets of cellulose acetate (Degree of Substitution=2.45) were provided by GIBAPLAST (Italy). These pellets have a 30% Glycerol triacetate or triacetin (TA, CAS number 102–76–1) content and specific gravity of 1.31. Nicefiller Ltd (Italy) supplied Layered Double Hydroxide (LDH) organically modified with approximately 20 wt% sorbate anion (listed in EC-Directive 10/2011) [34,35]. Cellulose acetate films, with and without 5 wt% of LDH (seen as active filler for food packaging application), were produced by extruding the composites with a twin-screw extruder (Thermo Scientific EuroLab 16 XL) at 40 rpm and 160 °C. Neat and filled film samples were obtained with a thickness of about 150 μm, and termed CAT and CAT-LDH, respectively.

The prepared films were cut into rectangular strips (1 cm × 2 cm), dried under vacuum for 24 h at 25 °C and totally immersed in the tightly sealed vials with 20 mL distilled water for migration tests of plasticizer. Strips were taken out for different characterizations after different immersion time. The surfaces of the strips were gently wiped, dried at 25 °C under vacuum for 24 h and then the samples were weighted by using an analytical balance. The migration quantity of TA was monitored until 48 h. The content of TA loss from the film was obtained as:

$$WL(\%) = \frac{M0 - Mdt}{M0} x100 \tag{1}$$

where M_{dt} is the weight of dry sample after immersion in water for a time interval t, and M_0 is the dry weight before immersion in water.

2.1.3. PBS-gelatin samples

The Polybutylene Succinate (PBS) Bionolle 1903 produced by Showa High Polymers (Japan) and gelatin from bovine skin type B (CAS 9000–70–8) purchased from Sigma-Aldrich (Italy) were used to prepare PBS/gelatin blends (80% and 20% wt/wt, respectively). An internal mixer (Rheomix 600 Haake, Germany) was used to prepare the blends at 120 °C, 80 rpm for 6 min. The blends were then processed in two ways. The first method involved compressing the material at 120 °C and 30 bar using a 300 P hot press (Collin, Germany) to create flat pieces (PBS/G_p) with an average thickness of about 800 μm. This thickness was chosen as representative of the common disposable products.

The second method involved extruding the blends with a twin-screw extruder (Thermo Scientific EuroLab 16 XL) at 40 rpm and 140 °C to obtain film specimens (PBS/G_f) with an average thickness of about 150 μm.

2.2. Analytical methods

TS (total solids) and VS (volatile solids) were determined following the standards DIN 38 414 - S2 and DIN 38 409 - H 1–3, respectively. The theoretical biochemical methane production (BPM) was calculated based on the elemental characterization ($C_xH_yO_zN_nS_s$) according to Eq. 2 [36]:

$$BMP = \frac{\mathrm{Vm} * \left(\frac{x}{2} + \frac{y}{8} - \frac{z}{4} - \frac{3n}{8} - \frac{s}{4}\right)}{12x + y + 16z + 14n + 32s} \tag{2}$$

Where Vm (22′414 mL/mol) is the molar volume of an ideal gas. The main physicochemical properties of the bioplastics analysed are pre-

Table 1
Characterization of bioplastics and inoculum adopted for the test.

Samples	**TS [%]**	**VS [% TS]**	**C [% dry base]**	**%O [% dry base]**	**%H [% dry base]**	**BMP_{th} [$mlCH_4$/gVS]**
CAT	85.34	100.00	50.69	43.25	6.06	490
CAT-LDH	87.46	98.74	48.80	41.38	5.82	472
PLA	100.00	100.00	50.00	44.41	5.60	467
PBS/G_f	97.89	99.92	54.70	34.86	6.87	558
PBS/G_p	96.38	99.89	54.70	34.86	6.87	558
Cellulose	97.00	100.00	45.40	N.A.	N.A.	454
Inoculum	**TS [%]**	**VS [%TS]**	**pH [-]**	**VOA/ TIC* [-]**	**IC [g/l]**	
Anaerobic sludge	3.14	64.31	7.62	0.165	1.26	

* : VOA = Volatile Organic Acid; TIC = Total Inorganic Carbonate.

Table 2
Number and weight of bioplastics specimens and cellulose adopted in the batch test.

Sample	**N.**	**g wet**	**g TS**	**g VS**
CAT	118	4.7371	4.0426	4.0426
CAT-LDH	76	4.6802	4.0932	4.0418
PLA	170	4.0441	4.0441	4.0441
PBS/G_f	-	4.1990	4.0470	4.0424
PBS/G_p	6	4.1791	4.0909	4.0875
Cellulose	-	2.0842	2.0217	2.0217

sented in Table 1.

2.3. Anaerobic digestion

The batch anaerobic digestion tests were conducted under mesophilic temperature conditions (37 ± 1 °C) and wet conditions (TS concentration lower than 10% w/w). The tests were carried out for a duration of 32 days, which is meant to represent a reasonable Hydraulic Retention Time (HRT) for an industrial anaerobic digester [37]. All bioplastic samples, except for PBS/G_p, which was ground to an average dimension of 10 mm, were cut into squares measuring 20 × 20 mm or at least an average area of 400 mm^2. Tests were performed in 0.5 L working volume bottles in a climate-controlled room: each sample was tested in triplicate. To ensure initial anaerobic conditions, a technical grade Nitrogen was flushed in the headspace volume for one minute [38]. Blank and a positive reference (micro-crystalline cellulose) tests were also conducted to determine the endogenous methane production and the inoculum activity, respectively.

The digestate from a wastewater treatment plant (Hamburg-Köhlbrandhöft, Germany) was used as the inoculum (Table 1). Before the test, the digestate was incubated at the test temperature for two weeks to minimize the endogenous methane production, reducing nearly to zero its methane production. The inoculum (400 g) and each bioplastic (around 4 g; Table 2) were mixed at an Inoculum-Substrate Ratio (ISR) of 2 (VS basis); for the reference sample (cellulose) an ISR of 4 has been adopted in order to achieve a biogas production similar to bioplastics samples [39]. The use of different ISRs between the test and control samples was necessary to avoid great differences on the respective biogas production [40]. The biogas volume produced was measured by liquid displacement of a eudiometric tube connected to the bottles. Biogas volume and composition were reported once per day: after every recording the bottles were shaken to ensure uniform distribution of microorganisms, nutrients, and substrate in the test suspension [41]. The methane yield of each sample was calculated according to VDI standard [40] in terms of $mlCH_4/gVS$ at standard conditions (0 °C and 101.325 kPa).

Gas composition in terms of CO_2, O_2, N_2, and CH_4 was measured through a gas chromatography system (HP 6890, Agilent) using Helium as a carrier with a thermal conductivity detector at 210 °C and 9 min detection time. Volatile Organic Acids (VOAs) and Total Inorganic Carbonate (TIC) were determined according to the Nordmann method [42]. Inorganic carbon (IC) was determined using multi EA 4000 analyzer (Analytik Jena AG) following DIN EN 13137.

2.4. Bioplastics biodegradation

The anaerobic biodegradability of bioplastics has been calculated according to ISO 14853 [43]. The percentage of biodegradation (B) of samples has been calculated using Eq. (3):

$$B = \frac{m_t \times 100}{m_v} \tag{3}$$

Where m_t is the total amount of carbon converted to gas [mg C], and m_v is the mass of carbon in the test material in each bottle [mg C]. The total amount of carbon converted to gas has been calculated using Eq. (4):

$$m_t = m_h + m_L \tag{4}$$

Where m_h is the net mass of carbon produced as gas in the headspace

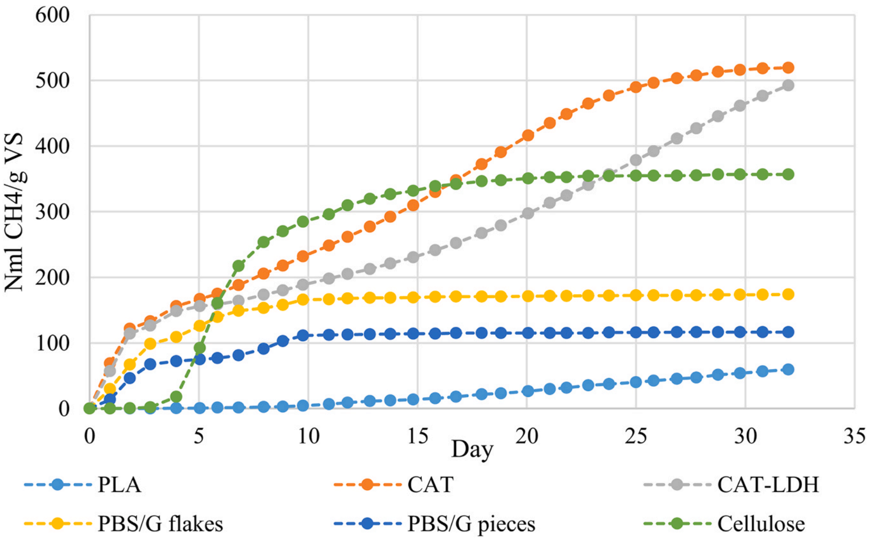


Fig. 1. Cumulative methane yield of bioplastics (average values of three tests).

Table 3
Final methane yield and digestate characteristics of the samples.

Samples	Methane yield [NmlCH$_4$/gVS]	pH [-]	IC [g/l]
CAT	519.32 ± 8.83	7.53	1.48
CAT-LDH	492.36 ± 17.65	7.49	1.45
PLA	59.38 ± 1.31	7.65	1.48
PBS/G$_f$	173.80 ± 10.84	7.85	1.90
PBS/G$_p$	116.40 ± 11.26	7.85	1.75

[mg C], $_{mL}$ is the mass of inorganic carbon in the liquid digestate [mg C]. In particular, m$_h$ and $_{mL}$ have been calculated through Eqs. (5) and (6) respectively:

$$m_h = \frac{^{12}C \times 0.1 \times (p - p_w) \times \Delta V_H}{RT} \tag{5}$$

$$m_L = \rho_{IC,net} \times V_L \tag{6}$$

Where ^{12}C is the relative atomic mass of carbon [12,000 mg/mol], 0.1 is the conversion factor for both hectopascals to pascals and litres to cubic meters; p is the atmospheric pressure of every readout [hPa], p$_w$ is the pressure of water vapour at the incubation temperature [hPa], ΔV_H is the difference between the initial and final volumes of headspace in each test bottle [l], R is the molar gas constant [8.314 J/mol*K], T is the incubation temperature [K]; $\rho_{IC,net}$ is the concentration of inorganic carbon in each test bottle [mg/l] and V$_L$ is the volume of liquid digestate [l]. In particular, ΔV_H consider the net volume produced by the sample only (net of the contribution of methane from the inoculum). In addition, $\rho_{IC,net}$ is the net IC formation: this value was determined at the end of the test, once the bottles were opened, subtracting the IC of the tested medium with the one of the blank (inoculum).

2.5. Bioplastics disintegration

According to standard methods [44], the degree of disintegration (D) of bioplastics during the anaerobic digestion was calculated according to Eq. (7):

$$D = \frac{(m_i - m_r)}{m_i} * 100 \tag{7}$$

Where m$_i$ is the initial dry mass of the specimen [g], m$_r$ is the residual dry mass of the specimen recovered [g]. Once the test was stopped and the bottles opened, the bioplastics fragments were retrieved from the digestate sieving it at 2 mm mesh. Any impurity from the inoculum attached to the plastic surface was manually removed. Bioplastics samples were then cleaned, dried in an oven for two days at 40 °C (as well as for the initial specimens) and then weighted.

3. Results and discussion

3.1. Anaerobic digestion

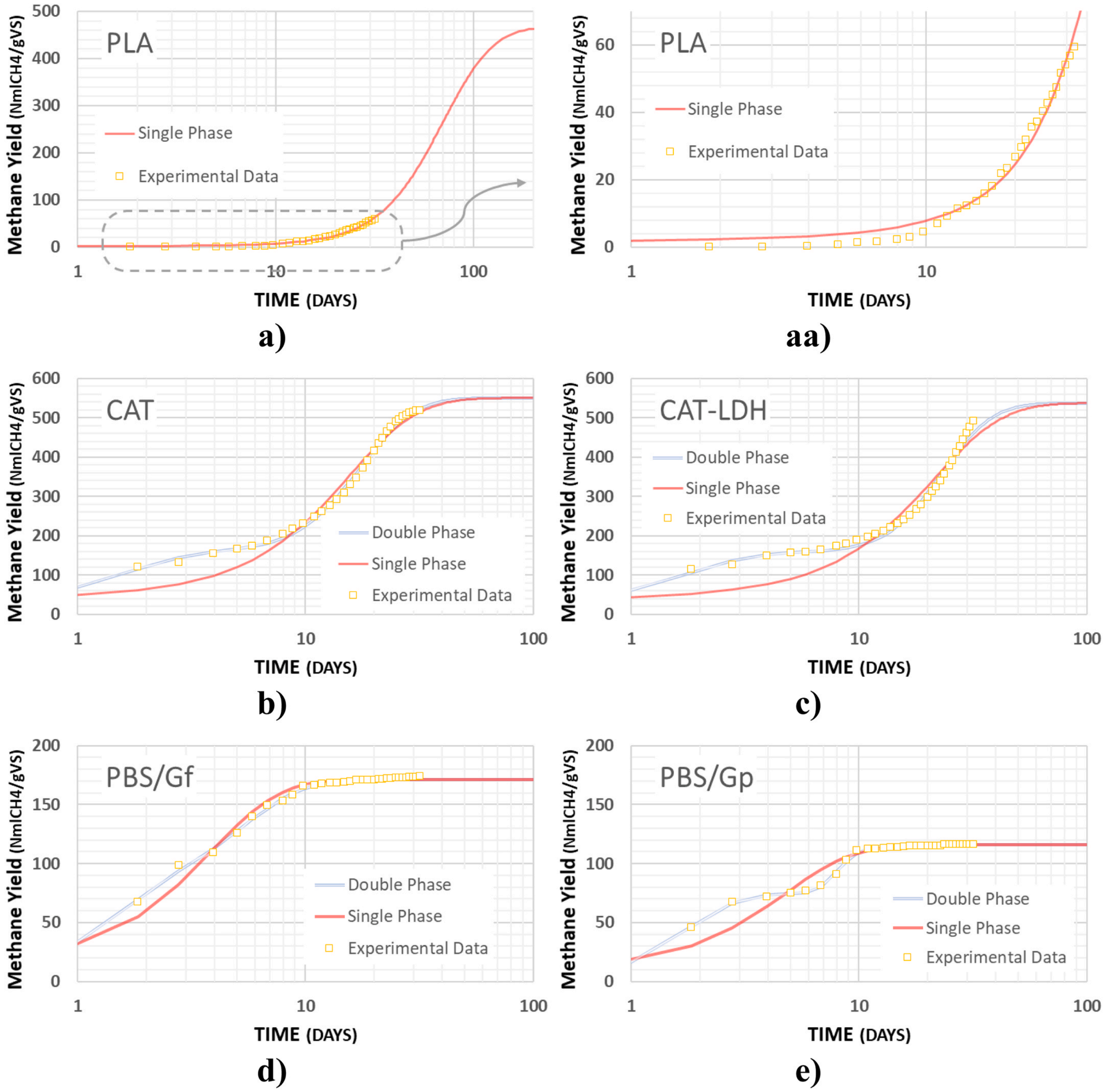
Fig. 1 shows the cumulative methane yield during the 32 days of batch anaerobic digestion of CAT, CAT-LDH, PLA, PBS/G$_f$, PBS/G$_p$ and reference (cellulose) while the final methane production values are reported in Table 3. Each test was conducted three times, and the results are presented as average values along with relative standard deviations. The suitability of the test was confirmed by the final methane yield of 356.8 NmlCH$_4$/gVS of reference (cellulose) [45].

The cellulose acetate based samples achieved the highest methane yield (around 500 NmlCH4/gVS), which value is similar to the one obtainable from common organic substrates currently adopted in anaerobic digestion [46]. Although the final methane yield of both cellulose acetate-based samples is similar, their methane generation exhibited different trends. During the first two days, both samples had a high methane yield (approximately 60 NmlCH$_4$/gVS per day), followed by a decrease in production rate over the next three days (about 16 and 13 NmlCH$_4$/gVS per day for CAT and CAT-LDH, respectively). These rates remained almost constant until the end of the test. The initial high methane production rate may be attributed to the quick expulsion of the plasticizer (triacetin) from the sample within the first few hours of immersion in water [47]. As measured from the migration tests of triacetin in water of CAT and CAT-LDH samples, a very high triacetin loss is measured just after 24 h of immersion with a WL (%) of around 24,6% and 28,6% for CAT and CAT-LDH samples, respectively. This loss become complete only after 48 h for both samples. The presence of triacetin reduced the typical lag phase of 2–5 days that usually characterizes degradation of cellulose-based materials [16]. The hydrophilic nature of the triacetin has, in fact, the potential to increase the permeability of water and oxygen of CAT, thereby accelerating its disintegration and biodegradation rates, compared to the neat CA. This behaviour is typical of plasticized systems. The presence of the LDH filler in the CAT-LDH samples slowed down the degradation rate of the polymer without affecting the total methane yield. The inorganic clay sheets present in the LDH additive acted as a barrier for both water and gas molecules, delaying polymer degradation [48]. At day 25, the methane generation of CAT started to decline, and by day 30, it reached a plateau phase. In contrast, CAT-LDH continued to produce methane throughout the 32-day test, with only a slight decrease on the last day (day 32). It is interesting to note that the experimental BMP values were consistently higher than the corresponding theoretical values for both CAT and CAT-LDH (Table 1). Similar results were found for several substrates characterized by a long lag phase and multiphase growth, probably attributed to a delayed inoculum hydrolisis [45]. This suggests that the theoretical calculations based on stoichiometric conversions may not fully capture the complexities of organic matter and its methane production [19] but also that this difference could be within the measurement error itself.

The methane yield of PLA was significantly lower than that of the cellulose-based samples, with a final value of 59.38 NmlCH$_4$/gVS. PLA is a polyester derived from renewable sources like corn starch or sugarcane and is commonly used for food packaging and disposable products [49]. However, due to its low biodegradability in mesophilic anaerobic conditions, its methane yield is lower than other biodegradable materials [50]. Indeed, about a biogas yield of 100 Nml/gVS was obtained from PLA film at mesophilic conditions, which is nearly similar to the value obtained by this study considering the methane only [4]. Fig. 1 shows that after an almost 10-day lag phase, the PLA samples start to produce methane and follow an increasing trend. PLA degradation, especially at mesophilic temperature, is slow and challenging [51]. Its high crystallinity degree impedes the diffusion of microorganisms and enzymes in its matrix, leading to a prolonged lag phase [52]. Its long lag phase and slow conversion to biogas are not compatible with the residence time in CSTR-type digesters.

PBS is an aliphatic polyester made from renewable resources, and it is used for food packaging and disposable products [53]. It is widely recognized as non-degradable in anaerobic environment [54], therefore, blends with highly degradable polymers or additives have been proposed to enhance its biodegradability in different environments [55]. In this case, 20% wt/wt of type B bovine gelatin was added to PBS to improve its degradation in anaerobic environments. The selection and optimization of the gelatin type and amount were carefully done to ensure that the mechanical, thermal, and barrier properties of the bioplastics are not compromised [56].

According to Fig. 1, the methane yield of both PBS-gelatin samples (PBS/G$_f$ and PBS/G$_p$) fell in between the methane yield of PLA and cellulose acetate-based samples. The values achieved in this studies revealed how the blend with gelatin increased the biogas yield, which in other study has been seen to be very low (11 Nml/gVS) [57]. The degradation rate of PBS/G$_f$ was faster than PBS/G$_p$, with the latter



a)

aa)

b)

c)

d)

e)

Fig. 2. Gompertz model description with single (n = 1) and double (n = 2) phase for a) PLA, b) CAT, c) CAT-LDH, d) PBS/G_f and e) PBS/G_p.

producing methane only in the first 3 days and from day 7 to day 10. The initial degradation of PBS/G_p was likely due to the presence of the gelatin phase in the blend. After about 10 days, a plateau with no significant increase in methane production is reached despite the presence of residual PBS matrix, indicating that the microorganisms responsible for methane production have completely converted the available gelatin phase. As expected, the size of the samples influenced their degradation rate, with flakes (150 µm thick) degrading at a faster rate than pieces (800 µm thick). This was evidenced by the higher methane yield of PBS/G_f, which suggests that the increased surface area of flakes facilitated the activity of microorganisms responsible for biodegradation. Similar differences are known for samples with different shapes, such as film and pellet [58].

Based on the results presented in Table 3, the digestate resulted with similar characteristics (TS ~ 2.2%; VS ~ 60%; VOA/TIC ~ 0.16 and pH in the range of 7–8.5), regardless the samples. In particular, the samples characterized by a longer plateau phase (especially PBS-gelatin samples) have a higher pH and IC, which can be assumed to be attributed to the dissolution of CO_2 in the liquid digestate.

3.2. Kinetic analysis

The anaerobic degradation performances of the substrates were gathered by fitting the cumulative methane yield curves with the Gompertz theoretical model, commonly used in anaerobic digestion experiments to describe the rate of biogas production as a function of time for several organic substrates [59,60]. However, the conversion of complex substrates containing different phases with dissimilar rate of

Table 4
Kinetic results of batch test data.

Samples	Single Phase		RMSE	Double Phase		BMP model ($mlCH_4/gVS$)	RMSE	BMP_{th} / BMP_{mod}
PLA	G_0	467	2.18	G_0^1	467	467	2.18	100%
				R_{max}^1	15.7			
	R_{max}	15.7		λ^1	22.7			
				G_0^2	-			
	λ	22.7		R_{max}^2	-			
				λ^2	-			
CAT	G_0	551	25.12	G_0^1	158.6	550	7.49	112%
				R_{max}^1	230.9			
	R_{max}	69.8		λ^1	0.5			
				G_0^2	392.4			
	λ	0.5		R_{max}^2	59.2			
				λ^2	6.4			
CAT-LDH	G_0	582	33.67	G_0^1	158.6	537	11.46	113%
				R_{max}^1	230.9			
	R_{max}	54.5		λ^1	0.5			
				G_0^2	379.1			
	λ	0.5		R_{max}^2	49.7			
				λ^2	11.2			
PBS/G_f	G_0	171.2	4.46	G_0^1	84.2	171	1.74	31%
				R_{max}^1	193			
	R_{max}	77.8		λ^1	0.5			
				G_0^2	87.2			
	λ	0.01		R_{max}^2	43			
				λ^2	2.4			
PBS/G_p	G_0	115.7	6.18	G_0^1	75.5	115	1.09	21%
				R_{max}^1	115			
	R_{max}	42		λ^1	0.6			
				G_0^2	40.2			
	λ	0.01		R_{max}^2	28.8			
				λ^2	6.07			

degradation result in stepped curves that cannot be described by a single Gompertz-type model. For this reason, a multi-step version of the modified Gompertz model is proposed here to analyse the experimental data [Eq. (8)]:

$$G(t)=\sum_{i}^{n} G_o^i \bullet \exp\left\{-\exp\left[\frac{R_{max}^i \bullet 2.7182}{G_0^i}\left(\lambda^i - t\right)+1\right]\right\} \tag{8}$$

Where n is the number of phases, t is the time of digestion, G(t) is the cumulative methane produced, G_0^i is the ultimate methane produced by the i-th phase, R_{max}^i is the maximum rate of methane produced by the i-th phase, and λ^i is the lag time. The experimental data and model results are compared in Fig. 2. The parameters of the model provided in Table 4 were derived through a nonlinear least-square regression analysis. This analysis utilized a Solver add-in program within Microsoft Excel to best match the average specific cumulative methane production curves. The effectiveness of the model was quantified using the Root Mean Square Error (RMSE) [Eq. (9)]:

$$RMSE=\sqrt{\frac{\sum_{i=1}^{n}\left(E_{m,1}-E_{c,1}\right)^2}{n}} \tag{9}$$

Where, n represents the number of measurements, $E_{s,i}$ and $E_{c,i}$ are the measured and the calculated cumulative methane production, respectively. The predicted specific methane yields, resulting from the nonlinear regression analysis, were graphed against the measured specific methane yields to establish an initial visual correspondence. It's crucial to emphasize that relying solely on the RMSE value is inadequate for assessing the model's appropriateness. A comprehensive evaluation should consider a mix of RMSE, visual assessment of the alignment between predicted and measured curves, and theoretical parameter values.

The application of Gompertz model simulation is problematic for PLA data obtained in our experiments. PLA is difficult to be degraded completely under mesophilic anaerobic conditions within 100 days. For this reason, we decided to use a single-phase Gompertz model ($n = 1$) with the G0 model parameter fixed to be equal to the theoretical value of BMP_{th} reported in Table 1. Under these assumptions, the model predicts that the complete transformation in methane require at least 200 days (see Fig. 2a), consistently with previous experimental results where the duration of biodegradation was ranging from 100 to 280 days [13,16,61–63]. However, due to the low biodegradation, also the accuracy of the kinetics parameters may be low as well.

The experimental data in Fig. 2, demonstrate that all systems analysed here (except for PLA) showed an evident stepped trend, suggesting the existence of different and progressive degradation phases. This behaviour was likely due to the varying accessibility of biodegradable compounds within the polymer structure or the need for acclimatization to this feedstock [64].

In the cellulose acetate-based and PBS-gelatin systems it is notable an inflection of the curve from day 6 to day 8. This trend may be due to the degradation of the leached plasticizer and the more accessible protein phase for cellulose acetate-based and PBS-gelatin, respectively. After about 10 days, the modelled PBS-gelatin samples exhibited a clear plateau, whose ultimate methane production values predicted by both the single- and double-phase models were lower than the theoretical one (Table 4). Specifically, the values from the double-phase model corresponded to about 31% and 21% of BMP_{th} for PBS/G_g and PBS/G_p, respectively. These values are consistent with the amount of gelatine (20%) in the initial PBS-gelatin blends, opening to the assumption that the conversion of this easily biodegradable additive could explain why the typical lag phase of PBS biodegradation was not observed in these experiments [55]. For cellulose acetate-based samples, the difference between BMP_{mod} and BMP_{th} (due to the reasons explained in the previous section) should be interpreted as complete (for CAT) or significant (for CAT-LDH) degradation of the blends during the experiments, as further confirmed by the next section.

3.3. Disintegration and biodegradation

In order to differentiate between physical and biological degradation of bioplastics, the degree of disintegration (D) and biodegradation (B)

Table 5
Disintegration vs. biodegradation values of bioplastics samples.

Sample	D [%]	B [%]
CAT	98.56 ± 0.14	99.18 ± 0.56
CAT-LDH	90.08 ± 2.08	89.70 ± 2.74
PLA	15.87 ± 1.14	10.98 ± 0.25
PBS/G_f	42.62 ± 0.83	30.90 ± 1.48
PBS/G_p	27.48 ± 0.44	20.23 ± 0.96

has been calculated for each sample. The final values of D and B for CAT, CAT-LDH, PLA, PBS/G_f and PBS/G_p are reported in Table 5.

In general, the results indicate that CAT was the most biodegradable among the tested bioplastics, while PLA was the least biodegradable. PBS-gelatin samples showed intermediate levels of biodegradability, which were influenced by the presence of gelatin and the size of the samples. These findings highlight the importance of taking into account the specific characteristics of different bioplastics when assessing their biodegradability under anaerobic conditions.

Regarding the cellulose-based samples, CAT and CAT-LDH achieved a disintegration degree of 98.6% and 90.1%, respectively. These values were very similar to the biodegradability degree, which were 99.2% and 89.7%, respectively. The component of B accounting the inorganic carbon dissolved in the digestate was negligible (<1%) due to the high methane production during the test. As shown in Fig. 3 (2a), only small amounts of CAT residues were retained during sieving, and single pieces were not detectable. CAT-LDH appeared yellow and thinner, which is a sign of surface degradation. A degradation of 66.8% and 51.4% could be found for CAT and CAT-LDH, respectively, in 21-days batch co-digestion with food waste [9]: the higher value in this study is due mainly to the longest time of test (32 days) but also for the presence of only bioplastic as substrate.

PLA reached the lowest value in both disintegration and biodegradation. Indeed, PLA samples remained almost unaltered due to their lower degradability, coherently with several studies, where nearly no degradation (< 1–7%) was observed in mesophilic conditions (35–37 °C) up to 40–150 days [65]. In particular, in this case the disintegration achieved higher value than the biodegradation: D resulted almost 50% more than B. In this case, the component of B accounting the inorganic carbon dissolved in the digestate was lower than 7% of the whole value. The slow methane production led to the CO_2 dissolving in the liquid digestate and then to the increase in IC (Table 3). From a visual inspection, PLA samples maintained their transparency because of their grater resistance to water infiltration than cellulose acetate samples.

PBS-gelatin samples achieved a final biodegradation of 30.9% and 20.2% for PBS/G_f and PBS/G_p respectively. The component of B accounting the inorganic carbon dissolved in the digestate was the highest (about 25%) for the fastest reaching of the plateau phase. On the other hand, D values appeared significantly higher: 42.6% and 27.5% for PBS/G_f and PBS/G_p respectively.

The degree of disintegration can be influenced by factors such as the shape and size of the sample, while biodegradation depends on the chemical composition and accessibility of the material to microorganisms. Indeed, PBS fragments in the liquid digestate were not converted to biogas through the action of microorganisms. The biodegradation is referred only to the gelatin fraction present in the sample, especially for PBS/G_p, where the degradation was easier. On the other hand, the present value has been, to our best knowledge, the highest registered among other studies [66,67].

4. Conclusions

In this work, different bioplastics were subjected to a 32-day batch anaerobic test. This timeframe was chosen as indicative of the average industrial digester residence time. The results emphasize the importance tailored treatment strategies for various bioplastics within industrial facilities: while cellulose-based bioplastics are suitable for biogas production, PLA and PBS-gelatin ones may not fully convert to biogas within the tested residence time.

The presence of additives or fillers can yield methane production trends that deviate from those exhibited by the pristine matrix. Although the modified Gompertz model can effectively predict ultimate cumulative methane production, an multi-step variant of this model enhances precision in characterizing the initial lag phase and the observed synergistic effects. By incorporating additional parameters, such as separate lag phases or intermediary steps, the multi-step Gompertz model provides a more comprehensive and realistic description of the intricate biological reactions, microbial adaptation, and gradual transitions occurring during biodegradation. However, it is important to acknowledge that the model coefficients and predictions are based on experimental data obtained under specific conditions. These conditions may not fully replicate real-world systems or account for the complexities and variations that can occur in natural environments. In order to evaluate the robustness, generalizability, and applicability of the model to various environmental contexts, a further validation using experimental data from varied conditions is essential.

CRediT authorship contribution statement

Giovanni Gadaleta: Conceptualization, Data curation, Formal

Fig. 3. Visual of pre (1) and post (2) digested CAT (a), CAT-LDH (b), PLA (c), PBS/G_f (d) and PBS/G_p (e).

analysis, Investigation, Writing – original draft. **Sabino De Gisi**: Conceptualization, Data curation, Funding acquisition, Methodology, Supervision, Validation, Writing – original draft. **Caterina Picuno**: Data curation, Supervision, Writing – review & editing. **Joern Heerenklage**: Formal analysis, Conceptualization, Data curation, Methodology, Resources, Supervision, Validation. **Kerstin Kuchta**: Supervision, Validation, Writing – review & editing. **Andrea Sorrentino**: Formal analysis, Funding acquisition, Writing – review & editing. **Michele Notarnicola**: Supervision, Writing – review & editing. **Maria Oliviero**: Investigation, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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