Original article

WM&R

Waste Management & Research
1–11

DOI: 10.1177/0734242X211063731
journals.sagepub.com/home/wmr
SAGE

Rigid and film bioplastics degradation under suboptimal composting conditions: A kinetic study

Federica Ruggero[1], Sara Belardi[1], Emiliano Caretti[2], Tommaso Lotti[1], Claudio Lubello[1] and Riccardo Gori[1]

Abstract

The present research investigates the degradation rate of bioplastics under various composting conditions, including suboptimal ones. Lab-scale tests were carried out setting three variables: temperature (37°C–58°C), humidity (30%–60%) and duration of the thermophilic and the maturation phases (15–60 days). The composting tests were carried out following modified guideline ISO 20200:2015 and lasted for 60 days. Bioplastics in the synthetic waste matrix consisted of Mater-Bi® film biobags and PLA rigid teaspoons. A kinetic study was performed, resulting in faster degradation rates for film bioplastics (first-order kinetics with k = 0.0850–0.1663 d^{-1}) than for rigid (0.0018–0.0136 d^{-1}). Moreover, film bioplastics reached a complete degradation within the 60 days of the test. Concerning the rigid products, 90% degradation would be achieved in 2–3 years for mesophilic conditions. Finally, in the undersieve of 0.5 mm some microplastics were identified with the ImageJ software, mainly relatable to rigid (PLA) bioplastics. Overall, the results disclosed that the combination of mesophilic temperatures and absence of moistening slowed down both the degradation and the disintegration process of bioplastics.

Keywords

Bioplastics, composting, suboptimal conditions, degradation, microplastics, Mater-Bi®, PLA, PBAT

Received 17th July 2021, accepted 13th November 2021 by Associate Editor Arne Ragossnig.

Introduction

Recent research about compostable bioplastics degradation highlighted the need to improve the basic knowledge about the delicate balance of temperature, humidity and timings, influencing this complex process in composting treatment (Emadian et al., 2017). Generally, in the industrial composting plants, thermophilic phase is expected to last a minimum of 20 days at 50°C–60°C (European Commission, 2000). For hygienization purposes, EU Regulation 2019/1009 required to maintain at least one of the following conditions: 70°C for 3 days, 65°C for 5 days, 60°C for 7 days or 55°C for 14 days (The European Parliament and the Council of the European Union, 2019). Therefore, it is possible that some industrial plants have a very short thermophilic phase. During compost maturation, the decomposition declines to a slow and steady pace at temperatures <40°C, with synthesis of humic substances (European Bioplastics, 2009).

Common technologies of industrial composting are windrows composting, aerated static piles and in vessel composting systems. These systems include rotting tunnels and the most recent technology of bio-oxidation in composting biocells. The diversity of composting technologies entails a variability of the main parameters, such as temperature, humidity and process duration, as well as of aeration, turning and moistening procedures. Considering the Italian composting plants, the open-air windrow composting, largely diffused in the southern part of the country, involves a thermophilic phase in a covered environment, lasting 40, 30 or 20 days (Pergola et al., 2017). Generally, a maturation phase in an open-air environment follows, with neither moistening nor aeration. During this phase, compost is organised in windrows which are static or weekly turned (Pergola et al., 2018). Similar conditions occur when bio-oxidation is ensured in static aerated platforms instead of channels (European Commission, 2000). Biocells are relatively recent technology: they find a good application for new plants construction and reconversion of old ones. Indeed, biocells are closed systems which prevent odours and litters and ensure a better control and monitoring of temperature, humidity, oxygen, pH, waste flows and aeration time

[1]Department of Civil and Environmental Engineering, University of Firenze, Firenze, Italy
[2]Department of Chemistry 'Ugo Schiff' and CSGI, University of Firenze, Firenze, Italy

Corresponding author:
Federica Ruggero, Department of Civil and Environmental Engineering, University of Firenze, Via di S. Marta 3, 50139 Firenze, Italy.
Emails: federica.ruggero@unifi.it; fruggero93@gmail.com

(Martalò et al., 2020). Industrial composting with biocells has generally a high-rate phase in thermophilic conditions carried out in one cell for 15 days or twice as long in two cells in series. It follows an open-air desiccation phase (European Commission, 2000).

The current research will implement a kinetic study of film and rigid bioplastics degradation under a wide variability of composting conditions. Similar studies have been recently developed to delineate decomposition trend of various organic waste, in particular green waste and sewage (Abu Qdais and Al-Widyan, 2016; Komilis, 2006; Manu et al., 2016). The study aims to delineate the reaction rates which characterise bioplastics degradation under different temperature, humidity and duration in composting. The results would be a useful reference for bioplastic waste management in the industrial composting plants, enhancing to foresee bioplastics degradation time in given composting conditions.

Materials and methods

Experimental setup and tested materials

The composting test was carried out following the guideline ISO 20200:2015 (ISO 20200, 2015), with temperature, duration and humidity modified. A 'synthetic' solid biowaste matrix was prepared based on the composition suggested in the guideline, dry matter basis (sawdust 40%; rabbit feed 30%; cow manure compost 10%; corn starch 10%, saccharose 5%; corn seed oil 4%; urea 1%); 500 g of synthetic waste matrix, with a water content of 50%, was incubated in 5 L polypropylene vessels covered with a lid. A total of eight vessels were used, to simulate the different composting conditions of interest. Moreover, on both the sides of the vessels, three millimetric holes were made to ensure gas exchange between the inner atmosphere and the outside environment.

As required by reference standard, turning and moistening were controlled and manually set daily during the thermophilic phase and weekly during the maturation. This procedure also ensured a good aeration of the biowaste matrix.

Due to the small amount of biowaste matrix used for the lab-scale experiment, it was necessary to keep the vessels in an oven to hold the temperature generated by self heating-effect. Therefore, two 250 L ventilated oven model M250-TB manufactured by Tecnolab (IT) were used to place the vessels. At the end of the composting test, the mass loss of synthetic biowaste matrices was monitored by measuring the total solids content, in accordance with the standard ISO 11465:1993 (ISO 11465, 1993). Moreover, the C/N ratio was measured before and at the end of the test. The C/N of the synthetic waste matrix before composting was 27 ± 2. The measurement of total organic carbon was provided using the Walkley–Black method and total nitrogen was measured in accordance with standard methods ISO 11261:1995 (ISO 11261, 1995).

The aim of the study was to delineate the reaction rates which characterise bioplastics degradation under different temperature, humidity and duration in composting. Therefore, the test was carried out under different operating conditions varying in duration of the thermophilic phase (15–30–45–60 days) and humidity. The temperatures were kept, respectively, at 58°C ± 2°C during the thermophilic phase and 37°C ± 2°C during the maturation phase. Two ranges of humidity were selected, called in this work 'low humidity' (L) and 'high humidity' (H). In high humidity conditions, the humidity was controlled in order to not decrease below 55% during the thermophilic phase and 50% during the maturation phase. In low humidity conditions, the humidity was controlled in order to not decrease below 50% during the thermophilic phase and 30% during the maturation phase. The process conditions of each vessel are graphically summarised in Figure 1.

The most favourable condition was 60 days of thermophilic phase (constant 58°C ± 2°C) with humidity not decreasing below 55% wm (A_H). On the contrary, condition D_L was the most unfavourable, with 15 days thermophilic phase (58°C ± 2°C and 50% humidity) followed by 45 days of maturation phase (37°C ± 2°C and humidity slightly above 30%).

The materials tested were both film (PBAT) and rigid (PLA). Film bioplastics were bags, available in Italian supermarkets, with the licence Mater-Bi® and labelled as compostable by OK compost Vincotte. To give a preliminary overview of the material composition, it is fair to report the study of Elfehri Borchani et al. (2015), who has analytically observed the presence of 20% starch, 10% additives and 70% PBAT in Mater-Bi® biopolymer (Elfehri Borchani et al., 2015). A total of 64 film samples, with 50 µm thickness and weight on average 0.0578 g, were cut 5 × 5 cm size from the bags. Rigid bioplastics samples were 64 teaspoons purchased from Ecozema shop (IT), labelled as compostable in accordance with the EN 13432 and available in Italian supermarkets. Samples had 250 µm thickness (concave part) and weighted on average 1.0051 g. The composition of the material is investigated by authors, by means of TGA and FTIR, as described later.

To allow an easy recovery and weighting, bioplastic samples were inserted in polyester nets with holes not larger than 1 mm size. Despite the usefulness of this method, it is fair to report that a net may reduce the surface directly available for the microbial community, and therefore be a further element of influence during the degradation process (Sintim et al., 2019). Before being analysed, all the bioplastic samples were carefully cleansed with distilled water and superficially dried with a tissue paper.

Kinetic study of bioplastics degradation

One rigid (PLA) and one film (PBAT) bioplastic sample were collected about once a week; the first three samples were reinserted in the matrix after the weighting procedure. Indeed, the net was removed, the sample was dried at 40°C ± 2°C to constant mass and weighted. In Tables S1–S4 of the supplementary materials, the weight of each sample at different times of the test is reported. Experimental weight loss was calculated based on equation (1)

$$\%Weight\,loss = \frac{(W_0 - W)}{W_0} \times 100 \tag{1}$$

where W_0 and W are the experimental weights before and at the sampling times of the test, respectively.

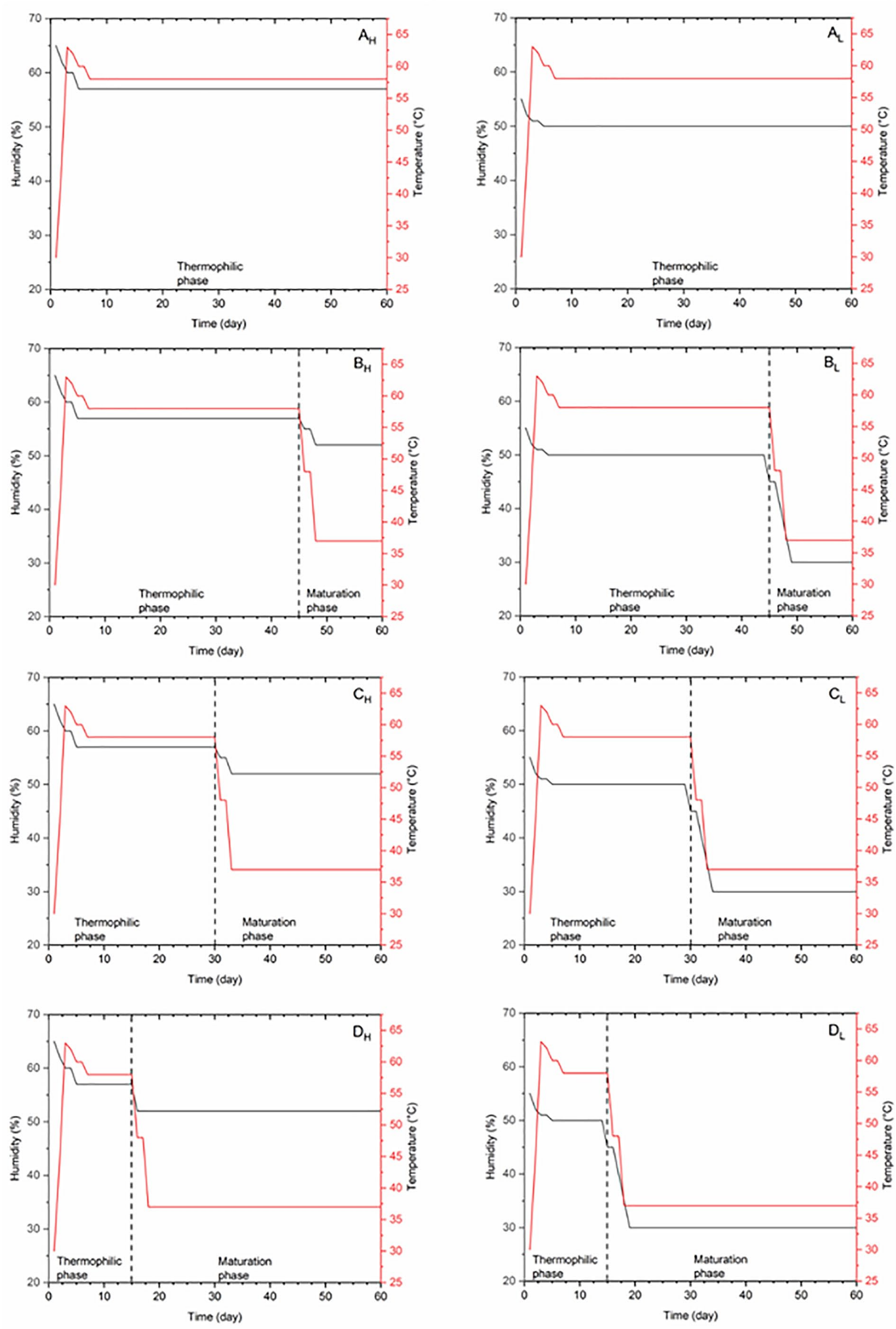

Figure 1. Composting process conditions in the eight variants of the tests.

The experimental data obtained in the present study were fitted in the following pseudo first-order kinetic model (equation (2))

$$\frac{dW}{dt} = -kW \quad (2)$$

where k is the degradation rate constant (day^{-1}) and t is the time (day).

Integrating the above equation and letting $W = W_0$ initially when $t = 0$, it gives equation (3)

$$ln\left(\frac{W}{W_0}\right) = -kt \quad (3)$$

The reaction rate constant (k) was obtained by plotting $\ln(W / W_0)$ versus time data for film and rigid Mater-Bi® bioplastics under the eight composting conditions.

Bioplastics characterization

Thermogravimetric analysis of bioplastic residues. Thermogravimetric Analysis (TGA) was performed only on rigid (PLA) bioplastics. The analysis was carried out on the pristine material and at the end of the 60 days test. It is fair to specify that the residue collected from the net at the end of the test was a mixture of bioplastics fragments and compost. A TA Instruments Q-600 (DTA-TG) apparatus using open aluminum pans under nitrogen atmosphere was used. Measurements were performed in a dry nitrogen flow of $100.0 \pm 0.5\,cm^3\,min^{-1}$ by increasing the temperature from room temperature up to 500°C at 10°C min^{-1}; 5 mg of material were submitted to the analysis. The main information provided by the elaboration of TGA is the characteristic temperature of the peak of conversion T_{peak}. Moreover, from the derivatives of the TGA curves, the percentage weight PA_i of each i component in the new materials was calculated with equation (4), from the study by Ruggero et al. (2020)

$$\int_{T_0}^{T_{inf}} \frac{dw}{dT} dT = PA_i\,(\%) \quad (4)$$

where T_0 and T_{inf} correspond, respectively, to the initial and the final temperatures of each peak.

Fourier-transform infrared of bioplastic residues. Fourier-transform infrared (FTIR) was performed on pristine rigid (PLA) and film (PBAT) bioplastics and on pure bioplastic residues collected from the net at different times of the test. In particular, rigid bioplastics were analysed at the end of the thermophilic phase and at the end of the maturation phase. Film bioplastics were analysed with FTIR at day 5, 10 and 15. The analysis was performed in total reflectance mode with a Shimadzu IRAffinity-1S equipped with a Miracle Pike ATR device. The instrument is supported by LabSolutions IR software. The investigated wavenumber range is 2400–600 cm^{-1}, with resolution 2 cm^{-1} and spectra are collected in absorbance. 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.

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 (EN 14045, 2003): distribution of particle size, consistency of the material, discolouring, erosion signs on the surface and lateral erosion signs.

Microplastics identification in compost

At the end of 60 days composting test, all the vessels of the eight variants contained a compost matrix, eventually with some bioplastic residues. The aim of the following procedure was to investigate whether some bioplastic residues were still present in the vessels of the eight variants. Therefore, for each vessel, the compost matrix was collected and dried at 105°C ± 2°C to constant mass. Then, the compost matrix was sieved with 2, 1 and 0.5 mm meshes. The oversieve of 2 mm was not used for this analysis. The three undersieves (of 2, 1 and 0.5 mm) were weighted and spread on a clean table. All the procedure was done for each vessel separately. The software ImageJ was used to investigate the presence of eventual bioplastic residues in the compost matrix of each vessel. Indeed, Image J measured the area occupied by these residues in the compost matrix collected from each vessel. So, photographs of the undersieves (of 2, 1 and 0.5 mm) were taken and uploaded on ImageJ. Using the function of adjust colour threshold, the software allows to set a threshold for microplastics identification within the compost matrix and provides the total area occupied by microplastics. In particular, the function was set with hue 0/255, saturation 0/255 and brightness in the range 232–247/255. The threshold colour was B&W with colour space HSB in dark background.

Results and discussion

Bioplastics characterization

Spectra of pristine materials are displayed in Figure 2(a). Concerning film biobags, the main peaks identified the material as Mater-Bi®, composed of starch and PBAT.

Already after 15 days the main peaks of both starch (1200–1080 cm^{-1}) and PBAT (1717, 1274, 1018, 726 cm^{-1}) were almost disappeared in all the composting conditions. In Figure 2(b), it was reported one example of spectrum done at days 5, 10 and 15 of film sample A_H.

Concerning the rigid material, FTIR analysis assessed the presence of PLA and PBAT (Figure 3(a)). Peaks referring to PLA were identified in 1748 cm^{-1}, corresponding to C=O group, 1450 cm^{-1} of $CH–CH_3$ groups, 1181 cm^{-1} relatable to C–O group and finally 1081 cm^{-1} related to C–C stretch in n-alkanes (Arrieta et al., 2014; Correa-Pacheco et al., 2020; Fortunati et al., 2014). The PBAT component was assessed through the peaks 1717 cm^{-1}, C–O group, 1274 cm^{-1}, the ester linkage, 1018 cm^{-1} corresponding to the phenyl, and 726 cm^{-1} corresponding to $[–C–H_2–]n_{\geqslant 4}$ (Elfehri Borchani et al., 2015; Weng et al., 2013).

All the main peaks of pristine film and rigid bioplastics are also marked in Figure 2(a).

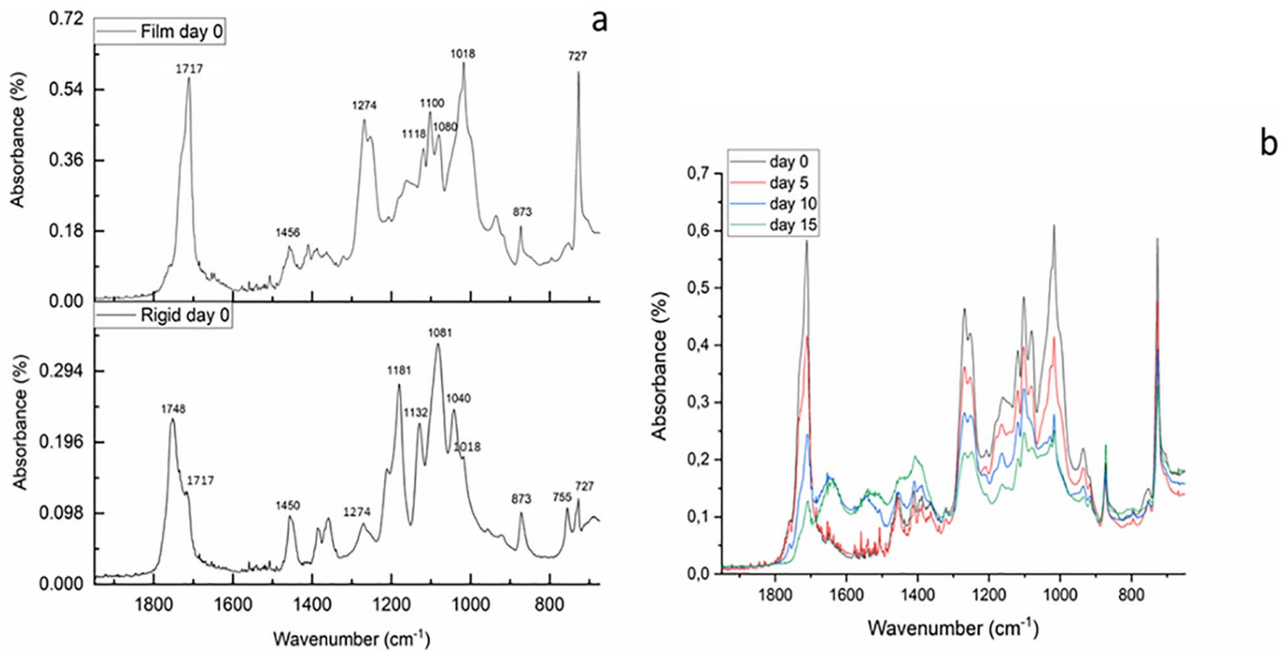

Figure 2. Spectra (wavenumber-area 1950 to 700 cm^{-1}) from FTIR analysis of (a) new film (PBAT) and rigid (PLA) bioplastic samples and (b) A_H film samples at days 0, 5, 10 and 15 of composting test.

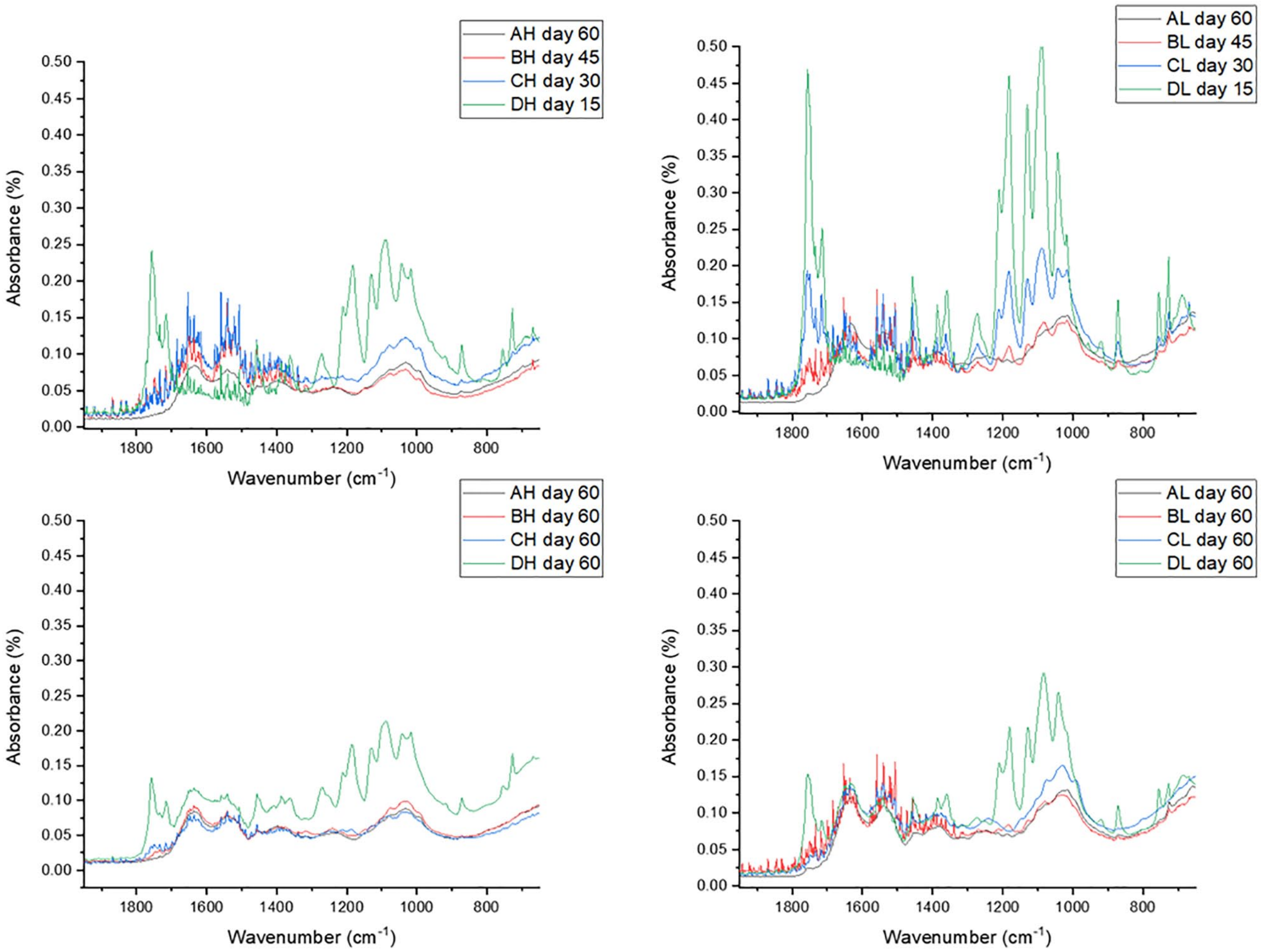

Figure 3. Spectra from FTIR analysis of rigid bioplastic samples (PLA) collected at the end of thermophilic phase (upper graphs) and at the end of the test (lower graphs) under the conditions of the variants A, B, C and D. Graphs on the left show results of variants with high humidity, right side graphs with low humidity.

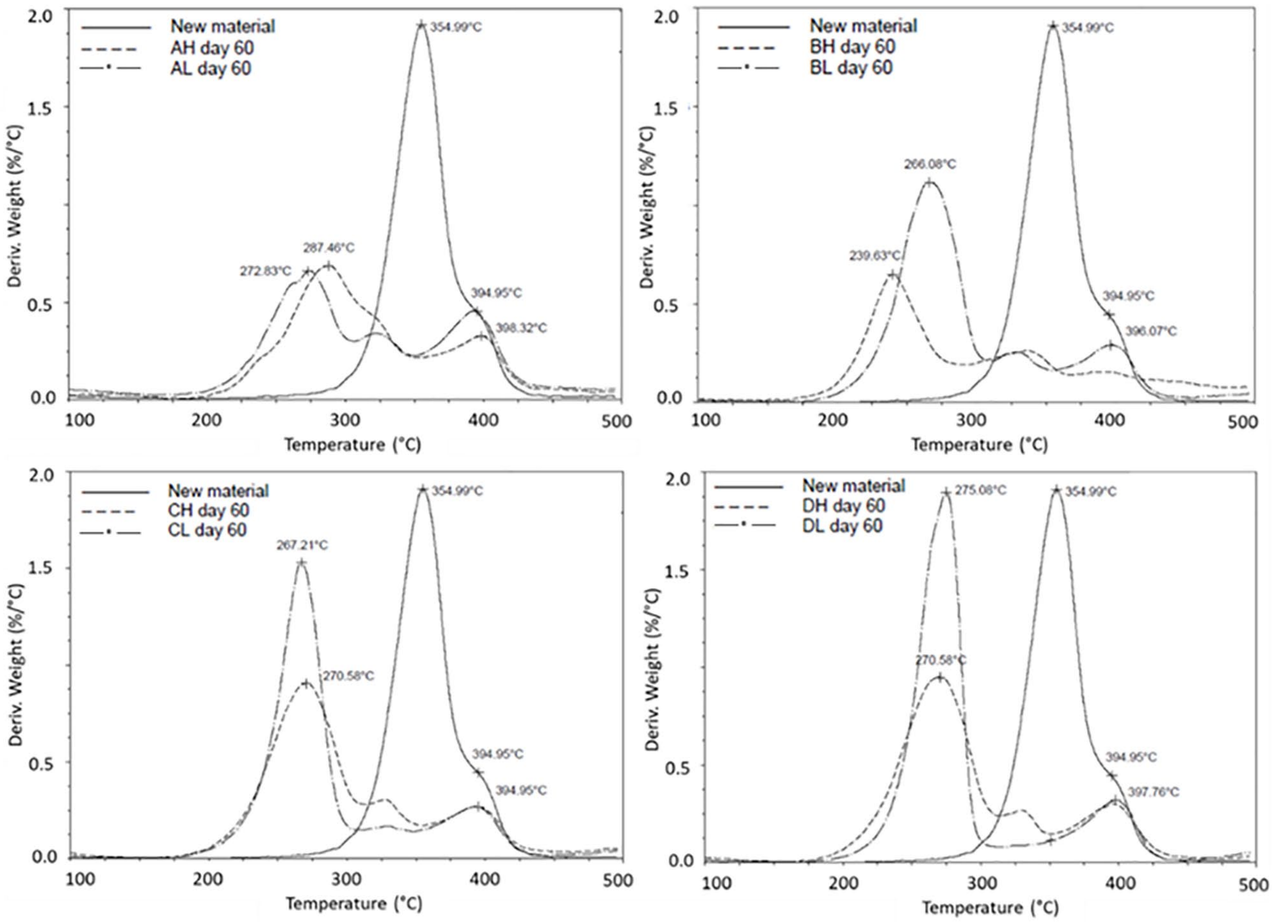

Figure 4. Graphs of the derivatives of TGA analysis of rigid bioplastic (PLA) samples collected at the end of the test, under the conditions of the variants A, B, C and D.

Concerning the rigid (PLA) bioplastics, the spectra depicted some differences between the samples of the eight operative conditions (Figure 3). Samples A and B showed similar trends under high- and low-humidity conditions. Indeed, all the main peaks are almost disappeared during composting process. In particular, the spectrum of sample B at the end of the 45 days thermophilic phase did not depict any differences respect to the spectrum at end of the maturation phase. Regarding sample C after the thermophilic phase (30 days), a major decrease in the main peaks in conditions of high humidity is observable. However, the disappearance of the main peaks in the spectrum of C_L at the end of the maturation phase showed that the degradation continued also under conditions of lower humidity. The main differences among the operative conditions occurred for samples D. Indeed, the graphs showed that especially under low-humidity conditions, all the main peaks of the material are still identifiable both at the end of the thermophilic phase (15 days) and of the maturation phase.

The TGA analysis provided a confirmation about the composition of bioplastic teaspoons (rigid bioplastic samples; Figure 4); following equation (4), composition ratio was 85:15 PLA and PBAT. So, it is confirmed that the material is mainly composed of PLA. The result is in line with research development about mixed biopolymers extruded to form film and rigid (PLA) bioplastics: different authors showed in their studies TGA and derivative graphs with the peculiar shoulder of PBAT in a temperature range from 390°C to 400°C, depending on the equipment and heating rate (Correa-Pacheco et al., 2020; Xiang et al., 2020; Xu et al., 2019).

Figure 4 reports the behaviour of the bioplastic teaspoons at the end of the test. The small peak at 395°C is related to the presence of a small amount of PBAT. This peak is almost stable: a slight increase occurred in some conditions, but it is basically due to cross-linking or recombination reactions which are typical of degradation (Kale et al., 2007). On the contrary, for the peak related to PLA, a substantial reduction in the main peak temperature at the end of composting period is noticeable, and it can be considered as an index of degradation (Luzi et al., 2015). This temperature shifted from 355°C to around 270°C in conditions C and D, down to a minimum of 240°C in B_H. A peculiar trend was shown in condition A, where at both low and high humidity, the PLA T_{peak} after composting was slightly higher than other conditions. However, it is fair to observe that these peaks are less sharp and less homogeneous, with a tendency to incorporate the small peak which rose at temperature around 320°C. This peak, which appeared in the TGA of day 60 in almost all the conditions, is relatable to the residual organic matter strongly attached to the surface of the material and not easily removable with the cleaning procedure, as observed in previous study (Ruggero et al., 2020). Therefore, in this work we refer to this material as rigid (PLA) bioplastic.

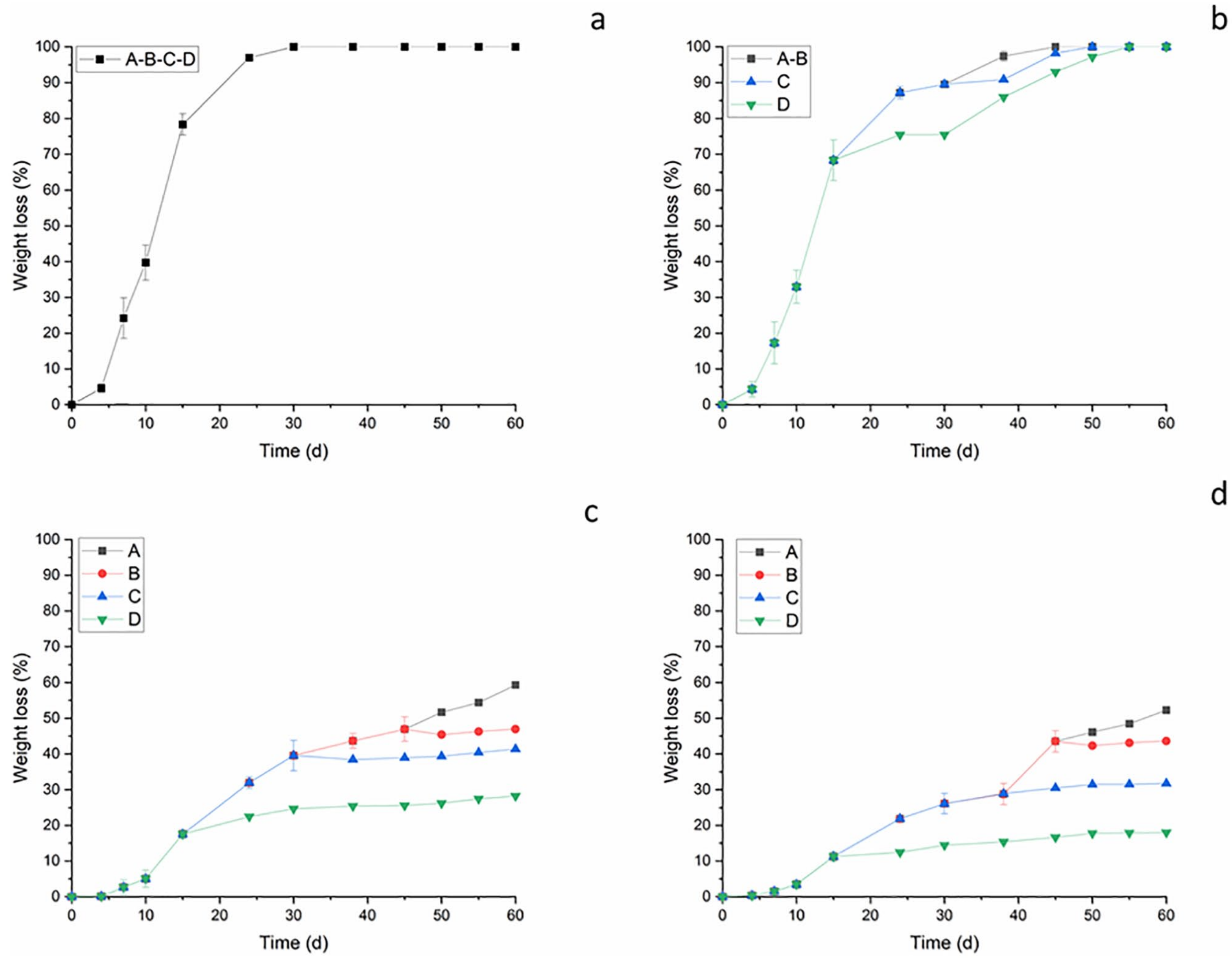

Figure 5. Weight loss calculated from experimental data with Equation 3.7: (a) film bioplastics (PBAT) in high-humidity conditions, (b) film bioplastics (PBAT) in low-humidity conditions, (c) rigid bioplastics (PLA) in high-humidity conditions and (d) rigid bioplastics (PLA) in low-humidity conditions.

Both A_H and A_L showed a degradation in particular for PLA compound. Furthermore, the results reported that B_H had the highest degradation in the area of 396°C which corresponds to stable PBAT compound. C_H, D_H and D_L showed the lowest degradation, confirming what already assessed with FTIR analysis. However, even for the less degraded samples, a decrease in the peak temperatures is generally observable, which can be associated with a shift from hardly degradable to easily degradable compounds.

Kinetic study of bioplastics degradation

The degradation of both rigid and film samples met a lag phase lasting for 4 days at the beginning of the composting process, similar to that observed by previous authors for several organic waste matrices (Abu Qdais and Al-Widyan, 2016). After the lag phase, the trend of weight loss followed a significantly different behaviour between film and rigid samples. Film bioplastics (PBAT) completely degraded within the 60 days of composting test; rigid samples (PLA) degraded up to a maximum of 60% for the most favourable condition (A_H). The curves of weight loss for both film and rigid bioplastics are presented in Figure 5.

Concerning film samples, a humidity not lower than 50% (conditions H) allowed to reach a complete degradation within 30 days. On the contrary, a humidity reduction during the maturation phase (condition L) resulted in slowing down the degradation of the material, which took up to 50–55 days (Figure 5(a) and (b)).

Considering the rigid samples, the trend of weight loss largely differed from one condition to another. Both in Figure 5(c) (condition H) and Figure 5(d) (condition L), the strong steepness change when the maturation phase (37°C ± 2°C) started is clearly visible. It is fair to remind that the maturation phase started after 15 days for sample D, 30 days for sample C and 45 days for B. Sample A was always kept at 58°C ± 2°C. Indeed, sample A showed an almost constant trend of degradation during the composting period. Moreover, in the same temperature conditions, Figure 5(d) shows that slower degradation and sharper steepness variations occurred in the case of a lower humidity of the biowaste matrix (condition L). Finally, an intensive degradation for A and B between 38 and 45 days is observable. It is interesting

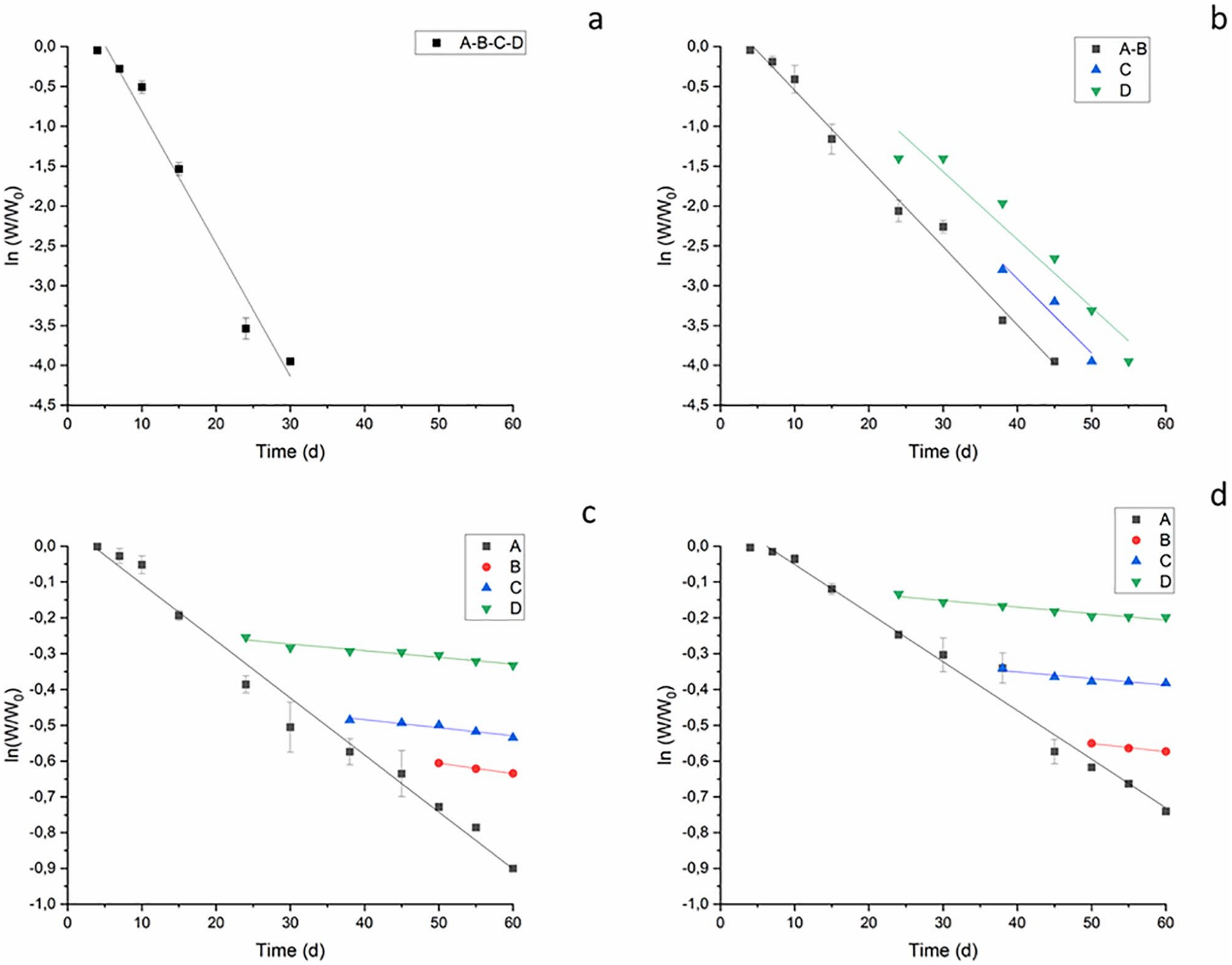

Figure 6. Pseudo first-order kinetic curves of bioplastics for (a) film bioplastics (PBAT) in high-humidity conditions, (b) film bioplastics (PBAT) in low-humidity conditions, (c) rigid bioplastics (PLA) in high humidity conditions and (d) rigid bioplastics (PLA) in low humidity conditions. Mind the different *y*-scale for film (PBAT) and rigid (PLA) plastics.

that this trend started at day 38 which was a sampling day, with consequent intensive turning and aeration of the biowaste matrix. After sampling bioplastics from the matrix, the vessels A and B were kept again at 58°C ± 2°C, in accordance with the operative conditions selected for the variants. Indeed, it is fair to assess that the strong aeration provided with turning, jointly with the thermophilic conditions of A and B, contributed to enhance and improve the degradation process.

Beside the results related to bioplastics, it is fair to mention some observations about the biowaste matrix. Indeed, weight monitoring of the synthetic waste matrix reported a weight loss ranging from 35% (A and B) to 10%–15% (C) and 0%–5% (D). From these values, it is assumable that the reduction of humidity, jointly within thermophilic phase shorter than 1 month, affected not only the degradation of the tested materials but also the degradation of the other waste in the biowaste matrix, especially the sawdust. A further index of the influence of unfavourable composting conditions on the synthetic matrix was provided by the C/N ratio. The initial value of 27 ± 2 decreased to a range of 11–18 for the conditions A and B and to 21–26 for C and D. Considering that the ratio C/N is one of the important parameters to determine the compost quality, a value between 10 and 20 is normally expected for a good compost quality (Veneto Agricoltura, 2009). By monitoring these basic indices, the study highlights that suboptimal conditions of temperature and humidity in composting may both prevent the complete degradation of rigid bioplastics and influence the final quality of compost.

Starting from weight loss measurement, the kinetic study was developed applying equation (3). The calculation of reaction rate *k* excluded the period of lag phase and started from day fourth. The kinetic of the thermophilic phase for bioplastics was elaborated with the values obtained while the samples A, B, C and D were at 58°C ± 2°C. Then, three different mesophilic kinetics were assessed for B, C and D, starting after the temperature decrease down to 37°C ± 2°C. The degradation kinetics for film and rigid bioplastics are shown in Figure 6, differentiated basing on set humidity conditions (L or H). The values of *k*, intercept and R^2 are reported in Table 1. The kinetic data were reasonably fit well to pseudo first-order reaction as shown by R^2 (~0.93–0.99).

Finally, for rigid bioplastics (PLA), from the reaction rate, the theoretical time required to complete the degradation process was extrapolated. It corresponds to 8 and 10 months for A_H and A_L, respectively. Times raised for B, C and D due to the reaction rate decrease during the maturation phase at 37°C ± 2°C. In temperature and humidity conditions of the maturation phase, B_H would take around 3 years for completely degrading; B_L and C_H not less than 4 years; C_L and D_H around 5 years; finally, D_L would degrade in 6 years.

Furthermore, it is fair to evaluate the duration to reach 90% degradation, which is the percentage required for bioplastics to comply with the international standard (i.e. EN 13432). While A_H and A_L can degrade up to 90% within 5 and 6 months, respectively, the operative conditions of the maturation phase slowdown the kinetic, and consequently, 90% degradation can be acquired within 2–3 years.

Table 1. Reaction rates of bioplastics degradation in composting, calculate from equation (3).

	k (d^{-1})	Film bioplastics (PBAT)		k (d^{-1})	Rigid bioplastics (PLA)	
		Intercept	R^2		Intercept	R^2
A_L	0.0981	0.432	0.9905	0.0136	0.085	0.9307
B_L	0.0981	0.432	0.9905	0.0023	0.439	0.9833
C_L	0.0934	0.822	0.9289	0.0018	0.278	0.9626
D_L	0.0850	0.981	0.9395	0.0018	0.097	0.9433
A_H	0.1663	0.851	0.9759	0.0159	0.055	0.9842
B_H	0.1663	0.851	0.9759	0.0029	0.461	0.9954
C_H	0.1663	0.851	0.9759	0.0023	0.394	0.9298
D_H	0.1663	0.851	0.9759	0.0019	0.217	0.9304

However, bioplastics degradation was not completely prevented during the maturation phase, where it continued at slow kinetics. It is assumable that the degradation was encouraged by mechanical factors, mainly stress and abrasion during turning, and by microorganisms infiltrated into the porous structure of the material. These microorganisms are protected against desiccation by the slime matrix secreted during microbial adhesion to bioplastic surface and made of polysaccharides and proteins (Lucas et al., 2008). The presence of proteinaceous material found a confirmation in peak 1550 cm^{-1} (Bonhomme et al., 2003), which rose in the FTIR spectra collected during the degradation process.

Microplastics from rigid samples (PLA) identified in compost

Microplastics detection in the retained matter >2 mm and 1–2 mm fractions were negligible, accounting no more than one item in each vessel. Indeed, it was expected that nets retained pieces ⩾1 mm size. On the contrary, in the undersieves <0.5 mm of the vessels of the eight variants, ImageJ software measured surface areas from 20 to 50 mm^2.

In Figure 7, the areas occupied by microplastics in each vessel are reported, beside an example of the analysis performed with

Sample	Area (mm^2)
A_H	40.3
B_H	48.6
C_H	50.3
D_H	30.6
A_L	46.0
B_L	33.4
C_L	28.8
D_L	20.1

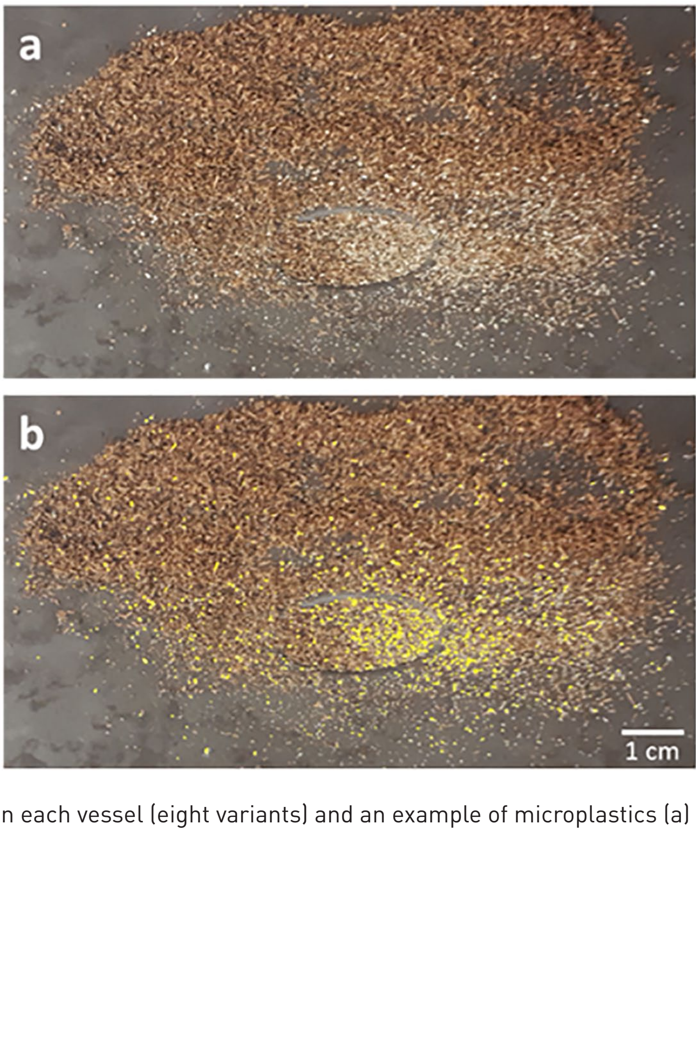

Figure 7. Areas (mm^2) occupied by microplastics in each vessel (eight variants) and an example of microplastics (a) without and (b) with threshold setting in ImageJ.

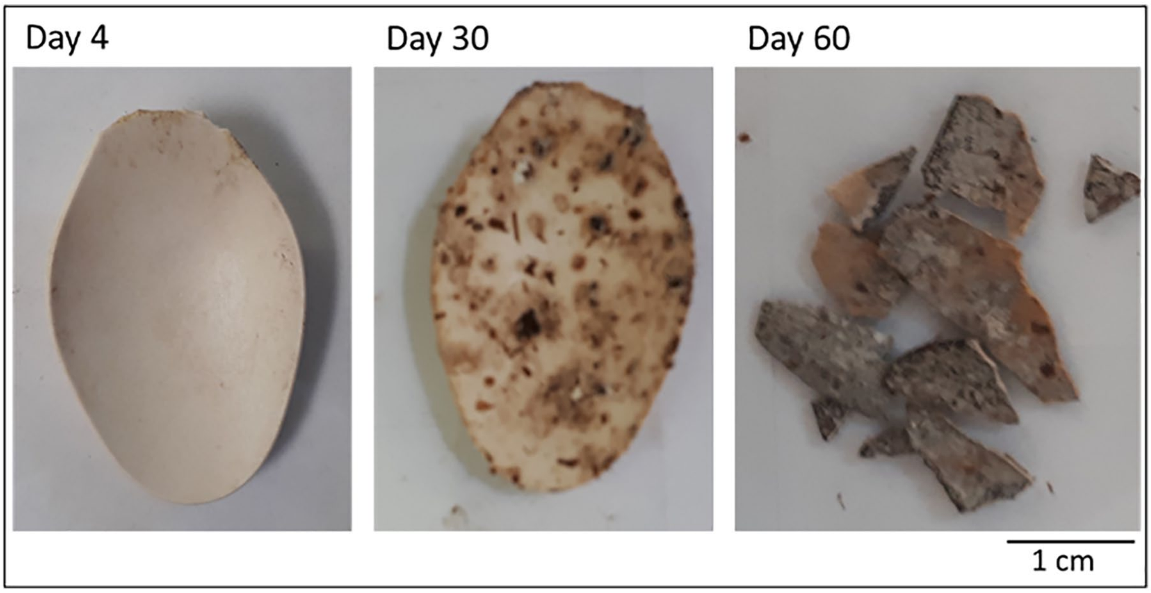

Figure 8. Residues of rigid (PLA) bioplastics collected in B_H vessel.

ImageJ, with and without the set threshold for microplastics identification.

As a general trend for B, C and D conditions, it was found that the area occupied by microplastics in each sample was higher in conditions H than L. The trend highlights that humidity had an important role in the disintegration process. Moreover, condition D (15 days of thermophilic phase) had the lowest abundance of microplastics in the undersieve of 0.5 mm. On the contrary, the largest areas were found in the conditions A, B and C_H, with longer thermophilic phases. Therefore, it was also confirmed the role played by high temperatures in disintegrating rigid bioplastics. It is fair to report that the important role of temperature in the disintegration of both film and rigid bioplastics was already assessed by previous studies (Ruggero et al., 2021; Weng et al., 2011).

In conclusion, a combination of mesophilic temperatures and absence of moisture slowed down both the degradation process and the disintegration of larger pieces into microplastics.

Overall, microplastics identification with ImageJ software was easily applicable, thanks to microplastics round shape and light colour, which enhanced threshold setting in dark matrix and dark background. Finally, visual identification of microplastics generally required a validation of the items identified as microplastics. Therefore, FTIR analysis was randomly carried out on the potential plastic items (Song et al., 2015). The analysis both confirmed the nature of the fragments and provided information about the type of bioplastics. As expected, microplastics derived from rigid (PLA) bioplastics, which only had degraded approximately 15%–60% within 60 days (Figure 5). Examples of pictures of teaspoons residues collected from the nets at different timings of the test are reported in Figure 8 (and supplementary materials).

Conclusion

The present research provided an improvement of the basic knowledge about the influence of optimal and suboptimal composting conditions on film (PBAT) and rigid (PLA) bioplastics degradation, which can be useful in the perspective of bioplastic waste management in industrial composting plants. To this purpose, the kinetic study was fundamental to deep analyse the degradation process. Due to the significant variation of conditions between the thermophilic and the maturation phase, the kinetic analysis was separately performed in the two phases.

Even though the kinetic study showed larger influence of composting conditions on rigid bioplastic (PLA) than film (PBAT), the maturation phase always led to a strong slowdown of the degradation rate. Humidity and temperature were decreased due to mesophilic conditions, which were found to significantly affect the degradation process.

Mater-Bi® bioplastic films reached a complete degradation within the 60 days of composting. However, constant moistening to maintain humidity above 50% allowed film bioplastics to degrade within 30 days. On the contrary, in condition L (low humidity) where the matrix was left to dry out, the degradation was not completed before 50–55 days. Concerning rigid bioplastic samples (PLA), the degradation rates were much slower. Even though the process was not prevented at all, the tested material did not completely degrade within the 60 days of composting.

Interestingly, dry matter (mass) and C/N of compost obtained from the biowaste matrix were monitored. The results highlighted that the parameters of compost obtained under suboptimal composting conditions did not fulfil the regulation requirements for compost quality. This issue may be further investigated in future research.

Finally, microplastics abundance in the undersieve of 0.5 mm was found to generally increase when bioplastics reached higher degradation. The results highlight that beside the degradation process, also disintegration has an important role during composting of bioplastics. Moreover, the results disclosed that beside the temperature, humidity had a role in the disintegration process.

Acknowledgements

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'.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship and/or publication of this article: Ente Cassa di Risparmio di Firenze is mentioned for funding part of this work. Moreover, this research has been part of the project 'Monitoraggio del processo di degradazione delle (bio)plastiche negli impianti di compostaggio e digestione anaerobica per il trattamento della frazione organica dei Rifiuti Urbani', funded by Consorzio Italiano Compostatori (CIC) and Novamont Spa.

ORCID iD

Federica Ruggero https://orcid.org/0000-0003-1779-7223

Supplemental material

Supplemental material for this article is available online.

References

Abu Qdais H and Al-Widyan M (2016) Evaluating composting and co-composting kinetics of various agro-industrial wastes. *International Journal of Recycling of Organic Waste in Agriculture* 5: 273–280.

Arrieta MP, López J, Rayón E, et al. (2014) Disintegrability under composting conditions of plasticized PLA–PHB blends. *Polymer Degradation and Stability* 108: 307–318.

Bonhomme S, Cuer A, Delort AM, et al. (2003) Environmental biodegradation of polyethylene. *Polymer Degradation and Stability* 81: 441–452.

Correa-Pacheco ZN, Daniel J, Ortega-Gudiño P, et al. (2020) PLA / PBAT and cinnamon essential oil polymer fibers and life-cycle assessment from hydrolytic degradation. *Polymers* 12: 3–32.

Elfehri Borchani K, Carrot C and Jaziri M (2015) Biocomposites of Alfa fibers dispersed in the Mater-Bi® type bioplastic: Morphology, mechanical and thermal properties. *Composites Part A: Applied Science and Manufacturing* 78: 371–379.

Emadian SM, Onay TT and Demirel B (2017) Biodegradation of bioplastics in natural environments. *Waste Management* 59: 526–536.

EN 14045 (2003) Packaging – Evaluation of the disintegration of packaging materials in practical oriented tests under defined composting conditions. Available at: https://www.sis.se/en/produkter/environment-health-protection-safety/wastes/other/ssen14045/

European Bioplastics (2009) Fact sheet: Industrial composting, pp.1–14. Available at: https://docs.european-bioplastics.org/2016/publications/fs/EUBP_fs_industrial_composting.pdf

European Commission (2000) Esempi di successo sul compostaggio e la raccolta differenziata Direzione generale Ambiente. Available at: https://postribu.files.wordpress.com/2009/01/esempi-di-successosul-compostaggio-e-la-raccolta-differenziata.pdf

Fortunati E, Luzi F, Puglia D, et al. (2014) Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves. *European Polymer Journal* 56: 77–91.

ISO 11261 (1995) Soil quality – Determination of total nitrogen – Modified Kjeldahl method. Available at: https://standards.iteh.ai/catalog/standards/iso/cde41e48-376f-423a-9794-26445243a323/iso-11261-1995#:~:text=190%2FSC%203-,Soil%20quality%20%2D%2D%20Determination%20of%20total%20nitrogen%20%2D%2D%20Modified%20Kjeldahl,pyridine)%20is%20only%20partially%20determined

ISO 11465 (1993) Soil quality – Determination of dry matter and water content on a mass basis – Gravimetric method. Available at: https://www.iso.org/standard/20886.html

ISO 20200 (2015) Test, standards publication plastics – Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale. Available at: https://www.iso.org/standard/63367.html

Kale G, Auras R, Singh SP, et al. (2007) Biodegradability of polylactide bottles in real and simulated composting conditions. *Polymer Testing* 26: 1049–1061.

Komilis DP (2006) A kinetic analysis of solid waste composting at optimal conditions. *Waste Management* 26: 82–91.

Lucas N, Bienaime C, Belloy C, et al. (2008) Polymer biodegradation: Mechanisms and estimation techniques – A review. *Chemosphere* 73: 429–442.

Luzi F, Fortunati E, Puglia D, et al. (2015) Study of disintegrability in compost and enzymatic degradation of PLA and PLA nanocomposites reinforced with cellulose nanocrystals extracted from *Posidonia Oceanica. Polymer Degradation and Stability* 121: 105–115.

Manu MK, Kumar R and Garg A (2016) Drum composting of food waste: A kinetic study. *Procedia Environmental Sciences* 35: 456–463.

Martalò G, Bianchi C, Buonomo B, et al. (2020) Mathematical modeling of oxygen control in biocell composting plants. *Mathematics and Computers in Simulation* 177: 105–119.

Pergola M, Persiani A, Palese AM, et al. (2017) Composting: The way for a sustainable agriculture. *Applied Soil Ecology* 123: 744–750.

Pergola M, Persiani A, Palese AM, et al. (2018) A combined assessment of the energy, economic and environmental issues associated with on-farm manure composting processes: Two case studies in South of Italy. *Journal of Cleaner Production* 172: 3969–3981.

Ruggero F, Carretti E, Gori R, et al. (2020) Monitoring of degradation of starch-based biopolymer film under different composting conditions, using TGA, FTIR and SEM analysis. *Chemosphere* 246: 125770.

Ruggero F, Onderwater RCA, Carretti E, et al. (2021) Degradation of film and rigid bioplastics during the thermophilic phase and the maturation phase of simulated composting. *Journal of Polymers and the Environment* 29: 3015–3028.

Sintim HY, Bary AI, Hayes DG, et al. (2019) Release of micro- and nanoparticles from biodegradable plastic during in situ composting. *Science of the Total Environment* 675: 686–693.

Song YK, Hong SH, Jang M, et al. (2015) A comparison of microscopic and spectroscopic identification methods for analysis of microplastics in environmental samples. *Marine Pollution Bulletin* 93: 202–209.

The European Parliament and the Council of the European Union (2019) Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003 (text with EEA relevance). *Official Journal of the European Union* 170: 1–114.

Veneto Agricoltura (2009) Il Compostaggio: Generalità E Normativa Di Riferimento. In: *Compost – Una Nuova Fonte Di Fertilità*, pp.7–18. Available at: https://www.venetoagricoltura.org/upload/pubblicazioni/COMPOST_E287/Low_01.pdf

Weng YX, Jin Y, Meng Q, et al. (2013) Biodegradation behavior of poly(butylene adipate-co-terephthalate) (PBAT), poly(lactic acid) (PLA), and their blend under soil conditions. *Polymer Testing* 32: 918–926.

Weng YX, Wang XL and Wang YZ (2011) Biodegradation behavior of PHAs with different chemical structures under controlled composting conditions. *Polymer Testing* 30: 372–380.

Xiang S, Feng L, Bian X, et al. (2020) Evaluation of PLA content in PLA/PBAT blends using TGA. *Polymer Testing* 81: 106211.

Xu C, Zhang X, Jin X, et al. (2019) Study on mechanical and thermal properties of poly(lactic acid)/poly(butylene adipate-co-terephthalate)/office wastepaper fiber biodegradable composites. *Journal of Polymers and the Environment* 27: 1273–1284.