



Full Length Article

Disposable Mater-Bi® bioplastic tableware: Characterization and assessment of anaerobic biodegradability

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ABSTRACT

In this study commercial starch-based (Mater-Bi®) disposable bioplastic tableware items, which are among the most widely used commercial products available on the market, were selected for lab-scale anaerobic degradability tests. Since the knowledge of the biodegradation profile of bioplastic products is still incomplete, the study was aimed at investigating the maximum biodegradation potential of the materials under ideal anaerobic conditions, as well as the biodegradability degree as a function of treatment time. The experiments were carried out under mesophilic and thermophilic conditions at different food to microorganism ratios and test material sizes, and the specific biogas production and associated kinetics were evaluated. Biogas production was observed only under thermophilic conditions, with conversion yields in the range 602–898 mL/gTOC for the tested cups and 1207 ± 52.8 mL/gTOC for the knives. The degrees of biodegradation and disintegration were found to be strongly dependent on the product composition. Physical, chemical and morphological analyses were used to characterize the tested materials before and after the degradation and potential correlations among process parameters and bioplastic characteristics were derived.

1. Introduction

The extensive production and use of conventional fossil-based plastics has come to the point of being a threat to the environment and human health. The rate of plastic consumption has been growing steadily in the last decades and is not matched by an equally developed waste management strategy, which causes plastic dispersion and accumulation into the environment. Therefore, biodegradable plastics have gained growing attention and are currently emerging in the market as a sustainable alternative to commodity plastics, although concerns have also been raised as to the overall environmental benefits of such materials including: the actual biodegradability in natural environments; the low recyclability potential; the misconception of consumers about the end-of-life routes; increased littering due to biased consumer perception of the environmental effects of bioplastic waste; increased land/water use intensity to produce bioplastic precursors; poor knowledge of the secondary products of bioplastic degradation [1]. The global production

of bioplastics reached 2.11 Mt in 2022 and is expected to increase to 6.30 Mt/y in the next five years [2]. Consequently, the share of bioplastic residues is expected to grow. In Italy, the amount of bioplastic is estimated to currently account for 4% by mass of the organic fraction of municipal solid waste [3] and it is therefore necessary to understand their fate before their amount becomes even more relevant. There are three main categories of bioplastics: bio-based and biodegradable, fossil-based and biodegradable, bio-based and non-biodegradable. Biodegradable plastics are potentially advantageous since they can be collected along with the organic fraction of municipal solid waste (OFMSW), and biological treatments (both aerobic and anaerobic) can be applied for the purpose of materials and energy recovery. However, so far it has not been assessed systematically whether biodegradable plastic products can be treated together with OFMSW [4]. Labelling of biodegradable products has not been properly regulated yet and this contributes to inadequate waste collection and treatment, which can in turn determine bioplastic leakage into the environment [5].

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Starch blends belong to this category of biodegradable plastics, with a contribution of 17.9% to the global bioplastics production in 2022. Starch is a polysaccharide composed by two main fractions, amylose and amylopectin, and has become particularly widespread for its availability and low cost [6]. Due to its poor tensile properties and high hydrophilic nature, it is usually modified into thermoplastic starch (TPS) to achieve a better processability [7] and often blended with other polymers or additives to obtain the required physical and mechanical properties [8]. For instance, fibrous inclusions are often used to reinforce the material [9,10] and fillers can be used to improve the barrier capacity, such as clay [11] or metal oxides [12]. One of the most common blends on the market is Mater-Bi®, a family of polymeric compounds based on TPS and commercialized with different chemical formulations depending on the co-polymer used (e.g. cellulose acetate (CAc), poly(vinyl alcohol) (PVA), poly(ϵ -caprolactone) (PCL), and poly(butylene adipate-co-terephthalate) (PBAT)) [13]. The presence of co-polymers and additives of different nature affects the material crystallinity, the thermal behaviour and ultimately the biodegradability [14,15], which can significantly change throughout different products of this bioplastic category. Therefore, products composition should be correlated to their ability to undergo biodegradation under different environmental conditions and to the timeframe required for this to get to completion. Currently, there is still a lack of information on the anaerobic biodegradability of commercial starch-based products [16]. Experimental investigations under anaerobic conditions are still limited and so far have been mostly focused on pure biopolymers [17]. Some researches testing TPS alone under thermophilic (52 °C) conditions reported a biodegradation degree of 81% in 127 days [18] and 77% in 30 days [19]. Narancic and colleagues tested it also under mesophilic (35 °C) aquatic anaerobic conditions and observed a biodegradation of 98% in 56 days [18]. A number of authors tested PCL/TPS blends and reported biodegradation levels of 70–80% in 58 days at 35 °C [20], 68% in 80 days at 52 °C [18] and 83% at 35 °C in 139 days [21]. Guo and colleagues tested some starch and PVA blends at 37 °C for 115 days and obtained a range of biodegradation of 68–75% [22].

Commercial products generally display a lower degradation degree compared to pure polymers. For example, Battista and colleagues reported that some starch-based cutlery remained non-degraded in 250 days at 37 °C [23], while in another study two different starch-based films were tested at 37 °C for 65 days and reached 18.3% and 10.2% biodegradation, respectively [24]. A number of authors who tested Mater-Bi® under mesophilic conditions (35 °C) reported a biodegradation of 30% in 40 days [25], 28% in 60 days [26] as well as 21% (film) and 10% (pellets) in 81 days [27]. Temperature was found to enhance biodegradation. For example, coffee capsules were degraded in 100 days by 12–24% under mesophilic conditions (38 °C) and up to 47–69% in thermophilic conditions (58 °C) [28]; in another study some starch-based shopper bags were degraded by a 6% at 35 °C and 55% at 55 °C in 90 days [29]. Calabrò and colleagues investigated the biodegradation of some Mater-Bi® bags and observed low methane production yields under both mesophilic and thermophilic conditions (144 L/kgVS at 35 °C and 186 L/kgVS) in 30 days [30]. Massardier-Nageotte and colleagues tested a Mater-Bi® film at 35 °C for 28 days under both aerobic and anaerobic conditions and observed 45% and 25% biodegradation, respectively, suggesting that composting conditions are more suitable for these kinds of materials [31]. Although the results from batch tests cannot entirely reflect the biodegradation process in full-scale anaerobic digesters [32,33], they can provide some useful insights on the process and the specific effects of the adopted operating conditions. The outcomes of the reported studies suggest that a low degree of biodegradation for the investigated bioplastics is expected for mono-digestion processes at the typical residence times (20–30 days) of real plants.

The behaviour of commercial blends to different environmental conditions is complex and difficult to predict. A thorough characterization of the polymeric matrix before and after the degradation process should be carried out to better understand the developing metabolic

pathways, as well as the evaluation of operating conditions influence. The nature and amount of undesired final products, such as microbio-plastics, should be evaluated. Given the wide variety of starch-based items commercialized, a systematic assessment of their behaviour is needed and can be only pursued by increasing the existing literature on the topic.

In the present study, commercial disposable Mater-Bi® items were tested in terms of their biodegradation profile under thermophilic and mesophilic anaerobic mono-digestion conditions. The objective was to investigate the maximum biodegradation potential of the materials under ideal testing conditions in terms of strictly anaerobic environment, homogeneity of feed material composition and mixing conditions, as well as control of the operating parameters (temperature, initial F/M ratio). Further insights into the influence of treatment time on biodegradability were also derived. To this aim, batch conditions were adopted as they are typically used to assess the biodegradability of a variety of substrates through specific test protocols (see e.g. [34]). An attempt was also made at relating the biodegradability degree and the associated rate to the degradation conditions and the materials properties, in order to derive potentially useful suggestions about the treatability of starch-based bioplastics through anaerobic digestion. Different physical, chemical and morphological characterizations were performed prior and after degradation in order to provide a thorough view of the anaerobic biodegradation of the materials of concern.

2. Materials and methods

2.1. Feedstock materials

Three disposable Mater-Bi® (MB) tableware items (two cups and one knife) were selected among the ones available in supermarkets and compliant with the EN 13432 standard (EN 13432:2008) (Table 1). The cups (MB1 and MB3) were manually cut into 1.5 × 1.5 cm squares, removing the edges and the bottom to ensure test material homogeneity in terms of thickness. The knife (MB2) was broken into sticks of 0.5 × 2 cm. In addition, MB1 and MB2 were also tested in powdered form (<0.1 cm, assessed through sieving), after mechanical grinding with a knife shredder using dry ice to prevent material softening and particle sticking effects. MB1 and MB3 were the same type of cup produced by the same manufacturer but were found to have different chemical structures and blend compositions and were therefore dealt with as different samples. Anaerobic sludge was collected at a full-scale mesophilic anaerobic digestion plant treating a mixture of organic residues from food industries, and was used as inoculum. The sludge was sieved at 0.84 mm to remove the coarser fraction (fibers and inorganic particles) and stored at –15 °C until the time of testing in order to ensure using homogeneous inoculum samples. Preliminary microbiological analyses conducted on the sludge detected the prevalence of acetoclastic methanogens including *Methanosarcina* and *Methanoculleus*. The sludge was then defrosted at room conditions every time a new set of experimental trials was started. Calcium lactate (LACT; C₆H₁₀CaO₆·5 H₂O) was used as a positive control material. The main characteristics of the sludge and substrates are shown in Table 1.

2.2. Analytical methods

SEM (Mira3, Tescan) equipped with energy dispersive spectroscopy (EDS) (Octane Elect, EDAX) was used to perform the morphological analysis of bioplastic items. Differential scanning calorimetry (DSC) (Netzsch DSC 214 Polyma) analysis was carried out to measure the glass transition (T_g), melting (T_m) and crystallization (T_c) temperatures. The analysis was performed under a 40 mL/min N₂ gas flow in cycle ranges from –40 to 210 °C at a heating/cooling rate of 10 °C/min. The thermal degradation of the selected items was evaluated using a SetSys Evolution TGA/DSC (Setaram Instrumentation) thermogravimetric analyser with a temperature range up to 800 °C and a heating rate of 10 °C/min in an N₂

Table 1
Main characterization parameters of substrates and inoculum.

Material	Type of item	TS [%ww]	VS [%ww]	TOC [gC/kgTS]	Hydrogen [gH/kgTS]	Thickness [mm]	Theoretical biogas production [LCH ₄ /kgTOC] [LCO ₂ /kgTOC]	
Inoculum	—	6.4 ± 0.01	4.2 ± 0.01	29.1 ± 2.4	n.a.*	—	—	—
MB1	Cup	99.7 ± 0.04	67.1 ± 0.02	356.3 ± 0.9	38.3 ± 0.8	0.07	640	1227.8
MB2	Knife	99.2	97.5 ± 0.02	502.7 ± 1.1	55.8 ± 0.2	1.17	958	909.9
MB3	Cup	99.8 ± 0.04	69 ± 0.02	386.5 ± 1.2	45.4 ± 0.9	0.07	748.3	1119.6
Calcium lactate (LACT)	—	77.5 ± 0.28	42.3 ± 0.31	317.9 ± 1.1	45.8 ± 0.7	—	636.6	1231.3

*not analysed

atmosphere. Fourier-transform infrared (FT-IR) spectra were recorded with 256 scans in the mid infrared range (400–4000 cm⁻¹) at a resolution of 3 cm⁻¹. The analyses were carried out with a Vertex 70 spectrometer (Bruker Optik GmbH) equipped with a single reflection Diamond ATR cell. SEM, TG and FT-IR analyses were also performed on the final digestates and on the residual bioplastic fragments at the end of the degradation process. The concentrations of total solids (TS) and volatile solids (VS) were measured according to the Standard Methods for the Examination of Water and Wastewater (method 2540 G) [35]. Elemental analysis was performed using the dry combustion method with elemental analyzer CHN600 (Leco Instr.). The total organic carbon (TOC) and soluble organic carbon (DOC) concentration was measured using a Shimadzu TOC analyser equipped with modules for the analysis of both liquid and solid samples. DOC, volatile fatty acids (VFAs) and soluble carbohydrates were analyzed in the liquid phase after sample centrifugation at 5500 rpm for 15 min with IEC CL10 Centrifuge (Thermo Scientific) and subsequent filtration through a glass microfiber filter (1.2 µm pore size). Carbohydrates were determined with spectrophotometric analyses using the colorimetric phenol-sulphuric acid method using glucose as the standard [36]. The concentrations of VFAs (acetic [HAc], propionic [HPr], butyric + iso-butyric [HBu], valeric + iso-valeric [HVal], caproic + iso-caproic [HCa], heptanoic [HHp]) and ethanol (EtOH) were determined using a gas chromatograph (Model 3600 CX, VARIAN) equipped with a flame ionization detector and a 30 m capillary column (TRBWAX) with an inner diameter of 0.53 mm. The temperatures of the detector and the injector were 270 and 250 °C, respectively. The oven temperature was initially set at 60 °C, held for 3 min at this value, subsequently increased to 180 °C at a rate of 10 °C/min and finally increased to 220 °C at a rate of 30 °C/min and held for 2 min. The biogas produced during the tests was periodically sampled from the gasbags used for gas storage and analyzed to determine its main constituents. After each analysis, the gasbags were emptied with a vacuum pump and reconnected to the reactors. The measured biogas composition was assumed to be the average composition of the biogas volume produced over each sampling period. The biogas analysis was performed with a gas chromatograph (Model 3600 CX, VARIAN) equipped with a thermal conductivity detector and a 2-m stainless-steel packed column (ShinCarbon ST) with an inner diameter of 1 mm. The operating temperatures of the injector and detector were 100 and 130 °C, respectively, with He as the carrier gas. The oven temperature was initially set at 80 °C and subsequently increased to 100 °C at 2 °C/min.

All the analytical determinations were performed in triplicate at the beginning and at the end of the experiments.

Table 2

Experimental design. Test codes refer to substrate type, F/M ratio and material size (pow = powder) used. The mesophilic tests are indicated with the letter “m” at the end of the code. All runs were stopped according to the Holliger’s criterion, with the exception of runs with the code t₁, t₂ and t₃, which refer to runs with time sets, corresponding to 18, 25 and 32 days of testing, respectively.

Run	Substrate size [cm]	F/M [gVS _{substrate} /gVS _{inoculum}]	T [°C]
MB1_1mMB1_0.5MB1_1MB1_1pow	1.5 × 1.51.5 × 1.51.5 × 1.5 < 0.1	10.511	38555555
MB2_1mMB2_1_t1MB2_1_t2MB2_1_t3MB2_1MB2_1pow	1.5 × 1.51.5 × 1.51.5 × 1.51.5 × 1.51.5 × 1.5 < 0.1	111111	385555555555
MB3_0.5MB3_1_t1MB3_1_t2MB3_1_t3MB3_1	1.5 × 1.51.5 × 1.51.5 × 1.51.5 × 1.51.5 × 1.5	0.51111	5555555555
LACT_1	—	1	38/55

2.3. Anaerobic biodegradation tests

Anaerobic biodegradation assays were carried out using the Gas Endeavour® apparatus by Bioprocess Control. The 500 mL reactors equipped with overhead mechanical stirring and maintained in a thermostatic bath were filled with 400 g of inoculum and substrate mixture using F/M ratios of 0.5 or 1 g VS_{substrate}/g VS_{inoculum} (Table 2). These values for the F/M ratio were chosen according to the existing literature, where 1 is the usual choice and 0.5 is adopted for more recalcitrant wastes [37,38]. The reactors were then flushed with nitrogen to ensure anaerobic conditions and incubated in a thermostatic bath at the fixed temperature of 55 °C for thermophilic tests and of 38 °C for mesophilic tests. The evolved biogas volume was measured through a flow cell unit with a 10-mL accuracy coupled with each reactor and then conveyed and stored into the gasbags. The instrument was also equipped with sensors for room temperature and pressure measurement that were used to convert the evolved gas volume to standard temperature and pressure conditions (T = 273.15 K, p = 101 kPa). Blank tests were conducted to evaluate the residual biogas production of the inoculum. Positive control tests using calcium lactate were also conducted to assess both the activity of the inoculum and the validity of the experiment (for the sake of reference, according to ISO 14853 [39] a test is valid if the reference material’s biodegradation exceeds 70% within 60 days). The details of the experimental runs are reported in Table 2.

The tests were carried out in duplicate and were stopped according to Holliger et al. when the daily methane production during three consecutive days was below 1% of the accumulated volume of methane [40]. Runs MB2_1 and MB3_1 were also carried out at intermediate sets of time to investigate the process evolution at different stages of progress. Three additional reactors for each test were run in parallel and stopped respectively at day 18 (t₁), 25 (t₂) and 32 (t₃). These intervals correspond to the time needed for the biogas production rate to increase to 50% of the maximum value (R) (t₁), to reach R (t₂) and to get back down to 50% of R (t₃). The results were modeled with the Gompertz equation (Equation (1)):

$$P(t) = P_m \cdot \exp \left\{ - \exp \left[\frac{R^* e}{P_m} (\lambda - t) + 1 \right] \right\} \quad (1)$$

where $P(t)$ is the cumulative biogas production at time t , P_m is the maximum biogas production and λ indicates the lag phase duration. Modelling was performed using the average biogas production of duplicate experiments and the fitting was found to be highly accurate, with values for the correlation coefficient (R^2) higher than 0.99. The process kinetics was evaluated through a parameter, $t_{x\%}$, which

represents the time required to reach a predetermined percentage, $x\%$, of the maximum conversion yield into biogas (with $x\% = 10, 25, 50, 75$ or 95%). The degree of biodegradation was calculated using Equation (2) [41]:

$$\text{Biodegradation}(t) = \frac{P_{net}(t) + P_{ICnet}(t)}{P_{th}} \quad (2)$$

where $P_{net}(t)$ is the actual cumulative biogas production (net of blank) at time t , $P_{IC}(t)$ is the actual dissolved inorganic carbon (IC) (net of blank), P_{th} is the theoretical biogas production calculated according to the Buswell equation [42], which is widely used to predict the stoichiometric amount of biogas generated assuming full conversion of the original material. The Buswell equation was applied using the elemental analysis results (expressed on a dry basis) assuming that the bioplastic materials only contained carbon, hydrogen and oxygen. The oxygen content of the samples was calculated by difference after determination of the C and H contents (see data in Table 1).

Bioplastics disintegration was evaluated at the end of each test. According to the EN 13432 standard [43], disintegration is considered to be complete if a maximum of 10 wt% of the initial material is retained by a 2-mm sieve. Bioplastics disintegration was evaluated at the end of each test using a 0.84-mm sieve, as this was previously used for inoculum pre-treatment, thus adopting a stricter assessment condition. The plastic fragments retained were carefully rinsed with deionized water and then dried at 35 °C until constant weight.

3. Results and discussion

3.1. Bioplastics characterization

All the selected products were morphologically characterized by SEM, as shown in Fig. 1. The polymeric matrices appeared to be complex and heterogeneous, with inclusions of different geometries. The microstructure of MB1 and MB3 was similar and displayed a ductile behaviour, which might be attributed to a high concentration of ductile polyester components in the blend. MB2 showed a brittle fracture surface with a sea island structure, suggesting a limited miscibility between the components, which were likely PLA and PBAT, which is usually added to improve PLA ductility [44]. The EDS analysis performed on MB1 indicated the presence of significant amounts of Mg, Si and Ti. This might suggest that titanium-based additives were used, while the co-presence of Mg and Si suggests the addition of a talc filler. The same fillers were detected in MB3 (Fig. 1c), which also displayed a less compact structure. On the other hand, EDS analysis for MB2 mainly detected carbon and oxygen, and this could mean that a lower content of additives was blended in the matrix and that the clearly visible fibers in Fig. 1b had a lignocellulosic nature.

Table 3 shows the DSC analysis results for the tested materials. No significant difference in the thermal behaviour of MB1 and MB3 was observed. During the first heating of the three samples a T_g of around 56–60 °C and a T_m in the range 163.7–169.7 °C were observed, which

Table 3

Thermal properties of the bioplastic samples obtained by DSC analysis.

	T_g [°C]	T_{cc} [°C]	T_m [°C]	ΔH_{cc} [J/g]	ΔH_m [J/g]
MB1	57	–	112.4; 168.6	–	23.7; 8.1
MB2	58.6	–	169.7	–	31.9
MB3	55.1	–	114.7; 163.7	–	27.2; 10.8

are typical of polylactic acid (PLA) polymers, which was likely used as a component in the blends. The starch melting peak is usually in the range 150–175 °C and a superimposition of the thermal response of starch and PLA is hypothesized [10,45]. A second melting peak at 112.4 and 114.7 °C was observed for MB1 and MB3, respectively, which can be attributed to PBS [46].

The FT-IR spectra are reported in Fig. 2. The typical polylactic acid (PLA) absorption bands can be observed in all spectra [47], however with a higher intensity for MB2, as demonstrated by the bands at 1758 and 1645 cm^{-1} ($\nu C=O$). At 1387 and 1357 cm^{-1} CH_3 deformation and asymmetric bending and C- CH_3 stretching (also detected at 1043 cm^{-1}) are visible. At 1268 cm^{-1} the -C-O-C stretching and CH bending modes were identified. C-O stretching of PLA was detected at 1180 and 1086 cm^{-1} . Characteristics C-O stretching (C-O-C and C-O-H) of starch at 1150–950 cm^{-1} were not detectable due to the superimposition with PLA absorption bands. The MB2 spectrum showed some minor bands that were assigned to poly(butylene adipate-co-terephthalate) (PBAT), which is used as co-polyester in the blend for mechanical purposes. Some of the bands commonly associated to PBAT were identified at 1717 cm^{-1} (C=O of the ester linkage) and 1453 cm^{-1} ($\nu C=C$ phenylene group) [48]; band at 1270 cm^{-1} may be associated to C-O asymmetric stretching, while bands at 870 and 729 cm^{-1} were associated to the out-of-plane bending vibration of the phenylene ring [49]. The presence of stearamide, a nucleating agent of PLA commonly used in Mater-Bi®, was associated to some additional absorption bands (3393, 3186, 2923, 2850 and 1648 cm^{-1}) [50]. In the MB1 and MB3 spectra, along with the PLA bands, absorptions commonly associated to Poly(butylene succinate) (PBS) were observed.

The asymmetric stretching of the -CH- groups was identified in the range 3000–2800 cm^{-1} and the corresponding symmetrical vibration was found at 1335 cm^{-1} [49]. The band at 1713 cm^{-1} is imputable to the carbonyl stretching (C=O) of the polymer's crystalline domain [49,51,52]. The bands at 1157 cm^{-1} and 953 cm^{-1} correspond to the -C-O-C- stretching of the ester bonds and to the -C-OH bending at the terminal acid groups, respectively [49]. Some additional bands were detected in the MB1 and MB3 spectra at 3675, 1006 and 667 cm^{-1} , which were ascribed respectively to O-H group, Si-O stretching and Si-O-Si bending of talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) [53] and confirmed what already observed from the EDS results. From the thermal degradation curves it was confirmed that the polymeric matrix of the products had two main constituents (Fig. 3b). The dTG first peak was attributed to starch and PLA degradation, which displayed a T_{peak} of 336 and 339 °C for MB1 and MB3, respectively (see values reported in Table 4). The higher T_{peak} associated with the first degradation step of MB2 (357 °C)

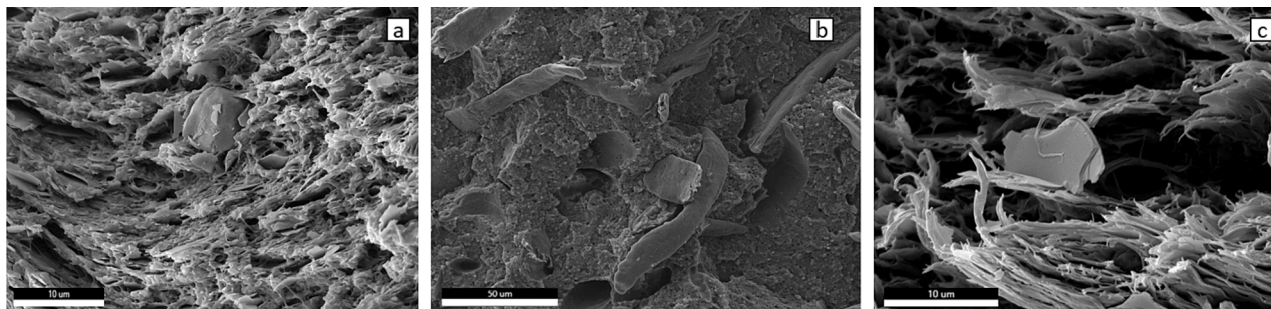


Fig. 1. SEM micrographs of a) MB1, b) MB2 and c) MB3.

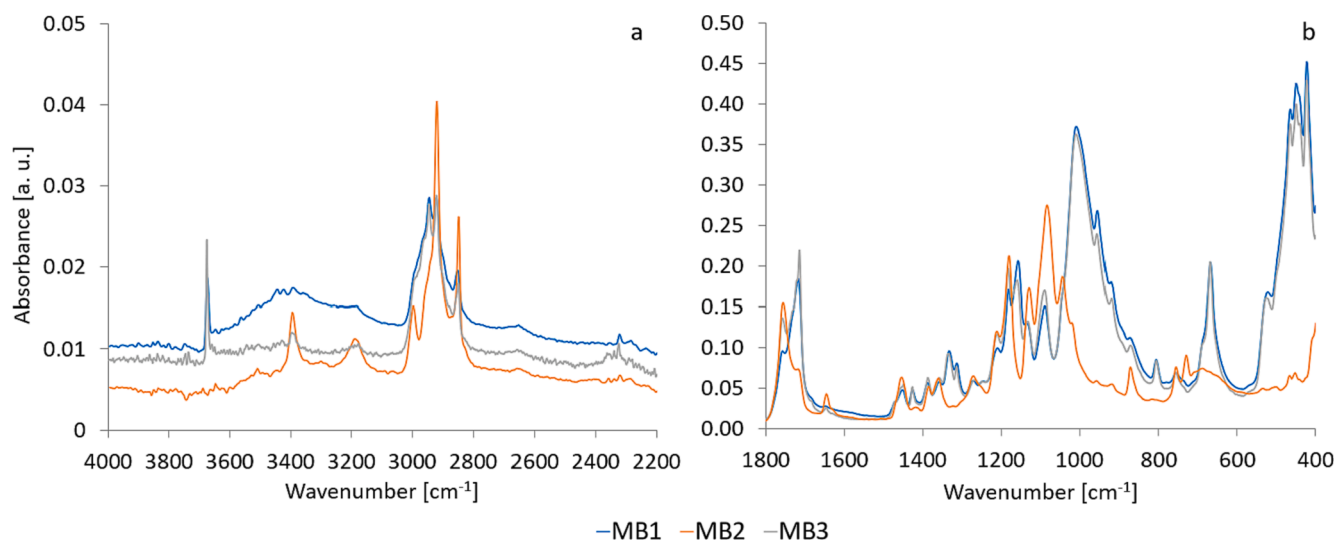


Fig. 2. FT-IR spectra of the tested materials.

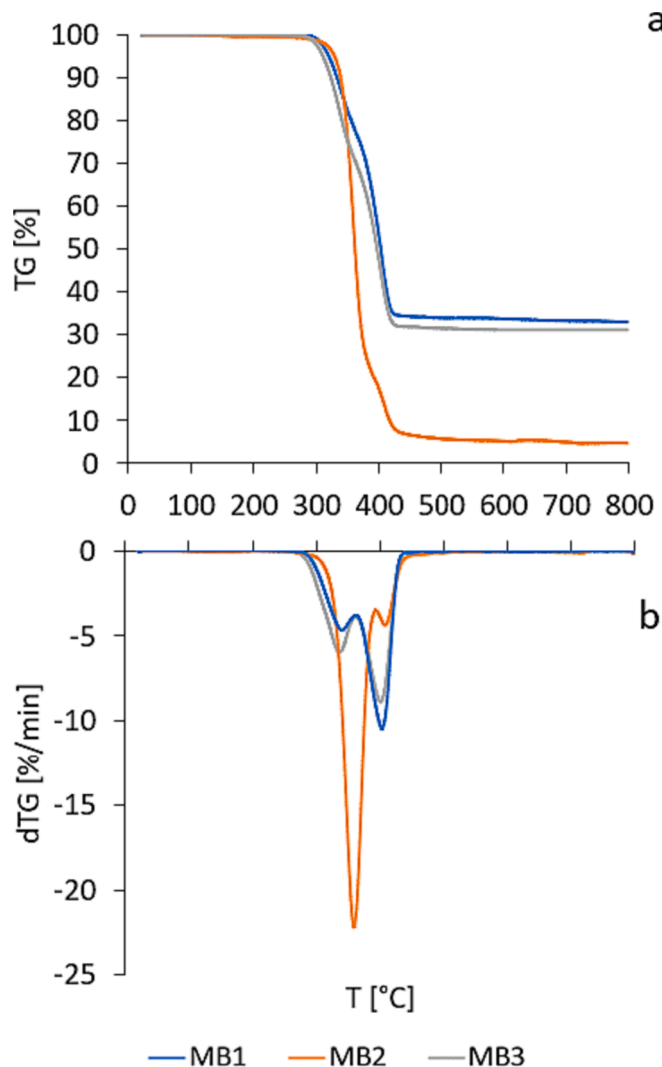


Fig. 3. Thermal analysis of the tested materials: a) TG and b) dTG.

a

Table 4

Onset temperature (T_0), maximum degradation temperature (T_{peak}) and residual mass for each tested material.

	T_0 [°C] *	T_{peak} [°C]	Residue [%]
MB1	329	339; 403	33
MB2	320	357; 408	4.7
MB3	310	336; 402	31.2

* Temperature value corresponding to a 5% mass loss

could have derived from the overlapping of starch and the compatibilising agent previously detected by infrared analysis, or from the interpenetrating networks formed by starch with the aliphatic polyester [54]. The second peak could be ascribed to the co-polyesters presence in each blend, which included PBAT and PBS for the knife and the cups, respectively [55–57]. Starch/PLA was a predominant component in MB2, moreover the lignocellulosic fibers could also have contributed to the first thermal degradation peak. From the comparison of MB1 and MB3, a change in the intensity of both peaks was observed (Fig. 3b): the second cup had a higher starch content and a lower polyester content compared to the other material.

This suggests a higher biodegradability potential of the new product. Moreover, the residual weight at the end of the thermal analysis tests for the Mater-Bi® samples was equal to 33%, 5% and 31% for MB1, MB2 and MB3, respectively (see Table 4), and this appeared to confirm the hypothesis that the additives in the cups had a more recalcitrant nature.

3.2. Biochemical methane potential (BMP) tests

The results of the biodegradation assays were evaluated in terms of the time evolution of bioplastics conversion into biogas during the tests, as well as total cumulative biogas yield attained. It should be mentioned that the biodegradation tests were found to display a very high replicability, with standard errors always below 5% of the calculated average values.

The activity of the inoculum used was testified by the fact that the positive control test showed no lag time in biogas production, indicating the absence of inhibiting effects of the inoculum storage method before testing. The calcium lactate used as the positive control material displayed a degradation yield of ~ 87% in 26 days under thermophilic conditions (biogas production 1016 ± 30 mL/gVS) and in 50 days under mesophilic conditions (982.4 ± 5 mL/gVS), confirming the reliability of the degradation tests performed on account of the fact that biodegradation was considerably larger than the threshold of 70%. Under

mesophilic conditions, the net biogas production for MB1 and MB2 was 130.6 ± 2.2 and 184.7 ± 4.3 mL/gTOC_{MB}, respectively, which corresponds to biodegradation degrees as low as 7 and 10%. Material disintegration was around 2% for the cups and 4% for the knives. It was concluded that mesophilic conditions did not promote degradation, therefore the corresponding tests results are not shown and the following data refer to thermophilic test conditions only. In order to compare the different materials tested, the experimental data were reported per unit of initial TOC of the feed material (MB). In particular, Fig. 4 shows the specific volume of evolved biogas for the different samples, while Fig. 6 reports the associated $t_{x\%}$ values derived from fitting of the cumulative biogas production.

In accordance to the criterion defined by Holliger et al. [40] on the basis of which a test is stopped once the residual methane production falls below 1% of the total cumulative biogas recorder for three consecutive days, the total duration of the thermophilic biodegradation tests for the different samples was found to lie in the range 40–48 days, with the only exception of MB2_1, which continued until day 60. While the above mentioned criterion may lead to an underestimation of the biogas production potential if a small residual biogas generation occurs for prolonged periods, we meant to overcome this issue by extrapolating the asymptotic value of the biogas production curves on the basis of a theoretical growth function. The Gompertz formulation, modified to describe a two-stage degradation process due to the presence of components with different biodegradation kinetics in the bioplastic blend, was found to adequately describe the experimental data, as indicated by the high R^2 values estimated from the fitting procedure (see Table 5).

The methane content was $59.0\% \pm 0.8\%$ (MB1), $56.5\% \pm 0.2\%$ (MB2) and $56.8\% \pm 1.3\%$ (MB3) of the total cumulative biogas production for the different runs. When adding up the amount of CO₂ dissolved in the liquid phase to the overall biogas volume, the contribution of methane to the total biogas generated was calculated to fall in the ranges $34.8\% \pm 5.1\%$ (MB1), $48.7\% \pm 0.6\%$ (MB2) and $43.5\% \pm 5.3\%$ (MB3). These values are in close agreement with the theoretical contributions calculated from the Buswell equation, which were calculated to be 34.3% (MB1), 51.3% (MB2) and 40.1% (MB3). On the other hand, the degree of biodegradation attained using Equation (2) was in the ranges 40–60% for cups (MB1, MB3) and 66–74% for the knife (MB2) (Fig. 6), suggesting that the blend composition was a limiting factor for products degradation, especially for the cups. The material disintegration at the end of the tests was in the range 31–42% for MB1 and MB3 and 95% for MB2. The runs on MB1 and MB3 (cups) compared in Fig. 4a show that MB3 attained a 25–30% higher biogas yield as predicted based on its composition. Furthermore, decreasing the F/M ratio from 1 to 0.5 appeared to result in an increase in biogas production, although the improvement attained was relatively limited (12% increase for MB1

and 18% increase for MB3). While exploring the influence of the F/M ratio on bioplastic biodegradation was not the aim of the present study, it is worth emphasizing that previous studies on PLA and PHB bioplastics revealed that lower F/M ratios had mainly an influence on accelerating the kinetics of the biodegradation process rather than on enhancing the ultimate methane yield [58]. In addition to that, we mention that F/M ratios in the range 0.5–1.0 are commonly adopted in batch BMP tests, with F/M ratios close to the lower limit of this range having been reported to be more suitable for recalcitrant substrates [59]. Particle size did not apparently affect the biodegradation degree, whereas it was found to reflect on the degradation rate. In this regard, the powdered MB1 sample displayed faster degradation kinetics particularly during the initial stages of the process, with a decrease by $\sim 10\%$ in the $t_{25\%}$ and $t_{50\%}$ values from those of 1.5-cm square MB1 particles (see Fig. 5). However, the differences in the degradation rate between the two samples tended to decrease gradually as biodegradation proceeded, so that the $t_{95\%}$ value was similar for the square and the powdered MB1 particles. This indicates that, while reducing the initial MB particle size was capable of accelerating the degradation process (as also reported previously [60]) likely by promoting biomass accessibility to the substrate, the biodegradation process was comparable in both cases irrespective of whether powdering was performed.

MB2 biogas production was twice the one observed for MB1 (Fig. 4b). This clearly depends on the specific chemical formulation of the two blends, which could affect the bioavailability of organic carbon and inhibit its degradation to different extents. Indeed, as previously determined, starch/PLA was the predominant component of the polymer matrix in MB2. Material pulverization was particularly effective for MB2, where an increase in both biogas production (13%) and an acceleration of the process kinetics (20% decrease of $t_{95\%}$) was recorded, likely due to the influence of particle thickness on the degradation process. However, runs MB2_1 and MB2_1pow displayed the highest values of $t_{95\%}$, which may have been caused by the lignocellulosic fibers embedded in the matrix.

The results of the experimental runs at different degradation times are shown in Fig. 7. In such tests, both the biodegradation and the disintegration degree were measured over time. The biological alteration of the material was not evident until day 18, increased thereafter to 7–9% at day 25, and attained 37% for MB2 and 22% for MB3 at day 32. The disintegration degree of MB2_1_t2 was over 55%; unfortunately, for the MB2_1_t3 and MB3_1_t3 runs it was not possible to retrieve information about the disintegration degree due to operational problems encountered during the corresponding digestion tests.

In addition, a mass balance of carbon was carried out to track the fate of the organic matter at intermediate stages (t_1 , t_2 and t_3) and at the end of the process (Fig. 8). The following contributions to the overall amount

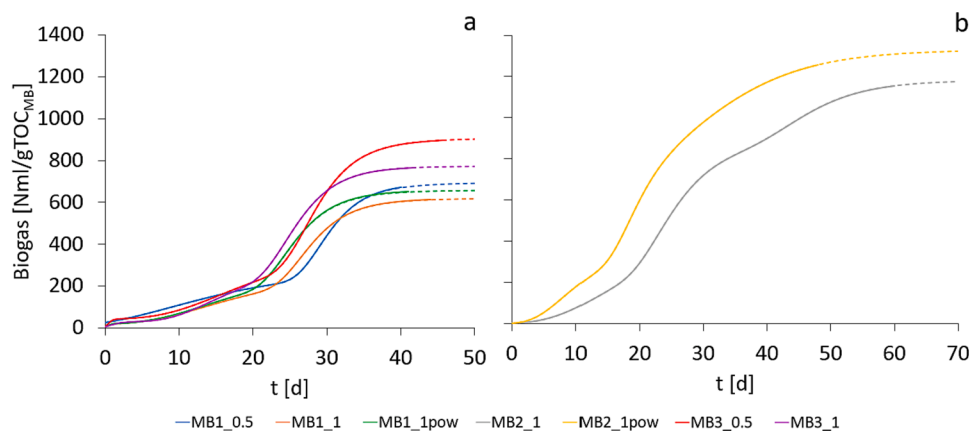


Fig. 4. Specific biogas production for thermophilic runs. Comparison among MB1 and MB3 tests at different F/M ratios and material sizes (a) and MB2 at different material sizes (b). The dashed lines indicate Gompertz interpolation projection beyond the test duration.

Table 5

Measured net biogas production (average value \pm standard deviation) at the end of the thermophilic biodegradation tests and parameters (average values) of the Gompertz fitting curves for biogas production.

Run	P_{net} (mL/gTOC)	P_{ICnet} (mL/gTOC)	P_m (mL/gTOC)	λ (d)		R (mL/gTOC/d)		R^2
				Stage 1	Stage 2	Stage 1	Stage 2	
MB1_0.5	593.6 \pm 12.0	512.4 \pm 17.6	698.1 \pm 7.0	0.0	25.8	9.5	50.0	0.997
MB1_1	562.3 \pm 17.2	251.9 \pm 55.7	621.7 \pm 3.4	3.2	23.5	10.0	41.3	0.998
MB1_1pow	611.0 \pm 5.8	184.0 \pm 16.2	659.7 \pm 6.2	3.8	20.9	11.4	44.9	0.998
MB2_1	1126.6 \pm 13.8	95.1 \pm 28.3	1181.3 \pm 15.1	5.4	20.2	23.2	28.5	0.999
MB2_1pow	1232.1 \pm 1.4	149.6 \pm 26.6	1330.2 \pm 4.2	3.5	11.3	31.1	54.6	0.997
MB3_0.5	848.3 \pm 7.2	255.7 \pm 5.8	907.7 \pm 5.6	3.0	23.6	13.1	57.9	0.999
MB3_1	749.6 \pm 16.2	0.4 \pm 0.1	772.7 \pm 17.2	5.9	21.3	15.5	49.0	0.999

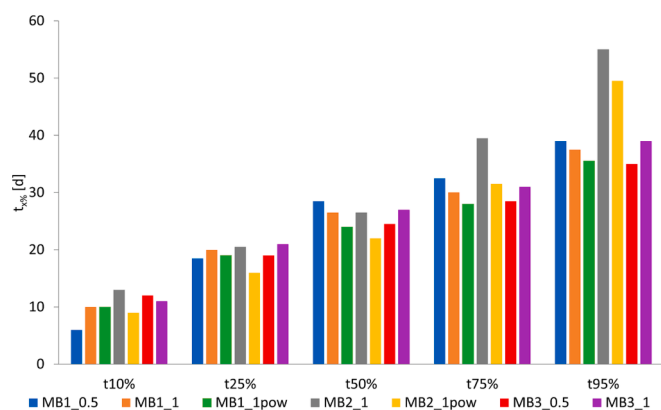


Fig. 5. Evolution of the $t_{x\%}$ parameter during the biodegradation process for the thermophilic experimental runs.

of carbon were considered: i) gasified carbon, as the sum of carbon in the evolved CO_2 (including the fraction dissolved in the liquid phase) and CH_4 ; ii) residual particulate carbon, obtained as the difference between the final TOC and DOC masses; iii) dissolved carbon in the form of undegraded carbohydrates and VFAs; iv) residual dissolved carbon, obtained as the difference between total DOC and the directly determined metabolic products (iii). A term referred to as “balance” was added to account for the carbon mass lost due to analytical inaccuracies or to sample heterogeneity in order to close the material balance. The values for the balance term ranged from -1 to 11% indicating a good degree of carbon recovery from the different analytical determinations for most of the runs, with the exception of MB2_1_t2 and MB3_1_t2. The presence of a considerable amount of non-degraded bioplastics in the

samples led to some interferences during the analytical measurement, and it was not always possible to accurately determine the TOC contribution. At time t_1 a reduction of particulate (13 and 17%) and residual dissolved carbon (17 and 29%) was observed; the sum of these two contributions was found to be mainly (65 and 58%) converted into VFAs, while gas production was still minor and comparable to that observed for the blank test. This indicates that the active biomass until time t_1 was mainly composed of hydrolytic and acidogenic microorganisms. In the subsequent biodegradation stages, particulate and dissolved carbon consumption proceeded along with VFA conversion, while the contribution of gas production increased as expected.

3.3. Digestate characterization

SEM analyses were conducted on the digestate samples taken at the end of the biodegradation tests in an attempt to determine the presence of residual microbioplastics. No residues were detected for the experimental runs MB2_1 and MB2_1powder, while it was possible to identify MB1 and MB3 particles in the respective digestate samples. In Fig. 9 the SEM results for sample MB1_1 at the end of the digestion process are shown as an example. Bioplastic particles down to $80\ \mu m$ were detected (Fig. 9a and b) that could easily be distinguished from the surrounding matrix due to their irregular edges and layering (Fig. 9c).

Moreover, the release of additives from the matrix resulting from material's surface erosion was observed (Fig. 9d). EDS analysis confirmed the presence of Mg and Si in such particles. Final digestates thermogravimetric analyses results are shown in Fig. 10. The peaks in the range $50\text{--}150\ ^\circ C$ are attributed to dehydration processes, as observed by other authors [61–63]. The inoculum response is shown for comparison in all the figures, and it is mainly composed of three degradation steps: (i) the first peak at $300\ ^\circ C$ corresponds to the thermal degradation of carbohydrates, of cellulose and hemicellulose [61]; (ii) at

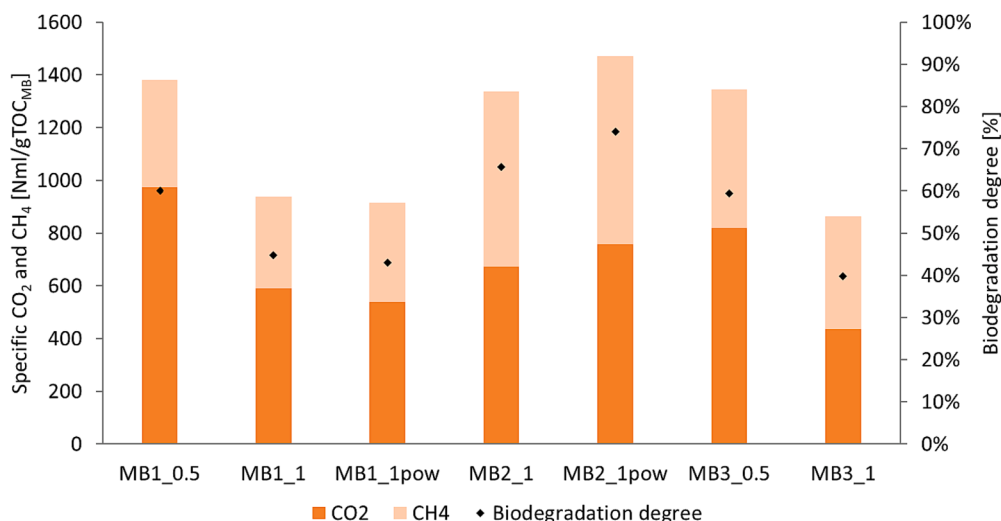


Fig. 6. Biogas composition (including IC contribution) and biodegradation degree for the experimental runs.

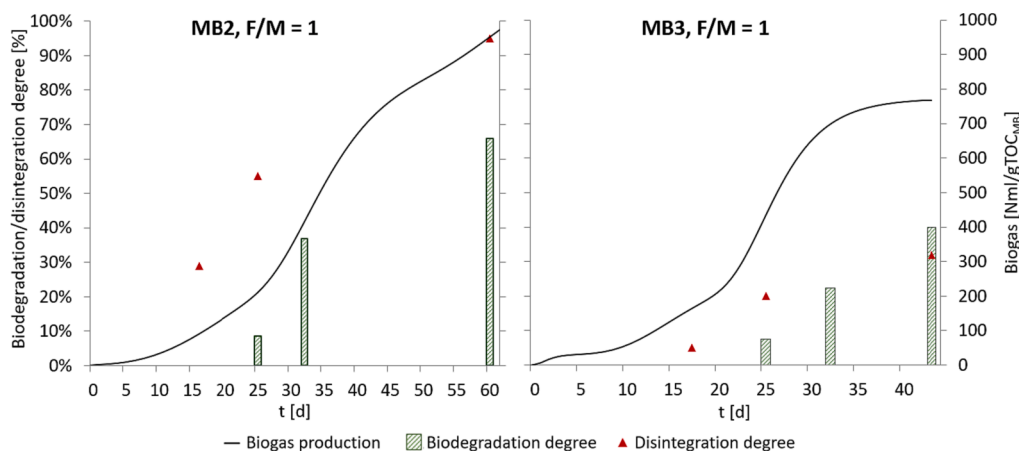


Fig. 7. Biogas production, biodegradation and disintegration degrees for the experimental runs with set of times.

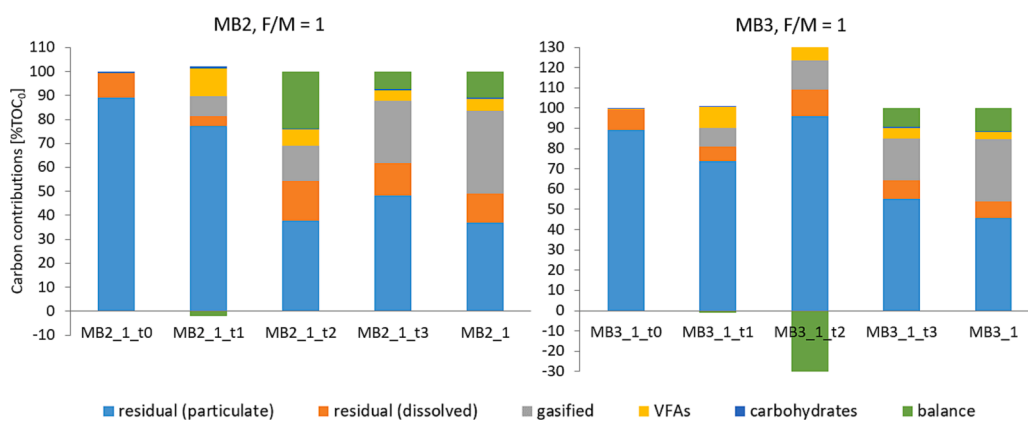


Fig. 8. Carbon mass balance for the experimental runs.

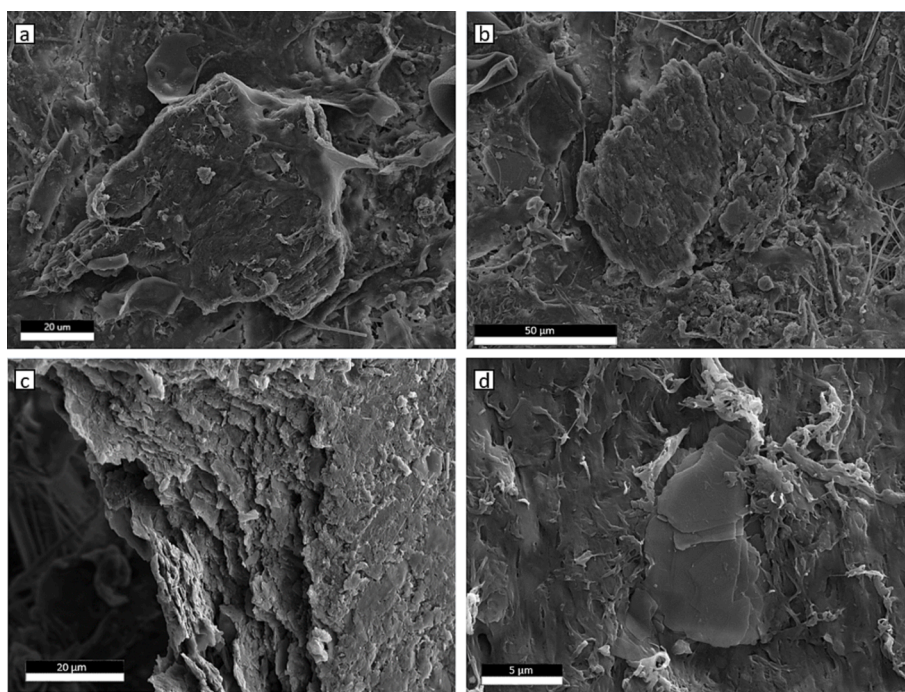


Fig. 9. A) and b) mb1 microplastics detected in the digestate; c) mb1 microplastic layering; d) surface of mb1 fragment showing an embedded particle.

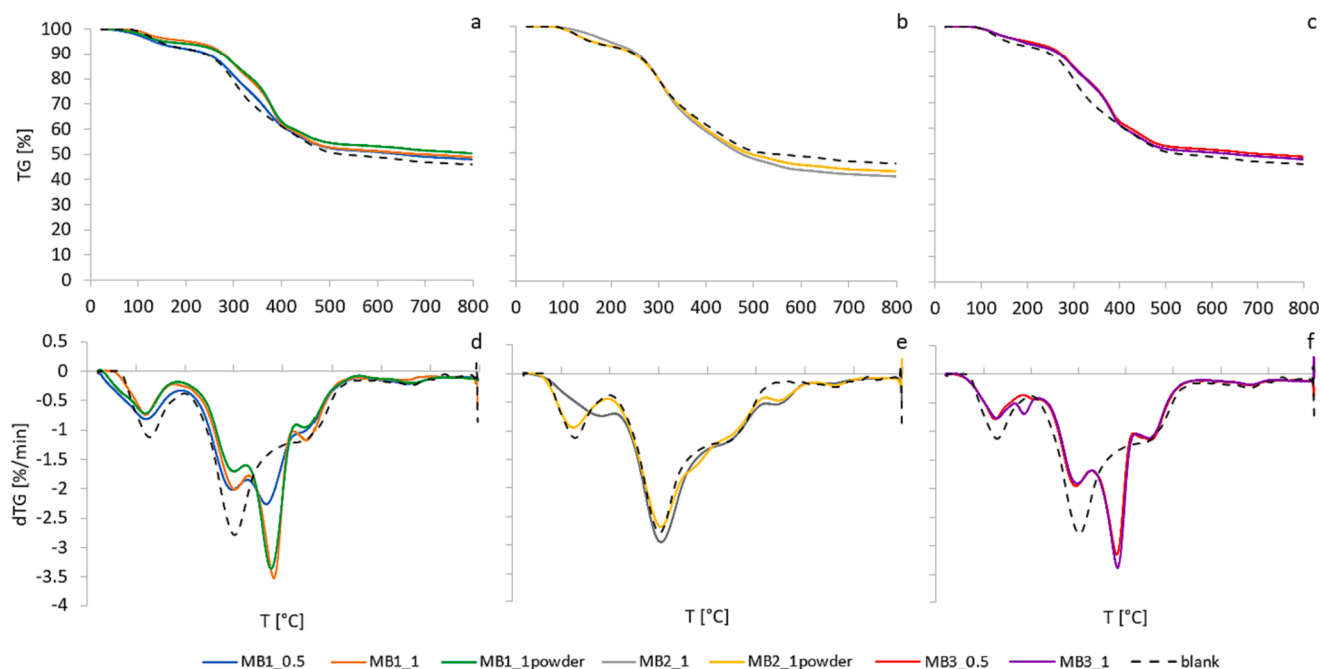


Fig. 10. TG (a, b and c) and dTG (d, e and f) results for the final digestates from runs on MB1, MB2 and MB3.

400–520 °C the thermal degradation of the aromatic structures occurs and (iii) the last peak in the 695–750 °C range is due to thermal degradation of inorganic material [63].

From the dTG results for the tests on MB1 and MB3, the peak associated to the starch/PLA component in the product was no longer detectable, suggesting that it was completely degraded (Fig. 10d and f). The peak attributed to PBS, instead, appeared to be shifted to the left (T_{peak} 380 °C), probably suggesting a worsening of the thermal capacity of the polyester phase. The intensity of this peak was not affected by

material pulverization, which confirms what was observed with the BMP tests. The thermal response of the MB2_1 and MB2_1powder samples was found to be mainly dictated by the inoculum, with the exception of a peak observed on the dTG curves at around 550 °C that was not observed for the other samples and was probably related to the thermal decomposition of some residual undegraded component of the original polymeric blend.

Additional TG and FT-IR analyses were conducted on the bioplastic fragments retrieved during the determination of material mass loss. The

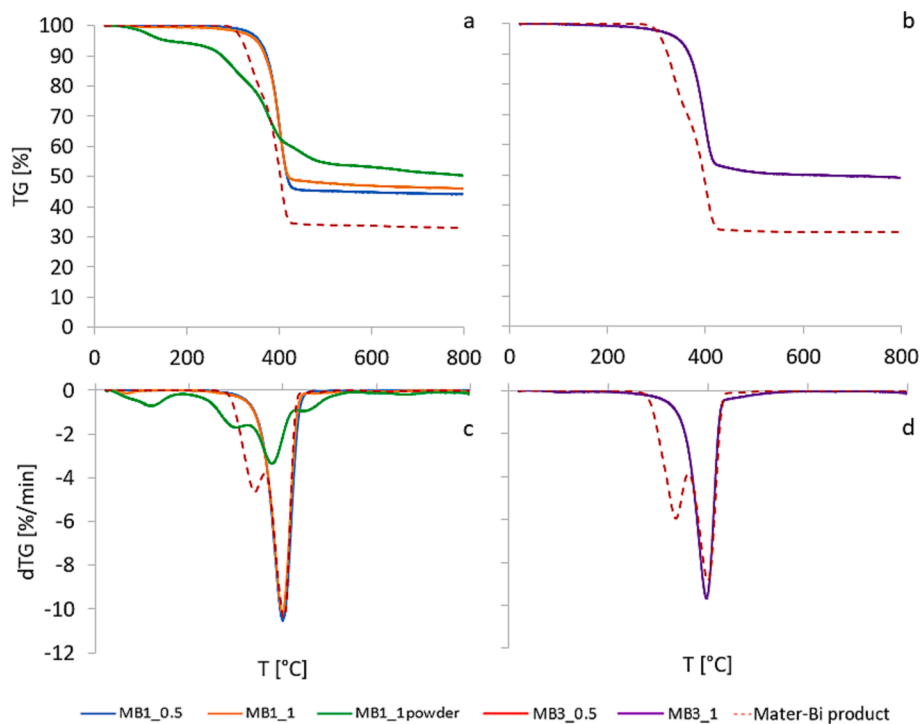


Fig. 11. TG (a, b) and dTG (c, d) results for MB1 and MB3 fragments retained with a 0.84 mm sieve from the digestate at the end of the tests; results are compared to the neat Mater-Bi® product.

TG analysis was carried out on the MB1 and MB3 fragments (size > 0.84 mm) recovered after the degradation process (Fig. 11). The starch/PLA component was found to have been fully degraded during the BMP tests, so that the corresponding peak on the dTG curve was no longer visible (Fig. 11c and d) and the fragments had a higher residual weight compared to the original product (Fig. 11a and b). The peak at 400 °C was still visible for all the recovered fragments with an intensity that was comparable to the neat product. The run MB1 powder displayed a different response that was attributed to a higher contamination of the sample by the inoculum at the time of testing, since in this case it was not possible to clean the material properly from microbial incrustations.

The FT-IR analyses carried out on the final digestates are shown in Fig. 12 in the wavenumber range between 1800 and 400 cm^{-1} , where the main absorption bands were detected. Runs on the MB2 sample did not show any characteristic peak of the original bioplastic, confirming that the undegraded portion of the material likely had a lignocellulosic nature that could not be distinguished from the composition of the inoculum (Fig. 12b). Runs on the MB1 and MB3 samples, which displayed a consistent residual portion of the initial bioplastic mass at the end of the test (69–58 wt%), still showed the characteristics absorption band of the original polymeric matrix. However, the bands at 1757 cm^{-1} , 1134 cm^{-1} , 1088 cm^{-1} and 755 cm^{-1} were no longer visible (Fig. 12a and c), confirming the degradation of the associated PLA component. A decrease in the intensity of the band at 1713 cm^{-1} , which was associated to PBS, was observed, as also previously indicated by other authors [64]. Upon inspection of the MB2 spectrum, no bands associated to the co-polyester could be detected, suggesting that PBAT was degraded probably as a consequence of its lower concentration in the polymeric matrix.

4. Conclusions

The anaerobic degradation of three Mater-Bi® disposable items (cups and knife) was assessed under thermophilic and mesophilic conditions. At 38 °C the material was found to be strongly recalcitrant to degradation and the biogas production of the test was comparable to the blank; the disintegration of the material was lower than 4%. All the experimental runs under thermophilic conditions attained a biogas production in the range 332–425 mL/gTOC_{MB} within 48 days, with the exception of MB2 which carried on until day 60. Material biodegradation and disintegration was mainly influenced by the chemical composition of the products, which were a blend of starch, polyesters (mainly PLA, PBAT and PBS) and organic/inorganic additives. MB cups had a high content of PBS and inorganic additives that limited both biodegradation (40–60%) and disintegration (40%). On the other hand, the biodegradation of the knife product, mainly composed of PLA, was ~70%. The characterization of the final digestates with

thermogravimetric and spectroscopic analyses helped drawing further considerations on bioplastics degradation. The PBS component was found to be particularly recalcitrant to microbial assimilation. The findings of this study emphasize the need for more detailed investigation of the bioplastics behaviour during biological treatments and, in particular, the need to understand the correlation between the process results and the products composition. In particular, the biodegradation profile under full-scale anaerobic digestion conditions should be explored more systematically in order to assess the treatability of bioplastic residues in waste management plants. To this regard, since bioplastic waste is expected to be collected together with the OFMSW (at least in short- to medium-term scenarios), the conditions under which the combined treatment of these two streams can be successful are yet to be assessed. A careful evaluation of the technological limitations of existing treatment facilities needs to be carried out to determine if specific operating strategies (e.g. recirculation of non-degraded bioplastics, dedicated pre-treatment, combination of anaerobic and aerobic treatment), can be implemented. Although the present study was based on batch biodegradation tests which do not entirely reflect the performance of full-scale anaerobic digestion, the results can still be interpreted in the sense that the investigated bioplastic materials, particularly under specific conditions (average digestion times, mesophilic regime), pose critical issues with regard to their expected biodegradability. In particular, on the basis of the observed biodegradation kinetics, the time required to reach a satisfactory biodegradation of the investigated bioplastics is not compatible with the typical residence time used in full-scale plants and this could lead to the contamination of the final products (compost and digestate), which could in turn be a carrier of residual bioplastics in the environment.

CRedit authorship contribution statement

Maria Paola Bracciale: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Giorgia De Gioannis:** Writing – review & editing, Methodology, Conceptualization. **Marica Falzarano:** Conceptualization, Methodology, Investigation, Data curation, Writing – review & editing, Writing – original draft. **Aldo Muntoni:** Writing – review & editing, Methodology, Conceptualization. **Alessandra Poletti:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Data curation, Conceptualization. **Raffaella Pomi:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Conceptualization. **Andreina Rossi:** . **Fabrizio Sarasini:** . **Jacopo Tirillo:** Writing – review & editing, Methodology, Investigation, Data curation, Conceptualization. **Tatiana Zonfa:** Methodology, Writing – review & editing.

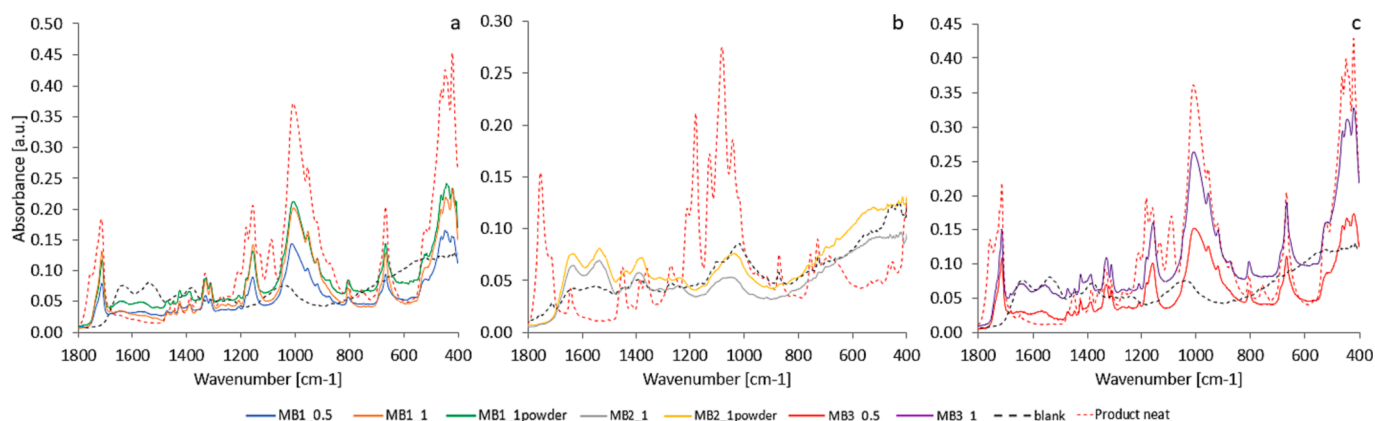


Fig. 12. FT-IR analysis of final digestates: runs with a) MB1, b) MB2 and c) MB3, compared with the spectra of blank test and of the respective neat Mater-Bi® product.

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.

References

- Nandakumar A, Chuah JA, Sudesh K. Bioplastics: A boon or bane? *Renew Sustain Energy Rev* 2021;147:111237. <https://doi.org/10.1016/j.rser.2021.111237>.
- Plastics Europe. Bioplastic Market Development Update 2020 2022.
- Compostatori CI, Centemero CICM, Compostabile M, Compostabile MN. Studio CIC - COREPLA 2020 : triplicano le bioplastiche compostabili nella raccolta dell' organico 2020.
- Calabrò PS, Grosso M. Bioplastics and waste management. *Waste Manag* 2018;78: 800–1. <https://doi.org/10.1016/j.wasman.2018.06.054>.
- Folino A, Pangallo D, Calabrò PS. Assessing bioplastics biodegradability by standard and research methods: Current trends and open issues. *J Environ Chem Eng* 2023;11. <https://doi.org/10.1016/j.jece.2023.109424>.
- Zdanowicz M. Starch treatment with deep eutectic solvents, ionic liquids and glycerol. A comparative study. *Carbohydr Polym* 2020;229:115574. <https://doi.org/10.1016/j.carbpol.2019.115574>.
- Jumaidin R, Mohd Zainel SN, Sapuan SM. Processing of thermoplastic starch. *Adv Process Prop Appl Starch Other Bio-Based Polym* 2020:11–9. <https://doi.org/10.1016/B978-0-12-819661-8.00002-0>.
- Ju Q, Tang Z, Shi H, Zhu Y, Shen Y, Wang T. Thermoplastic starch based blends as a highly renewable filament for fused deposition modeling 3D printing. *Int J Biol Macromol* 2022;219:175–84. <https://doi.org/10.1016/j.jbiomac.2022.07.232>.
- Bortolatto R, Bittencourt PRS, Yamashita F. Biodegradable starch / polyvinyl alcohol composites produced by thermoplastic injection containing cellulose extracted from soybean hulls (Glycine max L.). *Ind Crops Prod* 2022;176:114383. <https://doi.org/10.1016/j.indcrop.2021.114383>.
- Hejna A, Barczewski M, Kosmela P, Mysiukiewicz O, Aniśko J, Sulima P, et al. The impact of thermomechanical and chemical treatment of waste Brewers' spent grain and soil biodegradation of sustainable Mater-Bi-Based biocomposites. *Waste Manag* 2022;154:260–71. <https://doi.org/10.1016/j.wasman.2022.10.007>.
- Souza AC, Benze R, Ferrão ES, Ditchfield C, Coelho ACV, Tadini CC. Cassava starch biodegradable films: Influence of glycerol and clay nanoparticles content on tensile and barrier properties and glass transition temperature. *LWT - Food Sci Technol* 2012;46:110–7. <https://doi.org/10.1016/j.lwt.2011.10.018>.
- Oleyaei SA, Zahedi Y, Ghanbarzadeh B, Moayedi AA. Modification of physicochemical and thermal properties of starch films by incorporation of TiO2 nanoparticles. *Int J Biol Macromol* 2016;89:256–64. <https://doi.org/10.1016/j.jbiomac.2016.04.078>.
- Aldas M, Ferri JM, Lopez-Martinez J, Samper MD, Arrieta MP. Effect of pine resin derivatives on the structural, thermal, and mechanical properties of mater-bi type bioplastic. *J Appl Polym Sci* 2019;137:48236. <https://doi.org/10.1002/app.48236>.
- Agarwal S. Major factors affecting the characteristics of starch based biopolymer films. *Eur Polym J* 2021;160:110788. <https://doi.org/10.1016/j.eurpolymj.2021.110788>.
- Quecholac-Piña X, Hernández-Berriel M del C, Mañón-Salas M del C, Espinosa-Valdemar RM, Vázquez-Morillas A. Degradation of plastics under anaerobic conditions: a short review. *Polymers (Basel)* 2020;12:109. <https://doi.org/10.3390/polym12010109>.
- Cazaudehore G, Guyoneaud R, Evon P, Martin-Closas L, Pelacho AM, Raynaud C, et al. Can anaerobic digestion be a suitable end-of-life scenario for biodegradable plastics? A critical review of the current situation, hurdles, and challenges. *Biotechnol Adv* 2022;56:107916. <https://doi.org/10.1016/j.biotechadv.2022.107916>.
- Falzarano M, Poletini A, Pomi R, Rossi A, Zonfa T. Anaerobic biodegradability of commercial bioplastic products: systematic bibliographic analysis and critical assessment of the latest advances. *Mater* 2023, Vol 16, Page 2216 2023;16:2216. <https://doi.org/10.3390/MA16062216>.
- Narancic T, Verstichel S, Reddy Chaganti S, Morales-Gamez L, Kenny ST, De Wilde B, et al. Biodegradable plastic blends create new possibilities for end-of-life management of plastics but they are not a panacea for plastic pollution. *Environ Sci Technol* 2018;52:10441–52. <https://doi.org/10.1021/acs.est.8b02963>.
- Nunziato R, Hedge S, Dell E, Trabold T, Lewis C, Diaz C. Mechanical properties and anaerobic biodegradation of thermoplastic starch/polycaprolactone blends. 21st IAPRI World Conf Packag 2018;0:722–9. <https://doi.org/10.12783/IAPRI2018/24452>.
- Hubackova J, Dvorackova M, Svoboda P, Mokrejs P, Kupec J, Pozarova I, et al. Influence of various starch types on PCL/starch blends anaerobic biodegradation. *Polym Test* 2013;32:1011–9. <https://doi.org/10.1016/j.polymertesting.2013.05.008>.
- Cho HS, Moon HS, Kim M, Nam K, Kim JY. Biodegradability and biodegradation rate of poly(caprolactone)-starch blend and poly(butylene succinate) biodegradable polymer under aerobic and anaerobic environment. *Waste Manag* 2011;31:475–80. <https://doi.org/10.1016/j.wasman.2010.10.029>.
- Guo M, Trzcinski AP, Stuckey DC, Murphy RJ. Anaerobic digestion of starch-polyvinyl alcohol biopolymer packaging: Biodegradability and environmental impact assessment. *Bioresour Technol* 2011;102:11137–46. <https://doi.org/10.1016/j.biortech.2011.09.061>.
- Battista F, Frison N, Bolzonella D. Can bioplastics be treated in conventional anaerobic digesters for food waste treatment? *Environ Technol Innov* 2021;22: 101393. <https://doi.org/10.1016/j.eti.2021.101393>.
- Zhang W, Heaven S, Banks CJ. Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste. *Polym Degrad Stab* 2018. <https://doi.org/10.1016/j.polymdegradstab.2017.11.005>.
- Day M, Shaw K, Cooney D. Biodegradability: an assessment of commercial polymers according to the canadian method for anaerobic conditions 1, *. vol. 2. 1994.
- Puechner P, Mueller WR, Bardtke D. Assessing the biodegradation potential of polymers in screening- and long-term test systems. *J Environ Polym Degrad* 1995; 3:133–43. <https://doi.org/10.1007/BF02068464/METRICS>.
- Scandola M, Finelli L, Sarti B, Mergaert J, Swings J, Ruffieux K, et al. Biodegradation of a starch containing thermoplastic in standardized test systems. <http://DxDoiOrg/101080/10601329808001999> 2006;35:589–608. <https://doi.org/10.1080/10601329808001999>.
- Cazaudehore G, Monlau F, Gassie C, Lallement A, Guyoneaud R. Methane production and active microbial communities during anaerobic digestion of three commercial biodegradable coffee capsules under mesophilic and thermophilic conditions. *Sci Total Environ* 2021;784:146972. <https://doi.org/10.1016/j.scitotenv.2021.146972>.
- Vasmara C, Marchetti R. Biogas production from biodegradable bioplastics. *Environ Eng Manag J* 2016;15:2041–8. <https://doi.org/10.30638/eemj.2016.220>.
- Calabrò PS, Folino A, Fazzino F, Komilis D. Preliminary evaluation of the anaerobic biodegradability of three biobased materials used for the production of disposable plastics. *J Hazard Mater* 2020. <https://doi.org/10.1016/j.jhazmat.2019.121653>.
- Massardier-Nageotte V, Pestre C, Cruard-Pradet T, Bayard R. Aerobic and anaerobic biodegradability of polymer films and physico-chemical characterization. *Polym Degrad Stab* 2006. <https://doi.org/10.1016/j.polymdegradstab.2005.02.029>.
- Kosheleva A, Gadaleta G, De Gisi S, Heerenklage J, Picuno C, Notarnicola M, et al. Co-digestion of food waste and cellulose-based bioplastic: From batch to semi-continuous scale investigation. *Waste Manag* 2023;156:272–81. <https://doi.org/10.1016/j.wasman.2022.11.031>.
- Chowdhury RBS, Fulford DJ. Batch and semi-continuous anaerobic digestion systems. *Renew Energy* 1992;2:391–400. [https://doi.org/10.1016/0960-1481\(92\)90072-B](https://doi.org/10.1016/0960-1481(92)90072-B).
- Angelidaki I, Alves M, Bolzonella D, Borzacconi L, Campos JL, Guwy AJ, et al. Defining the biomethane potential (BMP) of solid organic wastes and energy crops: A proposed protocol for batch assays. *Water Sci Technol* 2009;59:927–34. <https://doi.org/10.2166/wst.2009.040>.
- Baird R, Bridgewater L. APHA, AWWA, WEF - Standard methods for the examination of water and wastewater 2017.
- Dubois M, Gilles K, Hamilton JK, Rebers PA, Smith F. Colorimetric method for determination of sugars and related substances. *Microb Cell Fact* 2002;8:59. <https://doi.org/10.1021/AC60111A017>.
- Gunaseelan VN. Anaerobic digestion of biomass for methane production: A review. *Biomass Bioenergy* 1997;13:83–114. [https://doi.org/10.1016/S0961-9534\(97\)00020-2](https://doi.org/10.1016/S0961-9534(97)00020-2).
- Chynoweth DP, Turick CE, Owens JM, Jergert DE, Peck MW. Biochemical methane potential of biomass and waste feedstocks. *Biomass Bioenergy* 1993;5:95–111. [https://doi.org/10.1016/0961-9534\(93\)90010-2](https://doi.org/10.1016/0961-9534(93)90010-2).
- ISO 14853:2016 Plastics — Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system — Method by measurement of biogas production n.d.
- Holliger C, Alves M, Andrade D, Angelidaki I, Astals S, Baier U, et al. Towards a standardization of biomethane potential tests. *Water Sci Technol* 2016;74: 2515–22. <https://doi.org/10.2166/wst.2016.336>.
- Yagi H, Ninomiya F, Funabashi M, Kunioka M. Thermophilic anaerobic biodegradation test and analysis of eubacteria involved in anaerobic biodegradation of four specified biodegradable polyesters. *Polym Degrad Stab* 2013;98:1182–7. <https://doi.org/10.1016/j.polymdegradstab.2013.03.010>.
- Buswell AM, Mueller HF. Mechanism of methane fermentation. *Ind Eng Chem* 1952;44:550–2. <https://doi.org/10.1021/ie50507a033>.
- EN 13432 - Packaging - Requirements for packaging recoverable through composting and biodegradation 2008.
- Fu Y, Wu G, Bian X, Zeng J, Weng Y, Polymeric F. Biodegradation behavior of poly (butylene adipate-co-terephthalate) (PBAT), poly(lactic acid) (PLA), and their blend in freshwater sediment 2020:4–6.
- Dolci G, Venturelli V, Catenacci A, Ciapponi R, Malpei F, Romano Turri SE, et al. Evaluation of the anaerobic degradation of food waste collection bags made of paper or bioplastic. *J Environ Manage* 2022;305:114331. <https://doi.org/10.1016/j.jenvman.2021.114331>.
- Su S, Kopitzky R, Tolga S, Kabasci S. Polylactide (PLA) and Its Blends with Poly (butylene succinate) (PBS): A brief review. *Polymers (Basel)* 2019;11. <https://doi.org/10.3390/POLYM11071193>.
- Beltrán FR, Arrieta MP, Moreno E, Gaspar G, Muneta LM, Carrasco-Gallego R, et al. Evaluation of the technical viability of distributed mechanical recycling of PLA 3D

- printing wastes. *Polym* 2021, Vol 13, Page 1247 2021;13:1247. 10.3390/POLYM13081247.
- [48] Ruggero F, Carretti E, Gori R, Lotti T, Lubello C. Monitoring of degradation of starch-based biopolymer film under different composting conditions, using TGA, FTIR and SEM analysis. *Chemosphere* 2020. <https://doi.org/10.1016/j.chemosphere.2019.125770>.
- [49] de Matos Costa AR, Crocitti A, de Carvalho LH, Carroccio SC, Cerruti P, Santagata G. Properties of biodegradable films based on poly(Butylene succinate) (pbs) and poly(butylene adipate-co-terephthalate) (pbat) blends. *Polymers (Basel)* 2020;12:1–17. <https://doi.org/10.3390/polym12102317>.
- [50] Cai YH. Influence of ethylene bis-stearamide on crystallization behaviour of poly(l-lactide). *Asian J Chem* 2013;25:6219–21. 10.14233/ajchem.2013.14326.
- [51] Ostrowska J, Sadurski W, Paluch M, Tyński P, Bogusz J. The effect of poly(butylene succinate) content on the structure and thermal and mechanical properties of its blends with polylactide. *Polym Int* 2019;68:1271–9. <https://doi.org/10.1002/PL.5814>.
- [52] Phua YJ, Chow WS, Mohd Ishak ZA. Reactive processing of maleic anhydride-grafted poly(butylene succinate) and the compatibilizing effect on poly(butylene succinate) nanocomposites. *Express Polym Lett* 2013;7:340–54. <https://doi.org/10.3144/EXPRESSPOLYMLET.2013.31>.
- [53] Socrates.. *Infrared characteristic group frequencies. Tables and Charts* 1994;296. [https://doi.org/10.1016/0003-2670\(94\)80274-2](https://doi.org/10.1016/0003-2670(94)80274-2).
- [54] Cerruti P, Santagata G, Gomez D' Ayala G, Ambrogi V, Carfagna C, Malinconico M, et al. Effect of a natural polyphenolic extract on the properties of a biodegradable starch-based polymer. *Polym Degrad Stab* 2011;96:839–46. <https://doi.org/10.1016/j.polymdegradstab.2011.02.003>.
- [55] Elfehri Borchani K, Carrot C, Jaziri M. Biocomposites of Alfa fibers dispersed in the Mater-Bi® type bioplastic: Morphology, mechanical and thermal properties. *Compos Part A Appl Sci Manuf* 2015;78:371–9. <https://doi.org/10.1016/j.compositesa.2015.08.023>.
- [56] Rizzarelli P, Rapisarda M, Perna S, Mirabella EF, La Carta S, Puglisi C, et al. Determination of polyethylene in biodegradable polymer blends and in compostable carrier bags by Py-GC/MS and TGA. *J Anal Appl Pyrolysis* 2016;117: 72–81. <https://doi.org/10.1016/j.jaap.2015.12.014>.
- [57] Junior IT, Dal Bosco TC, Bertozzi J, Michels RN, Mali S. Biodegradability assessment of starch/glycerol foam and poly(butylene adipate-co-terephthalate)/starch film by respirometric tests. *Brazilian J Food Technol* 2020;23:1–15. <https://doi.org/10.1590/1981-6723.24818>.
- [58] Cazaudehore G, Guyoneaud R, Lallement A, Gassie C, Monlau F. Biochemical methane potential and active microbial communities during anaerobic digestion of biodegradable plastics at different inoculum-substrate ratios. *J Environ Manage* 2022;324. <https://doi.org/10.1016/J.JENVMAN.2022.116369>.
- [59] Neves L, Oliveira R, Alves MM. Influence of inoculum activity on the biomethanization of a kitchen waste under different waste/inoculum ratios. *Process Biochem* 2004;39:2019–24. <https://doi.org/10.1016/j.procbio.2003.10.002>.
- [60] Ryan CA, Billington SL, Criddle CS. Assessment of models for anaerobic biodegradation of a model bioplastic: Poly(hydroxybutyrate-co-hydroxyvalerate). *Bioresour Technol* 2017. <https://doi.org/10.1016/j.biortech.2016.11.119>.
- [61] Karaeva JV, Timofeeva SS, Islamova SI, Gerasimov AV. Pyrolysis kinetics of new bioenergy feedstock from anaerobic digestate of agro-waste by thermogravimetric analysis. *J Environ Chem Eng* 2022;10:107850. <https://doi.org/10.1016/j.jece.2022.107850>.
- [62] Gómez X, Cuetos MJ, García AI, Morán A. An evaluation of stability by thermogravimetric analysis of digestate obtained from different biowastes. *J Hazard Mater* 2007;149:97–105. <https://doi.org/10.1016/j.jhazmat.2007.03.049>.
- [63] Pietro M, Paola C. Thermal analysis for the evaluation of the organic matter evolution during municipal solid waste aerobic composting process. *Thermochim Acta* 2004;413:209–14. <https://doi.org/10.1016/j.tca.2003.09.026>.
- [64] Bandini F, Taskin E, Vaccari F, Soldano M, Piccinini S, Frache A, et al. Anaerobic digestion and aerobic composting of rigid biopolymers in bio-waste treatment: fate and effects on the final compost. *Bioresour Technol* 2022;351:126934. <https://doi.org/10.1016/j.biortech.2022.126934>.