Degradation of bioplastics in organic waste by mesophilic anaerobic digestion, composting and soil incubation

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Abstract

The aim of the study was to assess the effects of high concentrations (10 % w/w, data projected for 2030) of commercial bioplastics, i.e. starch based shopping bags (SBSB) and polylactic acid (PLA) tableware, in the organic fraction of municipal solid wastes (MSW) on compost quality obtained by pilot-scale dry mesophilic anaerobic digestion and subsequent composting of the digestate.

After the biological processes, 48.1 % total solids (TS) of SBSB and 15 % TS of PLA degraded, resulting in a high bioplastics content (about 18 % TS) in compost. Subsequent compost incubation in soils indicated that bioplastics degraded by pseudo-zero order kinetics (0.014 and 0.010 mg C cm^{-2} d^{-1} for SBSB and PLA, respectively), i.e. complete degradation was expected in 1.6 years (SBSB) and 7.2 years (PLA), confirming the intrinsic biodegradability of bioplastics. Nevertheless, enhancing the rate and amount of bioplastics degradation during waste management represents a goal to decrease the amount of bioplastics reaching the environment.

Keywords

Anaerobic digestion; Biodegradability; Composting; Polylactic acid; Starch-based bioplastics.

1. Introduction

Bioplastics are a wide family of compounds that comprise (i) biodegradable and bio-based materials (e.g. starch-based bioplastics, polylactic acid - PLA), (ii) biodegradable and fossil-based materials (e.g. polycaprolactone) and (iii) non-biodegradable bio-based materials (e.g. bio-polyethylene) (Bátori et al., 2018).

Bioplastics have been introduced in recent decades as environmentally friendly and sustainable alternative materials to fossil-derived plastics. Recently their production started to increase worldwide, particularly in the EU, where in 2019 a new directive banned the use of single-use plastics (European Parliament, 2019). As consequence of that, bioplastics are likely to be substituted for the banned plastic items in the coming years. In addition, the use of bioplastics in food packaging applications is increasing, leading to a growing demand for bioplastics production (Zhao et al., 2020).

Nowadays, waste bioplastics are usually collected with the organic fraction of municipal solid wastes (OFMSW), representing an increasing fraction of this waste stream. For instance, bioplastics in Italy represented about 3-4 % (weight basis) of OFMSW in 2019 and this percentage is expected to increase rapidly in future years (ISPRA, 2020), posing important issues about biodegradation during waste management and final disposal. In fact, “bioplastics degradability” is certified under optimal standardized degrading conditions, i.e. thermophilic conditions, 1 % concentration of test material, and long-term tests (58 °C and 90 days) (ISO 20200, 2016), that are far from the real conditions of the bioprocesses used to treat organic wastes, i.e. anaerobic digestion (AD) and composting.

Therefore, degradation of bioplastics in OFMSW treatment facilities could become an increasing issue, since large volumes of these materials have to be treated in plants that were not designed for bioplastics processing resulting in contamination of digestate and/or compost with large amounts of non-degraded bioplastics. In fact, plastics, including bioplastics, are mechanically separated in the early stage of waste treatment (before the biological processes) and are often disposed of in landfill.

Mesophilic ADs (35-37 °C) of OFMSW are more widespread than thermophilic ADs (52-55 °C) (Kumar and Samadder, 2020) because mesophilic processes are more stable and require lower investment and energy. Moreover, AD of OFMSW is usually conducted with short hydraulic retention times (20-30 days) in order to optimise the biogas yields and volumes of waste treated (Panigrahi and Dubey, 2019, Shrestha et al., 2020). Certainly, composting of OFMSW is commonly carried out at industrial facilities operating under thermophilic conditions (maximum temperature 55-65 °C), and lasting about 90 days. Nevertheless, composting after AD does not often reach high temperatures (higher than 50-55 °C for long time) because the organic waste has been already partially biodegraded during the AD process (Tambone et al., 2015). This fact has a negative effect on the biodegradation of bioplastics during OFMSW management, resulting in low bioplastics degradation. Zhang et al. (2018) reported that four bioplastics certified under the EN 13432 (EN13432, 2002) composting standard converted less than 20 % of their carbon into biomethane during mesophilic AD. Calabrò et al. (2020) concluded that bioplastics cannot feed conventional anaerobic digesters, because they found fully recognizable compostable bags at the end of AD. However, other researchers reported higher kinetics constants of degradation under thermophilic composting conditions than those reported for AD for many bioplastics (Cucina et al., 2021, Gómez and Michel, 2013, Kalita et al., 2020). For instance, Báreková et al. (2021) have reported that food packaging and single-use items made of bioplastics (i.e. PLA, starch-based products) completely degraded after 12 weeks of composting in a real-scale facility. Therefore, more research is needed to better understand the fate of bioplastics under engineered environments such as AD and digestate composting (Battista et al., 2021, Folino et al., 2020).

Incomplete biodegradation of bioplastics at the end of OFMSW management results in high bioplastic contents of the final products, which presents an obstacle for the agricultural reuse of anaerobic digestate and compost because the product fails to comply with legal requirements. Indeed, Italian legislation concerning high quality compost production prescribes a 0.5 % w/w limit for the presence of plastics, metals and glass particles (particle size > 2 mm), without any

distinction between fossil-based plastics and bioplastics (Decreto Legislativo 29 Aprile 2010, 2010). Moreover, the fate of bioplastics residues in soil when digestate and compost containing bioplastics' residue are applied is still debated and is currently being studied. Although Emadian et al. (2017) stated that the vast biodiversity of soil microorganisms should enable the degradation of bioplastics in soil, several authors have reported a slow biodegradation of bioplastics in soil (Karamanlioglu et al., 2017, Narancic et al., 2018, Rudnik and Briassoulis, 2011). Nevertheless, the outcome of this process differs depending on the soil environment: for example, Weng et al. (2013) showed a significant degradation of PLA buried in soil after 4 months.

In this context, the aim of the present study was to evaluate the effects of the presence of a high concentration of bioplastics (PLA and starch-based polymer) in OFMSW on compost quality after mesophilic anaerobic digestion and digestate composting of a mixture made of OFMSW and bioplastics. In addition, residual processed bioplastics in compost were studied to observe their degradation in soil.

2. Materials and methods

2.1 *Tested materials*

The bioplastics studied in the present work were starch-based shopping bags (SBSB) and a mixture of PLA goods (dishes, glasses and cutlery) (PLA) available at Italian supermarkets. All the products sampled were labelled as compostable by the Italian Consortium of Composters (CIC) (Italy) and TÜV Austria (Austria).

Before the experiments, which included biomethane potential tests, pilot-scale trials, disintegration tests and a soil incubation procedure), the bioplastics were reduced in size by cutting them into pieces of about 5 x 5 cm, which is the size used at full scale to sieve OFMSW before dry anaerobic digestion.

The total amount of bioplastics dosed in the trials was decided by taking into consideration the trend of bioplastics in the OFMSW registered in the last 4 years in Italy, and current bioplastic production

trends (ISPRA, 2020, RameshKumar et al., 2020), so that a likely bioplastics content could be projected for 2030. By doing so, it was calculated that about 8-10 % bioplastics (w/w) in the separately collected OFMSW should represent a realistic projection for the data at that time. In this study, therefore, a mix of OFMSW and 10 % w/w bioplastics was tested, to assess degradability of the bioplastics through biological waste management.

For the anaerobic digestion and composting experiments, a local company that collects and treats anaerobically the OFMSW by dry digestion provided OFMSW and anaerobic digestate to be used as inoculum (Table S1). Both materials were collected and stored at 4 °C before the beginning of the experiments.

2.2 Biological treatments

2.2.1 Biomethane potential tests

Biomethane potential (BMP) tests were carried out to assess the potential for biomethane production from the bioplastics and all organic waste fractions tested in this work. Specifically, the following materials were studied: SBSB, PLA, bioplastics mix (50 % SBSB and 50 % PLA on weight basis), OFMSW and the mixture of bioplastics plus OFMSW (10 % bioplastics mix and 90 % OFMSW, on weight basis). The BMPs of all samples were determined by modifying a standardized method reported by Schievano et al. (2008). Briefly, 3.0 g of dried sample was added to 300 mL of inoculum in a 500 mL bottle (substrate to inoculum ratio 1:1 on total solids basis) and then the batch was sealed with Teflon hermetic caps, flushed with gaseous N_2 and incubated at 37 ± 2 °C. Control blanks were prepared using 300 mL of inoculum. The anaerobic digesters were provided with a system for biogas measurement and the biogas composition was periodically evaluated through gas-chromatography (Carlo Erba Megaseries 5300, capillary column 25-m × 0.32-mm diameter and flame ionization detector - FID). The carrier gas was N_2 at 20 kPa pressure and temperatures of injector and FID were 130 and 150 °C, respectively. Comparison of obtained peak areas was carried out with a standard gas mixture of 30:70 CH_4:CO_2.

133 Biomethane production of the blank control was subtracted from biomethane production of all the
134 batches to determine the BMPs. BMP tests were carried out for 60 days although bioplastics require
135 much more time to be degraded, in order to compare the results obtained with those of other
136 matrices. Moreover, it is common for AD biogas plants to work with an HRT lower than 60 days.
137
138 *2.2.2 Pilot-scale anaerobic digestion and composting*
139 AD was carried out under mesophilic (30 ± 2 °C, room temperature) and dry (40 % total solids, TS)
140 conditions, using a 60 L adiabatic pilot-scale anaerobic digester. Dry conditions were selected
141 because most of the facilities that treat OFMSW operate at a high TS regime (>15 %). About 40 kg
142 of a mixture made of 60 % w/w OFMSW, 30 % w/w inoculum and 10 % w/w bioplastics (mixture
143 of SBSB and PLA in a 50% w/w ratio) were placed in the digester, which was then hermetically
144 closed. Gaseous N_2 was flushed in the headspace of the digester before the start of the experiment.
145 Quantitative and qualitative biogas production was evaluated as described for BMP assays. After 35
146 days of AD the digester was opened to recover the digestate. Representative samples of digestate
147 were collected and stored at 4 °C prior to analytical determinations. About 10 kg of digestate were
148 placed in an aerobic adiabatic reactor (20 L volume) for the active phase of composting. Since AD
149 was carried out in dry conditions, there was no need to add bulking and/or absorbent agents for
150 composting. The reactor was provided with both temperature and oxygen probes to register
151 thermometric and oxygen trends; this latter was kept around 10 % (v/v) by air insufflation
152 controlled by feedback modality. A detailed description of the aerobic reactor can be found in
153 Tambone et al. (2015). The active phase of composting was considered complete when the
154 temperature of the mixture decreased to the environmental temperature (25 °C, occurred at 15^{th} d).
155 At the end of the active phase, the fresh compost was collected and placed in an open box for the
156 maturation phase that lasted for another 40 days (in total 55 days of composting, for a total
157 treatment of 90 days, AD plus composting). During maturation, the fresh compost was turned
158 periodically to ensure a proper oxygenation. At the end of the maturation, representative samples of

compost were collected. A sample of mature compost was sieved at 2 cm in order to simulate common practice at full-scale facilities in preparing the final compost. In addition, another sample of mature compost was sieved through a 1 cm sieve to evaluate the effect of the size reduction on compost quality. Representative samples of compost sieved at 2 and 1 cm were collected and stored at 4 °C prior to analytical determinations. Compost characteristics were also compared with the legal limits established by Italian legislation for high quality compost production (Decreto Legislativo 29 Aprile 2010, 2010).

2.3 Disintegration test

The disintegration of bioplastics under simulated composting conditions at laboratory-scale was carried out modifying the standard method ISO 20200 (ISO 20200, 2016). Briefly, the solid matrix used consisted of a synthetic solid waste inoculated with mature compost and the disintegration was determined after a composting cycle (58 °C, 90 days under forced ventilation), by sieving the final matrix through a 2 mm sieve in order to recover the non-disintegrated residues. The test was carried out using SBSB and PLA separately, testing a 10% w/w concentration of bioplastics instead of the 0.5 - 2.0 % w/w established by the method, in order to evaluate the disintegration of high concentrations of bioplastics in the synthetic organic waste under optimal composting conditions.

2.4 Biodegradation in soil

The biodegradation test was carried out following standard procedures reported in ISO 17556 (ISO 17556, 2019) using the bioplastics mix before (t_0) and after (t_{90}) biological treatments. In addition, non-treated (t_0) and treated (t_{90}) bioplastics (SBSB and PLA) were incubated separately. Positive (powdered cellulose for chromatography application) and negative (polyethylene) references were also included in the tests for comparison. The tested materials were mixed with a standard soil (pH of 7 and C/N of 40) composed of sand (70 % w/w), clay (10 % w/w), natural soil (16 % w/w) and mature compost (4 % w/w), using the 1.25 % w/w concentration of tested material established by

185 the standard procedure. The mixtures were incubated in glass flasks (2 L volume) under controlled
186 conditions (25 ± 2 °C in the dark) over 90 days during which CO_2 evolved was determined. In
187 parallel, the background CO_2 production was determined in flasks containing the soil without test
188 material. The evolved CO_2 was determined at established intervals by trapping it in NaOH solution,
189 1 mol L^{-1}, and titrating the residual NaOH with HCl 0.1 mol L^{-1}. Results were then expressed as
190 cumulative mg of carbon (C) evolved per g of C of tested material.
191
192 *2.5 Analytical methods*
193 Organic wastes, digestate and compost were characterized with particular reference to final sieved
194 compost.
195 Total solid (TS), volatile solids (VS), total organic carbon (TOC), Total N and ammonium-N, were
196 determined according to standard procedures (APHA, 2017). Organic N was calculated as the
197 difference between total N and ammonium N. pH and volatile fatty acids (VFA) were determined
198 according to standard procedures (US Department of Agricolture - US Composting Council, 2002);
199 VFA content was analyzed only for digestate. Heavy metals content was determined by inductively
200 coupled plasma mass spectrometry (Varian, Fort Collins, USA) preceded by acid digestion (EPA,
201 2007). Hexavalent chromium was analysed by a colorimetric method in aqueous extracts prepared
202 from dry samples (El Fels et al., 2015). Inert residues (plastics, metals, glass and stones),
203 determined by H_2O_2 digestion and subsequent isolation and weighing, and *Salmonella* spp. content
204 were determined following standard procedures (ANPA, 2001).
205 Germination index (GI) was determined following the method described by Solé-Bundó et al.
206 (2017). The number of germinated seeds and the primary root lengths were measured and the GI
207 was then determined as a percentage of the control.
208 Mass balance of bioplastics was performed by direct weighing after each process step and after the
209 disintegration test, taking into consideration TS and VS degradation (biomass degradation)
210 determined by using the ash preservation methods (Genevini et al., 1997). Briefly, after each

process (AD and composting), bioplastics (SBSB and PLA) were recovered from representative digestate and compost samples, washed in water, dried and weighed. The weights of recovered bioplastics from the digestate/compost samples were then referred to the total mass of substrate (i.e. digestate and compost), and the concentration of bioplastics (% w/w) was determined. Mass balance of VS at the end of composting was also determined following the ash preservation procedure described by Genevini et al. (1997).

2.6 Spectroscopic analysis and scanning electron microscopy

Bioplastics were characterized by spectroscopic investigation, using the Fourier Transform InfraRed (FT-IR) spectra, which were collected in total reflectance mode (ATR) with a Shimadzu IRAffinity-1S equipped with a Miracle Pike ATR device (Shimadzu Italia srl, Milano, Italy); peak areas were determined using Shimadzu LabSolutions IR software. The investigated wavenumber range was of 4,000-500 cm^{-1} and the resolution was of 2 cm^{-1}.

Investigated bioplastics were sampled directly from the organic matrices after each step of the biological treatments, i.e. before biological treatments, at the end of the pilot-scale AD (after 35 days) and at the end of the pilot-scale composting (after 90 days). Bioplastics were also sampled at the end of the disintegration tests (after 90 days) and at the end of the soil incubation test (after 90 days). Bioplastic samples were dried, cleaned and gently tooth-brushed in order to remove all the deposits formed on their surfaces.

Images of bioplastics before and after biological treatments were collected with a Scanning Electron Microscope (SEM) (ZEISS EVO NA15 apparatus, ZEISS International, Oberkochen, Germany). The bioplastics fragments were previously metallized with a 10 nm layer of gold.

2.7 Statistics

BMP assays, soil incubation procedures, disintegration tests and chemical analysis were replicated three times. Mean and standard deviation values were calculated according to standard procedures

and the results analysed by ANOVA (Microsoft Excel Software). Tukey's test was used to compare mean values and to assess the significance of the differences between mean values ($p < 0.05$).

3. Results and discussion

3.1 Biomethane potentials

Biomethane potentials of studied materials showed that OFMSW produced 170 NL kg TS^{-1} which was low, if compared to data reported in the literature (Raposo et al., 2012) (Table S2). This low biomethane potential was probably due to the composition of the OFMSW used in the experiments, which was rich in green wastes, which were abundant in OFMSW collected in the summer season. Bioplastics showed low biomethane potentials in the 60 days assays, i.e. 34, 119 and 78 NL kg TS^{-1} for PLA, SBSB and bioplastics mix, respectively. These results agreed with data reported by Cazaudehore et al. (2021) who reported poor biomethane potentials of bioplastics in mesophilic AD, independently of the composition and size of the polymer tested, and also with Battista et al. (2021), who reported that starch-based bioplastic and PLA materials remained almost undegraded after 250 days of AD. Among biodegradable bioplastics, only polyhydroxyalkanoates blends have been reported to degrade efficiently under mesophilic AD (Cucina et al., 2021, Ryan et al., 2017). Finally, the mixture of OFMSW and bioplastics produced about 100 NL kg TS^{-1} of biomethane. This figure is lower than that for OFMSW alone because of the presence of the bioplastics in the mix.

3.2 Pilot scale dry anaerobic digestion and composting

The AD process carried out in mesophilic pilot-scale conditions produced 135 NL kg TS^{-1} of biogas (Table 1) with an average content of biomethane of 59 % v/v. The total amount of biomethane produced by the mixture of OFMSW and bioplastics was then 81 NL kg TS^{-1}. This value represented about 80 % of the biomethane potential of the mixture of OFMSW and bioplastics confirming that the pilot-scale AD developed correctly. No literature data from other pilot-scale

anaerobic trials treating bioplastics were found which might provide a comparison with these results. Digestate characterization (Table 1) showed a reduction of total and volatile solids of 8.7 % and 12.4 % respectively (on an absolute basis) if compared to the initial mixture and this was due to hydrolyzation of organic matter and conversion of soluble organic matter to biomethane, respectively. pH remained almost unchanged during AD, as expected during dry AD processes (Matheri et al., 2018).

A sample of digestate (10 kg) coming from AD process was subsequently composted.

Table 1. Main operational and production parameters of pilot-scale anaerobic digestion.

Parameter	**Unit**		
Operational parameters			
Useful volume	L	60	
Average ambient temperature	°C	30 ± 2	
Hydraulic retention time	d	35	
Production parameters			
Biogas	NL kg TS^{-1}	135 ± 7[a]	
Average CH_4 content	%	59 ± 3	
Biomethane	NL kg TS^{-1}	81 ± 4	
Mixture and digestate characteristics		Mixture	Digestate
Total solids	%	40.4[b] ± 0.8	36.9 ± 0.2
Volatile solids	%	76 ± 0	73.5 ± 0.3
Ph		7.3 ± 0.0	7.5 ± 0.0
Volatile fatty acids	mg L^{-1}	7,280 ± 96	6,345 ± 154

[a]Mean Value ± SD; *n* = 3.
[b]Results are expressed on fresh weight bases except for volatile solids.

The increased temperatures observed in the mixture during the first days of composting indicated an efficient mineralization of easily degradable organic matter (Cucina et al., 2018) (Fig. S3). The temperature increased rapidly after the start of the experiment and reached the maximum value (57 °C) after 72 hours. The temperature remained near 55 °C for almost three days, allowing proper

277 sanitation of waste material from animal and plant pathogens, as well as inactivation of weed seeds
278 (Petric et al., 2012). Although minimal temperature requirements were met during the active phase
279 of digestate composting, it should be highlighted that thermophilic conditions were maintained for a
280 relatively short time if compared to temperature values usually detected during composting of
281 OFMSW and OFMSW digestate (Arab and McCartney, 2017, Awasthi et al., 2015). This was
282 probably because anaerobic digestion had already caused extensive degradation of the easily
283 degradable organic matter and did not allow the high temperature of the compost to be maintained
284 for very long (Tambone et al., 2015, Zeng et al., 2016).
285 During composting, TS content of composts increased because of water loss through evaporation,
286 whereas VS and TOC decreased due to organic matter mineralization. The VS reduction observed
287 was of 43.9 % of starting VS content and it was comparable to results found in the literature (Adani
288 et al., 2002, Cucina et al., 2018), indicating the correct development of the composting process.
289 Refined composts met all the legal limit values prescribed by Italian legislation concerning high
290 quality compost production with the exception of the inert materials content (Decreto Legislativo 29
291 Aprile 2010, 2010). The Italian norm prescribes a maximum content of inert materials (plastic,
292 glass, metals) with a size > 2 mm of 0.5 % (w/w) in compost, without distinction between fossil-
293 based plastics and bioplastics. Compost sieved at 2 cm showed 17.8 % TS of bioplastics content,
294 whereas bioplastics content was reduced to 5.3 % TS in the compost sieved at 1 cm. These contents
295 largely exceeded the legal limit value for compost commercialization, creating an important issue in
296 OFMSW management in the presence of a high and rising bioplastics production and use scenario.
297 Results of this work indicate that if bioplastics concentration in OFMSW rises by 2030 by as much
298 as expected, the issue of non-compliant composts will become more and more common if the
299 OFMSW is treated, above all, by mesophilic bioprocesses. Therefore, bioplastics' pre-treatment
300 used to accelerate their degradation under mesophilic conditions (i.e. thermal or alkaline pre-
301 treatments) (Battista et al., 2021) or post-treatments to remove residual bioplastics from compost

will be needed to minimize bioplastics' presence in the mature compost. Alternatively, thermophilic treatments should be evaluated and implemented (Calabrò et al., 2020).

Table 2. Compost characterization and limits established by Italian legislation for high quality compost production.

Parameter	Unit[a]	Compost 2 cm	Compost 1 cm	Limit value
Total solids	%	74.9[b] ± 1.0	75.1 ± 0.2	> 50
Volatile solids	%	70.7 ± 0.5[c]	63.0 ± 0.2[c]	
pH		8.4 ± 0.0	8.3 ± 0.0	6 – 8.5
Total organic C	%	31.1 ± 2.0[c]	24.5 ± 1.8[c]	> 20
Total N	%	1.7 ± 0.1	2.1 ± 0.2	
Organic N/Total N	%	94.1 ± 0.9	95.2 ± 0.4	> 80
Pb	mg kg^{-1}	23.4 ± 0.1	23.8 ± 0.1	140
Ni	mg kg^{-1}	59.3 ± 0.8	58.3 ± 0.7	100
Cd	mg kg^{-1}	0.4 ± 0.0	0.4 ± 0.0	1.5
Cr	mg kg^{-1}	150 ± 8	140 ± 7	
Cr VI	mg kg^{-1}	< 0.5[d]	< 0.5[d]	0.5
Zn	mg kg^{-1}	152 ± 10	139 ± 7	500
Cu	mg kg^{-1}	74.1 ± 5.4	78.1 ± 3.5	230
Hg	mg kg^{-1}	0.03 ± 0.00	0.03 ± 0.01	1.5
Germination index	%	121 ± 7	130 ± 10	> 60
Salmonella spp.	Absence/Presence in 25 g	Absence	Absence	Absence
Bioplastics > 2 mm	%	17.8 ± 0.9[c]	5.3 ± 0.5[c]	<0.5[e]

[a]Results are expressed on dry weight bases except for TS and pH.

[b]Mean Value ± SD; $n = 3$.

[c]Statistically different at $p < 0.05$.

[d]Detection limit of the method.

[e]Limit value for inert materials (plastic, glass, metals).

3.3 Bioplastics degradation

FT-IR investigation confirmed that SBSB were composite materials mainly composed of starch and polyesters (Fig. 1A and 2A) confirming previous data (Marichelvam et al., 2019), whereas PLA goods were mainly composed of polylactic acid with small amounts of additives. For SBSB it was

312 possible to recognize two diagnostic peaks for the starch (3,400 and 1,050 cm^{-1}) and two for the
313 polyester component (1,730 and 730 cm^{-1}), useful to record bioplastic fate during bioprocesses
314 (Table S4). SEM micrographs of bioplastics before treatments (Fig. 3A) indicated a heterogeneous
315 structure for SBSB, whereas PLA showed a more homogeneous microstructure, confirming FT-IR
316 data. Specifically, SBSBs were characterized by circular spots probably made of starch dispersed in
317 a matrix likely composed of polyesters.
318

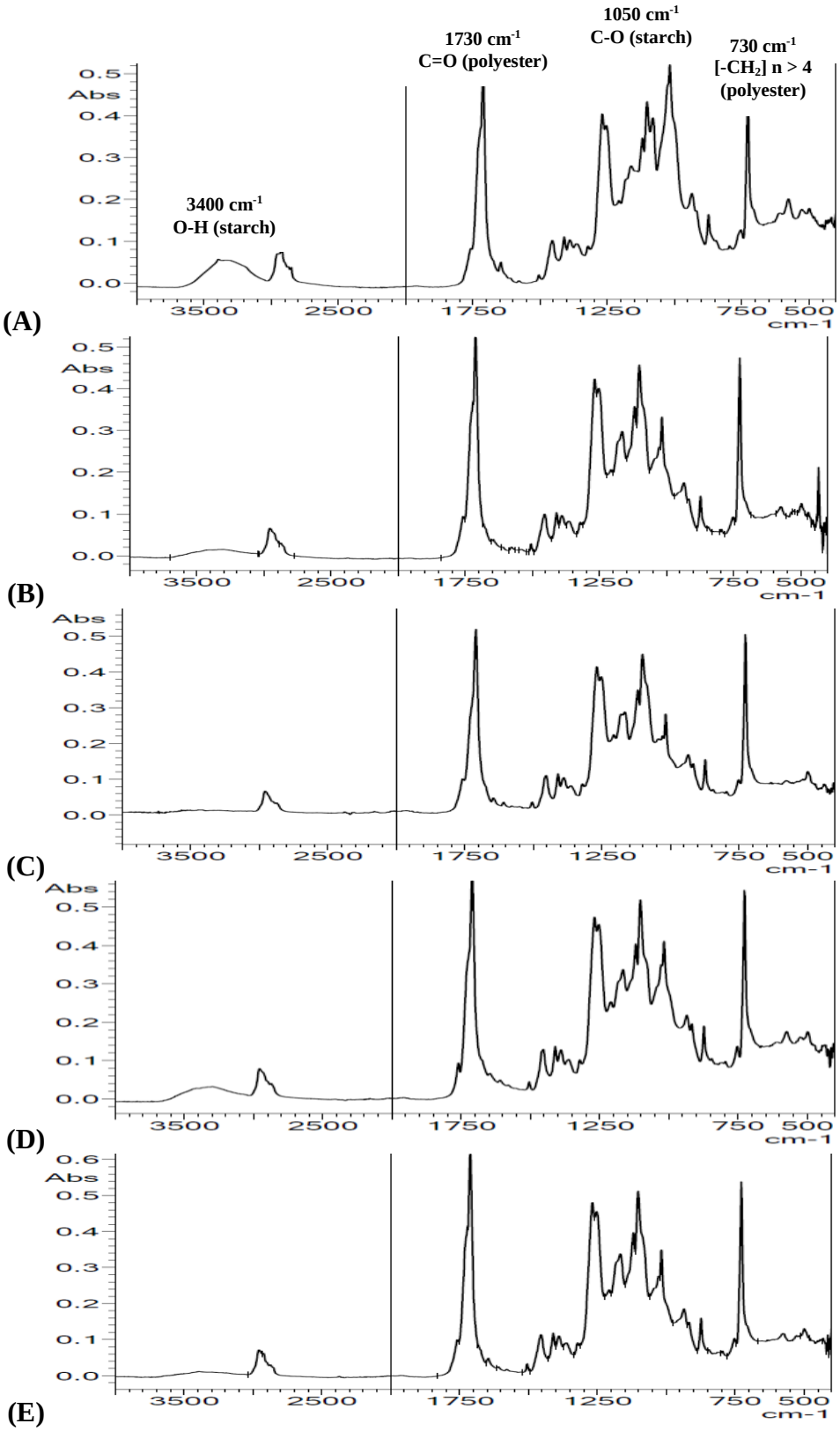

Figure 1. FT-IR spectra of starch-based shopper bags (SBSB) at (A) t_0, (B) at the end of anaerobic digestion (t_{35}) and (C) after composting (t_{90}), (D) at the end of the disintegration test and (E) at the end of the incubation in soil.

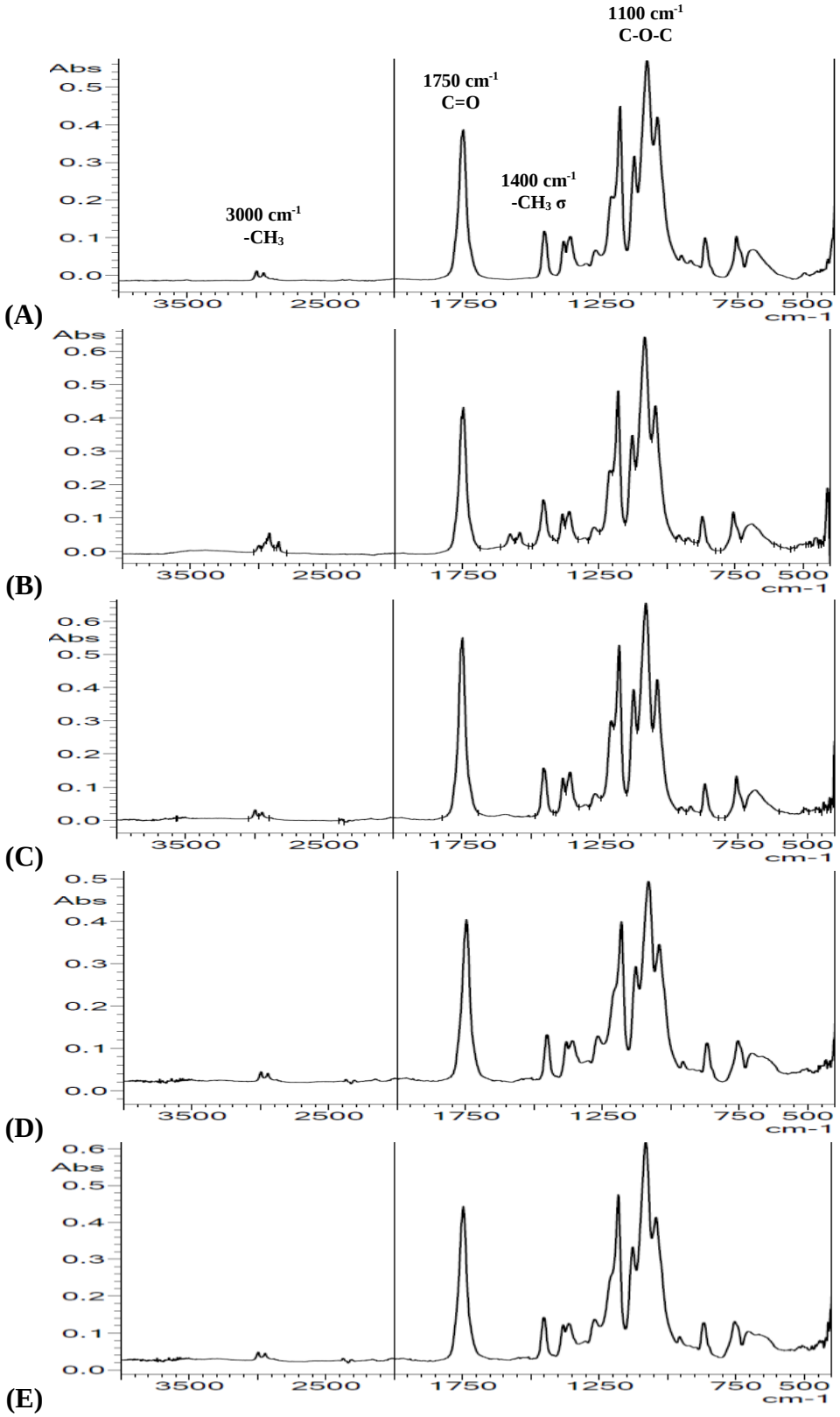

Figure 2. FT-IR spectra of PLA products at (A) t_0, (B) at the end of anaerobic digestion (t_{35}) and (C) after composting (t_{90}), (D) at the end of the disintegration test and (E) at the end of the incubation in soil. PLA FT-IR spectra were obtained from PLA glasses.

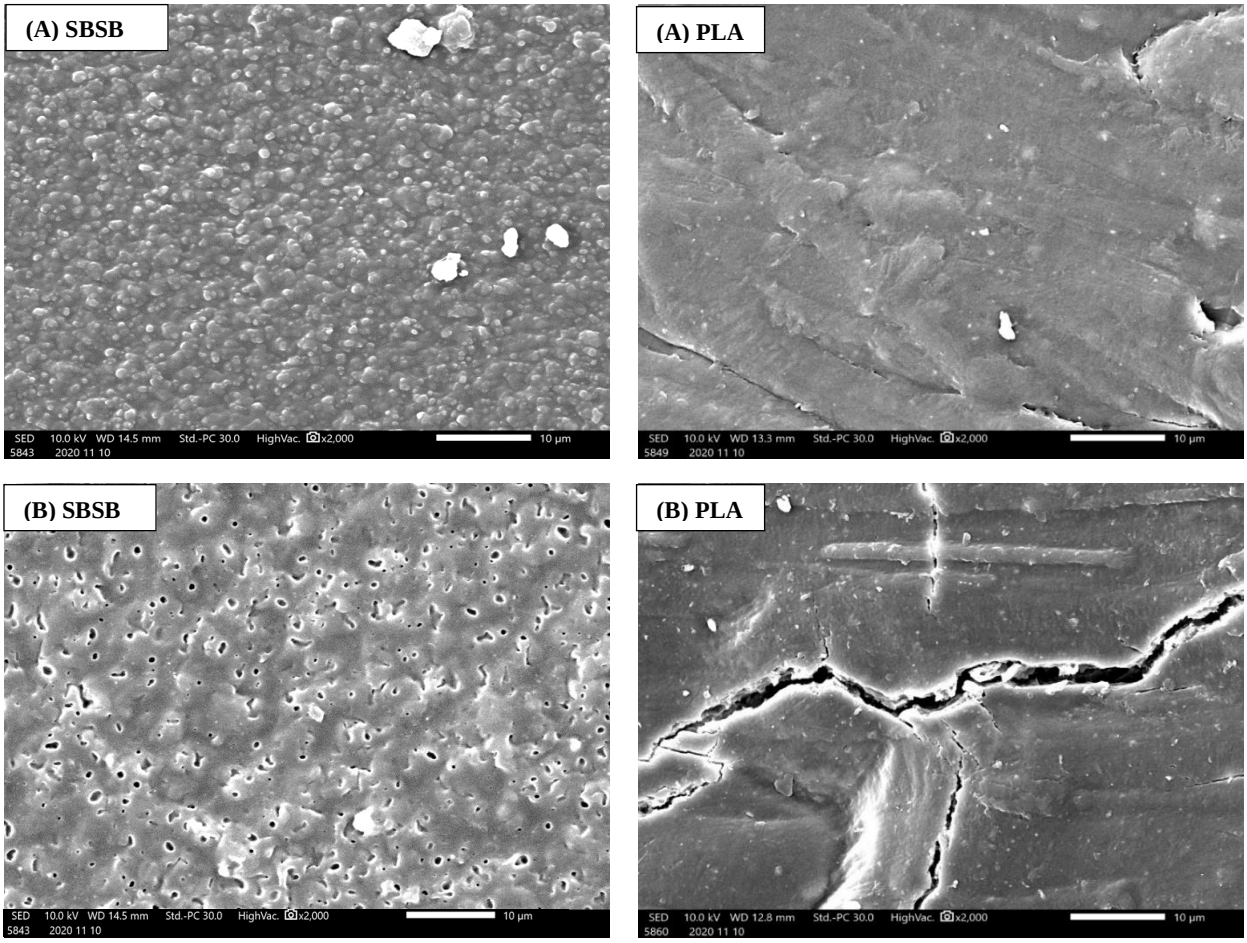

Figure 3. SEM pictures of bioplastics at (A) t_0 and (B) at the end of composting (t_{90}). SBSB: starch-based shopper bags; PLA: Polylactic Acid products. PLA SEM pictures were obtained from PLA glasses.

321

322 Mass balance of the bioplastics mix showed an overall bioplastics reduction of about 15 % as TS
323 during the pilot-scale AD (Table 3). SBSB showed a higher degradation in comparison with PLA
324 (29.5 and 3.7 %, respectively) in accordance with the results of the BMP assays carried out in this
325 work and with recent literature dealing with bioplastics degradation under anaerobic conditions
326 (Bátori et al., 2018, Battista et al., 2021, Folino et al., 2020). Bioplastics have been reported to
327 degrade differently under anaerobic conditions, according to their chemical composition and the
328 operational conditions of the plant (Folino et al., 2020). For example, PLA degraded efficiently only
329 under thermophilic (55 °C) conditions, since it is known that reaching the glass transition
330 temperature (55-60 °C) enhances its degradation by changing PLA's mechanical properties (Marek

and Verney, 2016), in contrast to other bioplastics that efficiently degraded in mesophilic conditions. Therefore, the mesophilic conditions used in this work during the pilot-scale AD explain the low rate degradation of PLA.

Table 3. Mass balances of bioplastics after pilot-scale biological processes and disintegration test.

		Time (d)	**Material**	**Degradation** (% TS)
Biological processes	*Anaerobic digestion*	35	SBSB[a]	29.5 ± 4.1[c]
			PLA[b]	3.7 ± 2.6
	Active phase of composting	50	SBSB	32.5 ± 6.3
			PLA	10 ± 0
	Maturation phase of composting	90	SBSB	48.1 ± 3.0
			PLA	15 ± 2
Disintegration test		90	SBSB	67.3 ± 1.2
			PLA	24.0 ± 0.4

[a]SBSB: starch-based shopper bags.

[b]PLA: Polylactic Acid products.

[c]Mean Value ± SD, n = 3.

FT-IR analysis of SBSB after AD (Fig. 1B) showed a preferential consumption of the starch with respect to the polyester component, resulting in an increased ratio between polyester and starch peaks areas (Table 4). Conversely, the PLA spectrum after AD did not differ from its initial spectrum (Fig. 2B), as confirmed by the peaks ratio (Table 4).

Bioplastics degraded by about 30 % on a TS basis at the end of the maturation phase (90 days). As already observed after AD, SBSB showed a higher degradation than PLA (48.1 % and 15.0 %, respectively). These results were in accordance with the findings reviewed by Folino et al. (2020) who reported that starch-based bioplastics and PLA products degraded by about 45 % and 15 % after composting, respectively. FT-IR spectra after composting (Fig. 1C and 2C) confirmed the differences observed after AD for SBSB and PLA degradation. While PLA spectrum and peaks area

ratio were the same as those of the initial material (Table 4), the starch component of SBSB resulted preferentially degraded by the end of composting, leading to the concentration of the polyester component. For example, the ratio between diagnostic peaks areas of polyester and starch at the end of composting increased from the initial value of 8.5 to 66.5. SEM investigation confirmed that PLA and SBSB underwent different pathways of degradation during biological treatments (Fig. 3B). PLA-SEM micrographs showed an almost unchanged microstructure, with the exception of macro-breaks probably caused by mechanical agents. Conversely, a considerable change in the microstructure of SBSB was highlighted by SEM investigation (Fig. 3). Small holes could be observed in correspondence with the starch spots that were evident before AD and composting, confirming that degradation of this material starts preferentially from the starch component.

Table 4. Ratio between peaks area of IR spectra in bioplastics sample before and after the biological treatments.

	SBSB[a]	**Time** (d)	**1730 cm^{-1}/3400[b] cm^{-1}**	**1730 cm^{-1}/1050[b] cm^{-1}**
Biological processes	*Before biological processes*	0	8.5	1.6
	After anaerobic digestion	35	24	3
	After maturation phase of composting	90	66.5	3.5
	After incubation in soil of bioplastic recovered from compost	180	133	4.3
Disintegration test	*Before biological process*	0	8.5	1.6
	After biological process	90	18.4	3.1
	PLA[a]	**Time (d)**	**3000 cm^{-1}/1750[c] cm^{-1}**	**1400 cm^{-1}/1750[c] cm^{-1}**
Biological processes	*Before treatments*	0	0.04	0.27
	After anaerobic digestion	35	0.05	0.28
	After maturation phase of composting	90	0.05	0.26
	After incubation in soil of bioplastic recovered from compost	180	0.04	0.25
Disintegration test	*Before biological process*	0	0.04	0.27
	After biological process	90	0.04	0.26

[a]SBSB: starch-based shopper bags; PLA: Polylactic Acid products.
[b]Wavenumber: 1730 cm^{-1} attributed to polyester and 3400 and 1050 attributed to starch (see also Figure 1 and S4).
[c]Wavenumber: 3000 cm^{-1}, 1400 cm^{-1} and 1750 cm^{-1} diagnostic peaks of PLA (see also Figure 2 and S4).

364 *3.4 Disintegration test*

365 In order to evaluate the degradation of highly concentrated bioplastics in organic wastes under
366 optimal composting conditions, adapted disintegration tests for SBSB and PLA were carried out
367 following standard procedures (ISO 20200, 2016) and using a 10 % w/w concentration of
368 bioplastics. At the end of the 90 days assay (58 ± 2 °C), SBSB was degraded by about 70 % TS and
369 PLA was degraded by about 25 % TS (Table 3). These values were significantly higher than those
370 from the degradation observed at the end of the composting trial carried out in this study, because of
371 the high temperature profile maintained through the disintegration test, i.e. 58 °C. Although the
372 studied bioplastics were all certified as compostable, neither SBSB nor PLA showed a complete
373 disintegration and this was probably due to the high concentrations of bioplastics tested in
374 comparison with the standardized test ISO 20200 (2016). In fact, the standard method prescribes a
375 0.5 – 2.0 % w/w concentration of bioplastics in the synthetic waste to ensure the optimal ratio
376 between tested materials and composting biomass. The correlation between the quantity of
377 bioplastics added and the disintegration, which occurred should be further investigated. FT-IR
378 spectra of bioplastics at the end of the disintegration test (Fig. 1D and 2D) showed that, also under
379 optimal composting conditions, the starch was degraded faster than the polyester component in the
380 SBSB, while PLA showed an unchanged chemical composition. In fact, in SBSB the ratio between
381 diagnostic peaks areas of polyester and starch at the end of the disintegration test increased from 8.5
382 to 18.4, whereas no differences were observed for ratio between diagnostic peaks areas in PLA
383 (Table 4). Interestingly the increase of ratio between polyester and starch peaks area after the
384 disintegration test was significantly lower than the increase observed at the end of the biological
385 processes. Since the test duration was the same (90 days), it is reasonable to suppose that this
386 difference might be attributable to the different process temperatures. The disintegration test carried
387 out at 58 °C for 90 days may also have promoted the degradation of the polyester component,
388 leading to a lower increase of the ratio between polyester and starch diagnostic peaks area. This was
389 in accordance with Gil-Castell et al. (2020) who reported that polyesters such as poly(3)-

hydroxybutyrate-co-3-hydroxyhexanoate (PHBH) biodegraded effectively only at temperatures higher than 58 °C.

Based on the results described, it was found that starch-based bioplastics degraded under mesophilic conditions following a pathway where the starch component was degraded faster than the polyesters component, modifying the chemical composition of starch-based bioplastics in time. Conversely, PLA bioplastics seemed to be degraded following a *take away* mechanism, where extracellular enzymes hydrolysed polylactic acid polymers into monomers. The so-obtained monomers can then enter the microbial cell and be metabolized, leading to a slow but constant degradation of PLA. Following this mechanism, PLA polymer does not undergo chemical changes with time and this was in accordance with the results reported in the present work (FT-IR spectra, SEM images) (Fig. 1, 2 and 3).

Summarising, increasing amounts of bioplastics in OFMWS gives rise to both possible advantages and disadvantages. Concerning positive aspects, bioplastics have the potential to increase the biomethane potential of OFMSW. It is reasonable to suppose that in 2030 the contribution of bioplastics in biomethane potential of OFMSW can reach about 40 %, taking into consideration 10% bioplastic content (w/w), if the biomethane potential could be reached, depending on process conditions (Table S5). Nevertheless, the low degradation rate of bioplastics under mesophilic anaerobic conditions leads to the necessity for further investigation on bioplastics pre-treatments to enhance biomethane potential and increase degradation kinetics. The slow degradation of bioplastics during mesophilic AD also raises issues on compost quality, since large amounts of bioplastics are expected to remain at the end of the conventional 90 days of biological treatments (AD and digestate composting).

On the other hand, because bioplastics are certified as biodegradable and they often have biological origin, they could be considered as biodegradable components like the other polymers composing compost (e.g. cellulose, hemicellulose, lignin). This concept will be discussed in the next section.

3.5 Fate of bioplastics in soil

3.5.1Biodegradation of bioplastics in soil by standardized trials

Incubation of bioplastics in soil was carried out to evaluate the fate of bioplastics residues in the soil environment after AD and composting and the results are reported in Table 5.

After 90 days of soil incubation, about 327 mg C g C $^{-1}$ evolved from cellulose (positive reference material), whereas no significant mineralization was observed from polyethylene (negative reference material).

Bioplastics showed a linear biodegradation and this was an indication that reaction rates were obeying a pseudo-zero order kinetics and that biodegradation rates were constant and independent of amounts of bioplastics. Chinaglia et al. (2018) and Chamas et al. (2020) reported that the constant rate could be explained by considering that the biodegradation rate depended on the available C-polymer at the surface and not on the total C-polymer. Based on these considerations, a pseudo-zero order kinetic model was assumed to evaluate the rate of biodegradation of bioplastics in soil in comparison with literature data (Table 5).

Table 5. Biodegradation of bioplastics observed at the end of the soil incubation test and kinetics parameter of biodegradation compared to literature.

Material	Biodegradation (mg C g C tested material^{-1})	Biodegradation (%)	Test duration (d)	k[a] (mg C g C^{-1} d^{-1})	k[a] (mg C cm^{-2} d^{-1})	$t_{1/2}$[b] (d)	Degradation (d)	Reference
Cellulose	327	32.7	90	3.63	-	138	275	This work
Polyethylene	0	0	90	0.00	-	-	-	This work
Bioplastics mix t_0	54	5.4	90	0.60	-	833	1,667	This work
Bioplastics mix t_{90}	28	2.8	90	0.31	-	1,607	3,214	This work
SBSB[c] t_0	343	34.3	90	3.81	0.032	131	262	This work
SBSB[c] t_{90}	154	15.4	90	1.71	0.014	292	584	This work
PLA[c] t_0	50	5	90	0.56	0.010	900	1,800	This work
PLA[c] t_{90}	34	3.4	90	0.38	0.010	1,324	2,647	This work
Starch-based bioplastic	-	14.2	110	1.30[d]	-	385[d]	769[d]	Gòmez and Michel (2013)
Starch-based bioplastic	-	37	90	4.11[d]	-	122[d]	243[d]	Accinelli et al. (2012)
PLA bioplastic	-	10	98	1.02[d]	-	490[d]	980[d]	Wu et al. (2012)
PLA bioplastic	-	20	600	0.33[d]	-	1,515[d]	3,030[d]	Urayama et al. (2002)
Polyethylene	-	-	-	-	-	> 2,500 years	> 5,000 years	Chamans et al. (2020)

[a]k: kinetic constant.
[b]$t_{1/2}$: half-life time.
[c]SBSB: starch-based shopper bags; PLA: Polylactic Acid products.
[d]Estimated in this work assuming a pseudo-zero order kinetic model.

445 Non-treated bioplastics mix (t_0) evolved about 54 mg C g C^{-1} after 90 days of incubation
446 in soil, representing 5.4 % w/w of the tested material. Assuming a pseudo-zero order
447 kinetic model, non-treated bioplastics mix should complete its degradation in soil after
448 4-5 years, on average. Nevertheless, because the mix was composed by two different
449 bioplastics, the data reported can be misleading. It is more interesting to consider each
450 single bioplastic.
451 Non-treated SBSB (t_0) evolved about 343 mg C g C^{-1} in the 90 days of incubation in soil
452 (representing 34.3 % w/w of the tested material), whereas PLA degraded 5 % w/w of
453 the tested material (50 mg C g C^{-1} evolved from soil in 90 days). Starting from these
454 results it was calculated that SBSB and PLA were expected to degrade in soil under
455 mesophilic conditions in about 1 and 5 years, respectively. These results were in
456 accordance with literature concerning biodegradation of bioplastics in soil (Emadian et
457 al., 2017; Folino et al., 2020). Indeed, a large range of biodegradability of bioplastics in
458 soil has been reported, depending mainly on the type of the selected soil environment
459 (i.e. pH, microbial community and season) and on the polymer tested (i.e. polymer
460 composition, particle size and surface area) (Chamas et al., 2020, Cucina et al., 2021,
461 Folino et al., 2020). For instance, PLA products were found to degrade in soil in the
462 range 10 % - 20 % (weight basis), whereas starch-based bioplastics showed a
463 degradation between 10 % and 40 % (weight basis), under similar mesophilic
464 conditions. Results of this work also agreed with the kinetics and degradation times
465 calculated from available literature data, which reported a range of 1-2 years and 3-10
466 years for the complete degradation in soil of starch-based bioplastics and PLA,
467 respectively (Table 5) (Accinelli et al., 2012, Gómez and Michel, 2013, Urayama et al.,
468 2002, Wu, 2012).

When the bioplastics mix recovered from compost (t_{90}) was incubated in soil, a slower mineralization was detected in comparison with the non-treated bioplastics mix (t_0). About 28 mg C g C^{-1} evolved from non-treated bioplastics after 90 days of incubation in soil, which represented almost 3 % w/w of the tested materials. Assuming a pseudo-zero order kinetic model, the treated bioplastics mix was expected to degrade completely in soil in about 8-9 years, on average, under mesophilic conditions. Again, these data can be misleading because the mix was composed of two different bioplastics.

SBSB and PLA recovered from compost and incubated separately (SBSB t_{90} and PLA t_{90}), showed a slower degradation in soil in comparison with non-treated materials. The kinetic constant of biodegradation in soil decreased from 3.81 to 1.71 mg C g C^{-1} d^{-1} for SBSB and from 0.56 to 0.38 mg C g C^{-1} d^{-1} for PLA. Therefore, time calculated for the complete degradation of SBSB and PLA after biological treatments increased to 1.6 and 7.2 years, respectively.

Since the bioplastics mix recovered from compost (t_{90}) and the non-treated bioplastics mix (t_0) were incubated in the same soil under the same experimental conditions, differences in biodegradability may be attributed to differences in the tested materials: AD and composting may have partially degraded the bioplastics, leading to the concentration of components characterized by slower degradation in soil.

Regarding SBSB, FT-IR spectra and SEM images (Fig. 1 and 3) confirmed that biological processes (AD and composting) had preferentially degraded some components of bioplastics (i.e. starch), leading to the concentration of more recalcitrant compounds (i.e. polyesters). This may have led to a slower degradation of the starch-based bioplastics recovered from compost in the soil (Table 5). Conversely, FT-IR and SEM investigations showed unaltered composition and microstructure of studied PLA

after biological treatments (Fig. 2 and 3). The slower degradation of treated PLA with respect to the non-treated PLA was the result of a varied ratio between PLA goods after biological treatments. Indeed, at the beginning of the biological treatments PLA goods were represented by dishes (30 % w/w, thickness 100 µm), glasses (30 % w/w, thickness 100 µm) and cutlery (35 % w/w, thickness 1 mm). In mature and sieved compost, the PLA goods ratio was modified and the thicker materials (cutlery) represented about 60 % w/w of the entire PLA, meaning that a preferential degradation and subsequent sieving of the thinner types of goods had occurred. If the biodegradation kinetic constant in soil was then referred to the surface area instead of the mass, as suggested by Chamas et al. (2020), non-treated PLA and treated PLA showed the same value (0.010 mg C cm^{-2} d^{-1}) (Table 5). This means that PLA biodegradation in soil proceeded through the previously mentioned *take away* mechanism and that expressing the biodegradation of bioplastics referring to the surface area could be more appropriate for 3D plastic items. Both changes in chemical composition of SBSB and the varied ratio between PLA goods after biological treatments explain the decreased biodegradability of the bioplastics mix recovered from compost during the incubation in soil.

SBSB and PLA recovered from compost were also analysed by means of FT-IR analysis at the end of soil incubation (90 days after soil incubation) (Fig. 1E and 2E). SBSB showed a completely different FT-IR spectrum with respect to the initial one (Fig. 1A). Diagnostic peaks of starch had almost completely disappeared, meaning that microorganisms from different environments (e.g. anaerobic digestion, composting, and soil) followed the same degradation pathway for SBSB and that they started the degradation from the starch component. Concerning PLA, FT-IR spectrum did not show

517 significant differences with respect to the initial one, and the ratio between diagnostic
518 peaks areas remained almost unchanged (Table 4).
519
520 *3.5.2 Bioplastics in soil: wide-ranging consequences*
521 From an environmental point of view, the results discussed above are encouraging,
522 because they confirm that bioplastics effectively degrade in the soil environment and,
523 thus, accumulation of bioplastics appears to be unlikely, unlike that of fossil-based
524 plastics that require hundreds or thousands of years to degrade in soil (Chamas et al.,
525 2020). This study confirmed the intrinsic biodegradability of bioplastics, which means
526 that these materials tend to biodegrade similarly to natural polymers in non-optimal
527 environmental conditions, even if the rate of biodegradation will be slower than under
528 optimal laboratory conditions (Degli Innocenti and Breton, 2020). Nonetheless, further
529 investigation is needed to assess the formation of bioplastic microplastics in soil and
530 their possible eco-toxicological effects.
531 Biodegradation in soil could occur after both accidental (e.g. littering) and voluntary
532 (e.g. agronomic use of compost) disposal of bioplastics, avoiding environmental issues
533 typical of fossil-based plastics. Indeed, if bioplastics are intrinsically biodegradable in
534 the natural environment, biodegradation reduces the likely permanence time and the
535 risks resulting from the materials' persistence and accumulation (Degli Innocenti and
536 Breton, 2020). Considering the standard density of an agricultural soil (1.5 Mg m^{-3}) and
537 a 30 cm deep fertilization using a compost containing 17.8 % TS of bioplastics, the
538 concentration of bioplastics in soil should not exceed 0.11 % w/w. Assuming that the
539 ecological risk derived from bioplastics residues in soil after compost application can be
540 calculated from the multiplication *concentration · residence time* (Degli Innocenti and

Breton, 2020), it is clear that both factors are reduced by dilution of bioplastics in soil (concentration) and intrinsic biodegradability of bioplastics (residence time).

Results of this work highlight the potential role of waste management in reducing the factor *concentration* in the definition of the ecological risk derived from bioplastics. In fact, integrated AD and composting carried out in mesophilic conditions degraded about 30 % TS of the bioplastics, whereas an average 45 % TS of bioplastics were degraded during the disintegration test carried out in thermophilic conditions (Table 3). In the same time (90 days), degradation of bioplastics in soil did not exceed 5 % TS. Thus, further efforts should be made to increase bioplastics degradation during waste management and consequently reduce the amount of bioplastics that could reach the soil environment.

The increasing amounts of bioplastics in OFMSW also challenges the existing regulations concerning compost quality. The existing regulations do not discriminate between fossil-based plastics and bioplastics. Consequently, it is reasonable to expect that there will be an increase in the amounts of composts that do not meet quality requirements, increasing costs and environmental impacts of OFMSW management. Bioplastics residues in compost should not be taken to count as inert materials (plastics, metals, glass) since they have been proved to degrade in natural environments (e.g. soil, water) (Emadian et al., 2017, Folino et al., 2020). Therefore, regulations might be adapted to the new framework by excluding bioplastics from the fraction of “inert materials”.

4. Conclusions

This paper aimed to evaluate the effects of increasing bioplastics amounts on OFMSW waste management through biological treatments. Bioplastics degraded poorly during mesophilic AD and digestate composting, leading to a high amount of bioplastics residues in compost, which therefore did not meet the current regulatory requirements. Bioplastics' intrinsic biodegradability in soil was demonstrated, showing that these biopolymers degrade in soil in much shorter times than fossil-based plastics. Enhancing bioplastics' degradation during the waste management processes and updating actual regulations concerning compost quality may represent the main challenges for future studies dealing with the effects of bioplastics on waste management.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at:

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