Chemosphere 246 (2020) 125770

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Monitoring of degradation of starch-based biopolymer film under different composting conditions, using TGA, FTIR and SEM analysis.

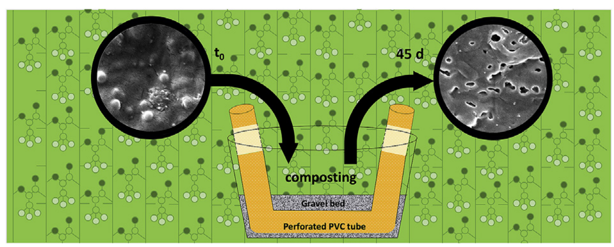
Federica Ruggero [a, *], Emiliano Carretti [b], Riccardo Gori [a], Tommaso Lotti [a], Claudio Lubello [a]

[a] Department of Civil and Environmental Engineering, University of Firenze, Italy
[b] Department of Chemistry "Ugo Schiff" and CSGI, University of Firenze, Italy

HIGHLIGHTS

- A synergic analytical approach improves knowledge of Mater-Bi® biodegradation.
- TGA, FTIR and SEM provide synergic analytical approach to biodegradation monitoring.
- Biodegradation of Mater-Bi® in composting is related to the process conditions.
- Starch and additives in Mater-Bi® film are biodegradable within 5 composting days.
- PBAT biodegradation is highly influenced by moisture and temperature conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 August 2019
Received in revised form
19 December 2019
Accepted 26 December 2019
Available online 30 December 2019

Handling Editor: Tamara S. Galloway

Keywords:
Biodegradation
Mater-Bi®
Composting
Process conditions
Analysis

ABSTRACT

This paper presents the results of a composting lab-scale test carried out on Mater-Bi® film, a starch-based biopolymer. The test material is composed by starch, additives and polybutylene adipate terephthalate (PBAT). The test lasted for 45 days and was developed in three replicates under different temperature and moisture conditions, with the aim to assess the influence on Mater-Bi® degradation of less favourable composting conditions as short thermophilic phase, absence of moistening, and a combination of the two factors. The chemical nature and the morphology of the material and of its single components have been investigated before, during and at the end of the composting process, by means of different analytical techniques. ThermoGravimetric Analysis (TGA) allowed to obtain activation energy and weight loss; Fourier Transform InfraRed spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were used to study changes in the polymeric and morphological structure, and visual analysis provided information on the size of the Mater-Bi® particles. The results show that the biodegradation of PBAT is strongly influenced by the environmental conditions (temperature and moisture); on the contrary, in all the three replicates, both starch and additives are completely biodegraded within the first days of the process.

1. Introduction

The use of bioplastic-made packaging, such as shoppers or

* Corresponding author. Via di Santa Marta 3, 50139, Firenze, FI, Italy.
E-mail address: federica.ruggero@unifi.it (F. Ruggero).

https://doi.org/10.1016/j.chemosphere.2019.125770
0045-6535/

coffee capsules, is part of the current perspective to reach the ambitious objective of 100% packaging recycling by 2030, proposed in the Strategy for Plastics (European Commission, 2018).

Bioplastics are considered more environmentally-sustainable than traditional plastics as, by definition, they are either bio-based, biodegradable, or feature both properties (European Bioplastics, 2008). Bio-based plastics limit extraction and use of fossil resources by using (partly) biomass; furthermore, biodegradability is an add-on property of certain types of bioplastics which offers additional means of recovery at the product's end-of-life and the promotion of a Circular Economy system.

There are several bio-based and biodegradable polymers available on the market, such as starch-based bioplastics, polylactic acid (PLA), polyhydroxy butyrate (PHB), polyhydroxyalkanoates (PHA), polybutylene adipate therephatlate (PBAT) (Emadian et al., 2017). It's fair to say that the biodegradability of a material also depends on the environmental conditions under which the degradation occurs thanks to the action of microorganisms available in the considered environment. For this reason, the study of bioplastic's fate in the environment must take into account specific conditions that bioplastic will be subjected to. The present article focuses on industrial aerobic composting, which is a process characterized by the following consecutive phases: (i) one or more mechanical pretreatments, to ensure an initial shredding and removal of coarse inorganic materials (glass, metals, plastics). (ii) a lag phase of few days during which the biological process starts, (iii) a thermophilic phase (or high-rate phase) of almost three weeks with temperature ranging between 55 and 60 °C, (iv) a maturation phase (or curing phase; duration between 1 and 2 months) with cooling down to room temperature. (v) a final refining with sieves of millimetric mesh is generally provided to obtain acceptable compost quality. In details, the thermophilic phase is submitted to manual operations of moistening and turning to ensure a moisture content not lower than 50–55% and a good aeration of the organic waste heaps. Aeration system can involve also air blowing from the bottom. While the thermophilic phase is characterized by intensive processes of sanitation and degradation of easily biodegradable organic compounds, the maturation phase leads to the stabilization of the organic matter through enrichment by means of humic acids.

Bioplastic-based items can be treated in composting plants in the case the material has proven its compostability according to the harmonised European standard, EN 13432:2000 (EN 13432, 2000) (for packaging) or EN 14995:2006 (for plastic materials not used as packaging).

The technical content of the two standards is identical, meaning that any plastic material that complies with UNI EN 13432 also complies with UNI EN 14995, and vice versa. These standards are the most important technical references for manufacturers of materials, public authorities, composters, certifying bodies and consumers. According to the European Standard EN 13432, a compostable material must have the following characteristics: (i) biodegradability, which is determined by measuring the actual metabolic conversion of the compostable material into carbon dioxide. This property is quantitatively measured using the standard test method, EN 14045 (which is also published as ISO 14855: biodegradability under controlled composting conditions). The acceptance level is 90%, which must be reached in less than 6 months. (ii) Disintegrability, that is the fragmentation and loss of visibility in the final compost (absence of visual contamination). This is measured with a composting test (EN 14045, 2003). The test material is degraded, together with organic waste, for 3 months. After this time, the compost is sieved with a 2 mm sieve. The residues of test material with dimensions higher than 2 mm are considered as not having disintegrated. This fraction must be less than 10% of the initial mass. (iii) Absence of negative effects on the composting process and (iv) low levels of heavy metals (below the predefined maximum values), and absence of negative effects on the quality of the compost (e.g. reduction of the agronomic value and presence of eco-toxicological effects on the growth of plants). A plant growth test (OECD test 208, modified) is carried out on compost samples where the degradation of the test material has taken place. There must be no difference from control compost. Other chemico-physical parameters that must not be different from those of the control compost after the degradation are the pH, salinity, volatile solids, N, P, Mg, K. Each of these requirements must be met simultaneously for a material to be defined as compostable.

Most of the above cited bioplastics (e.g starch-based bioplastics, PLA, PBAT) have been tested under composting conditions, in accordance with the specific requirement of EN 13432, to be labelled as compostable in the biological aerobic and anaerobic processes for the treatment of the organic fraction of municipal solid waste (Ruggero et al., 2019; Zhang et al., 2018). Previous studies dealing with bioplastics degradation under industrial composting conditions have been focused on test conditions required by international standards to assess biodegradability (e.g. ISO 14855) or degree of disintegration (e.g. ISO 20200, EN 14806), always including a thermophilic step at 58 ± 2 °C for a period ranging from 45 days to 6 months. Some authors have indicated that the entity of the biodegradation of different bioplastic types in these conditions ranges between 70% to more than 90% (Gómez and Michel, 2013; Weng et al., 2011; Balaguer et al., 2016). On the contrary, other authors who carried out the tests under mesophilic conditions, have observed a degradation level not exceeding 43% (Accinelli et al., 2012; Emadian et al., 2017).

This paper presents a test carried out on Mater-Bi® film, a starch-based biopolymer. Samples of the material were placed under three different conditions (temperature and moisture), manually controlled during the test to assess their effects on bioplastic degradation. By imposing these process conditions, the aim is to simulate real composting treatments, which can face with less homogeneous and favourable conditions than those commonly used in the standardized tests. The effect of the abiotic process conditions on the test material as a whole and on each single component of Mater-bi® bioplastic film (starch, additives and PBAT), was studied by means of ThermoGravimetric Analysis (TGA), Fourier Transform InfraRed spectroscopy (FTIR), visual analysis and Scanning Electron Microscopy (SEM). In order to follow the whole biodegradation process, samples were analysed at different intervals during the composting process.

2. Material and methods

2.1. Composting test: experimental set up

In the composting test, the waste matrix (initial weight: 5 kg) was composed of food waste and green waste (20% grass, 10% wood chips, 20% vegetables, 30% fruits, 4% tuna, 6% yogurt, 9% cow manure inoculum). The biodegradation test was carried out in a 12 l vessels made of polypropylene, designed by authors to be used as trapezoidal shaped composters. Each vessel was 20 cm high, 20 cm deep, with top base 30 cm and bottom base 33 cm. Following the indications of the standard EN 14045 (2003), the vessel was provided with three temperature probes; then, at the bottom it was placed a system composed by a perforated PVC tube to ensure a good aeration of the heap and a drainage system to avoid that compost will flood. It consists on a grain layer, covered with a still net of 1 mm mesh (Fig. S1 of Supplementary material). In order to maintain the thermophilic and mesophilic temperatures of the composting process, each vessel was placed in the shelves of a 250 l ventilated oven model M250-TB manufactured by Tecno-lab (Italy). Moreover, turning and moistening were controlled and manually set daily during the high-rate phase and every two days during the curing phase.

2.2. Analytical methods

The main composting parameters of the waste matrix were measured at the beginning of the test: the values provided in the standard EN 14045, 2003 for the compost quality required in composting tests were taken as reference. The initial moisture content of the matrix was approximately 60% (Table 1), measured with total solids (TS) content analysis, in accordance with the standard ISO 11465 (1993). The measurement of total organic carbon was provided using the Walkley-Black method: this method involved oxidation of organic matter by potassium dichromate ($K_2Cr_2O_7$) with sulfuric acid (H_2SO_4) to heat the dilution, followed by colorimetric titration (Matus et al., 2009). Total nitrogen and pH were measured in accordance with standard methods ISO 11261 (1995) and ISO 10390 (2005). Initial values of C/N ratio and pH were of 26 and 6.7, respectively. The values in the reference standard EN 14045 are a moisture content not lower than 50%, C/N ratio ranging from 20 to 30 and a pH not lower than 5. The same analyses are done on compost obtained at the end of the composting test and the results are compared with values obtained on a 2 months old stabilized compost provided by the Italian Consortium of Composters CIC (*Consorzio Italiano Compostatori*).

2.3. Tested material and experimental conditions

Regarding the test material, 1 wt% of Mater-Bi® bags available in the supermarkets was added after having cut them into pieces of 5 × 5 cm size. The material of the bags, available in Italian supermarkets, has the licence Mater-Bi® and is labelled as compostable by OK compost Vincotte. To give a preliminary overview of the material composition, it's fair to report the study of Elfehri et al., who has analytically observed the presence of 20% starch, 10% additives and 70% PBAT in Mater-Bi® biopolymer (Elfehri Borchani et al., 2015).

Three replicates were used for the test (Table 1): in the oven, two replicates (A, B) were manually kept in a high-rate phase at 58 ± 2 °C for 5 days (d), followed by a curing phase of 40 d with temperatures at 35 ± 5 °C. In replicate A the moisture content was manually maintained above 45% for all the test, while in B the moisture content went down to 20% during the curing phase. Finally, replicate C was maintained in a high-rate phase of 20 d, followed by a curing phase of 25 d, with moistening conditions equivalent to replicate A. In Fig. S2, temperature and moisture trends of the three replicates are shown.

2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q-600 (DTA-TG) apparatus using open aluminum pans under nitrogen atmosphere. Measurements were performed in a dry nitrogen flow of 100.0 ± 0.5 $cm^3\ min^{-1}$ by increasing the temperature from room temperature up to 500 °C at 10 °C min^{-1}. The main information provided by the elaboration of TGA, in particular by the first derivative of the TGA curves, is related to three aspects. First, from the first derivative of the TGA curves it is possible to obtain the characteristic temperatures of the peaks associated to the thermal reactions of the components of Mater-Bi®. They are indicated as T_0, T_f and T_{peak} and correspond respectively to the initial, to the final and to the maximum temperature of every peak. Moreover, from the derivative of the TGA curves, it is possible to obtain both the composition of Mater-Bi® in terms of weight of each single component at a given aging time and the activation energy of every thermal reaction undergone by the components of Mater-Bi®. More in detail, in order to calculate the activation energy, the Friedman equation was applied (Friedman, 1967).

$$\ln\left(-\frac{d\alpha}{dt}\right) = \ln A + n\ \ln(1-\alpha) - \frac{E_a}{RT} \quad (1)$$

The elaboration of Equation (1) was carried out with the Broido method (Mano et al., 2003). E_a is the activation energy [kJ/mol] of the thermal degradation reaction of the polymers constituting Mater-Bi® (PBAT and starch), A is the Arrhenius constant, while α is equal to $(w_0\text{-}w_t)/(w_0\text{-}w_{inf})$ where w_0 is the weight of the sample before the analysis (when $t = T_0$), w_t is the weight at time t, and w_{inf} is the weight of the sample at the end of the conversion (when $t = T_{inf}$). Moreover, n is the order of the reaction, R corresponds to 8.314 $\left[\frac{J}{mol\ K}\right]$ and T is the temperature [K]. The T range for data elaboration was chosen in agreement with the value of $\frac{d\alpha}{dt}$ that must be constant. In fact, by considering constant this parameter and n = 1 (Mano et al., 2003), Equation (1) becomes linear as follows:

$$\ln\frac{1}{(1-\alpha)} = -\frac{E_a}{R\,T} + const. \quad (2)$$

Then, by plotting $\ln(-\ln(1-\alpha))$, versus 1000/T, through a linear fitting, it is possible to obtain $-\frac{E_a}{R}$ that corresponds to the slope of the curve. A decrease of the activation energy during the composting process is expected because the biodegradation implies a simplification of the polymeric structure due to hydrolysis reactions and further transformation of Mater-Bi® in simpler and more stable compounds.

The weight of Mater-Bi® components derived from data analysis of the TGA is expressed through the following equations:

$$\int_{T_0}^{T_{inf}} \frac{dw}{dT}\ dT = (PA_i)_j\ (\%) \quad (3)$$

Equation (3) is applied separately on starch, additives and PBAT (indicated with j, j = 1,2,3), providing the peak area (that is proportional to the amount of the jth substance still present into the degraded Mater-Bi® at time i) of each component at different i-times of the degradation process $(PA_i)_j$. Equation (4) normalizes the peak area over the initial peak area $(PA_0)_j$, providing the fraction (%) of the jth Mater-Bi® component degraded during the composting process at time i.

$$100 - \frac{(PA_i)_j}{(PA_0)_j} x\ 100 = (WL_i)_j\ (\%) \quad (4)$$

where $(WL_i)_j$ is the percentage weight loss that corresponds to the

Table 1
Process conditions (temperature, moisture and duration of the phases) of the experimental composting tests.

	Thermophilic (or high-rate) phase			Maturation (or curing) phase		
	T (°C)	Moisture (%)	Time (d)	T (°C)	Moisture (%)	Time (d)
A	58 ± 2	55–60	5	35 ± 5	45–50	40
B	58 ± 2	40–50	5	35 ± 5	20–30	40
C	58 ± 2	55–60	20	35 ± 5	45–50	25

amount of the *j*th component degraded at time *i*. Then, in accordance with Elfehri et al.(Elfehri Borchani et al., 2015), it is finally possible to derive the weight fraction of starch, additives and PBAT present in the sample of Mater-Bi® before the test and at time *i*, when the biodegradation is in progress. This allows to make some considerations on the degradation trends of the single components within the biopolymer.

$$\frac{(PA_i)_j}{\sum_{j=1}^{3}(PA_i)_j} x\,100 = (WF_i)_j(\%) \quad (5)$$

where $(WF_i)_j$ is the weight fraction of the single element *j*th in the degraded Mater-Bi® at time *i*. In Table S1 of the supplementary material is provided an example of calculation, applying the described equations.

Moreover, in order to assess the capability of bioplastics to absorb water on their surface as a function of time of the composting process, a gravimetrical determination of the water uptake (*WU*) was experimentally measured and elaborated in accordance with Equation (6):

$$\frac{w_h - w_i}{w_{nd}} x\,100 = WU(\%) \quad (6)$$

where w_{nd} is the initial weight of the piece before degradation and w_i is its weight at time i during the degradation test. w_h is the weight of the sample after having been removed from the matrix, carefully cleansed with distilled water and superficially dried with a tissue paper.

2.5. Spectroscopic analysis

The Fourier Transform InfraRed (FTIR) spectra were collected in total reflectance mode (ATR) with a Shimadzu IRAffinity-1S equipped with a Miracle Pike ATR device. Fragments of bioplastics recovered during the composting process were previously dried, cleaned and tooth-brushed in order to remove all the deposits formed on their surface. The investigated wavenumber range is 2400-600 cm^{-1} and the resolution is 2 cm^{-1}. The variation of peaks intensity and wavenumbers provides qualitative information about the chemical change of the polymeric structure and about the specific degradation process of starch and PBAT.

2.6. Scanning electron microscopy

Images of degraded and not degraded Mater-Bi® have been collected with Scanning Electron Microscope (SEM), ZEISS EVO NA15 apparatus. The pieces of bioplastics were previously metallized with a 10 nm layer of gold.

2.7. Visual inspection

Bioplastics recovered from the waste matrix were reported in photographs to visually define the material in accordance with the following criteria as described by EN 14045, 2003: distribution of particle size, consistency of the material, discolouring, erosion signs on the surface and lateral erosion signs.

3. Results and discussion

3.1. Thermogravimetric analysis

3.1.1. Characteristic temperatures

In Table S4 are reported the values of T_0, T_{inf} and T_{peak} for starch and PBAT. For both the compounds it is possible to observe a decrease of these parameters, already after 5 d of composting, indicative of a degradation process. During the further 40 d, data reveal that the temperatures fluctuate in a range from 2 to 20° around the values assessed at the fifth day. In particular for starch, the decrease of T_0 from 275 to 212 ± 10 °C, was likely to be due to an effective change in the polymeric structure of this material (Weng et al., 2013). Concerning the different process conditions of the three replicates, the graphs in Fig. 1 reported the TGA curves (images a, b, c and d) and their corresponding first derivative (DTGA, images e, f, g and h). It is clear that replicate B undergoes minor changes during degradation than A and C. Moreover, as peak related to additives disappears just after 15 d, this component was not included in the data elaboration for the activation energy.

3.1.2. Activation energy

The calculation of the activation energy was developed considering a range of temperatures equal to T_{peak} ± 10 °C. Moreover, in order to evaluate the influence of the choice of the temperature range in the obtained E_a value, two more data elaborations were carried out: in the first, the T range was equal to T_{peak} ± 7 °C and in the second to T_{peak} ± 13 °C. The standard deviation of the E_a values obtained with the three datasets ranges from ±0.15% up to ±1.8% of the mean value, thus confirming that the choice of the temperature range in the surrounding of T_{peak} doesn't affect meaningfully the final result. In Fig. S3 are reported the linear equations for starch and PBAT, of data elaborated with Broido method for E_a calculation. The good quality of the linear fitting is confirmed by the R^2 value.

In Table S3 are summarized the activation energies of starch and PBAT for replicates A, B and C. As observed for characteristic temperatures, also the E_a value decreased mainly at the beginning of the composting test (first 5 d). The E_a value of starch dropped from 287.3 kJ/mol, for a not degraded sample (Mano et al., 2003), to 125.3, 142.1 and 117.3 kJ/mol for A, B and C replicate respectively. On the contrary, the E_a value of PBAT underwent a lower decrease, from 251.5 kJ/mol typical of a not degraded Mater-Bi® sample, to 217.5, 231.0 and 210.4 kJ/mol, respectively. In the following 40 d, the activation energies of starch and PBAT decreased much more slowly and settled on values slightly lower than those at the 5th day.

3.1.3. Polymeric weight trend

Considering first the variation of weight for starch, additives and PBAT separately (in Table S5 are reported peak area and weight loss), it's possible to outline some considerations about the influence of moisture content and temperature on each single component of Mater-Bi®. The weight loss and the weight fraction, based on Equations (4) and (5) respectively, are shown in Fig. 2 for days 0 and 45.

It's fair to notice that starch and additives follow a trend that is almost constant for the three process conditions A, B and C: they present an average weight loss of 40.5 ± 3% and of 85%, respectively (Fig. 2a). On the contrary, for PBAT it's necessary to observe the behaviour of the polymer individually in the three replicates: while in case of a low moisture content (condition B) the weight loss is only of 17.2%, under a more favourable condition with a moisture content between 55% and 45%, PBAT presents a degradation of 79.9% in A (thermophilic phase of 5 d) and 90.4% in C (thermophilic phase of 20 d). Furthermore, in Fig. S4 is depicted the weight trend of the whole Mater-Bi® material. Concerning the weight fraction of starch, additives and PBAT, Fig. 2b reports values at day 0, which comply with the ones observed by Elfehri et al., depicted in paragraph 2.3 (Elfehri Borchani et al., 2015). Comparing the initial weight fraction of the test material with the composition at the end of the composting process, it's confirmed that for the B replicate the composition has a small variation, with an increase of PBAT

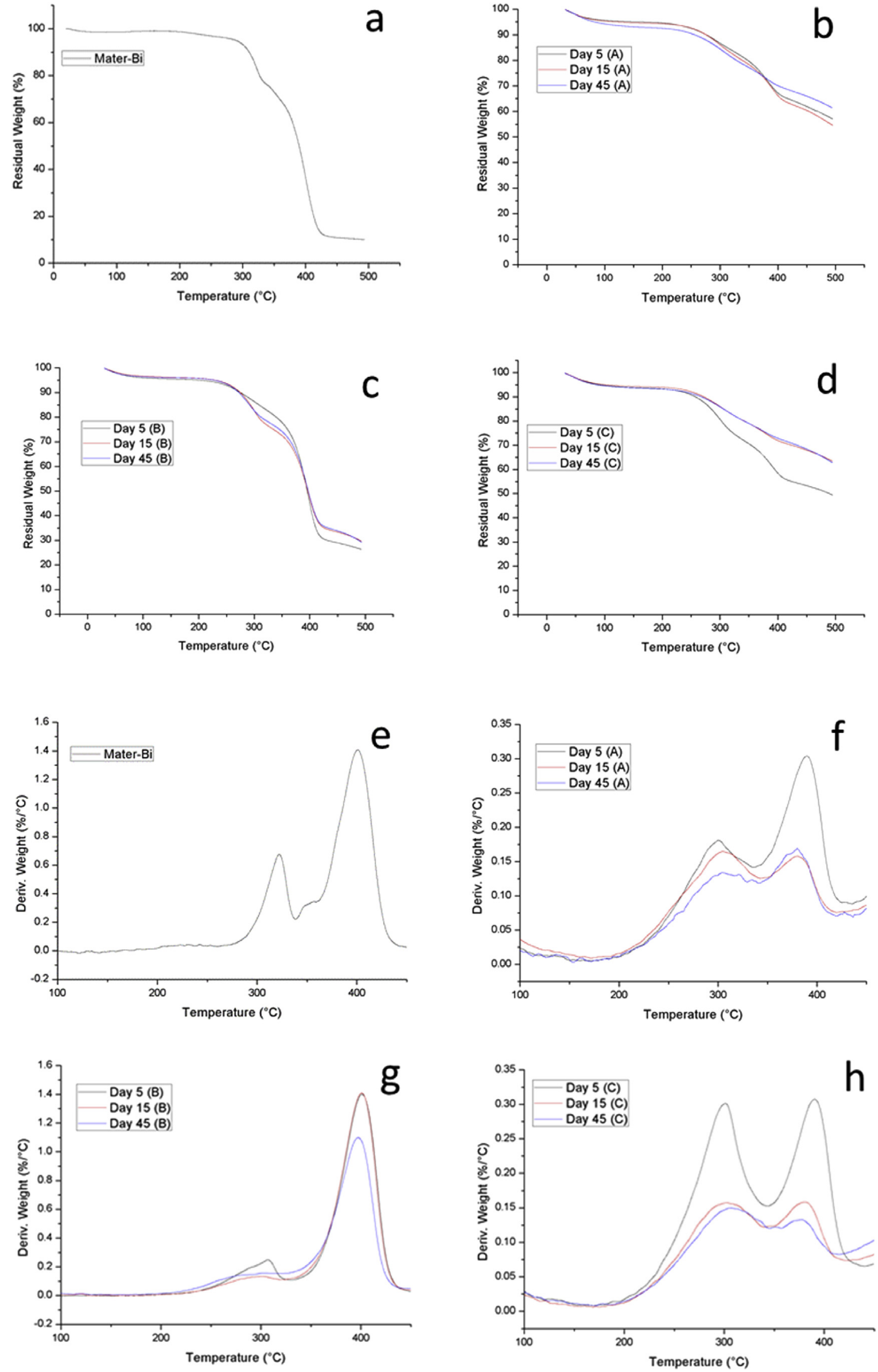


Fig. 1. Representative examples of TGA and DTGA graphs: a) TGA of Mater-Bi® before composting process; b), c) and d) represent the TGA graphs during composting (day 5 and 15) and at the end of the process (day 45) respectively for samples A, B and C. e) DTGA of Mater-Bi® before composting process. f), g) and h) represent the DTGA graphs during composting (day 5 and 15) and at the end of the process (day 45) respectively for samples A, B and C.

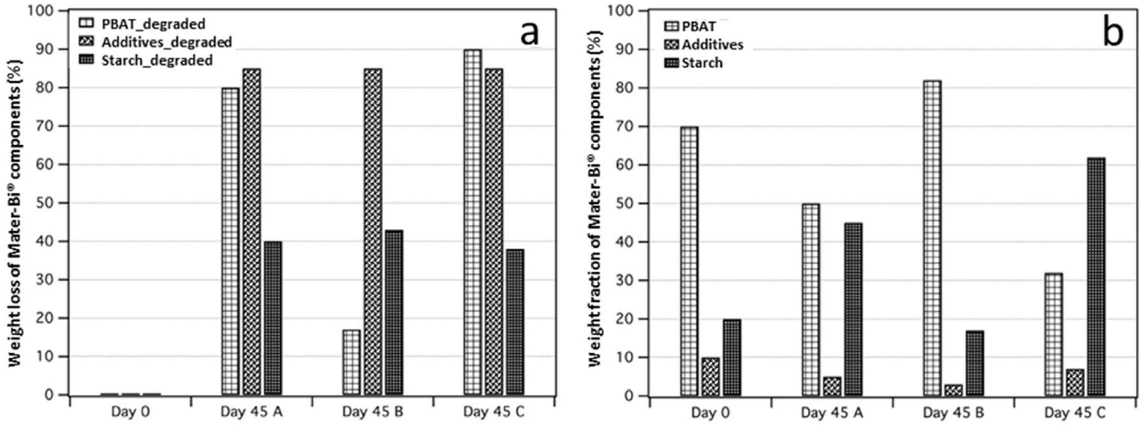


Fig. 2. The graphs show a) the weight loss WL (%) and b) the weight fraction WF (%) of each Mater-Bi® component at day 45 for samples A, B and C in comparison with day 0. The calculations are based on Equations (4) and (5) respectively.

percentage due to its much lower degradation with respect to the other components. On the contrary, for samples A and C there is a prevalence of starch at the end of the biodegradation process. It's fair to conclude that PBAT is the polymeric component of Mater-Bi® more subjected to the influence of moisture and temperature trends; moreover, being the influence of moisture much more relevant than that of temperature, it is possible to affirm that water plays a primary role in the biodegradation of Mater-Bi®. Water within the waste matrix firstly allows the exchange of nutrients through the cellular membrane of the microorganisms that concur to the degradation of the bioplastic; secondly water is a vehicle for the movement of extracellular enzymes and soluble substrates, and finally is the medium in which chemical reactions take place. Moreover, high water availability allows the entrance of the microorganisms, present in the matrix, inside of the material, promoting the biodegradation activity (Alvarez et al., 2006). However, the necessary condition to promote the biodegradation of the Mater-Bi® is a moisture content higher than 40% in the organic waste matrix not only during the period of bio-oxidation, but also during the curing-phase. Below this threshold is observed a slowing down of the biological activity, that stops for moisture values lower than 25%. In these conditions the degradation process seems stabilized, but previous reports showed that if water is added again, the biological activity is able to restart (e.g. Chiumenti and Chiumenti, 2002). To directly consider the capability of bioplastic pieces to absorb water on their surface, a measure of the water uptake was done in accordance with Equation (6). The values of water uptake, as an average of the three replicates, increased until the 30th day and then stabilized around 5% (Fig. S5).

3.2. Spectroscopic analysis

The ATR-FTIR allowed to detect the chemical composition of Mater-Bi® during the composting process. The most significant spectra are reported in Fig. 3, with Mater-Bi® at day 0 and samples from A, B and C replicates at days 5, 15 and 45. The figure reports the spectra in the wavenumber range between 1800 and 600 cm^{-1}, where the main diagnostic peaks are present (see Table 2); the whole spectra are reported in Fig. S6. In Table 2 the most important absorption bands of the collected spectra are compared with those identified by other authors for Mater-Bi® (Elfehri Borchani et al., 2015), for starch (Mihaela et al., 2018) and PBAT (Weng et al., 2013; Herrera et al., 2002).

The peaks attributed to PBAT are the ones at 1717, 1274 and 726 cm^{-1}: while for replicate C an almost complete disappearance of these signals is observed as the biodegradation process proceeds, for sample A and even more for B, they are still present even after 45 d. The observations confirm the results already outlined with the TGA: the biodegradation of PBAT is strongly influenced by temperature and moisture.

Moreover, the spectra reported in Fig. 3 show that, after 5 d, in the regions between 1650 and 1600 cm^{-1} and between 1450 and 1400 cm^{-1}, there is the appearance of two new peaks attributable to amidic groups of proteinaceous materials. These peaks are due to the compost remained on the surface of bioplastic samples analysed; in fact the spectrum of the compost obtained at the end of the lab-scale test (Fig. S7) confirmed the presence of these two new peaks appearing in the considered range.

3.3. Scanning electron microscope

The SEM micrographs of not degraded Mater-Bi® (day 0) are reported in Fig. 4 and Fig. S8. The images indicate the presence of a heterogeneous microstructure; the main evidences of the material is the presence of some circular spots which dimensions range in the order of few hundreds of nm probably composed by starch (Deschamps et al., 2008), (Szymońska et al., 2009) dispersed in a continuous 3D polymeric matrix that is supposed to be composed mainly by PBAT (Muthuraj et al., 2015).

Fig. 4 shows that, upon degradation, strong changes in the microstructure of Mater-Bi® occur. With the progress of the composting process, images reported in Fig. 4 indicate the progressive disappearance of the circular spots with the formation of small holes (in the order of hundreds of nanometres) in correspondence of the grains that were present before composting. Being that from TGA we observed that the composting process progressively induces a strong degradation of the starch constituting the original Mater-Bi®, it is reasonable to suppose that these circular spots are made mainly by starch.

3.4. Visual inspection

The visual inspection carried out on pieces recovered during the test (Fig. 5), outlines several interesting considerations. Just after 5 d the material presented signs of erosion, and the aspect was greatly changed due to the contact with the organic waste matrix. Bioplastic pieces presented organic matter deposition on the surface. The organic matter remained strongly attached to bioplastics, thus encouraging the exchange of microorganisms between the materials. Moreover, Fig. 5 clearly shows the different behaviour of

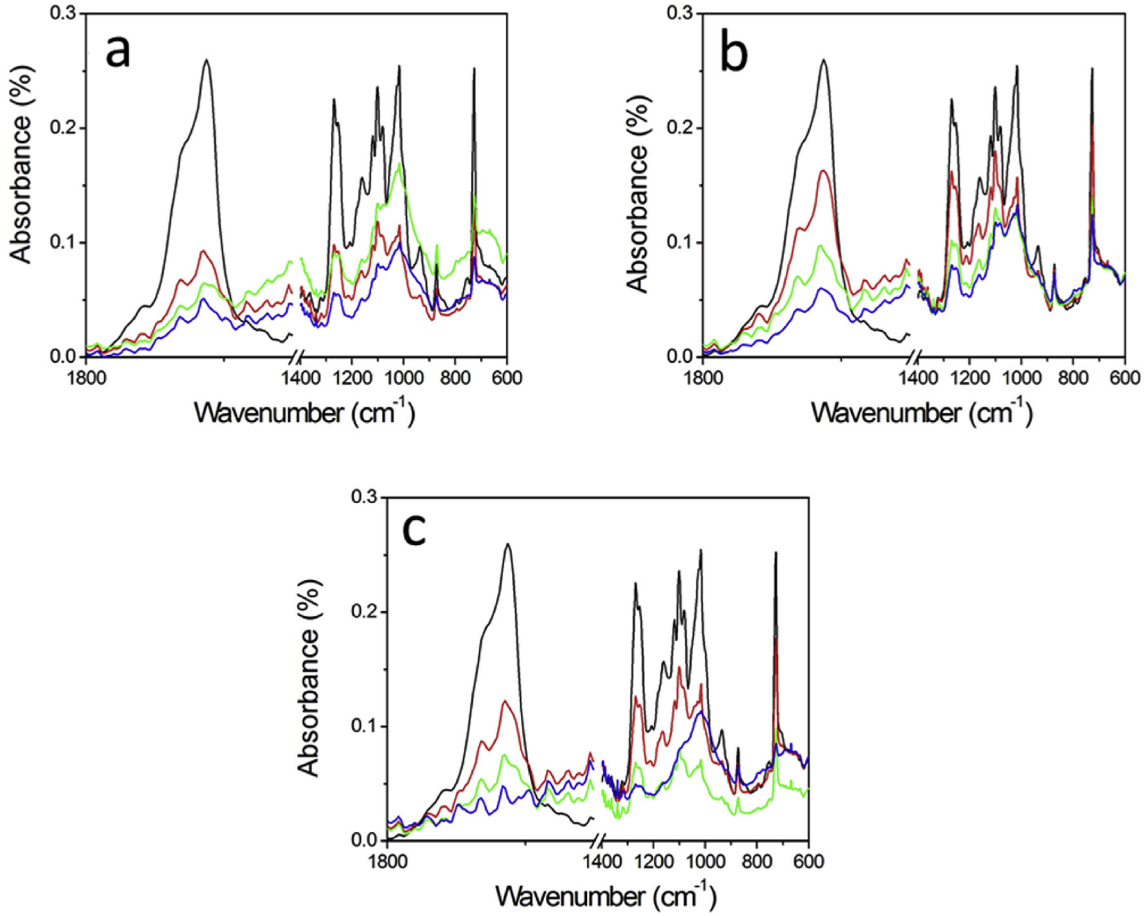


Fig. 3. Comparison between spectra obtained with FTIR analysis at different days: black corresponds to day 0, red to day 5, green to day 15 and blue to day 45. a) spectra of samples A, b) spectra of samples B, c) spectra of samples C. The range of wavenumber is the most significative for the observations of the main chemical changes. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
In the first column of the Table are presented the wavenumbers identified during the study with the FTIR analysis. The absorption bands were compared with those in literature; in the second and third columns are reported the assignment of the molecular bond and the material (starch or PBAT) which the authors attribute to the wavenumbers.

Wavenumbers (cm^{-1})	Assignment	Material	Reference
1717	C=O	PBAT	(Elfehri Borchani et al., 2015), (Weng et al., 2013); Herrera et al. (2002)
1506	benzene	PBAT	Weng et al. (2013)
1456	phenylene group	PBAT	Elfehri Borchani et al. (2015)
1409	$C-H_2$	PBAT	Weng et al. (2013)
1274	C−O	Starch	(Elfehri Borchani et al., 2015), (Weng et al., 2013)
1163	CH_2OH	Starch	Mihaela et al. (2018)
1118, 1081	C−O	Starch	Elfehri Borchani et al. (2015)
1018	phenyl ring	PBAT	(Weng et al., 2013; Herrera et al., 2002)
726	$[-C-H_2-]n \geq 4$	PBAT	(Elfehri Borchani et al., 2015), (Weng et al., 2013)

replicates A and B with respect to C. Bioplastics from replicate C were almost completely disintegrated just after 15 d, a trend which is strictly attributable to the temperature that was maintained at 58 ± 2 °C. However, it's fair to notice that for the three replicates, after 45 d under the described conditions some micro-pieces were still recoverable: their aspect, particularly in replicate C, was very similar to compost, even though FTIR and SEM still detected the presence of bioplastic within the sample.

3.5. Compost characterization

At the end of the 45 d of composting test, C/N and pH analyses were carried out on mature compost. Compost was previously sieved with 4 mm mesh: in fact, in full scale plants there is generally a final refining with removal of not degraded wood chips and refuses. Moreover, using just few grams of compost for the analysis, the presence of lignin pieces could strongly alter the results, particularly for the total carbon. The refined compost was homogeneous in the three replicates, resulting in C/N and pH equal to 16.1 ± 1.8 and 8.7 ± 0.1 respectively. The same analyses carried out on a 2 months old stabilized compost provided by CIC resulted in C/N 16.2 and pH 8.7.

Moreover, compost from the lab tests was analysed through TGA and FTIR; the profile of the TGA curve (Fig. S9a) shows that the

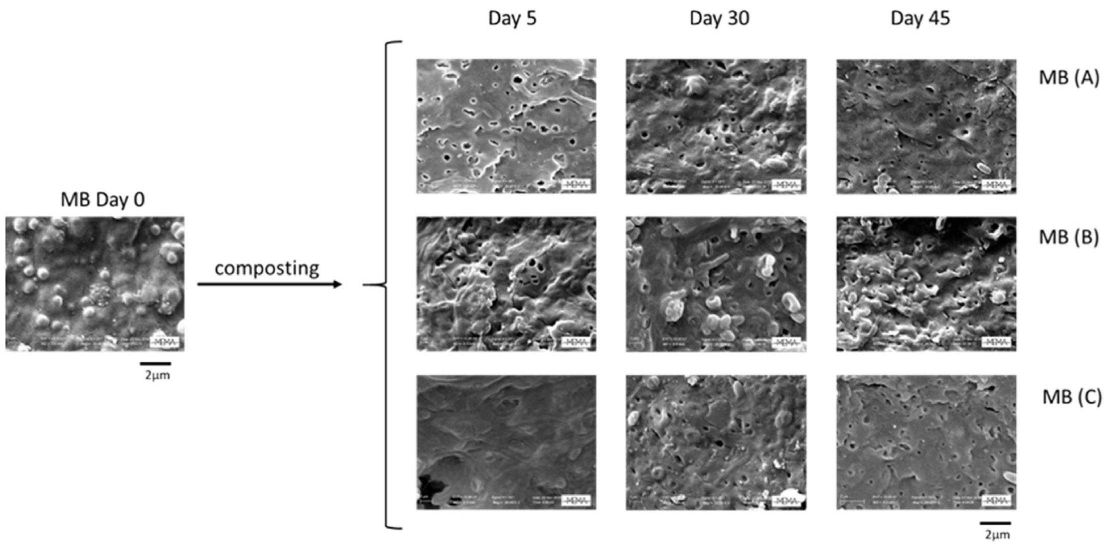


Fig. 4. SEM micrographs of degraded samples A, B and C during (day 5 and 30) and at the end (day 45) of the composting process, x20000.

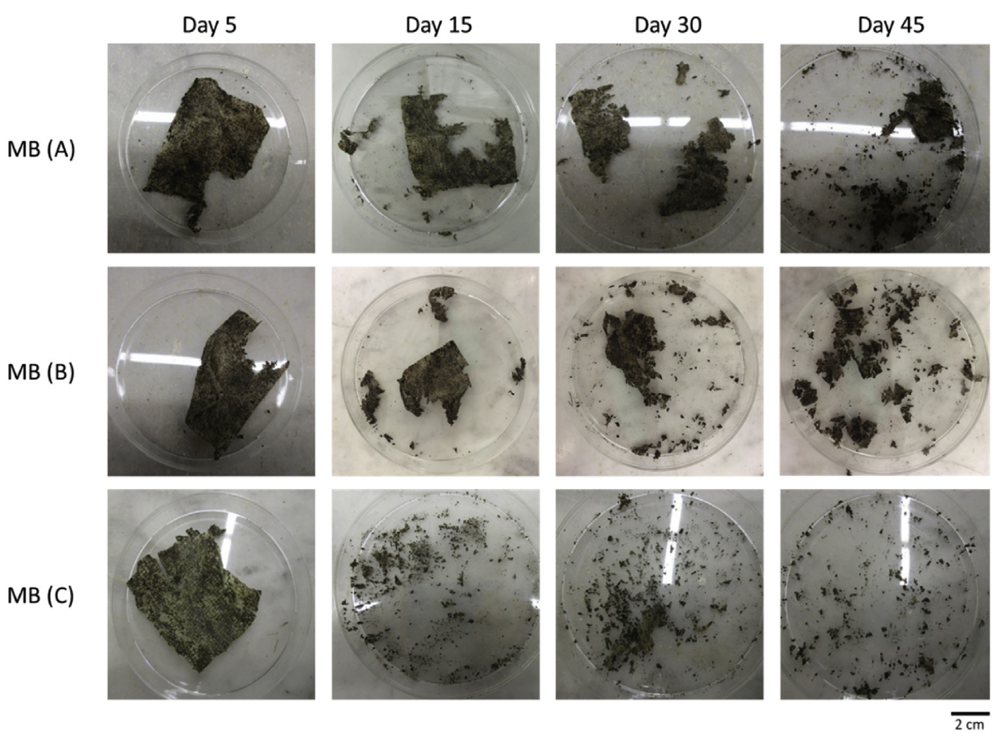


Fig. 5. Representative pictures, taken during the laboratory tests, of degraded samples A, B and C during (day 5, 15 and 30) and at the end (day 45) of the composting process. MB is used in the figure as abbreviation of Mater-Bi®.

thermal behaviour of the pure compost is similar to the one of bioplastics (Fig. 1b–d). Second, the graph of the first derivative of the TGA curve (Fig. S9b) reveals a peak almost in the same T range typical of starch (Fig. 1f–h).

Finally, as previously discussed, FTIR carried out on compost (Fig. S7) shows two peaks in the wavenumbers range 1650-1600 cm^{-1} and 1450-1400 cm^{-1}, both due to amidic groups of the proteinaceous materials appertaining to the bacteria acting the biodegradation. These peaks are present also in the biodegraded bioplastics, due to the residues of these microorganisms not completely detached from the film surface during the cleaning procedure before the FTIR analysis.

4. Conclusions

The composting of Mater-Bi® inside a heterogeneous organic waste matrix and under different process conditions allowed to study the effect of the environmental conditions on the biodegradation of its single polymeric components (starch, additives and PBAT). From TGA analysis it is possible to obtain activation energies of the thermal degradation processes underwent by Mater-Bi® components. These data together with the study of the weight variation of bioplastic samples, indicate that the first 5 d of the composting process play a fundamental role in the biodegradation of Mater-Bi®: both the weight and the activation energy of starch and additives (these parameters are used as markers to follow the biodegradation) undergo a strong decrease in the first period of the composting process. This trend is also confirmed by FTIR and SEM data. On the other hand, as indicated by the trend of both the weight of the bioplastic and E_a, the biodegradation process continues in the following period, even if at a lower rate. Taking into account the different process conditions tested, the data indicate that while the biodegradation of starch and additives aren't influenced by the decrease of temperature and moisture occurring as the maturation phase starts, the biodegradation of PBAT is strongly slowed down for replicates A and B during the maturation phase. The most influent parameter for the biodegradation of PBAT is the moisture content that determines the microbial activity and prevents the transformation of the biopolymer into a stable organic matter. This is the case of replicate B, where the moisture content passes from 40 to 50% in the thermophilic phase up to 20–30% in the maturation phase. Moreover, being starch a natural polysaccharide, used as a readily biodegradable source of energy by microorganisms, its degradation rate is faster than the rate of synthetic biodegradable polymers (Wang et al., 2015), as demonstrated by the strong decrease of its E_a. On the other hand, PBAT is a synthetic aromatic-aliphatic co-polyester with a molecular structure more complex than starch (Ra et al., 2018); then, it takes a longer period to be completely assimilated by microorganisms and transformed into stable products and it is much more subjected to process conditions like an insufficient moistening content.

In conclusions, to carry out an exhaustive analysis of the biodegradation process, this study highlights the necessity to use a synergic approach based on the use of different instrumental techniques, giving complementary information. This approach allows a complete kinetic analysis of the composting process and shows the influence of the environmental conditions on the biodegradation of starch, additives and PBAT, allowing to extend the knowledge on the behaviour of Mater-Bi® in a composting process.

CRediT authorship contribution statement

Federica Ruggero: Conceptualization, Methodology, Writing - original draft, Data curation. **Emiliano Carretti:** Software, Formal analysis, Resources. **Riccardo Gori:** Writing - review & editing. **Tommaso Lotti:** Investigation, Resources. **Claudio Lubello:** Project administration, Supervision.

Acknowledgments

The lab-scale composting tests were carried out in the laboratory of Sanitary Engineering at the Department of Civil and Environmental Engineering (DICEA) of the University of Firenze. The TGA and FTIR analyses were carried out in the laboratories of the CSGI Consortium and of the Department of Chemistry "Ugo Schiff", while the SEM analysis at the MEMA centre ever in the University of Firenze.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.125770.

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