



# Chemical-Physical Characterization of Bio-Based Biodegradable Plastics in View of Identifying Suitable Recycling/Recovery Strategies and Numerical Modeling of PLA Pyrolysis

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Received: 28 November 2022 / Accepted: 1 May 2023 / Published online: 30 May 2023  
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## Abstract

Several bio-based and biodegradable polymers have been lately introduced on the market as potential substitutes for conventional plastics in order to decrease the environmental impacts related to plastics manufacturing and especially end of life disposal. The most applied route for the management of these types of bioplastics once they enter the waste stream is co-treatment with biowaste in anaerobic digestion and/or composting plants that may lead to their recycling as digestate and/or compost. Several studies however, have reported the incomplete biodegradation of these materials at lab-scale and/or in conventional treatment plants and the significant content of small inert particles, including microplastics, in the final products. This could represent an obstacle to the agricultural use of the produced digestate and/or compost. It is therefore necessary to study all the possible options for the recycling of these types of materials based on the specific characteristics of the polymers that constitute them. In this study, four different types of bio-based biodegradable plastics were characterized by chemical-physical analysis. In particular, the main properties investigated included the content of volatile and non-volatile phases, crystallinity, main elemental composition, content of different phases by spectroscopic investigation using Fourier Transform InfraRed spectra and of metals and metalloids of potential environmental concern. The results of the thermogravimetry analysis indicated that all of the recycling/recovery options considered (compost production via biodegradation, chemical recycling and energy recovery) could be potentially applicable for the examined bioplastics, since they showed to contain polymers that volatilize below 550 °C. The highest volatile matter contents were measured for PLA cups and starch-based films, while the highest ash contents were found for the other two types of rigid bioplastics, which also showed the highest concentrations of elements of potential environmental concern, that were anyhow quite limited, and reduced higher heating values estimated by elemental analysis compared to PLA or starch-based films. In addition, the rigid bioplastics tested exhibited a higher degree of crystallinity, which could be associated to a lower biodegradability. With regard to chemical recycling processes, the results of the chemical-physical investigations indicated that pyrolysis could be a technically viable process to apply for the treatment of all of the bioplastic samples examined. Thus, PLA, which is manufactured through lactic acid condensation, chemical recycling by rapid depolymerization through pyrolysis was evaluated applying a numerical model implemented in Aspen plus®. Results indicated that the best yields in terms of lactide recovery could be obtained at an temperature of 400 °C and 10 s residence time and that other valuable products may be obtained potentially by fractional condensation.

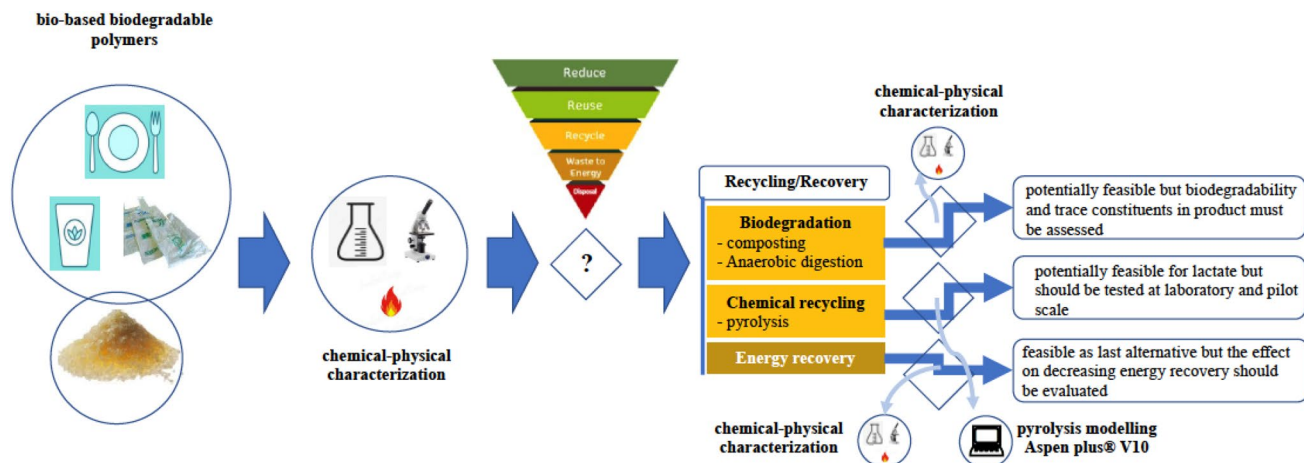
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## Graphical Abstract



**Keywords** Bioplastics · Recycling · Environmental sustainability · Chemical-physical characterization · Poly(lactic acid); pyrolysis

## Statement of Novelty

To evaluate different opportunities for the recovery and/or recycling of a waste material, it is essential to characterize its main properties. In this study, a systematic analysis of the chemical-physical properties of the most widely used types of bio-based and biodegradable plastics that have been recently introduced on the market and have already become a new type of waste that needs to be managed, was conducted. Indeed, to study the potential recycling opportunities of these types of polymers through biodegradation or chemical recycling processes, only partial characterization data can be found in the literature. Regarding PLA-based bioplastics, a numerical model to simulate their treatment by pyrolysis to recover lactate was implemented. This allowed to carry out a first assessment from a circular economy perspective on whether chemical recycling of this type of bioplastic would be technically feasible and potentially beneficial.

## Introduction

According to Plastics Europe, in 2020, global plastics production reached 367 million tons [1]. Eurostat, reports that about 15.4 million tons of plastic packaging was generated in the EU in 2019, of which 6.3 million tons (41%) were recycled and 5.6 million (36%) tons recovered as energy [2]. There is no indication on the remaining amount that can be assumed to have been landfilled. A report of the European Community indicates that 27% of plastic

packaging was disposed of in landfills in 2018 [3]. The effects of plastic pollution are however increasingly visible. The lack of control over production and disposal and of coherent recycling policies have favored the uncontrolled dumping of these materials and their accumulation on land and in water bodies, such as rivers and seas [4–7]. It is estimated that 2 to 5% of the produced plastics ends up in oceans, causing adverse effects to coastal and marine ecosystems. Microplastics are a particular concern, as they can be ingested by wildlife, potentially causing physical harm, affecting fertility and acting as a vector for toxins [8]. To address this problem, the European Commission published in January 2018 a strategy for managing plastics in a circular economy perspective. The strategy identifies several criticalities, including the low reuse and recycling rates of plastic waste, the greenhouse gas emissions associated with plastics production and incineration, and the presence of plastic waste (including microplastics) in oceans [9]. Key objectives identified in this European strategy include [9]: (1) the reusability or possibility of recycling plastics effectively (by 2030); (2) replacement or phasing out of substances that hinder the recycling processes of plastics; (3) development and use of innovative materials and alternative raw materials for plastics production that present greater environmental sustainability than the non-renewable alternatives. With specific regard to this latter objective, bioplastic materials presenting comparable technical characteristics to conventional plastics have been lately started to be employed in the manufacturing of single use items, such as packaging materials, disposable tableware and shopping bags.

The European Bioplastics Agency classifies bioplastics into three categories: biodegradable and produced from renewable resources, biodegradable and produced from non-renewable resources, and non-biodegradable but produced from renewable resources [10]. Currently, 44.5% of bioplastics production is related to non-biodegradable bioplastics of biogenic origin, while biodegradable polymers of biogenic or fossil origin amount to 55.5%. In the pursuit of increasing environmental sustainability and achieving the goals identified in the European plastics strategy, biodegradable plastics from renewable sources are of particular interest since their production and end-of-life management should both lead to reduced environmental impacts compared to conventional plastics. In fact, instead of using fossil resources such as oil for their production, a theoretically carbon neutral source such as biomass is used; in addition, end of life management should be significantly improved owing to their biodegradation [10]. Focusing on the biodegradable and produced from renewable resources category, the following types of bioplastics that are commonly employed to manufacture single-use items can be cited: starch-based materials [11], polylactic acid or polylactide (PLA) [12], polyhydroxyalkanoates (PHA), polyhydroxybutyrates (PHB) [13], polybutylene succinate (PBS) [14] and polybutylene adipate terephthalate (PBAT) [15].

The global production of bioplastics is expected to reach 2.4 million tons by 2024, and this highlights the need to find an effective way to manage these materials once they enter the waste flow. According to the European bioplastics association, over 60% of global bioplastics are of the biodegradable type and the forecast predicts that they will reach 70% in 2026 [16]. Biodegradable bioplastics present the advantage of being able to be theoretically treated in waste management processes such as composting and anaerobic digestion plants [10]. As defined in the standards UNI EN 13,432:2002 for packaging items [17] and UNI EN 14,495:2007 for other materials [18], biodegradability is the breakdown of an organic chemical compound by microorganisms in the presence of oxygen to carbon dioxide, water and mineral salts or any other elements present and new biomass (aerobic degradation), or in the absence of oxygen to carbon dioxide, methane, mineral salts and new biomass (anaerobic degradation). A plastic material is considered aerobically biodegradable if at least 90% of its C content is converted to CO<sub>2</sub> during a composting test carried out for a maximum period 6 months at 58 ± 2 °C [17], following the method reported in ISO 14855-1:2012 [19], and anaerobically biodegradable if the biodegradation % based on biogas production is higher than 50% [17]. In this latter case, the test is performed at 35 °C for a maximum of 90 d, following ISO 14853:2016 [20]. In addition, to establish if a bioplastic material can be classified as recoverable by composting and biodegradation, two other properties besides

biodegradability are defined and evaluated: disintegration and compost quality [17, 18]. Disintegration is the physical decomposition of a material into small fragments [21] and is usually investigated using the standardized methods EN 14806:2005 [22] and ISO 20200:2004 [23]. Specifically, after being exposed to composting for a maximum of 12 weeks, no more than 10% of the weight of the initial sample should be retained by a 2 mm sieve [17]. Finally, compost quality evaluations are aimed at establishing that materials defined as organically recoverable do not compromise the quality of the compost that can be obtained by treating the material under controlled conditions. Besides the content of metals and of other constituents of potential environmental concern, also the presence of microplastics (MPs) is an aspect that has been lately also started to be investigated in relation to compost quality [24]. The presence of microplastics has been found to determine several effects on organic matter humification and fungal community succession during the composting process, specifically, the addition of any type of MP showed to decrease the maturity and polymerization of compost, while polyethylene (PE) and PHA microplastics were found to increase the risk of the presence of phytopathogenic fungi in compost [25]. A recent review found that estimated microplastic contents reported for compost, digestate and food waste vary widely [26]. It also highlighted that several studies indicate potential negative effects of MPs in soil–plant systems, such as increased water repellence and porosity, decreased soil bulk density, delayed or reduced seed germination, reductions in plant growth or uptake into plant tissues, changes in soil microbes, oxidative stress and other effects on soil macrofauna, besides ingestion and bioaccumulation in some livestock species. The study concludes however that the existing data are not sufficient to fully evaluate the risks of microplastics in agricultural soils [26]. It should be however considered that MPs from biodegradable bioplastics present a different behaviour from MPs from conventional plastics, as they may subsequently degrade in the soil [27].

According to Italian legislation, biodegradable bioplastic materials should be collected with the organic fraction of municipal solid waste (OFMSW) that be treated in both aerobic and anaerobic plants receiving organic waste [28]. To provide compost and/or digestate that is safe for use, it is necessary to ensure the biodegradation and stabilization of the organic waste, together with a low content of potential pollutants [29]. Therefore, current research is evaluating the biodegradation of bioplastics and investigating the processes that occur in the biowaste treatment plants in order to understand the fate of bioplastics and the quality of the generated products to be used in agriculture. Recent publications report critical issues associated with the mechanical pre-treatments applied in biowaste treatment plants: when size separation is employed, most bioplastics end up in the processing residues

[30], similarly to traditional plastics [31]. Furthermore, this has a drag effect on the organic waste, leading to a significant increase in the amount of residues that need to be managed [30].

In some cases, composting and anaerobic digestion were reported not to ensure the complete degradation of bioplastics [27, 32, 33] due to conditions occurring during the full-scale process that are different from those adopted in the standardized methods for establishing biodegradability at laboratory scale [34]. Furthermore, for some types of bioplastics such as PLA, contrasting results on degradation were reported in the literature. A maximum degradation of 75% was recorded during the composting process performed under thermophilic conditions ( $58 \pm 2$  °C) for 90 days, following EN 14806 and ISO 20200:200 [35]. In addition, the thickness of some rigid PLA items were found to slow down the composting process, requiring to modify plant management settings in order to ensure biodegradability [36]. With regard to the anaerobic biodegradation of PLA, some studies reported it not to be optimal [37, 38], while an overall degradation of 70% under thermophilic conditions for 60 days, higher than that found for starch based bio-plastics, was reported instead by [27]. It should be anyhow mentioned that this latter study also reported that based on experimental kinetic studies complete degradation of the residual bioplastic after waste treatment was much slower for PLA compared to starch-based bioplastics (248–500 days vs. 174–183 days, respectively) [27]. Among the factors influencing biodegradation, crystallinity should also be mentioned. Especially in the case of PLA, it was found that hydrolytic compounds were two orders of magnitude lower in the case of semicrystalline phases compared to amorphous ones; consequently, during anaerobic digestion at 35 °C, semicrystalline PLA was found not to produce a statistically significant amount of biogas, while amorphous PLA generated a small amount of biogas [39].

Incomplete biodegradation of some polymers results in reduced energy efficiency in the case of biomethane production by anaerobic digestion, and a deteriorating quality of the end-products (compost and digestate) related to their substantial (bio)plastic contents [38, 40]. Alternatively, processes applied to manage conventional plastics such as combustion and co-incineration for energy recovery, or others such as e.g. pyrolysis, gasification that allow the recovery of liquid and gaseous hydrocarbons to use as fuels or raw materials for the production of further products, could be employed instead also to treat bioplastics [41].

Among the latter types of processes mentioned above that can be defined as chemical recycling strategies [42], pyrolysis consists in the thermal degradation of the organic matrix in the absence of oxygen [43]. Several studies showed that, depending on different parameters such as temperature, residence time, inert material used, etc., interesting products

such as gas, oil and char can be obtained. These products also include the bioplastic precursors fed to the considered processes, such as lactic acid and lactide in the case of PLA, and this implements circularity and can reduce environmental impacts [37, 44]. For example, 97% of PLA is made-up of volatile substances [45], which would make it suitable for thermal degradation processes such as pyrolysis that leads to the production of a bio-oil from which precursor products for the reformulation of new bioplastics, such as those previously mentioned, can be recovered.

In order to identify the most suitable options to manage bioplastic items at their end of life prioritizing the recovery of materials, but also ensuring their environmental compatibility, it is necessary evaluate their main properties. To the best of our knowledge, only partial characterization data that can be employed for this assessment can be found in the literature for some of the items that have been recently introduced on the market.

In this study, four types of items classified as bio-based biodegradable plastics according to standard UNI EN 13,432: 2002, differing by polymer type and shape (i.e.: starch-based plates and film bags, bioplastic B-plates and PLA cups), were characterized to determine their main chemical-physical properties. Specifically, the investigations performed included proximate analysis via thermogravimetry, crystallinity, main elemental composition, contents of different phases by spectroscopic investigation using Fourier Transform InfraRed (FTIR) spectra and of metals and metalloids of potential environmental concern. The obtained results were evaluated in view of establishing the potential suitability of recycling/recovery routes and also compared with the respective properties of conventional plastics, i.e.: polyethylene (PE), high-density polyethylene (HDPE) and low-density polyethylene (LDPE), reported in previous studies or specifically analyzed. With regard to PLA, a chemical recycling process was assessed, i.e. rapid depolymerization through pyrolysis aimed at obtaining the lactide precursor, by means of a numerical model implemented in Aspen plus®.

## Materials and Methods

Four different types of commonly marketed single-use bioplastic items were characterized in this study: PLA cups; B-bioplastic plates; Mater-Bi® (starch-based) plates; Mater-Bi® shopping bags (Table 1). It was decided to characterize in particular rigid types of biodegradable bio-plastics since, as discussed in Sect. "Introduction", previous studies indicated that these materials may present a lower degradability, especially in full scale plants. For Mater-Bi, film materials were also tested as a comparison.

**Table 1** Classification of the samples

Bioplastics sample	Type	Texture	Abbreviation
PLA cups	PLA-based	Rigid	BR-1
B-Bioplastic plates	Commercial vegetable-based	Rigid	BR-2
Mater-Bi® based plates	Starch-based	Rigid	BR-3
Mater-Bi® based bags	Starch-based	Film	BF-1

Before characterization, all the samples were ground with a knife mill (Retsch GM200) to obtain a sample size presenting a diameter ( $\phi$ ) below 850  $\mu\text{m}$ . The effects of grinding varied depending on the sample: while plates (BR-2 and BR-3) and film bags (BF1) yielded a homogeneous product in terms of shape and size (Fig. 1 a, b and c), the cups (BR-1) were found to show a predominance of one dimension over the others due to the fibrous nature of the material (Fig. 1 d). For all the types of bioplastics tested, the analyses were performed on samples with a particle size between 500 and 850  $\mu\text{m}$ .

The investigation of the chemical-physical characteristics was performed employing the following techniques: thermogravimetric (TGA) and Differential Scanning Calorimetry (DSC) analysis; elemental composition (CHNS(O)); spectroscopic investigation using FTIR spectra; content of metals and metalloids in the solid matrix by microwave acid digestion of the samples coupled by Inductively Coupled Plasma Optical Spectroscopy (ICP-OES) analysis.

Rapid depolymerization through pyrolysis was evaluated for PLA by means of a numerical model implemented in Aspen plus®.

## Analytical Methods

The thermo-gravimetric analysis was carried out according to the ASTM E914 standard [46] using the instrument TGA701 (LECO Corp) and evaluating the results according to the following standards: UNI EN ISO 18122:2016 (for

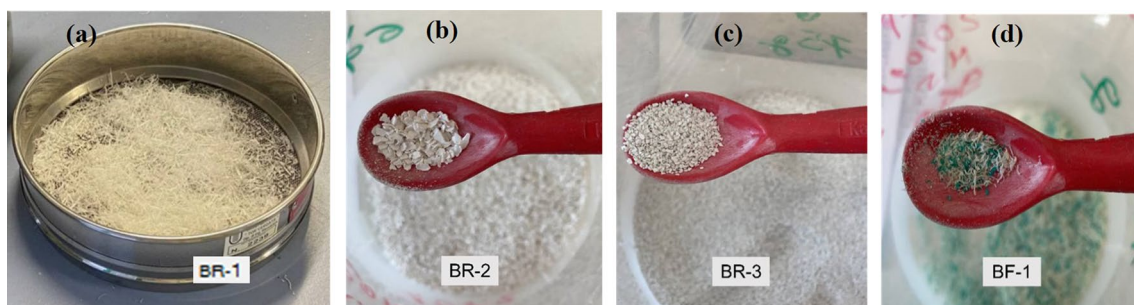
the ash content) [47] and ISO 18123:2015 (for the volatile matter content) [48]. The thermogravimetric analysis was performed using the following temperature ramp: 1) a first heating step from room temperature to 105 °C with a rate of 6 °C/minute in order to remove the moisture present in the sample; 2) a second heating step from 105 to 550 °C with a rate of rate of 10 °C/minute in order to remove the volatile fraction present in the sample; 3) a third heating step from 550 to 815 °C with a rate of 10 °C/minute in order to remove the fixed carbon present in the sample; 4) final cooling.

Crystallinity ( $\chi$ ) was analysed according to ISO 11357–1:2023 by differential scanning calorimetry [49]. A DSC1 STAR System Instrument (Mettler-Toledo GmbH, Gießen, Germany) was used. Energy and temperature calibrations were carried out using an indium standard. All the samples were analyzed using the following 3 step procedure: 1) a first heating step from 25 to 190 °C (heating rate of 10 °C/min; 2) a cooling step from 190 to 25 °C (cooling rate of 10 °C/min) and a second heating step from 25 to 190 °C (heating rate of 10 °C/min) under a constant nitrogen flow of 50 mL/min to prevent any oxidative degradation of the samples. The mass of the DSC bulk samples ranged between 3 and 6 mg. The following formula was used to calculate the degree of crystallinity in accordance with [50, 51].

$$\text{Crystallinity}(\chi) = \frac{\Delta H_m}{\Delta H_m(\infty)} \times 100 \quad (1)$$

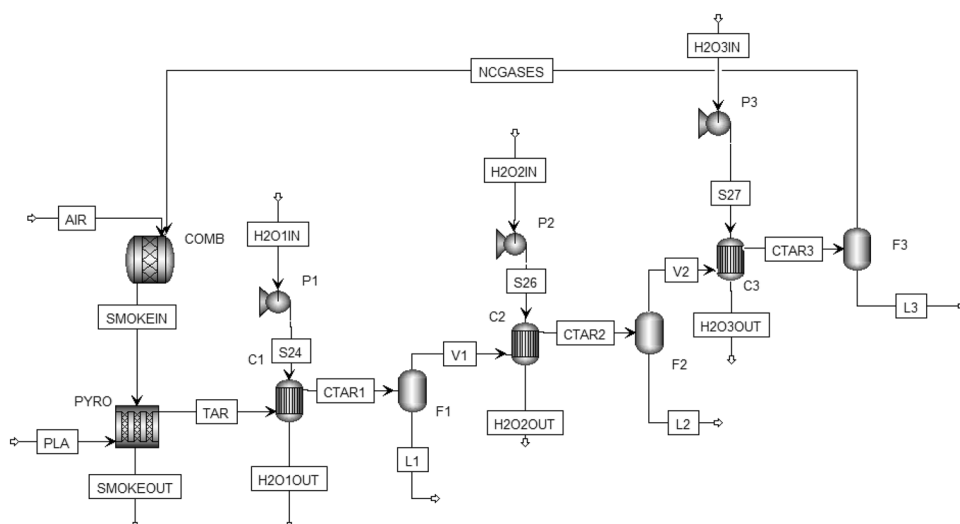
where  $\Delta H_m$  is the melting enthalpy measured for the sample (in J/g) and  $\Delta H_m(\infty)$  is the melting enthalpy (in J/g) reported for a purely crystalline sample of the same polymer; in this study, the  $\Delta H_m(\infty)$  values reported in [52, 53] were considered.

The CHNS(O) analysis was performed with Elemental Macro's Vario MACRO-cube analyzer, using the “coal50” standard, with flash burning of the samples with a temperature column of 1150 °C (FLASH 2000 – Organic Elemental Analyzer). Elements such as C, H, N and S were determined following the ISO 16948:2015 standard [54] and the instrument's calibration was performed employing



**Fig. 1** Effect of grinding on the samples in terms of shape and size

**Fig. 2** Layout of the pyrolysis reactor and of the fractionation stages implemented in the Aspen Plus model



a sulfanilamide standard. The oxygen content was obtained by difference, as commonly performed in previous studies (e.g. [55]).

FTIR analysis is a spectroscopic technique exploiting electromagnetic radiations with a wavelength ranging from 2,500 to 22,000 nm. It provides rapid analytical data, which if properly processed, provide chemical information concerning the samples with regard to their manufacturing processes, differences or similarities in chemical composition, appearance and physical characteristics. The spectroscopic investigation was performed using Fourier Transform InfraRed (FT-IR) spectra collected with a PerkinElmer SPECTRUM 100 spectrometer. The wavenumber range investigated was of 450–4,000  $\text{cm}^{-1}$  and the resolution was of 2  $\text{cm}^{-1}$ .

The higher heating value (HHV) of each sample was calculated using the empirical correlation of Milne et al. reported in Eq. (2) using the experimental data on the elemental composition of the samples [56]:

$$\text{HHV} \left[ \frac{\text{MJ}}{\text{Kg}} \right] = \frac{338.2C + 1442.8(H - \frac{O}{8})}{1000} \quad (2)$$

The content of metals in the solid matrix was analyzed by microwave acid digestion followed by ICP-OES analysis of the resulting digestate solutions. Specifically, following the UNI EN 13657:2004 standard [57], 0.5 g of dried sample was placed in contact with a solution of aqua regia (a mixture of  $\text{HNO}_3$  and  $\text{HCl}$ , in a 1:3 ratio) and subjected to the microwave power program established by the standard employing an Ethos Easy Microwave Acid Digestion System (Milestone). After cooling, the resulting solution was filtered to  $d < 0.45 \mu\text{m}$  and diluted with ultrapure water in order to determine the metal content

using an Agilent 5800 ICP-OES. All the analyses were performed in triplicate.

## Pyrolysis Modeling

The simplified model for the chemical recycling of PLA was implemented in Aspen plus® V10 software [58] considering that, as reported in the literature, the following five reactions would occur, namely: cis-elimination, ester exchange, chain scission and unzipping, Zn-catalyzed reaction and two other secondary reactions for the formation of non-condensable gases [59–62]. For the development of the following model, the absence of char and presence of only condensable tar and of non-condensable gas at the reactor outlet was assumed on the basis of the high volatile content and negligible fixed carbon and ash contents resulting from the thermo-gravimetric analysis. Furthermore, the absence of solid particles within the vapour was hypothesized. It was also assumed that the PLA structure is a short-chain molecule i.e.,  $\text{C}_{30}\text{H}_{42}\text{O}_{21}$ , to overcome some criticalities of the software to process high molecular weight compounds. The reactor temperature was hypothesized to increase linearly along the reactor axis. In addition, a simplified model was chosen for the heat exchange banks, which simply required the heat exchange surface. The absence of a pressure drop among the heat exchangers was considered. As a final assumption, liquid-in-chamber flash separation and a combustion chamber efficiency of the residual gas mix of 60% were considered [63, 64]. For the thermo-kinetic model, as described in [61, 64], 7 reactions and 15 species were accounted for. The reactions and the kinetic parameters adopted in the model are reported in Table 2.

Since several side reactions were neglected, some products generally found in the bio-oils of PLA pyrolysis in experimental studies were not considered. Figure 2

**Table 2** Reaction scheme and kinetic parameters implemented in the thermo-kinetic model [64]

Reaction (n.)	Reactions	A (1/s)	$E_a$ (kJ/mol)
1	$PLA \rightarrow 2,5L\text{-lactide} + 2,5D\text{-lactide} + H_2O$	300.000	31.150
2	$2 PLA \rightarrow 2,5L\text{-lactide} + 5 C_3H_4O_2 + H_2O$	100.000	32.224
3	$PLA \rightarrow 10 C_2H_4O + 10 CO + H_2O$	100.000	32.205
4	$2 PLA \rightarrow 5 C_2H_4O + 5 C_3H_4O + 5 CO_2$	100.000	33.916
5	$PLA \rightarrow 5L\text{-lactide}$	100.000	31,527
6	$PLA \rightarrow 3 C_2H_4 + 0,5 O_2 + C_3H_6 + 5 CO_2 + 2 C_2H_4O + 4 C_3H_4O_2$	250.000	31.766
7	$Mesolactide \rightarrow 0,75 H_2 + 3 CO + 0,5 CO_2 + 0,25 C_4H_{10} + 0,5 C_3H_8$	1.000.000	30.811

describes the flowsheet of the process aimed at maximizing the yield of PLA precursors, namely lactide (in its various stereoisomers), by fast pyrolysis. The process was simulated in ASPEN PLUS V10 using the POLYNRTL method for calculating the thermodynamic properties of components and mixtures that implements Van Krevelen's method for estimating polymer properties and is also suitable for the stage-separation of hydrocarbons at the outlet of the reactor [63].

A PLA flow rate compatible with a lab-scale set-up, i.e. 1 kg/h, was considered in the simulation. The process starts by feeding the PLA with nitrogen into a plug flow reactor (PFR) in which the reactions reported in Table 2 take place at an average temperature of 400 °C in the center of the reactor. As mentioned before, at the outlet of the reactor there are only vapors, which are sent to a first heat exchange bank to decrease the temperature to about 220 °C, so that the lactides, namely L-lactide and D-lactide, presenting respectively a boiling temperature of 250 and 285 °C, can be separated. A flash separator is then considered to simulate the separation between liquid and vapor. The vapors leaving the head then enter a second exchanger, which like the first exchanger, has a heat exchange surface area of 0.024 square meters. The outlet gas flow then enters a second flash separator to again separate the liquid phase from the vapor, and the remaining vapors, which mainly contain CO, acetaldehyde, acrylic acid, CO<sub>2</sub>, ethylene, propane, propene and butane, enter a third column also cooled by water. It should be noted that in reality cooling is simply

performed by exchange with the external environment and the temperature will reach 16 °C, lower than the boiling temperature of acetaldehyde, which is why this compound is found also in liquid form after the third flash separator. At the head of this separator, non-condensable constituents such as CO, CO<sub>2</sub>, ethylene, propane, propene and butane and some acetaldehyde, are released. These non-condensable gases can be recirculated to the reactor simulating the combustion chamber, along with air. The flue gases generated by the reactions shown in Table 2 can be used to generate the heat required to meet the thermal demand of the process, making the system autothermal. The operating conditions of the modeled pyrolysis process were: reactant residence time of 10 s, reactor at a constant temperature of 400 °C and vapor specific flow rate of 0.026 m/s, resulting in a vapor residence time in the reactor of 2 s.

## Results and Discussion

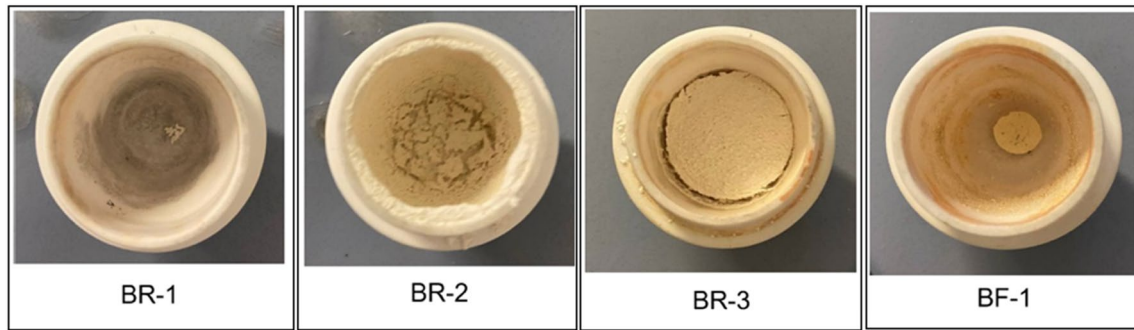
### Thermogravimetric and DSC Analysis

The results of the TGA analysis performed on the bioplastics samples considered in this study are reported in Table 3. A good homogeneity of the composition of each type of product examined can be noted, as attested by the small value of the standard deviation calculated for the results of the analytical replicas. The volatile matter content varied between 64.45 (BR-3) and 97.35% (BR-1), while a low moisture

**Table 3** Results of the thermogravimetric analysis, reported in % on a weight basis (% w.b.), of the tested types of bioplastics compared to plastics of fossil origin [65–68]

Samples	Moisture (%w.b.)	Volatile matter (%w.b.)	Ash (%w.b.)	Fixed carbon (%w.b.)
BR-1 <sup>a</sup>	2.52 (0.31)	97.35 (0.36)	0.08 (0.06)	0.05 (0.10)
BR-2 <sup>a</sup>	1.19 (0.19)	81.23 (0.17)	17.03 (0.04)	0.55 (0.03)
BR-3 <sup>a</sup>	0.61 (0.15)	64.45 (0.02)	33.13 (0.04)	1.81 (0.15)
BF-1 <sup>a</sup>	1.98 (0.02)	92.42 (0.21)	0.25 (0.03)	5.35 (0.21)
PE [65, 67]	0.02–0.2	99.6–99.85	0.15–0.2	–
HDPE [66, 68]	0.01–0.40	99.38–99.77	0.22	–
LDPE [66, 68]	0.03–0.19	99.65–99.85	0.12–0.15	–

<sup>a</sup>The standard deviation value for each parameter and sample is reported in brackets



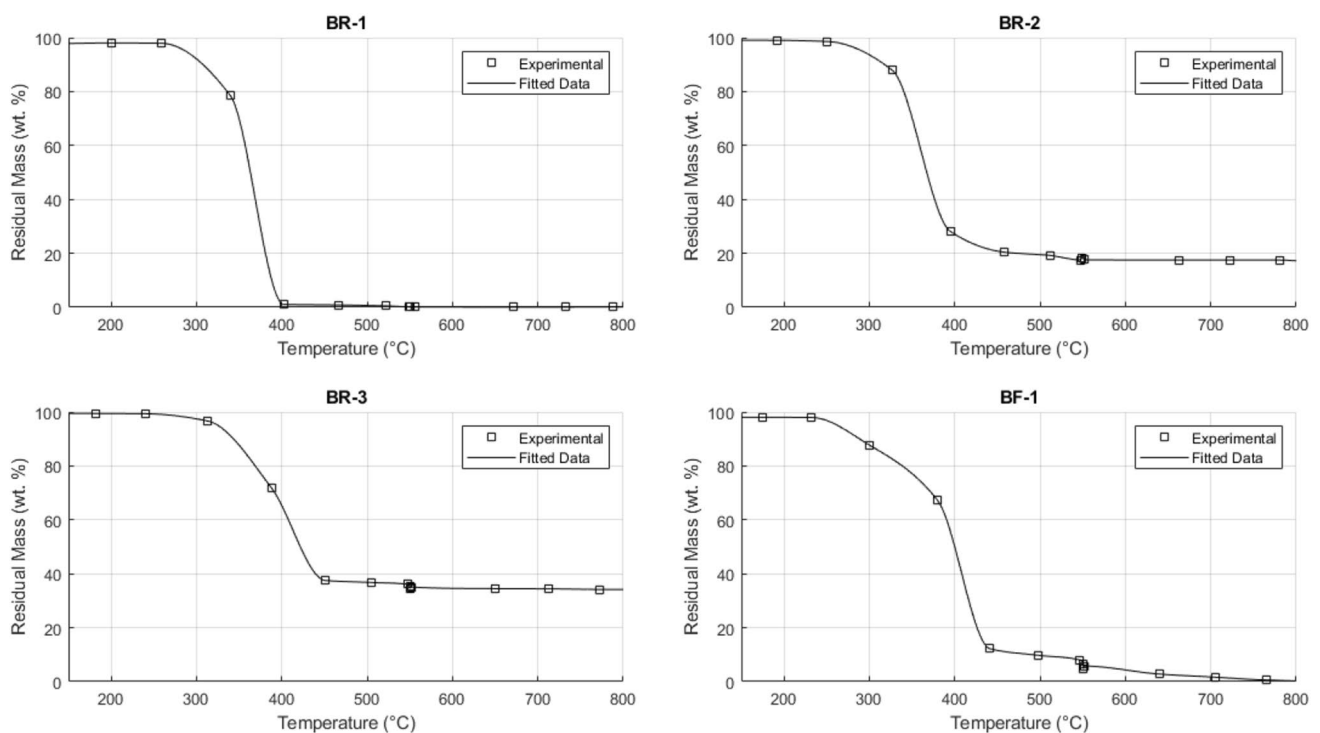
**Fig. 3** Pictures of the residues from the TGA test

content (varying between 0.61% for BR-3 and 2.52% for BR-1) was found for all of the tested samples. The ash content values showed significant variations in relation to both the biopolymer type (PLA, Mater-Bi® or B-bioplástico) and the consistency and type of item examined (cups, plates or shopping bags). This can also be appreciated through the visual survey of the residues of each sample at the end of the TGA test (Fig. 3). BR-1 exhibited a nearly negligible ash content that was lower than that of all the other types of bioplastics examined. As previously mentioned, Mater-bi® was the only biopolymer tested for two different types of items: shopping bags (BF-1) and plates (BR-3). A much lower ash content was found for the shopping bags (BF-1:

0.25%) compared to the same type of biopolymer in rigid form (BR-3: 33.13%). For the same type of item (plates), a lower ash content was found for BR-2 (17.03%) compared to BR-3.

Compared to the bioplastic materials analysed in this study, the proximate analysis data reported for the types of fossil-derived plastics typically employed to produce items employed for the same purposes, showed to be characterized (Table 3) by a lower moisture content (below 0.4%), a higher volatile matter content (greater than 99.38%) and a very low ash content (less than 0.22%).

Figure 4 shows the percent mass loss as a function of temperature measured for the different types of bioplastic



**Fig. 4** Thermogravimetric analysis—Mass-loss profile versus temperature for BR-1, BR2, BR-3 and BF-1 samples



samples tested. The trends confirm the results of previous studies. In fact, a single stage of decomposition was detected for BR-1 [69]. This characteristic is peculiar to PLA, while for other biopolymers, such as BF-1, the trend of mass loss has been reported to be characterized by two stages, as highlighted by two slopes [70]. All of the bioplastics samples tested consisted mainly of a volatile fraction (from a minimum of 64 to a maximum of 97%) and presented a very low moisture content (from a minimum of 0.61% to a maximum of 2.52%). The high values of volatile fraction are significant in terms of both bio-treatment and chemical recycling, indicating for example pyrolysis as a potentially viable process for bioplastics recovery. In fact, the volatile fraction showed to contain polymers that volatilize in a temperature range between 105 and 550 °C, characteristic to pyrolysis processes.

In addition, DSC analysis was performed to evaluate the crystallinity of the samples. Results are shown in Table 4. For BR-2, it was not possible to define the degree of crystallinity because the polymer constituting the item is not well defined, therefore the melting enthalpy of the purely crystalline polymer to employ in Eq. (1) could not be established.

Analyzing the results, it can be observed that the BF-1 sample tested presented a much lower crystallinity value in comparison to the rigid bioplastic items. This result could indicate that these latter samples (BR-1 in particular) may present a lower biodegradability in comparison to BF-1, since as discussed in Sect. "Introduction", it is reported in

the literature that bioplastics with a semicrystalline structure are more difficult to biodegrade than films [39].

## Elemental Composition

The results of the CHNS(O) analysis performed on the bioplastics samples considered in this study are reported in Table 4. Also the results of this analysis indicated the homogeneity of the composition of each type of investigated bioplastics, in relation to the limited value of the standard deviation calculated for the replicas and provided further evidence on the differences between the types of bioplastic items tested. The carbon and oxygen contents were the main elements that differed mostly among the biopolymer samples and in comparison to fossil-derived plastics considered as terms of comparison [65–68]. The carbon content (C) varied between 37.14 and 59.53%, highlighting that the materials produced with PLA (BR-1) and those marketed as films for shopping bags (BF-1) have a higher amount of carbon and, as already seen, also a lower ash content. The oxygen content varied between 26.43 and 43.17%, confirming also for this element a higher content in BR-1 and BF-1. The Hydrogen content, the highest of which was found for sample BF-1 (5.12%), showed to be positively correlated to the Higher Heating Value (HHV) of the sample. Nitrogen was present in small amounts, below 0.03%, similarly to sulfur, below 0.06%, except for sample BF-1 in which a value of 0.48% was found.

Compared to the bioplastic samples analyzed in this study, the conventional plastics (PE, HDPE, LDPE), exhibited (see Table 5) higher carbon values, varying between 82.77 and 85.81%, with differences ranging from a minimum of 23.24% (HDPE vs. BF-1) to a maximum of 48.67% (PE vs. BR-3) [65, 66]. They also presented higher hydrogen contents, with values varying between 13.86 and 16.92%, with differences ranging from a minimum of 8.74% (PE vs. BF-1) to a maximum of 13.67% (HDPE vs. BR-3), comparable sulfur concentrations in HDPE and LDPE to those found

**Table 4** DSC analysis results

Samples	$\Delta H_m$ (J/g)	$\chi$ (%)
BR-1	29.03	30.9
BR-2	25.00	n.d
BR-3	28.13	16.7
BF-1	1.24	0.73

**Table 5** Results of the elemental composition of the tested bioplastics compared to plastics of fossil origin [65–68]

Samples	C (% w.t.)	H (% w.t.)	N (% w.t.)	S (% w.t.)	O <sup>a</sup> (% w.t.)	HHV <sup>b</sup> (MJ/kg)
BR-1 <sup>c</sup>	52.74 (0.37)	4.04 (0.13)	0.03 (0.02)	0.02 (0.01)	43.17	15.89
BR-2 <sup>c</sup>	45.56 (0.65)	3.64 (0.16)	0.04 (0.01)	0.06 (0.04)	33.67	14.58
BR-3 <sup>c</sup>	37.14 (0.26)	3.25 (0.11)	0.03 (0.01)	0.03 (0.02)	26.43	12.48
BF-1 <sup>c</sup>	59.53 (1.92)	5.12 (0.28)	0.03 (0.01)	0.48 (0.36)	34.81	21.28
PE [65, 67]	85.53–85.81	13.86–14.22	0–0.12	0.06	0–0.25	49.40
HDPE [66, 68]	82.77–86.99	12.12–16.92	0–0.27	0.07–0.29	0–0.56	52.40
LDPE [66, 68]	83.00–85.60	13.40–16.75	0–0.26	0–0.25	0–0.74	52.23

<sup>a</sup>Calculated by difference

<sup>b</sup>Calculated using the following equation [56]:  $HHV \text{ (MJ/kg)} = 0.001 * [338.2 * C(\%) + 1442.8 (H(\%) - O(\%)/8)]$

<sup>c</sup>The standard deviation value for each parameter and sample is reported in brackets

in BF-1, while similar ones in PE to those in the remaining types of bioplastics tested. The conventional plastics examined exhibited also an approximately 40% higher heating value than that of the tested bioplastics, which can be attributed to the lower carbon and hydrogen content and the higher oxygen and ash contents (Table 3) present in the components of biological origin. However, the calorific value of the BF-1 sample was significant, considering that its net calorific value (NCV) would lead to its classification as class 2 solid recovered fuel [71] ( $\geq 20$  MJ/kg), unlike BR-1 (NCV class 3,  $\geq 15$  MJ/kg) and BR-2 and BR-3 (NCV class 4,  $\geq 10$  MJ/kg) which showed to present a reduced heating value and hence worst NCV classification. As a reference, the analyzed conventional plastics exhibited a NCV class of 1 ( $\geq 25$  MJ/kg).

### Spectroscopic Investigation by FTIR

The results of the spectroscopic investigation performed on the biopolymer samples considered in this study are

reported in Fig. 5. Comparing the spectra obtained for all of the tested samples to what reported in previous studies [34, 36], the evident peaks retrieved at  $2,950\text{ cm}^{-1}$  and  $1,447\text{ cm}^{-1}$ , can be associated to C–H stretching, the intense peak at  $1,715\text{--}1,730\text{ cm}^{-1}$  to C=O stretching, while the broad fingerprint band at  $1,400$  and  $950\text{ cm}^{-1}$  to the overlapping of several absorption spectra. In addition, a large band in the  $3,500\text{ cm}^{-1}$  region representing amine (N–H) and in particular hydroxy (O–H) compounds typical of starch [36], was found to be particularly evident for sample BF-1, while significantly lower for the other types of bioplastics analyzed. Small peaks around  $2,000$  and  $1,900\text{ cm}^{-1}$  related to C–H bending only for samples BR-1 and BF-1.

Compared to the conventional types of plastics examined, i.e. fossil-derived plastics: Polystyrene (PS) cups—a, and plates—b, and PE film—c, it can be seen (Fig. 6) that the main differences in the FTIR spectra are the presence of C=O groups not evident in conventional plastics, while a lower intensity of peaks related to C–H bending.

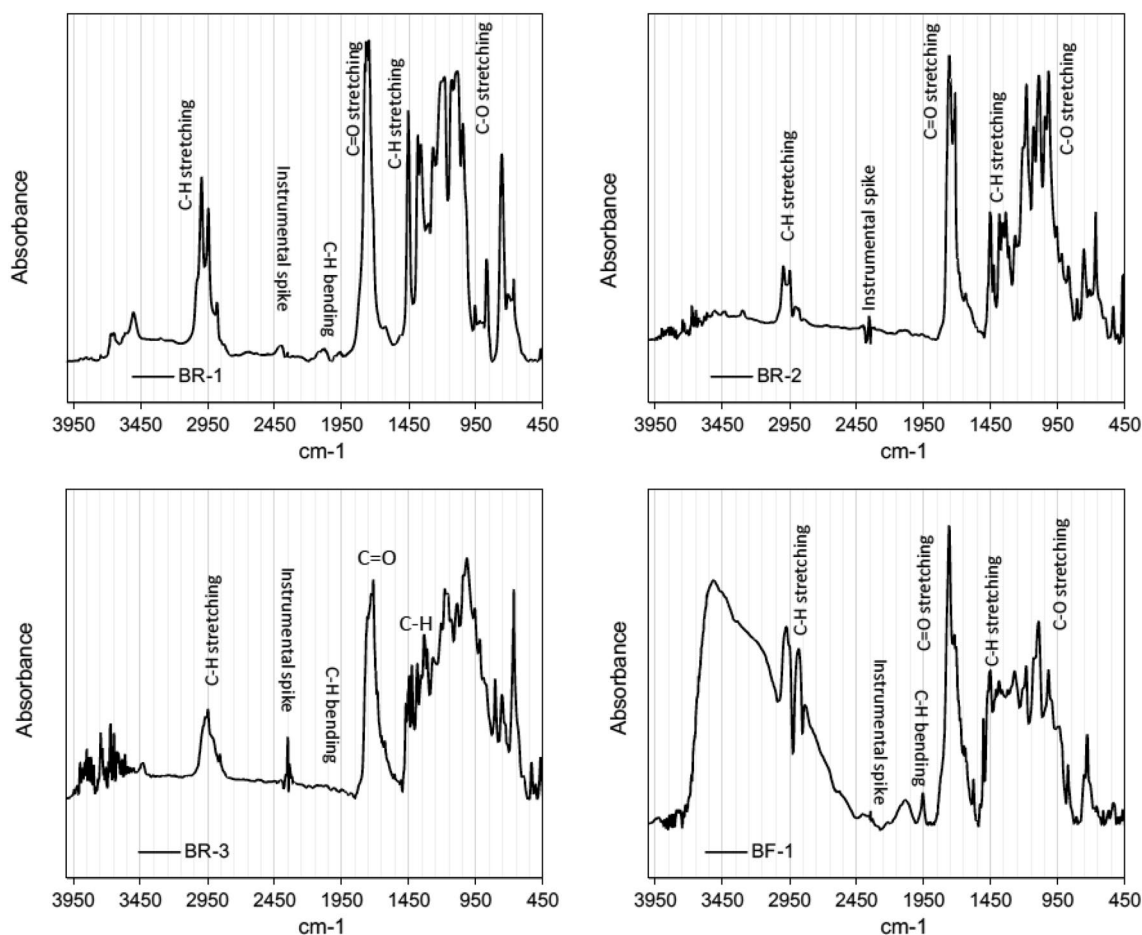
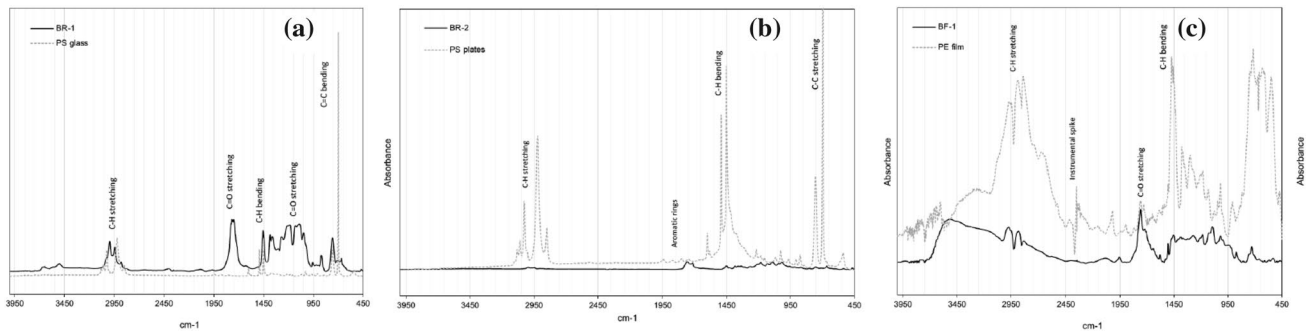


Fig. 5 FTIR Spectra performed on the bioplastics samples



**Fig. 6** Comparison between the FTIR Spectra resulting for bioplastics and for PS (cups—a, and plates—b) and PE (film—c)

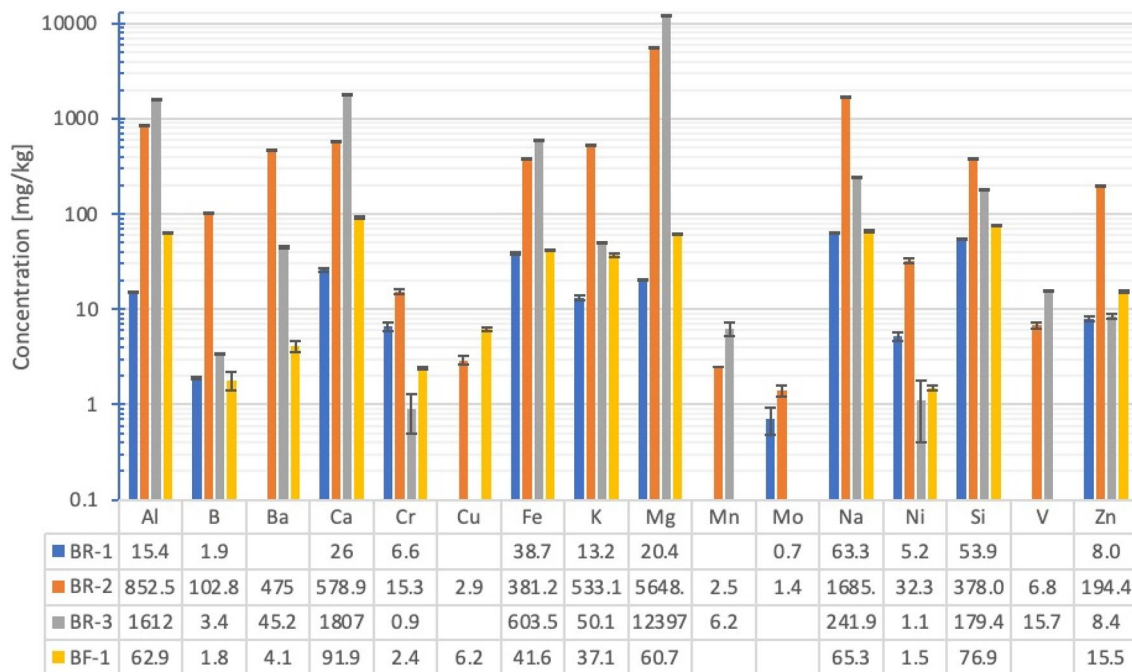
### Contents of Main and Trace Elements

In this study, the contents of the following elements were analyzed in the types of biopolymers tested: Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mn, Mg, Mo, Na, Ni, Pb, Sn, Se, Si, V, Zn. In Fig. 7, for each sample, the detected concentration values for only the chemical elements that were above the instrument’s detection limits are shown. For all the samples, the concentrations of As, Be, Cd, Co, Hg, Pb, Sn, Se were below the respective detection limit, while others were undetectable only in specific samples, i.e.: Ba (BR-1), Cu (BR-1, BR-3), Mn (BR-1, BF-1), Mo (Br-3, BF-1) and V (BR-1, BF-1).

The results obtained highlight generally a good homogeneity of the composition of each type of investigated

bioplastics, as attested also for this analysis by the limited value of the standard deviation calculated for the results of the analytical replicas. The results confirmed the non-hazardousness of these materials with reference to the maximum contents established for environment and human health protection in the EU’s CLP Directive [72].

Examining the results, it can be observed that BR-2 and BR-3, the starch-based rigid plastics (plates) tested, presented the most chemical elements with the highest concentrations (see Fig. 7). In addition, BR-1, the PLA-based rigid plastics analyzed, was found to present the highest number of chemical elements investigated with the lowest concentrations, although for some metals BR-3 and BR-4 (starch-based Mater-Bi®) were also found to exhibit the lowest concentrations (see Fig. 7). In particular, the type of



**Fig. 7** Concentrations of major and trace elements above the respective detection limits in the tested bioplastics samples

bioplastics that presented the highest contents of most of the tested elements was BR-2 (Figs. 7), for which an unspecified formulation is reported (commercial vegetables-based).

Compared to conventional plastics (see Table 5), referring to the data available in the literature for PE, HDPE, LDPE and considering the following metals: Pb, Cr, Cd, As, Cu, Zn, Mn, Se and Ba, it can be seen that bioplastics showed concentration values of the investigated elements below the detection limit for Pb (<6.2 mg/kg), Cd (<0.6 mg/kg), As (<3.8 mg/kg) and Se (LOD <3.8 mg/kg); however it should be noted that in this latter case the detection limit was quite comparable to the concentrations of this element reported in the literature for conventional plastics. Cu, as well as Mn and Cr, were detected in both bioplastics and conventional plastics. In particular, Cu in conventional plastics was found to be between one and three orders of magnitude higher than in bioplastics, depending on the type of plastics considered. Cr was generally found in higher concentrations in conventional plastics except for BR-2, for which a Cr concentration higher than that reported for LDPE, but lower than that of the other two types of plastics, was retrieved. Mn, detected only in samples BR-2 and BR-3, showed a lower concentration but of the same order of magnitude as the plastics taken as reference. For Zn and Ba, the concentrations reported for conventional plastics were generally higher than those measured in the bioplastics samples tested, with the exception of BR-2 for which higher concentrations were found.

In addition, the concentrations of the elements of potential environmental concern found in the biopolymer samples were compared to the limit values established by the Italian legislation for the production of high-quality compost [75] (see Table 6). This comparison was performed in order to assess whether the bioplastics treated by biostabilization to produce compost may potentially exert a negative effect on compost characteristics related to its content of regulated metals and/or metalloids, thus limiting its utilization. As can be note in Table 6, all regulated metal and metalloid concentration values retrieved in the bioplastic samples were found to be well below the established national limit values,

apart for Hg and Cr(VI). It should be noted however that in the case of Hg, the instrument's detection limit was higher than the compost criteria; while for Cr, the total Cr content was measured and it was compared to the CrVI limit. Hence for these two elements, further analyses employing a more sensitive method or characterizing the oxidation state of the element should be performed, respectively. It should also be considered that bioplastics will be present in the waste matrix sent to biostabilization in limited amounts, not above 10%, as indicated in [38]. Therefore, considering the concentrations of metals and metalloids present in the as-received bioplastics, it is highly unlikely that this contribution would result in an increase in the metal and metalloid contents of the produced compost such that the limit values established in the compost regulation would be exceeded (Table 7).

### PLA pyrolysis Modelling

The main products expected as a result of the pyrolysis of PLA are L-lactide, D-lactide, meso-lactide, lactic acid, acetaldehyde, CO, CO<sub>2</sub> and other non-condensable gases such as ethylene, propane, propylene, butane and trace hydrogen [62] and [76]. Analysing the results obtained from the Aspen simulation in terms of yields as a function of temperature, which are also confirmed by TGA data reported in the literature [45, 62], it can be seen (Fig. 8) that before 260 °C the other reactions do not take place and only drying of the processed material occurs. PLA pyrolysis reactions are activated around 260 °C, and the peak reaction rate is reached between 350 and 380 °C. Around 300 °C, meso-lactide (not shown in the figure) is the fastest-forming product, but as the temperature increases, it contributes to the formation of L-lactide and D-lactide. Between 350 and 380 °C there is a rapid increase in L-lactide and D-lactide; around 400 °C their production stabilizes. Simulations also showed that at 360 °C lactic acid begins to form and its content increases with increasing temperature. The simulated mass fraction of PLA (Fig. 8) seems to approximate well the trend resulting from the TGA results reported in the literature [45, 62].

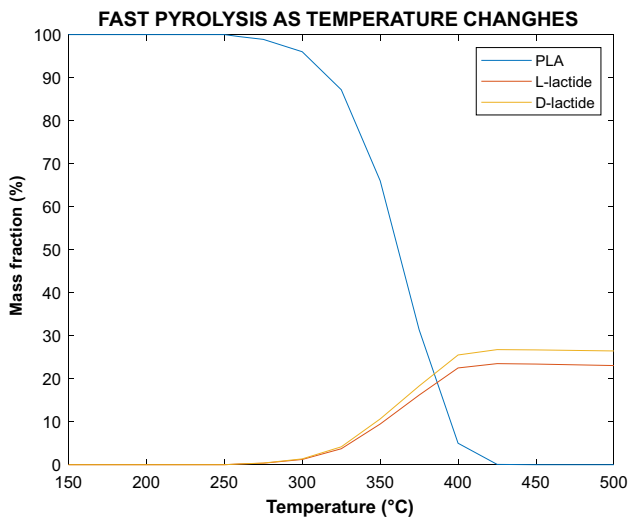
**Table 6** Results of major and trace element contents of the tested bioplastics compared to plastics of fossil origin [73, 74]

	Metal Concentration (mg/kg)								
	Pb	Cr	Cd	As	Cu	Zn	Mn	Se	Ba
<b>Bioplastics</b>									
BR-1	<6.2	6.6	<0.6	<3.8	0.5	8	<0.6	<3.8	<0.6
BR-2	<6.2	15.3	<0.6	<3.8	2.9	194	3	<3.8	475.0
BR-3	<6.2	1.0	<0.6	<3.8	0.3	8	6	<3.8	45.2
BF-1	<6.2	2.4	<0.6	<3.8	6.2	16	<0.6	<3.8	4.1
<b>Plastics [73, 74]</b>									
PE	13.4–458	18.6–87	2.4	5.0	20–23.5	45.5–97	8.0	5.6	77.6
HDPE	16.2	20.9	10.5	11.6	99.0	98.4	6.8	3.0	136.6
LDPE	6.3	9.7	7.3	11.2	28.6	22.5	6.1	4.2	65.8

**Table 7** Concentrations of the elements of potential environmental concern in the tested bioplastics samples compared to the limits for high-quality compost established by the Italian legislation [75]

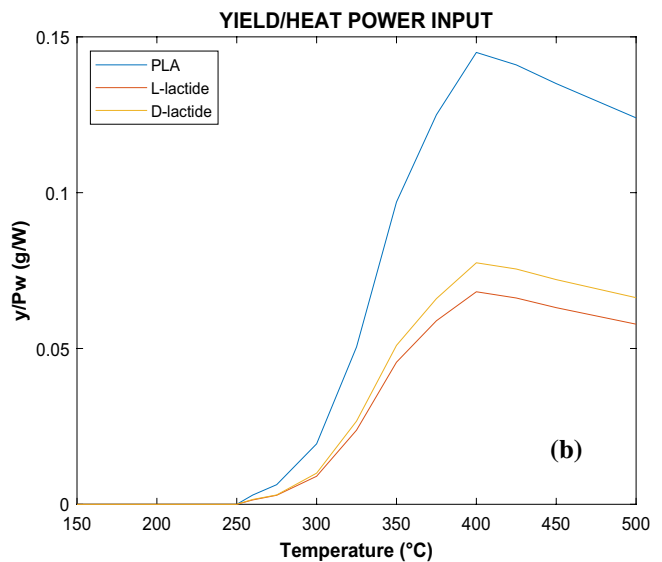
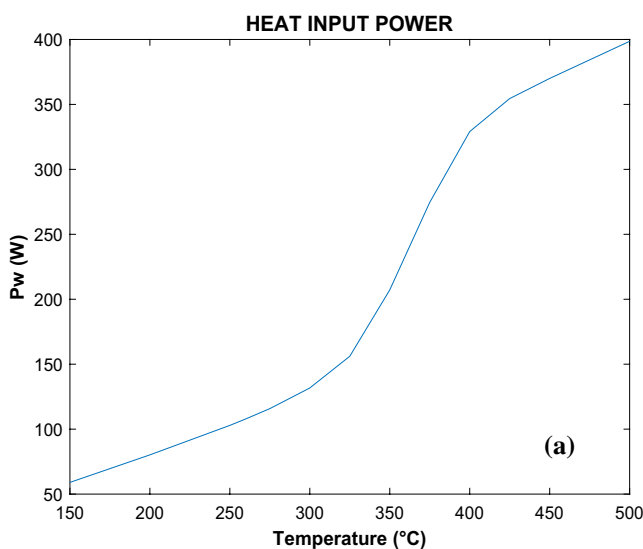
	Concentrations (mg/kg d.m.)							
	Cu	Zn	Pb	Cd	Ni	Hg	Cr(VI)	Tl
Compost [75]	≤ 230	≤ 500	≤ 140	≤ 1.5	≤ 100	≤ 1.5	≤ 0.5	≤ 2*
Bioplastics								
BR-1	< 0.6	8.0	< 6.2	< 0.6	5.5	< 3.8	6.6	–
BR-2	2.9	194.4	< 6.2	< 0.6	32.3	< 3.8	15.3	–
BR-3	< 0.6	8.4	< 6.2	< 0.6	1.1	< 3.8	0.9	
BF-1	6.2	15.5	< 6.2	< 0.6	1.5	< 3.8	2.4	

\*For compost containing algae



**Fig. 8** Trends in mass fraction of reactant and products as a function of temperature

Figure 9a shows the simulated trend of the heat power required by the reactor that increases significantly in the range between 350 and 380 °C. Figure 9b exhibits the simulated yield to power ratio (g/W) as a function of temperature. In this trend, it is evident how the increase in this ratio corresponds to an increase in the formation of PLA precursors (L-lactide and D-lactide). If we focus on the two PLA precursors, we have that the ratio trend increases up to a temperature of 400 °C where there is a yield/power of 0.145 g/W. After this peak, the yield vs. power input decreases almost linearly, emphasizing that 400 °C is the optimal temperature to sustain the process. Therefore, to obtain 0.145 g of L-lactide, 1 W of power is theoretically required. This behaviour is identical for both lactides, with the only difference being that L-Lactide has a higher yield for the same power requirement than D-Lactide. Furthermore, following the yield/power trends, the increase in yield is greater than the increase in power input up to 400 °C.



**Fig. 9 a** Trend of simulated reactor power input; **b** Variation of simulated yield to power ratio

Above this temperature, the heat power demand increases more than the precursor output. This allows us to establish that the optimal maximum temperature for the production of these precursors by pyrolysis is 400 °C, in agreement with what reported in the literature [60].

In the simulation, an attempt was made to obtain the highest possible purity of PLA precursors in the three oils resulting from the fractional condensation of the pyrolytic process. The graphs shown in Fig. 10 summarize the results obtained both in terms of the mass fractions in the oils and in terms of the yields with respect to the initial matrix. Considering the optimum temperature of 400 °C and simulating a first cooling column at 220 °C (blue bars), mainly D-lactide and L-lactide could be obtained, with a yield of 18% and 21%, respectively, compatible with their higher boiling temperatures compared to those required for condensation.

These two compounds are usually used together, in different proportions, for PLA production [77]. Their purity would be significant, based on the values found for the mass fraction of 44% for D-lactide and 52% for L-lactide, and further considering that acrylic acid and acetaldehyde, which are not PLA precursors, would be present in the marginal amounts of 1.4% and 0.1%, respectively. This marginal presence is justified by the boiling temperatures of acrylic acid and acetaldehyde, which are below 200, and 141 and 20.2 °C, respectively. A second condensation was simulated at a temperature of 105 °C. At this temperature, the condensation of L-lactide is completed (Fig. 10, mass fraction, red bar), but there would be also a noteworthy condensation of acrylic acid, which, together with other compounds

(acetaldehyde, acrylic acid, acrolein and water), would result in a substantial reduction of the purity of the PLA precursors (D-lactide and L-lactide) that condense in this second stage. Finally, a third cooling column was simulated at a temperature of 20 °C. Among the condensed products (Fig. 10, yellow bars), the following compounds were found in an appreciable content: acrylic acid, water, acetaldehyde, acrolein, and a negligible fraction of L-lactide. The main compounds obtained from the simulation and discussed here are in agreement with those identified in a previous study [78]. Adding the values resulting from the simulation for the lactide stereoisomers after the first, second, and third condensation step, it can be observed that the expected lactide yield would be of 48.7%. This value is comparable to those reported in studies by other authors [44, 76]. Based on these results, it can be estimated that for every kg of PLA-based bioplastics waste, 0.45 kg of new PLA-based bioplastics could be generated through chemical recycling, assuming a 94% yield of the lactide to PLA conversion process [79].

The developed model also estimated the composition of the gas (non-condensable products) leaving the third condensation column (Fig. 11). This gas is composed not only of carbon monoxide and carbon dioxide, but also of hydrocarbons (such as ethylene, propylene, propylene, and butane) that can contribute significantly to meeting the energy requirements for the operation of the pyrolysis reactor.

These non-condensable high-calorific gases were evaluated for their possible use, via recirculation, as a substitute for the required fuel (e.g., methane gas) to be provided as an energy source. For this purpose, the energy required to

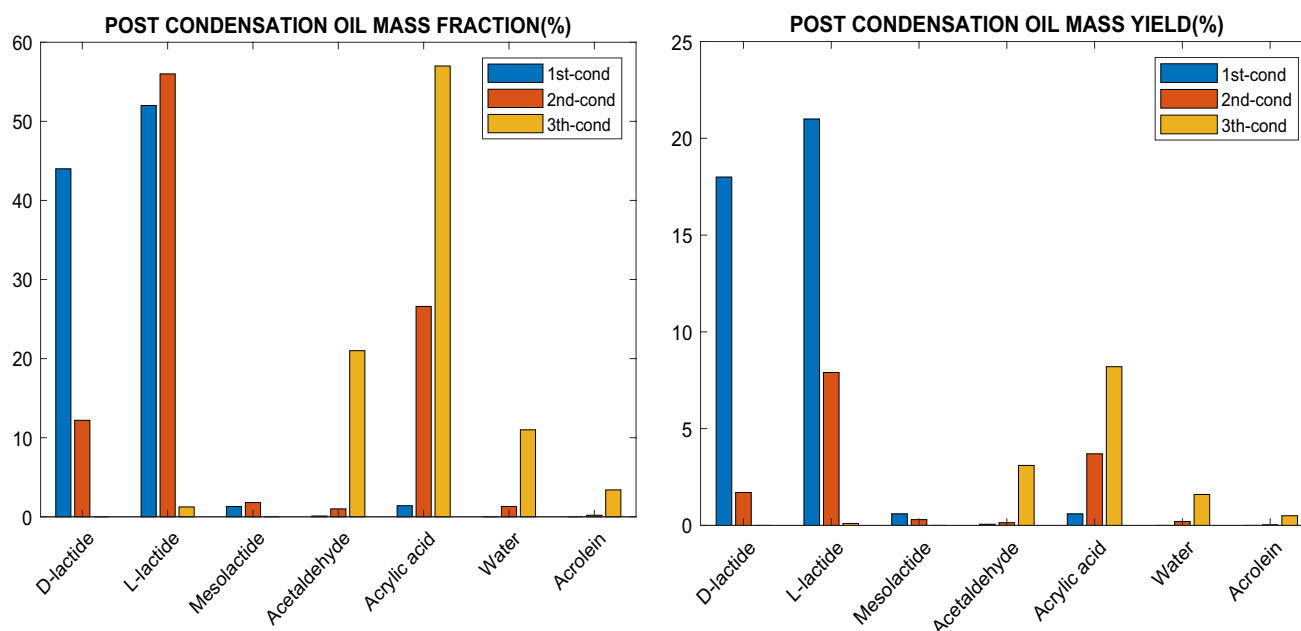
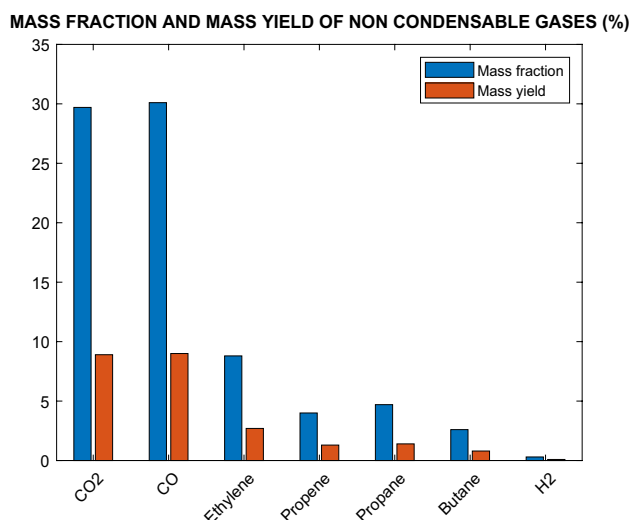


Fig. 10 Mass fraction and mass yield of oil post-condensates



**Fig. 11** Results for non-condensable gases

operate the reactor in the simulated modes was compared with the heat output that could be generated using the gas produced by the pyrolysis process. The calorific value of non-condensable gases can be determined from information available in the literature [80]; the lower calorific value of the mixture ( $LHV_{gnc}$ ) can be calculated using Eq. (3) below:

$$LHV_{gnc} = \sum_i x_i * LHV_i = 25.1 \text{ MJ/kg} \quad (3)$$

Where  $x_i$  and  $LHV_i$  are the mass fraction and the low heat value of the generic gaseous component (i), respectively.

This energy content was compared to the energy required for the simulated pyrolysis process, considering the volume of the pyrolysis reactor and energy losses (assumed to be 40%) due to thermal losses. From the ratio of the difference between the power that can be generated from the gas resulting from the pyrolysis reaction and the power required for the pyrolytic process, considering an operating temperature of 400 °C, and the power required by the process itself, a power surplus of about 105% would be necessary.

## Conclusions

In this study, the chemical-physical properties of four types of items classified as bio-based biodegradable plastics, differing by polymer type and shape, i.e.: starch-based plates and film bags, bioplastic B-plates and PLA cups, were examined. The aim of this characterization was to obtain more insight on the properties of these materials in view of establishing the potential suitability of recycling/recovery routes, such as compost production via

biodegradation, chemical recycling and thermal treatment with energy recovery, once they enter the waste stream. In fact, although bio-based biodegradable plastics waste should be collected and managed with the organic waste fraction, which is generally treated by aerobic and/or anaerobic biodegradation, some issues regarding its treatability in full scale-plants, in particular of rigid items, have been highlighted. Specifically, incomplete biodegradation or diversion into the processing scraps flow during the initial size separation of the feed waste, have been reported. In this study, we hence focused on some of the properties of these materials that could indicate the suitability of other treatments besides biodegradation, and for this reason, also compared the results obtained to those reported in the literature for analogous items made of conventional plastics.

The results of the characterization phase indicated that the types of analyzed bioplastics exhibited an organic matter content above 64%, a fixed carbon one below 5.4%, and a total carbon content above 37%. The highest volatile matter contents were measured for the PLA cups and starch-based films, while the highest ash contents were found for the other two types of rigid bioplastics examined. The results of the thermogravimetry analysis hence do not rule out any of the considered management strategies for the examined bioplastics, since they showed to contain polymers that volatilize below 550 °C. The rigid bioplastics however, exhibited a higher degree of crystallinity, a property that has been reported in previous studies to be associated to a lower biodegradability of bioplastic materials. Recovery as compost should be anyhow specifically investigated though biodegradation tests, carried out under the conditions characteristic of full-scale plant operation.

The concentrations of elements of potential environmental concern measured in the tested samples showed to be quite limited, generally lower than the ones reported for conventional plastics, and possibly indicating that the compost produced from organic waste containing the materials would continue to comply with the limits for agronomic use. It should be highlighted anyhow that the bioplastic items presenting the highest ash contents, especially the one for which the polymer composition is not provided, presented the highest contents of elements of potential environmental concern, indicating the importance of monitoring this parameter in all of the different types of bioplastic items recently introduced on the market. In addition, the possible presence of residual elements that are often associated to plastics and microplastics in the products of biological stabilization processes, needs still to be assessed. In this context, FTIR analysis could be a useful tool to investigate the general nature of the solid particles eventually found in the compost product to assess their potential biodegradability and final behaviour in the soil.

With regard to chemical recycling processes, the results of the thermogravimetric analysis indicated that pyrolysis could be a technically viable process to apply for the treatment of all of the bioplastic samples examined. It was hence decided to evaluate a chemical recycling process for PLA-based bioplastics by modeling the rapid pyrolysis process and the pyrolysis oil separation step by fractional condensation. This last step was specifically studied since it is particularly critical for cost-effective separation of high-purity chemical species. As observed from the numerical results obtained, the best efficiencies in terms of recovery of lactides, PLA precursors, should be obtained at the pyrolysis temperature of 400 °C. In addition, the first condensation oil, which has a high lactide purity (over 96%), would be separated from the condensation oil. This would be an important achievement in view of the production of second-generation PLA, which would offer important environmental benefits in terms of savings in land use and carbon dioxide emissions. In addition to lactide, significant amounts of acrylic acid, which could be used in the paint, adhesives and water treatment industries, and modest amounts of acetaldehyde, often used in the chemical industry, were found in the oils that could be potentially obtained.

Finally, should further investigations indicate some critical issues for the recycling of the tested bioplastics items by biodegradation or, in the case of PLA, by chemical recycling, the analyses performed in this study indicated that thermal treatment with energy recovery could be potentially feasible. For some samples tested, i.e. the starch-based and vegetable-based rigid items, however, the estimated HHV values were lower than 15 MJ/kg.

**Acknowledgements** Sara Franceschin is fully acknowledged for the preliminary contribution to this study carried out during her Master thesis.

**Author Contributions** FL: conceptualization, data curation, methodology, supervision, writing—original draft, writing—review & editing. GC, LB: methodology, validation, formal analysis, data curation, Writing—original draft, writing—review & editing. SC, VM: methodology, validation, supervision, writing—original draft, writing—review & editing. AF, PM, MM, DS: investigation, methodology, data curation, validation writing—original draft, writing—review & editing. All authors read and approved the final manuscript.

**Funding** Open access funding provided by Università degli Studi di Roma Tor Vergata within the CRUI-CARE Agreement. The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

**Data availability** Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

## Declarations

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

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