Analysis of potential recycling/recovery strategies for bioplastic municipal solid waste based on their chemico-physical properties and numerical modeling of pyrolysis process as recycling strategy

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Abstract
Owing to its low cost and versatility, plastics has become one of the most employed substances for a wide range of applications. According to Plastics Europe, in 2019, global plastic production reached 368 million tonnes (Plastics Europe, 2020). The expectation is that the production will further increase to about 600 million tons in 2025 (plasticsoupfoundation.org). However, its production based on fossil fuels and its frequent incorrect disposal at the end of life entails environmental sustainability issues (Folino et al., 2020). For this reason, in the perspective of pursuing environmental sustainability and promoting circular economy, bioplastics seem to be the designated substitute, since they present similar characteristics but should exert lower environmental impacts regarding both production and end of life management.

In this study, the most widely used bioplastics, i.e. those based on polylactic acid (PLA) and on starch, are characterized both chemically and energetically and are compared with conventional plastics which they replace in common use. Based on their chemico-physical properties, end-of-life management strategies, including chemical recycling and energy recovery, are then assessed for each product considering energy balances and environmental aspects.

Keywords: bioplastics; recycling/recovery; environmental sustainability; physico-chemical characterization.

Introduction
According to European Bioplastics (2021), “Bioplastics are not just one single material. They comprise a whole family of materials with different properties and applications.” A plastic material is defined as a bioplastic if it is either biobased, biodegradable, or features both properties (European Bioplastics, 2021).

The family of bioplastics is divided into three main groups:
- bio-based or partly bio-based, non-biodegradable plastics such as bio-based PE, PP, or PET (so-called drop-ins) and bio-based technical performance polymers such as PTT or TPC-ET;
- plastics that are both bio-based and biodegradable, such as PLA and PHA or PBS;
- plastics that are based on fossil resources and are biodegradable, such as PBAT.

Currently, bioplastics represent approximately only 1% of the annual plastic production (Plastics Europe, 2020). The most common bioplastics (European Bioplastics 2021, b) are: polyactic acid (PLA - 18.7%) and starch-based bioplastics (starch blends - 18.7%). Aerobic composting is the preferred disposal strategy due to the intrinsic biodegradability of biodegradable biopolymers. However, alternative disposal strategies for municipal solid bioplastic waste – incineration, mechanical and chemical recycling- are matter of study, as reported in Figure 1. The selection of the optimal route is deeply affected by the type of product and the biopolymer physico-chemical characteristics (European Bioplastics, 2016).

Figure 1 - End-of-life routes for biodegradable and non-biodegradable bioplastic waste (Fredi et al., 2021)
Among the possible end-of-life routes for bioplastics, recycling/recovery within organic waste management is the most direct. In Italy for example, current legislation (Italian Legislative Decree 116, 2020) establishes that biodegradable plastics should be collected with organic waste and follow the same management routes. Therefore, bioplastics in Italy should be mainly managed at its end of life through bio-treatments in anaerobic digestion and/or composting plants leading to the generation of biogas, digestate and/or compost. The biodegradability of bioplastic materials is certified through a standardized procedure in which optimal degradation conditions, i.e. thermophilic conditions (58 °C), a concentration of 1% of the test material and long contact time (90 days) are applied; these conditions differ significantly from the real process conditions that usually occur in anaerobic digestion and/or composting plants treating organic waste. This has been shown especially for anaerobic digestion processes carried out both in mesophilic conditions (Cucina et al., 2021) and in thermophilic conditions (Bandini et al., 2020). Furthermore, for most of the bioplastics produced, marketed, and mainly used today, the incomplete biodegradation of bioplastics results in a high content in small sizes of these substances in the final products, representing an obstacle for the agricultural reuse of digestate and/or compost (Bandini et al. 2022), (Lehner et al., 2019). To summarize, these studies outlined how aerobic digestion and/or aerobic composting presents several drawbacks and alternative end-of-life strategies must be taken in consideration.

**Method**

Characterization is the first step that is required to assess the effectiveness of process such as a sustainable disposal route. A concentration of heavy metals is below certain limits is required to obtain an end product from aerobic composting of quality compatible with the environment in which it will be used. Acid digestion through microwave irradiation is a widely used method to accelerate the biodegradation process and ICP-OES an advanced methodology to identify and quantify the inorganics included in the biopolymers. For energy recovery process – incineration – high energy densities, low moisture content and appropriate physico-chemical characteristics are required so that combustion process is effective. In chemical recycling process, depolymerization reactions occur to degrade polymer backbones into their monomers for a new synthesis and other high valuable chemicals recovery (Badia & Ribes-Greus, 2016) (Lamberti et al., 2020). Thermo-gravimetric analysis provide data to understand the thermal kinetics of degradation and assess the potentiality of pyrolysis process as an effective chemical recycling strategy.

In this study, the most widely used commercial for recycled tableware and food packaging sector, i.e. those based on polylactic acid (PLA) and on starch, are characterized both chemically and energetically and are compared with conventional plastics which they replace in common use.

The materials tested in this study (Table 1) are: PLA glasses; B-bioplastic plates (an unspecified plant-based bioplastic); Mater-Bi plates; Mater-Bi bags.

**Table 1:** Sample’s classification

<table>
<thead>
<tr>
<th>Sample</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA Glasses</td>
<td>BR-1</td>
</tr>
<tr>
<td>B-bioplastic plates</td>
<td>BR-2</td>
</tr>
<tr>
<td>Mater Bi plates</td>
<td>BR-3</td>
</tr>
<tr>
<td>Mater Bi bags</td>
<td>BF-1</td>
</tr>
</tbody>
</table>

**Results**

First results of the characterization highlight that heavy metals concentration is under the limit values established by the EU legislation (Decision (EU) 2015/2099). As reported in Figure 2, in every bioplastics are completely absent arsenic, beryllium, cadmium, cobalt, mercury, lead, antimony and selenium. The other metals are contained in traces. Thus, these preliminary results highlight that composting could be an applicable recycling route. The method used for the heavy metal’s characterization is the UNI EN 13657.

The elemental analysis show that oxygen is highly present in the samples considered, with values that exceeds over the 30% in almost all the cases. This has a strong impact on the high heating values and lowers the prospects of incineration as an effective end-of-life path.

Thermogravimetric analysis were performed to evaluate the suitability of bioplastics to undergo to thermal recycling process. A significant percentage of volatile matter was evidenced for all the biopolymers tested, with values of over 97% d.b. for poly(lactic acid) glasses. Ash contented presents significant variation among the samples, deeply influenced by the shape, i.e. bags or plates, and feedstock (BF BR … ).
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Thermogravimetric analysis (TGA) were performed to evaluate the suitability of bioplastics to undergo to thermal recycling process. A significant percentage of volatile matter was evidenced for all the biopolymers tested, with values of over 97% d.b. for poly (lactic acid) glasses (Figure 3). Ash contented presents significant variation among the samples, deeply influenced by the shape, i.e. bags or plates, and feedstock (BF BR …).

Considering the high presence of volatile matter coupled with its low calorific power limits in biodegradation exhibited by PLA solid waste reported in the literature and the preliminary results of the characterization, fast pyrolysis process for PLA depolymerization was considered as high potential. A numerical model has been implemented in Aspen Plus © to simulate the pyrolysis process of PLA waste applied to a lab-scale screw reactor (Figure 4). Particular attention was paid...
in the implementation of kinetic model based on previous studies of analytical pyrolysis (Chrysafi et al., 2021) (Das & Tiwari, 2017). The model was validated against experimental data (TGA) and the product composition was compared respect to related studies (Undri et al., 2014) (Saeaung et al., 2021). Numerical simulation results show that PLA bioplastics building blocks (lactides) and valuable chemicals (acrylic acid, acetaldehyde) can be recovered by fractionation of pyrolysis oil. The model was used to scale-up to assess the economic feasibility of a potential plant for bioplastic waste disposal.

Figure 4: Plant diagram of the pyrolysis process for the recycling of PLA implemented in Aspen Plus

Conclusion
This study aims to contribute to the assessment of the more effective and sustainable end-of-life route for solid bioplastic waste. Accurate characterization is crucial to evaluate and compare the feasibility of different recycling routes. At the knowledge of the authors, literature lack of a deep study on both chemical and energetic parameters on a such large field of commercial biopolymers. The results show that composting could ideally be a viable path for all the samples analyzed, however respirometry tests need to be carried out to reinforce this preliminary conclusion. Chemical recycling route is a promising alternative route for PLA waste, according to the principle of preservation of natural sources and circular economy. The numerical model provided precious data regarding to the feasibility of pyrolysis process, but further investigation is required for model validation.

References


Chrysafi, I., Ainali, N. M., & Bikiaris, D. N. (2021): “Thermal degradation mechanism and decomposition kinetic studies of poly(Lactic acid) and its copolymers with poly (hexylene succinate)”. Polymers, 13(9). https://doi.org/10.3390/polym13091365


