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Polymer recycling in an open-source additive manufacturing context: Mechanical issues

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ABSTRACT

Nowadays, the low recycling rate of polymers is still a challenge to humankind due to energy, economic and logistical issues. In the context of additive manufacturing, there is an exponential use of thermoplastic materials in the industrial and public open-source additive manufacturing sector, leading to an increase in global polymer consumption and waste generation. However, the coupling of the open-source 3D printers with polymer processing could potentially offer the basis for a new paradigm of distributed recycling process. It could be a complementary alternative to the traditional paradigm of centralized recycling of polymers, which is often uneconomical and energy intensive due to transportation embodied energy. In order to achieve this goal, a first step is to prove the technical feasibility to recycle thermoplastic material intended for open-source 3D printing feedstock.

The contribution of the present study is twofold: first, a general methodology to evaluate the recyclability of thermoplastics used as feedstock in open-source 3D printing machines is proposed. Then, the proposed methodology is applied to the recycling study of polylactic acid (PLA) material addressed to the fused filament fabrication (FFF) technique, which is currently the most widely used. The main results of this application contribute to the understanding of the influence of the material's physico-chemical degradation on its mechanical properties as well as its potential distributed recyclability.

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1. Introduction

Polymer materials play an important role in our modern society thanks to a range of unique properties. They present characteristics such as a very wide range of operating temperatures, high thermal/electrical insulation, corrosion- and light- resistant and sufficient mechanical properties (high strength-to-weight ratio, stiffness, toughness and ductility). These properties are adequate for the manufacturing of a wide range of low-cost, low-weight, high-performance products which are fundamental for technological and societal development [1,2]. However, one of the main issues is the environmental impact of the plastic residues accumulated in the natural environment and in landfills, due to their longevity which can reach several decades (if not millennia) to degrade [3,4].

In the industrial ecology for polymers, different strategies have been studied for plastic waste management, ranging from reuse and recycling (Mechanical, Chemical, Feedstock) to thermolysis/recovery processes [3,5,6]. From the energy and environmental perspective, the research works of Arena et al. [7], Perugini et al. [8], Lazarevic et al. [9], Piemonte [10] have highlighted that the mechanical recycling strategy is the most suitable plastic waste management option for relatively clean and homogeneous plastic and bioplastic waste streams compared to landfilling or incineration alternatives.

Mechanical recycling allows directly recovering plastic solid waste for reuse in the manufacture of new plastic products [3,6,8,11]. This process entails the technologies for the separation of polymer types, decontamination, size reduction, remelting and production of new plastic products from plastic wastes. However, there are several obstacles in the mechanical recycling process to consider that influence the viability of this recycling strategy. Main obstacles are related to economical, logistical and technical considerations of the degradation of recyclable materials [3,6]. From the economical and logistical perspective, there is no net benefit from recycling plastic materials [12]. The low weight-to-volume ratio and the heterogeneity of plastic wastes make less economically viable to invest in the necessary transport, collection and sorting facilities. Moreover, the price of recycled plastic is limited by the price of virgin plastic [3]. From technical perspective, the

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quality is the main issue when dealing with mechanically recycled products. One important element to consider in this process is the heterogeneity and compatibility issues of the polymers. The more complex and contaminated the waste, the more difficult is the mechanical recycling process. There is a need for a greater understanding of recycled plastic material characteristics and its ability to be recycled. As a consequence of the precedent factors, one can see that according to the U.S. Environmental Protection Agency, there were 33.3 million tons of wasted plastic in 2014. Only 3.1 million tons (equivalent to 9.5%) were recycled [13]. In the case of Europe, 25.8 million tons of post-consumer plastics waste were generated in 2014. 7.7 million tons (equivalent to 29.7%) were recycled [14].

In recent years, several types of polymer materials have been used in the additive manufacturing (AM) sector in order to produce plastic prototypes [15]. Additive manufacturing (AM) is the general name for direct fabrication from prototypes (for verification of form, fit and function design) until end-use products using technologies that deposit material layer-by-layer [16,17]. Due to the expiration of early additive manufacturing machinery patents as *Fused Deposit Modeling* (FDM) in the mid-2000s, a new form of open-source additive manufacturing (also known as open-source 3D printing) has been taking place as a result of the conjunction of the digital fabrication capabilities of AM with the communication technologies and the commons-based peer production (CBPP) practices (self-selection of tasks by the participants, collaboration as peers, modularity) [18,19]. Projects such as **RepRap** (or **Rep**licating **Rap**id-prototyper) and Fab@Home are extrusion-based systems, which use a fused-filament fabrication (FFF) approach in order to make engineering components and other products from a variety of thermoplastic polymers. These types of projects are available to everyone, and provide an opportunity to (co-)design globally (taking from and contributing to a knowledge commons) and produce locally, responding to specific needs [18,20–23]. Thanks to the democratization of these projects, the fabrication of functional pieces/prototypes has become accessible for everyone for a marginal cost [18,24]. Moreover, the affordable costs of 3D printers can positively impact communities like Fablabs, university laboratories or schools, and open new dimensions to science education that can make a marked impact in developing countries [25]. Furthermore, this technology have been proved to be useful tools in several fields, such as education [26,27], medicine [28–31], scientific equipment [32–34] and sustainable development [35].

Recently, the adaptation of open-source (OS) 3D printers with domestic waste plastic extruders has been explored as a new prospective approach to polymer recycling in order to prepare 3D printer feedstock. The major interest of this approach is the reduction of cost and greenhouse gas emissions related to waste collection and transportation as well as the environmental impact of manufacturing custom plastic parts. This distributed polymer recycling approach could be an additional alternative to the conventional centralized polymer recycling [36–39]. Taking into account the significant growing adoption of open-source (OS) 3D printing, distributed polymer recycling approach could be highly relevant as current recycling rates are particularly low. Currently, numerous open-source plastic extruders and projects for transforming post-consumer plastic into feedstock for 3D printers have been proposed: Lyman Filament Extruder [40], the Filabot [41], Recyclebot [36], RepRap Recycle Add-on [42], Precious plastic [43], Plastic Bank [44]. Polylactic Acid (PLA) and Acrylonitrile-Butadiene-Styrene (ABS) filaments, ranging from 1.75 to 3 mm of diameter, are the two most common polymers in the open-source (OS) 3D printing context. From an economical point of view, commercial filament costs are in the range between \$18.86 and \$175.20 per kg, which is 20 to 200 times above the cost of raw plastic. Kreiger et al. [37] and Wittbrodt et al. [45] proved the economic feasibility for a distributed model with local plastic material recycling (recycled filament) for OS 3D printers in which 1 kg of recycled filament was fabricated from about 20 milk jugs for under 10 US cents using the prototype of open-source plastic extruder called “Recyclebot”. In terms of energy, Baechler et al. [36], and Kreiger and Pearce [39] have shown a proof of concept for recycling of high-value polymer waste where savings were between 69% and 82% embodied energy for distributed recycling over a centralized recycling approach. Therefore, there is an interest in recycling polymeric materials for a 3D printing open-source context. In the context of commercial AM, there have been several studies in order to characterize the recycled material properties of metal powders for electron beam melting process [46,47], and polymer powders for selective laser sintering process [48,49]. However, there remains a need for an efficient method that can allow to understand the polymer recycling process in the context of open-source 3D printing. Therefore, a first step one has to study is the physical characterization at the micro- and macro-level of the recycled material in order to assure new potential uses.

The contribution of the present research, being a continuation of our previous paper on polymer recycling presented at the SFF symposium in 2015 [50], is twofold: first, a general methodology to evaluate the recyclability of polymers used as feedstock for 3D printing machines is proposed. Then, the proposed methodology is applied to the PLA recycling study in order to be used by extrusion-based systems using fused filament fabrication (FFF), which is now the most widely used technique. The main results of this application contribute to the understanding of the influence of the material's physico-chemical degradation on its mechanical properties and thus on its potential distributed recyclability.

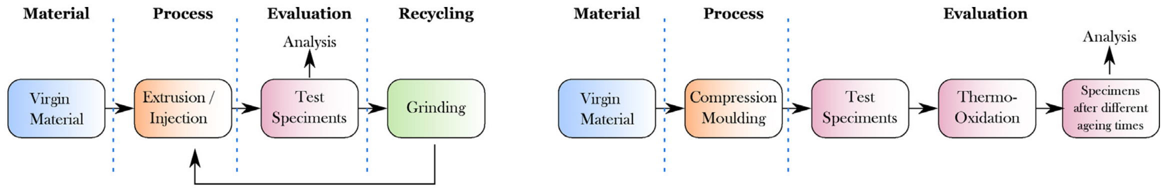
The remainder of this paper is organized as follows: In Section 2, we present a polymer recycling background in order to put the scientific basis for the proposed methodology. In Section 3, the proposed methodology to evaluate the recycling feasibility for open-source additive Manufacturing (OS AM) is detailed. Afterwards, Section 4 shows in a detailed manner the application of the methodology to the case of PLA. In Sections 5 and 6, experimental results are presented and their implications for the future recycling process are discussed. To finish, in Section 7, conclusions and perspectives for future research are presented.

2. Polymer recycling background

In the extensive polymer literature, one can see that the polymeric materials are exposed to thermo-mechanical and thermo-oxidative degradation [51–57]. Thermo-mechanical degradation occurs when the material is processed, more precisely when high shear forces and high temperatures cause chain scission and chemical reactions. On the other hand, thermo-oxidative degradation produce physical and chemical changes in the polymeric structure due to exposure of specific environmental conditions during service life. Thermo-mechanical and thermo-oxidative degradations are responsible for changes in structural and morphological characteristics of the polymers such as mechanical-rheological-thermal properties, degree of crystallinity, viscosity, and molecular composition [55]. This information can be used as quality assessment of the recycled material, and can also provide important inputs about the control of the processing conditions/parameters during the recycling process.

Modeling the life cycle of recycled products is an usual experimental frameworks to investigate the mechanisms and effects of the degradation processes to which recycled products are exposed. These frameworks to investigate the thermo-mechanical and thermo-oxidative degradation are illustrated in Fig. 1:

The procedures for modeling the life cycle of recycled plastics can be decomposed in four phases *Material*, *Process*, *Evaluation* (and



(a) Multiple processing approach to evaluate thermo-mechanical degradation.

(b) Methodology for thermo-oxidation degradation.

Fig. 1. Life cycle modeling of recycled polymers.

Adapted from [55].

Recycling for multiple processing Fig. 1a). For both cases, *Material* is the initial step which has as main goal to characterize the initial condition of the polymer. Fig. 1a presents the methodology of multiple processing in order to analyze the structural and morphological changes induced by consecutive processing steps. In this sense, multiple extrusion or injection moulding process is a well-tried approach to assess the recyclability of polymeric materials in order to simulate the extended life cycle. The main aim of this approach is to obtain information about the progressive material degradation due to the *Process* phase. In this way, it is possible to optimize the processing conditions during the mechanical recycling in order to avoid further degradation. For example, the choice of temperatures range and/or further addition of stabilizers and other additives are possible options.

On the other hand, Fig. 1b plots the approach for modeling the service life trough different accelerated ageing tests. The goal of this test is to simulate accurately the environmental conditions applied to the polymer materials during the life service (humidity, temperature, air, chemical environment – e.g. radiation, biological and microbial attack, pH or salt content –) [55]. Parameters such as temperature, time and type of environment are carefully selected to model real conditions. In conclusion, these two strategies enable us to study the degradation processes undergone by synthetic polymers during their first use and sub-sequent mechanical recycling processing. Recent approaches have tried to combine reprocessing and accelerated ageing to obtain an overall picture of the extent of the degradation processes that affect the polymers during the entire life cycle [55].

Moreover, it is necessary to define the quality characteristics which are assessed in the phase *Evaluation* in the model presented in Fig. 1. These quality characteristics have to consider the macro/microscopic properties in order to fulfill the requirements of manufacturers and consumers, and to guarantee the performance of recycled products in second-market applications [51]. Traditionally in the plastic industry (plastic producer or processor), the melt flow index (MFI) is one property that is needed in order to evaluate whether the same process can be used irrespective of whether it uses virgin or recycled polymers. This will indicates if it is possible to process the recycled polymeric materials in the same set-up as usual. However, several additional properties are needed in order to have a holistic assessment of the material degradation. Karlsson [51], Vilaplana and Karlsson [55] developed a conceptual framework with three main axes in order to evaluate the quality assessment of recycled plastics, as detailed in Fig. 2:

They can be defined as follows:

Degree of degradation (DD): it determines the evolution of polymer degradation at macro-microscopic scale due to the processing and service life.

Degree of Mixing (DM): it is related to the presence of polymeric impurities as a consequence of impure plastic waste streams and poor separation in recycling plant.

Low molecular weight compounds (LMWC): it is related to the presence of additives, contaminants and degradation products in the polymer structure. These elements are important in order to fulfill legislation requirements.

For each axis, there are numerous analytical strategies and characterization tests in order to appropriately evaluate the degradation of the material. Badia and Ribes-Greus [58] present a set of multi-level characterization tests and analytical techniques for the recycled polymers commonly used to evaluate the performance and/or degradation state of the resulting material. Finally, it depends on the investigator to select the property (or properties) to study during the mechanical recycling process. Therefore, the adequate experimental protocols are implemented.

To the best of our knowledge, little evidence is available about experimental methodologies integrating these recycling concepts in the context of the open-source additive manufacturing, nor correlating the material degradation with the properties of the printed object. Therefore, in the next section we propose a systematic methodology to evaluate the recyclability of thermoplastics for OS AM based on these scientific literature.

3. Methodology to evaluate 3D printing polymer recycling

The main goal here is to present a generic methodology to evaluate the opportunity, interest and processes to recycle thermoplastic polymers in order to use them as feedstock for open source 3D printers. Within the framework of the present methodology, a first assumption is the use of virgin materials as initial material to ensure the initial conditions of the procedure. A second strong assumption is to have closed-loop cycles where the initial materials is fully recycled, and there is no addition of material in the middle of the recycling process. The proposed methodology is shown in Fig. 3. It has been structured in five main steps that will be described in the following subsections:

3.1. Step 1 "Material definition"

The main purpose of this step is to define the material to be studied. The polymer characteristics given by the supplier have to be taken into account for initial establishment of the processing parameters. Also, the material quantity needed for the overall experimentation has to be estimated.

3.2. Step 2 "Process assignment"

This step is divided into two parts: *Recycling chains (Fig. 3:2.1)* and *3DP Feedstock (Fig. 3:2.2)*.

- The ***"Recycling Chains"*** step has two main goals. In the first place, the identification of the recycling process chains that are necessary to characterize the material degradation. In the second place,

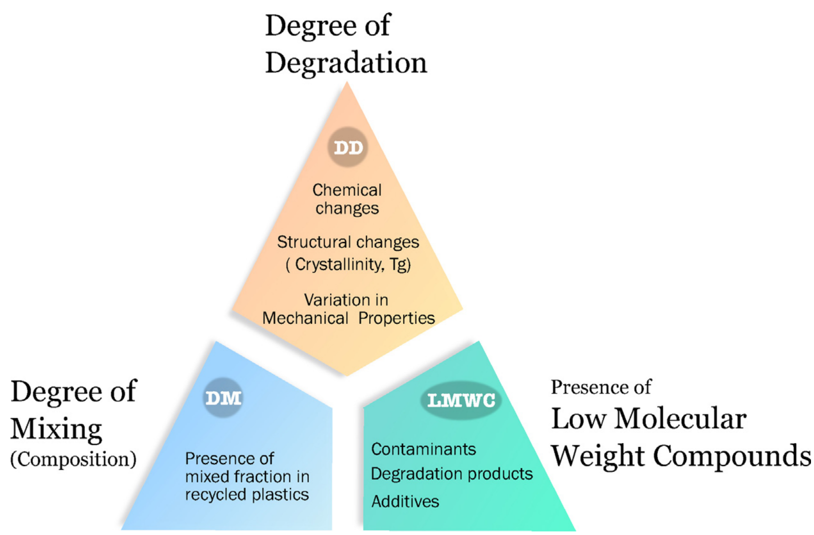


Fig. 2. Key properties for quality assessment of recycled plastics.

Source [51,55]

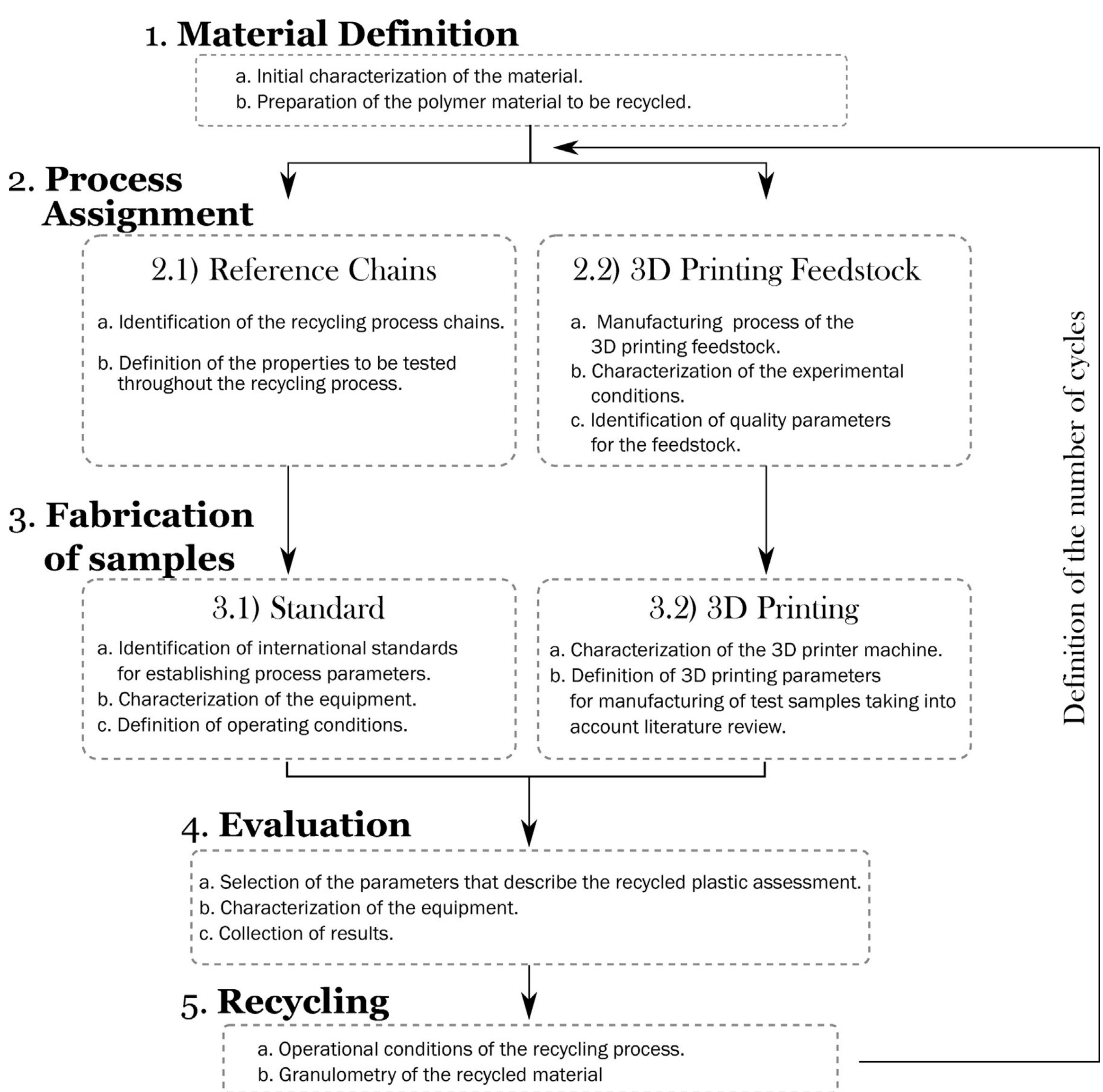


Fig. 3. Proposed methodology to evaluate the recycling process in the 3D printing chain.

the definition of the material properties to be tested during the recycling process.

Considering the recycling process chains, we propose at least four recycling chains are needed to compare the material degradation in order to highlight the effects of the different processes on the material,

- *Reference:* used as degradation reference for the recycled material.
- *3D Printing:* used to evaluate the degradation of the material as a result of the 3D printing process with samples made using a 3D printer with established parameters.
- *Feedstock:* used to evaluate the degradation impact due to the manufacturing of the raw material for the 3D printing machines considered (i.e. filament, grain, powder, . . .).
- *3DP (Reference):* used to evaluate the degradation of the material as a consequence of the 3D printing process using the reference equipment.

The comparison of the two former recycling chains (*Reference* and *3D printing*) enable us to observe the differences of the material degradation between a standard (e.g. injection) and the 3D printing manufacturing process. Considering the two latter (*Feedstock* and *3DP (Reference)*), they allow us to estimate the impact of the printing process on the material degradation.

On the other hand, regarding the definition of the properties to be tested, different mechanical, chemical and rheological properties are able to illustrate the polymer degradation as stated in Section 2. The experimenter has to determine his/her choice taking into account the international standards.

• The ***"3DP Feedstock"*** step refers to the definition of how the raw ma material will be manufactured. It is necessary to specify the different processes that will be used to get the feedstock in usable form for the OS 3D printers. The different manufacturing parameters of the feedstock and the definition of the obtained quality are addressed here.

3.3. Step 3 "Fabrication of samples"

The main goal of this step is to characterize the *Standard (Fig. 3:3.1)* and the *3D printing (Fig. 3:3.2)* manufacturing processes.

1. The *"Standard"* process refers to the characterization of the traditional equipment used in the literature of polymer recycling. This will serve as reference for the purpose of comparing the obtained results with the 3D printing process. For that reason, in function of the properties to be studied, the identification of the appropriate international standards and the scientific literature are necessary in order to determine the equipment and manufacturing parameters of the samples.
2. For the *"3D Printing"* process, there are two main goals: (1) to characterize the open source 3D printer, and (2), to establish the manufacturing parameters of the samples. Literature review about the selected properties in the additive manufacturing context can give an initial insight into important parameters to consider.

3.4. Step 4 "Evaluation"

Within this step, the set of variables that describes the targeted properties are defined Likewise, the definition of the test conditions/equipment is addressed. The tests are conducted in order to collect the data according to the international procedures taking into account the recycling process chains and the number of recycling cycles.

3.5. Step 5 "Recycling"

To finish, the main goal is to adapt the recycled plastic material for reprocessing. The recycling process is made individually for each recycling process chain. A characterization of the recycling equipment used and a description of the characteristics of the recycled material obtained is made.

4. Application case: recycling study of PLA for fused filament fabrication (FFF) 3D printers

In order to illustrate the application of the proposed methodology, this section will describe the recycling process of the polylactic acid (PLA), which is one of the most widely used material in the open source context. More precisely, we consider the Fused Filament Fabrication (FFF) technique with the open-source RepRap machine [21–23]. The main interest of using open-source (FFF) 3D printers is that these systems are more widely used than any other additive manufacturing system [19].

4.1. Material definition: Polylactic Acid (PLA)

Polylactic Acid (PLA) is one of the most important bio-based, biodegradable and biocompatible polymers [59–63]. PLA is a thermoplastic aliphatic polyester obtained from the ring-opening polymerization of lactide, which may be derived from renewable resources such as potato, starch, sugar cane and corn sugar [64–66]. PLA offers great promise in a wide range of commodity applications such as bottles, trays, containers and so on. Moreover, PLA can be processed by injection moulding, blow moulding, or be extruded into films, fibers, and sheets [59,67–70]. Therefore, PLA is considered a promising alternative to reduce the municipal solid waste (MSW) disposal issues by offering additional end-of-life scenarios [71].

The selected material for this study was PLA type 4043D, a product of NatureWorks supplied by NaturePlast (Caen, France). This material is intended for fabrication of 3D printers feedstock according to the manufacturer's specifications.

a Initial characterization of the material: The selected PLA has a density of 1.24 g/cm^3, tensile yield strength of 60 MPa, tensile modulus of 3600 MPa, tensile strength at break of 53 MPa, tensile elongation of 6%, MFI = 6 g/10 min at 210 °C, a glass transition temperature (T_g) of 55–60 °C.
b Preparation of the material: Prior to processing, virgin pellets were uniformly dried for 4 h at 80 °C in a dehumidifier with the purpose of removing humidity as much as possible.

4.2. Process assignment

4.2.1. Recycling chains: thermo-mechanical degradation

a. *Identification of the recycling process chains*:

Based on the thermo-mechanical degradation framework, a scheme for establishing the four recycling process chains was adapted as illustrated in Fig. 4. These experimental strategies allow us to compare the material degradation, as specified in the methodology Section 3.2.

In the *Process* stage, we consider that the material will be degraded by the three operations injection, extrusion and 3D printing, taking into account the respective recycling chain.

b. *Definition of the properties to be tested*:

In this study we will consider the *Degree of degradation (DD)* as indicator of the quality of the recycled material. Consequently the variation of mechanical properties will be studied through the recycling process. Based on the literature of recycling of PLA

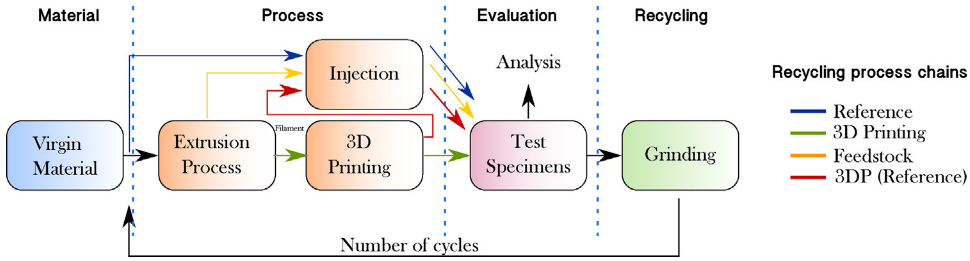


Fig. 4. Definition of the recycling process chains.

(Appendix A), the micro injection moulding, by means of the micro-compounding process, is selected as *Standard* process. The characterization of the equipment and the parameters used are discussed in more detail in Section 4.3.1.

4.2.2. 3D printing feedstock: extrusion

a. *Manufacturing process of the 3D printing feedstock*:

A considerable number of open source 3D printers are inscribed in the context of extrusion-based systems, where the loading of material is in form of continuous filament plastic of 1.75–3 mm in diameter [17,72]. In that respect, extrusion of the polymer into monofilament may be achieved by melt spinning, which is one of the most important techniques for continuously melt processing of PLA [68,69]. For the purpose of this experiment, we will consider this process as a sum of three systems namely the feeding system, extrusion process and conveyor system, as it can be seen in Fig. 5.

b. *Characterization of the experimental conditions*:

The feeding system is performed using a twin screw volumetric feeder K-TRON (K-MV-KT20). The feed rate used was established at 0.53 ± 0.04 kg/h. Concerning the extrusion process, a laboratory scale extruder (HAAKE^{TM}Rheomex CTW 100 OS counter-rotating conical twin screw) was used. The temperature profile selected was 160, 170, 180 °C and the screw speed was set up to 60 rpm. Finally, a conveyor system was adapted with the purpose of controlling properly the take-up speed of the filament after the extrusion process.

c. *Identification of quality parameters for the feedstock*:

The parameter selected for establishing the quality of feedstock was diameter regularity. The filaments obtained were in a range of 1.5–1.8 mm. Appendix B present an explanation of the approach used for the relationship of the manufacturing conditions with the diameter obtained.

4.3. Fabrication of samples

4.3.1. Standard: micro injection moulding process

a. *Identification of international standards*:

This study is focused on *Degree of degradation* in terms of variation of the mechanical properties of the recycled material. Therefore, tensile properties were studied according to ISO 527-1B. The tensile specimen is a dog-bone geometry of 150 mm in length and central dimensions of $10 \times 4\,\text{mm}^2$.

b. *Characterization of the equipment*:

The micro-compounding process was selected as our standard manufacturing process. Using micro-compounders, it is possible to analyze a small amount of material (i.e. 3–15 g) with a similar processing history as in conventional twin-screw extruders. A twin-screw micro-compounder machine (DSM-Xplore 5 cm^3 Micro-Compounder, Model 2012) was selected for this experimentation.

c. *Definition of the operating conditions*:

A constant temperature from the feed throat to the die of 180 °C and a screw speed of 100 rpm in co-rotating mode were the parameters adopted. The extruded material was taken at after a mixing time of 3 min. The temperatures of the melt and the mold were 190 °C and 45 °C respectively. The melt was directly injected using the transfer cylinder of DSM Xplore 10 ml injection molding machine in order to obtain mechanical samples. The injection and holding pressures were set to 9 bars for 30 s. Specimens were carefully removed from the mold after 5 min of cooling.

4.3.2. 3D printing process: fused filament fabrication (FFF)

The goal of this step are, first, to characterize the open source 3D printer, and second, to establish the manufacturing parameters of the mechanical samples using the OS 3D printer. One of the principal characteristics of open-source 3D printing is that it has been an object of social experimentation, where numerous enthusiasts and communities have developed a significant number of 3D printer machine architecture [18]. Therefore, due to the high customization nature, there are different machine architecture configurations which result in inherent variability among different 3D printers. It is necessary to characterize the open source 3D printer with the purpose of guaranteeing reproducibility of the printed parts [73].

a. *Characterization of the 3D printing machine*:

Fig. 6 a presents the two types of 3D printers, named *Mondrian* and *FoldaRap*, selected for the fabrication of the samples in this study [74,75]. They can be considered as representative 3D printer among the set of OS 3D printer machines [73]. The work capability are $140 \times 140 \times 155\,(\text{mm}^3)$ and $200 \times 200 \times 200\,(\text{mm}^3)$ for *FoldaRap* and *Mondrian* respectively. In both 3D printers, the extrusion system can be displaced in the horizontal plane XY. In the case of the *Foldarap*, the printed head can be displaced in the *Z*-axis while in the case of the *Mondrian*, print bed can be displaced in this axis. The heated print bed is made of aluminium joined with a peltier cell and a top layer of kapton is used with the purpose of improving the adherence of the piece with the print bed.

b. *Definition of 3D printing parameters*:

From the point of view of dimensional accuracy, there have been attempts in order to characterize the dimensional performance of the open source 3D printers [73,76–78]. It was found that according to the International Standard Tolerance Grade of these types of machines, it could be situated between IT14 and IT16. Moreover, parameters such as layer thickness, raster width and nozzle speed movement can have an impact on the machine accuracy [73].

On the other hand, considering the mechanical properties in additive manufacturing technology based on extruded-based systems, one important conclusion of the literature is the orthotropic behavior of the printed parts. Therefore, the properties are directionally dependent.

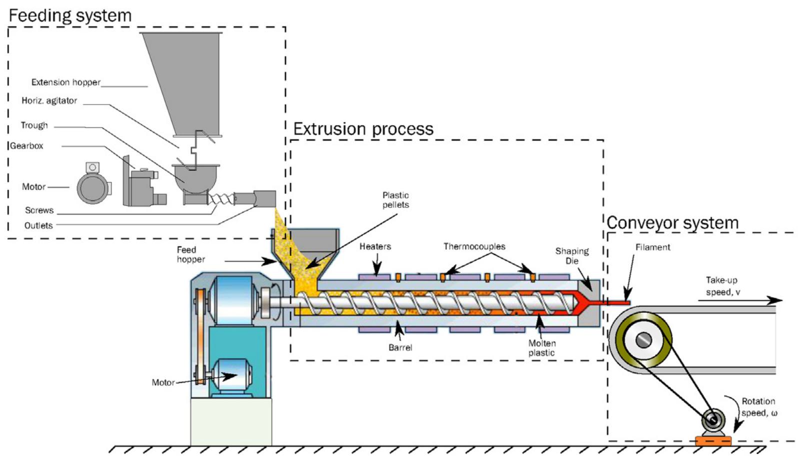
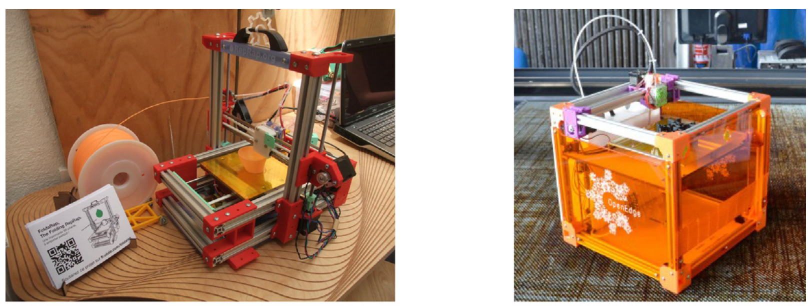


Fig. 5. Schematic diagram of the extrusion process for the fabrication of 3D printing feedstock.



(a) 3D printer -FoldaRap-

(b) 3D printer -Mondrian-

Fig. 6. Open-source 3D printers used for the fabrication of the recycled test samples.

Mechanical integrality of the printed part is directly related to factors like the energy adhesion/cohesion between the layers and deposited beads, the growth of the contact area formed between the adjacent beads, the molecular diffusion and randomization of the polymer chains across the interface, and a minimum residence time at elevated temperature in order to assure adequate levels of diffusive bonding [79–82]. Moreover, the thermal history of interfaces plays an important role in determining the bonding quality. Uneven heating and cooling cycles due to the inherent nature of the printing process results in stress accumulation in the built part, which is primarily responsible for week bonding and thus affects the strength. For that reason, there is a dependence of the mechanical properties on toolpaths and build part orientation. Therefore, mechanical properties are a function of parameters of fabrication because they affect meso-structure and fiber-to-fiber bond strength [83–91].

The constitution of the stiffness matrix for an orthotropic material would require the fabrication of specimens in six different orientations as made in the research made by [85,92,93]. However, for the purposes of this study, we selected only one build orientation with two different types of toolpaths 0/90, 45/45. Fig. 7 shows the parameters used in the fabrication.

4.4. Evaluation: mechanical properties

The parameters to describe the mechanical properties of the recycled samples are:

a. *Selection of parameters*:
   - Elastic modulus E [MPa]: ratio of stress (nominal) to corresponding strain below the proportional limit of the material. In the diagram of Fig. 8, it is the slope in the stress-strain diagram between 0.05% (ϵ_1) and 0.25% (ϵ_2) strain. This value can be calculated by linear regression between the strain values ϵ_1 and ϵ_2
   - Tensile strength (σ_m [MPa]): Maximum stress sustained by the test specimen
   - Tensile strain ϵ_m [mm/mm]: Strain at the moment of maximum stress
   - Tensile strength at break (σ_B [MPa]): Stress at which it occurs the rupture
   - Nominal strain at break (ϵ_B [mm/mm]): Strain at the moment of rupture

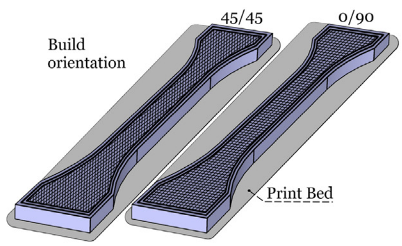
b. *Characterization of equipment*:
   Tensile tests were achieved by means of an Instron 5569 (Instron, USA) universal electromechanical testing instrument. The loading speed was 1 mm/min, and a 50 kN load cell was used. An extensometer was used with a nominal length of 50 mm to determine elastic modulus.

c. *Collection of results*:
   Once the specimens are tested, Table 7 (Appendix C) is proposed in order to collect the necessary data for further statistical analysis for each recycling process chains.

4.5. Recycling process: plastic shredding

Size reduction of the samples of each recycling cycle is required in order to reprocess the material.

a. *Operational conditions of the recycling process*:



Parameters	Value	Units
Toolpaths	0/90 − 45/45	
Layer thickness	0.2	mm
Bed temperature	60	°C
Nozzle temperature	195	°C
N° of perimeters	2	
Top solid layers	2	
Bottom solid layers	2	
Fill density	100	%
Travel speed	140	mm/s
Nozzle diameter (FoldaRap)	0.5	mm
Nozzle diameter (Mondrian)	0.4	mm
Bead width	*Printer's nozzle*	mm
Nozzle speed	40	mm/s
G-code	Slic3r	

Fig. 7. Parameters used for the fabrication of printed mechanical samples.

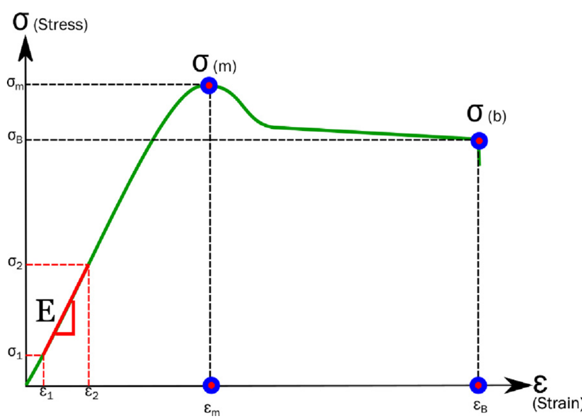


Fig. 8. Stress–strain curve.

A cutting mill machine SM 300 Retsch® with a selectable speed range from 700 to 3000 rpm was used. The selected speed was 700 rpm.

b. *Granulometry of recycled material*:
The final fineness achieved was in a range of 0.2–2 mm.

4.6. Experimental strategy

Fig. 9 summarizes the experimental strategy followed for each recycling process chain. Each chain is described in terms of the operational steps (*A, B, C* . . .) to be followed in order to deploy the complete recycling process. Five recycling cycles were made. For each recycling chain, eight samples in each cycle were considered for the analysis.

Fig. 9a corresponds to the *Reference* and *3DP reference* process chains. Comparing these two processes, it is possible to identify the difference on material degradation using a traditional manufacturing process and the 3D printing process.

On the other hand, Fig. 9b presents the *Feedstock* and *3D Printing (Reference)* process chains. we can see that the only difference in this two processes is the 3D printing process phase. The main goal of comparing this two process is to quantify the impact of the 3D printing process on the material degradation.

5. Experimental results and discussion

In this part, the results obtained for the four process chains proposed in the case of PLA recycling for fused filament fabrication (FFF) 3D printers will be presented.

5.1. Reference process chain

As outlined earlier, the purpose of this process chain is to set a degradation reference for the recycled material, following the operational methodology shown in the first row of Fig. 9a. The results obtained in this process chain will then be compared with *3D printing process chain* in order to compare the material degradation between these two manufacturing processes.

Fig. 10a presents the stress–strain curves for reference process chain samples in function of the number of cycles. In Fig. 10b, it can be seen that here the recycling process induces a low diminution (3.7%) of the elastic modulus at the end of the fifth cycle. The mean elastic modulus value throughout during the five cycles was $E = 3449 \pm 81$ MPa.

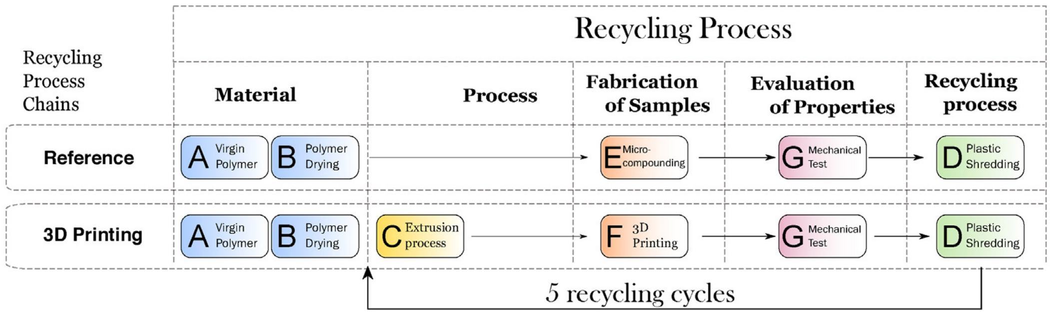
This result is in good agreement with previous studies in which injection moulding was used for the recycling process [94,95]. Therefore, one can consider that the material strength in the elastic zone is slightly affected by the recycling [58].

In Fig. 10c, a progressive diminution of tensile strength σ_M (19.81%) and stress at break σ_B (15.95%) can be observed after the five cycles. In the same way, there was a significant reduction in the tensile strain ϵ_M (27.31%) and the nominal strain at break ϵ_B (40.65%) of the material as detailed in Fig. 10d. This trend is consistent with the results of previous PLA recycling studies [63,65,96].

In general terms, the degradation mechanisms for PLA, based on the postulated mechanistic routes of polyesters, could be resumed as follows [58,97]:

- Hydrolysis: formation of hydroxyl and carboxyl linear oligomers.
- Esterification and resterification.
- Intramolecular transesterification.
- Intermolecular transesterification: which interchange ester units between different chains, leading to an increase in the heterogeneity of the polymer.
- Thermo-oxidation: which leads to chain scission reactions:
  - acyl-O and alkyl-O β-C initiated homolytic chain scissions at temperatures above melting.
  - radical reactions induced by oxygen, which may produce random chain cleavage, leading to the formation of mainly linear hydroxyl and carboxyl terminated species.

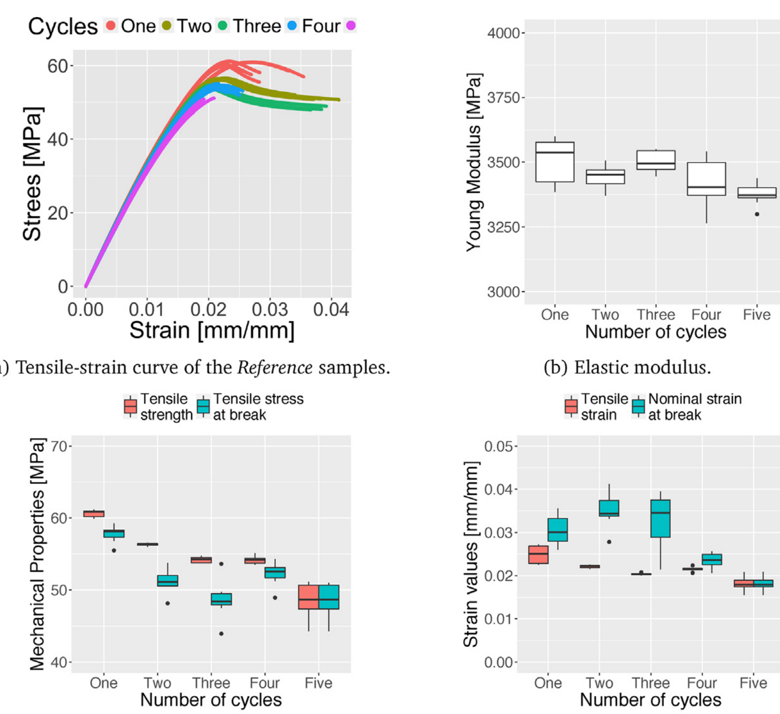
Therefore, the mechanical properties reduction observed here can be related to the chain scission of the polymeric chains, which leads to a progressive embrittlement of the reprocessed material. In fact, it can be seen that the tensile strength value (σ_M) as well as the tensile strain value (ϵ_M) are converging to a same value with respect to the tensile strength at break (σ_B) and the nominal tensile



(a) Methodologies for comparing the material degradation using a standard and 3D Printing process.

(b) Methodologies to evaluate the impact of 3D printing process on material degradation.

Fig. 9. Operational methodologies for each recycling process chains.



(a) Tensile-strain curve of the *Reference* samples.

(b) Elastic modulus.

(c) Tensile properties.

(d) Strain values.

Fig. 10. Mechanical properties of the *Reference* process chain samples.

strain value (ϵ_B) as the number of cycles increases (Fig. 10a and Table 1). Factors such as a decrease in the polymer chain length, reduction in the molecular weight, and increase in the degree of crystallinity induce the crack propagation above the elastic domain [63,94,98]. An experimental observation is that nominal strength at break after the first cycle seems relatively weak with respect to studies of mechanical properties using the same material PLA 4043D [99,100]. This could be attributed to differences in operating conditions during processing. Nevertheless, the reduction trend of this strain value is coherent with the literature of PLA recycling.

Table 1
Mechanical properties of the recycled *Reference* samples.

Number of cycles	Samples	Elastic modulus E [MPa]	Tensile strength σ_M [MPa]	Strength at break σ_B [MPa]	Tensile strain ϵ_M [mm/mm]	Nominal strain at break ϵ_B [mm/mm]
One	8	3507.5 ± 87.2	60.6 ± 0.4	57.7 ± 1.1	0.025 ± 0.0022	0.030 ± 0.0035
Two	8	3443.7 ± 42.4	56.3 ± 0.1	51.1 ± 1.6	0.022 ± 0.0004	0.035 ± 0.0040
Three	8	3502.1 ± 41.0	54.2 ± 0.4	48.6 ± 0.4	0.020 ± 0.0002	0.032 ± 0.0069
Four	8	3418.2 ± 95.2	54.1 ± 0.5	52.2 ± 0.5	0.021 ± 0.0006	0.023 ± 0.0017
Five	8	3375.6 ± 42.2	48.6 ± 2.3	48.5 ± 2.3	0.018 ± 0.0016	0.018 ± 0.0016

5.2. 3D printing process chain

The main purpose of this process chain is to obtain directly recycled printed test samples. The operational methodology illustrated in the second row of Fig. 9a was followed. As mentioned in Section 4.2.2, feedstock in the form of filament was fabricated for each recycling cycle. For the purpose of ensuring the quality of the printed samples, filament diameter measurements were taken considering the mean value in the printing parameters.

Fig. 11 and Table 2 show the mechanical properties from the printed samples using the parameters mentioned in Section 4.3.2. The two types of toolpaths (0/90–45/45) were tested in order to evaluate the changes in the mechanical performance of the samples. We can observe from Fig. 11b–d that both types have similar reduction trends. The mechanical properties of the final parts considerably depend on two important elements, the building direction and the toolpaths used in each layer [85]. The obtained results could confirm that the toolpath characteristics (0/90, 45/45) for the selected build orientation had virtually no influence on the mechanical properties. Nevertheless, we have to take into account that printing strategies using higher fraction of extruded polymeric fibers oriented along the load direction exhibit improved strength [93]. A complete study of the mechanical properties of the recycled material implies the fabrication of six different orientations for each recycling cycle in order to establish the stiffness matrix.

Considering the samples with *One* cycle, the obtained results are coherent with those reported in the literature by [91,101]. We corroborate that the printed components from open-source machines are comparable in tensile strength and elastic modulus to the parts printed on commercial 3D printing systems [91].

The recycled printed samples are presented in Fig. 11a. Fig. 11b shows that the elastic modulus presents a slight growth as the number of cycles increases for both types of toolpaths. On the other hand, from Table 2 and Fig. 11c and d one can observe the existence of a significant deterioration of mechanical properties. For the samples 45/45, there is a reduction of tensile strength σ_M (41.27%), the tensile strength at break σ_B (40.08%), tensile strain ϵ_M (53.08%) and nominal strain at break of about ϵ_B (56.53%). Similar trends were obtained for the samples 90/90, the reductions were tensile strength σ_M (38.15%), tensile strength at break σ_B (39.29%), tensile strain ϵ_M (52.20%) and nominal strain at break ϵ_B (57.43%).

5.3. Feedstock process chain

The main purpose of this recycled process chain is to quantify the material degradation due to the feedstock manufacturing process of 3DP material. The first row of Fig. 9b present the operational methodology used. After each extrusion, the micro-compounding process was used in order to obtain the mechanical test sample. It means that the number of times that the material is processed will be proportional to the number of cycles plus one from the micro-compounding process.

Considering the literature for the multiple extrusion approach to assess the recyclability, the study conducted by Zenkiewicz et al. [102] shows the effect of multiple processing (up to ten times) of PLA (type 2002D NatureWorks®, USA). They conclude that after ten extrusions, there are reductions in tensile strength (5.2%) and the tensile strength at break (8.3%). On the other hand, the elastic modulus did not significantly vary with the number of the extrusion processes. In our case, one can see that there is practically no variation in the elastic modulus. These results are in concordance with the literature of PLA recycling and with our *Reference* process chain of Section 5.1. However, considering the tensile properties, Table 3 shows a considerable reduction in tensile strength σ_M and tensile strength at break σ_B of about 47.40% and 42.50% respectively, after the five cycles. In the same way, a considerable reduction of the tensile strain ϵ_M and nominal strain at break ϵ_B values of about 58.57% and 70.84% was observed.

5.4. 3D Printing (Reference) process chain

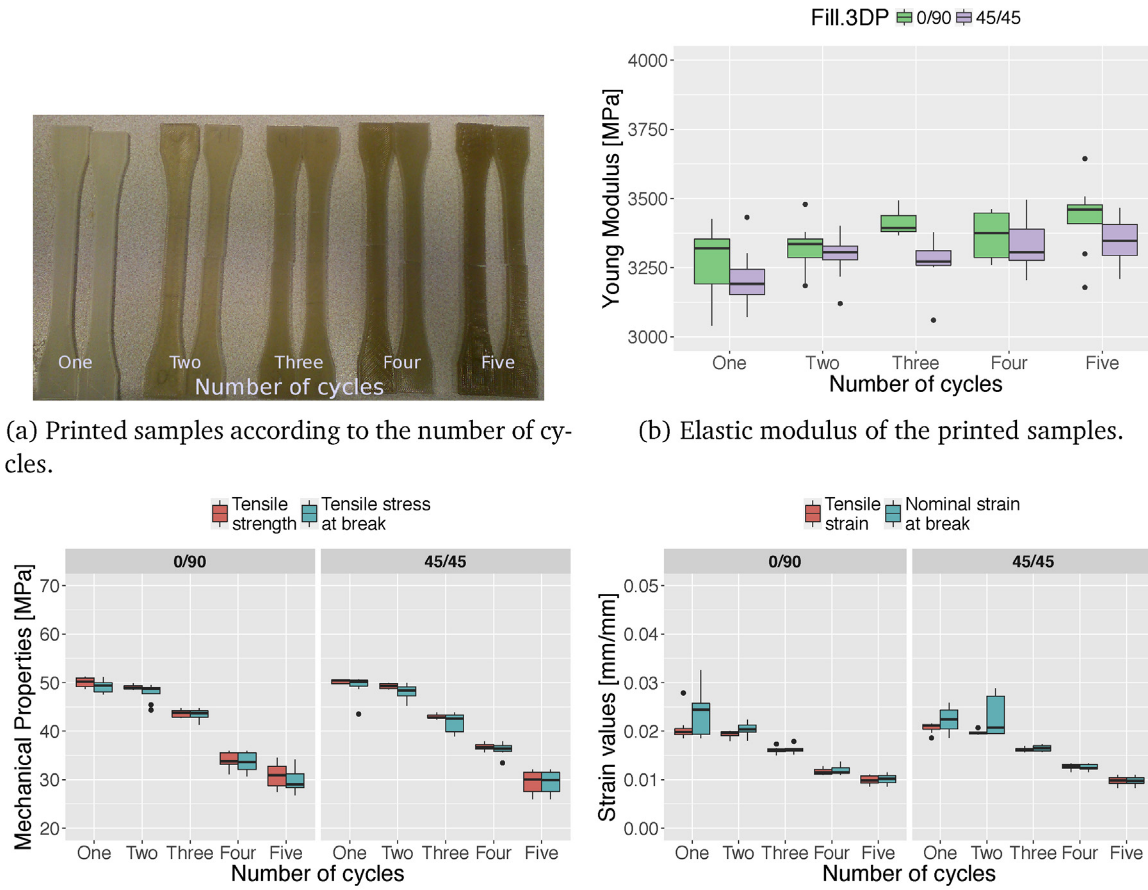
The main goal of this recycling process chain is to evaluate the mechanical properties after the printing process. The second row of Fig. 9b sumps up the operational methodology used.

Once the material was printed at every cycle, it was collected, milled and injected in the micro-compounder in order to obtain mechanical samples. Albeit, it must be recognized that using this approach, inevitably one additional degradation process will be applied to the material, this recycling process chain can allow us to have a quantitatively measurement of the material after the printing process.

Table 4 presents the evolution of the mechanical properties of the material after the printing process. One can see that the elastic modulus E remains approximately constant through the five cycles; nevertheless, one can observe a strong variability in the results during the fifth cycle which could be attributed to the difficult fabrication of the test samples due to the fluidity of the material. It has to be noted that this process chain presented the highest reduction in mechanical properties through the five cycles. Tensile strength σ_M decreased 71.34%, tensile strength at break σ_B 72.58%, tensile strain ϵ_M 78.93% and nominal strain at break ϵ_B 86.49%. In fact, the results in the table indicates that in the fourth and fifth recycled material, there could be a influence of the micro-compounding process on account of the appreciable reduction in tensile strength.

6. Comparison of the different recycling process chains

In this section, two different comparisons of the obtained results in terms of elastic modulus E and tensile strength (σ_M-σ_B) / strain (ϵ_M-ϵ_B) for the previous recycling process chains will be carried out. First, the *Reference* and the 3D printing process chain will be compared in order to qualify the differences between injected samples and 3D printed test samples (0/90–45/45). Then, a comparison between *Feedstock* and *3D Printing (Reference)* process chains will allow us to qualify the material's degradation due to the 3DP printing process.



(a) Printed samples according to the number of cycles.

(b) Elastic modulus of the printed samples.

(c) Tensile properties of the printed samples.

(d) Strain values of the printed samples.

Fig. 11. Mechanical properties of the *Reference* process chain samples.

Table 2
Mechanical properties of the recycled *3D Printing* samples.

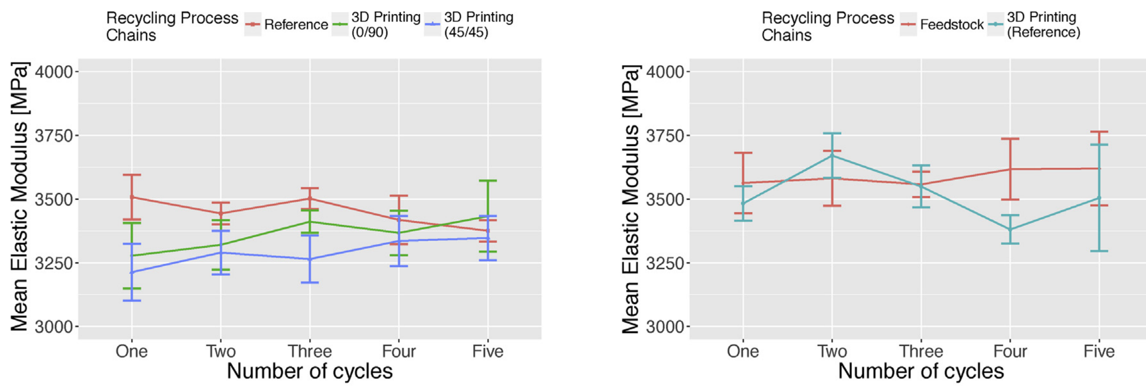
Number of cycles	Toolpaths	Samples	Elastic modulus E [MPa]	Tensile strength σ_M [MPa]	Strength at break σ_B [MPa]	Tensile strain ϵ_M [mm/mm]	Nominal strain at break ϵ_B [mm/mm]
One	0/90	8	3277.7 ± 128.5	50.1 ± 1.0	49.3 ± 1.4	0.021 ± 0.0030	0.024 ± 0.0047
Two	0/90	8	3320.6 ± 96.9	49.0 ± 0.4	47.9 ± 1.9	0.019 ± 0.0008	0.020 ± 0.0014
Three	0/90	8	3411.3 ± 43.8	43.7 ± 0.8	43.5 ± 1.1	0.016 ± 0.0007	0.016 ± 0.0008
Four	0/90	8	3367.5 ± 87.5	34.0 ± 1.7	33.6 ± 2.1	0.012 ± 0.0006	0.012 ± 0.0010
Five	0/90	8	3432.6 ± 138.9	31.0 ± 2.6	29.9 ± 2.7	0.010 ± 0.0009	0.010 ± 0.0011
One	45/45	8	3213.3 ± 111.5	50.2 ± 0.4	49.2 ± 2.4	0.021 ± 0.0010	0.022 ± 0.0026
Two	45/45	8	3290.0 ± 85.8	49.3 ± 0.6	48.1 ± 1.6	0.020 ± 0.0005	0.023 ± 0.0041
Three	45/45	8	3264.8 ± 92.1	43.0 ± 0.5	41.8 ± 2.0	0.016 ± 0.0005	0.017 ± 0.0006
Four	45/45	8	3335.7 ± 98.2	36.8 ± 0.8	36.3 ± 1.4	0.013 ± 0.0006	0.013 ± 0.0006
Five	45/45	8	3347.4 ± 87.0	29.5 ± 2.4	29.5 ± 2.4	0.010 ± 0.0010	0.010 ± 0.0010

Table 3
Mechanical properties of the recycled *Feedstock* samples.

Number of cycles	Samples	Elastic modulus E [MPa]	Tensile strength σ_M [MPa]	Strength at break σ_B [MPa]	Tensile strain $\epsilon_M \sigma_B$ [mm/mm]	Nominal strain at break [mm/mm]
One	8	3562.9 ± 118.6	59.3 ± 1.5	53.5 ± 2.9	0.023 ± 0.0021	0.032 ± 0.007
Two	8	3581.4 ± 118.6	54.7 ± 0.6	51.8 ± 3.4	0.020 ± 0.0004	0.023 ± 0.0031
Three	8	3557.6 ± 49.5	51.4 ± 2.6	50.8 ± 3.0	0.018 ± 0.0017	0.018 ± 0.0019
Four	8	3617.0 ± 119.3	40.3 ± 7.3	39.2 ± 7.6	0.013 ± 0.0027	0.012 ± 0.0028
Five	8	3619.9 ± 144.9	31.1 ± 7.1	30.7 ± 7.5	0.009 ± 0.0026	0.009 ± 0.0025

Table 4
Mechanical properties of the recycled *3D Printing (Reference)* samples.

Number of cycles	Samples	Elastic modulus E [MPa]	Tensile strength σ_M [MPa]	Strength at break σ_B [MPa]	Tensile strain $\epsilon_M \sigma_B$ [mm/mm]	Nominal strain at break [mm/mm]
One	8	3482.7 ± 67.8	59.3 ± 0.5	53.6 ± 2.7	0.0242 ± 0.0010	0.0333 ± 0.0054
Two	8	3670.7 ± 87.1	53.6 ± 0.9	50.4 ± 1.7	0.0179 ± 0.0008	0.0218 ± 0.0044
Three	8	3549.2 ± 82.4	48.0 ± 1.7	47.6 ± 1.5	0.0159 ± 0.0012	0.0159 ± 0.0012
Four	8	3380.6 ± 55.7	30.0 ± 2.5	29.1 ± 3.4	0.0093 ± 0.0008	0.0094 ± 0.0008
Five	8	3504.6 ± 209.0	17.0 ± 3.2	15.8 ± 4.3	0.0051 ± 0.0010	0.0048 ± 0.0009



(a) Mean elastic modulus value of the *Reference* and *3D printed* recycled samples

(b) Mean elastic modulus value of the *Feedstock* and *3D printed (Reference)* recycled samples

Fig. 12. Evolution of elastic modulus in the recycling process chains.

6.1. Elastic modulus

Fig. 12 shows the elastic modulus of the four recycling process chains. If we consider the injected samples (*Reference* in Fig. 12a and *Feedstock* and *3D Printing (Reference)* in Fig. 12b), we can conclude that the elastic modulus remains virtually constant during the recycling process within a range of variation between 3200–3500 MPa).

On the other hand, if we consider the printed test samples (*3D Printing* 45/45 and 0/90 in Fig. 12a), a slight and continuous increase of elastic modulus is observed in the recycled samples. At the fifth cycle, the elastic mean value increased 4.1% and 4.7% for the samples 0/90–45/45 respectively.

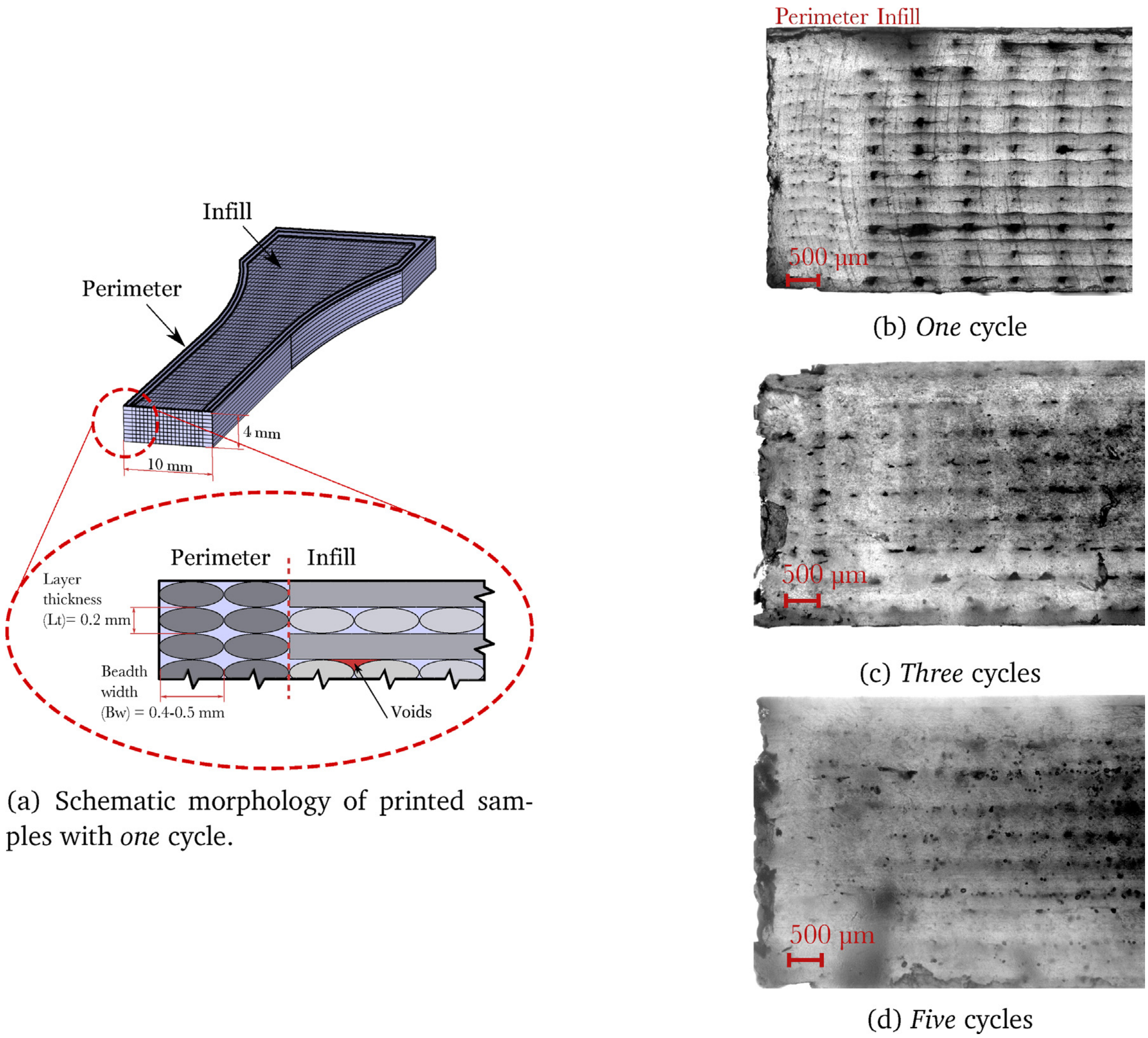
It could be argued that due to the change of material viscosity, which is a consequence of the recycling process, the mesostructure and fiver-to-fiber bond characteristics of the printing samples will also change as the number of recycling processes increases. According to the literature, one of the internal defects that affects the structural quality of printed part are the voids, pores, and sub-perimeter voids due to the rounded shape of the deposited material [72,81]. In the printing process, the printed material will spread into an oblong shape in function of the process characteristics (e.g. nozzle diameter, nozzle speed, layer thickness.) and the final shape will rely on the viscosity of the melt, and the relative surface energies of the bead and the surface where the layer is deposited [72]. Ultimately, the overall mechanical properties will depend on the growth of the neck formed between the adjacent filaments (and layers), the molecular diffusion and randomization of the polymer chains across the interface, the thermal history imposed on the material during the printing process, the size/geometry/distribution of the internal defects and the material properties themselves [82].

Therefore, one hypothesis for explaining the similar behavior between *Reference* and *3D Printing* process chains in terms of the elastic modulus at the end of the fifth cycle is that there is an appreciable reduction of the internal defects caused by the reduction in material viscosity, which facilitates the homogenization of the deposited layers. It could be assumed that the internal mesostructure of the printed samples could be similar to its relative injected one. Nevertheless, this reduction in viscosity is one consequence of the material degradation. And as a result of this degradation, the tensile properties are affected as can be seen in the next section.

For testing this hypothesis, we performed a microscopic (optical) observation in order to register the morphology changes in the cross-section of the recycled printed samples. A ligth optical microscope Zeiss Imager A1(Germany) with objectives of 2.5× was used to determine the homogeneity deposition in the printing process. For each recycling cycle, a cross-section of 5 mm length was carefully removed at the rupture zone from the printed specimen. Fig. 13 shows the representative microscopy images of the samples. The plots Fig. 13b–d were taken from a border of the specimen in order to see the perimeter and a portion of the infill morphology. These figures present the evolution of the morphology of *One, Three* and *Five* cycles at 2.5×.

As can be seen for the cycle *One*, it is possible to differentiate the perimeter and the infill of the cross-section area. Moreover, as expected from the literature of FDM [81,82,103–105], we can distinguish the presence of internal defects such as voids and staircase effect. From a quantitative perspective, the void geometry/density could be performed in order to correlate these parameters with the macroscopic properties as showed in the research made by [103,106]. For our purposes, a qualitative analysis of the morphology of the recycled samples shows that there is a change in terms of the size/ geometry and the mesostructure of the printed part as the number of cycles increases. These results are in concordance with our previous predictions.

The main consequence of the degradation mechanisms is a reduction in molar mass of the PLA, in terms of number-average molar mass M_n and viscous molar mass M_V due to chain scission.



(a) Schematic morphology of printed samples with *one* cycle.

(b) *One* cycle

(c) *Three* cycles

(d) *Five* cycles

Fig. 13. Optical microscopy images for recycled samples (toolpath = 0/90) from the *3D printing* process chain.

This reduction in molar mass can be correlated to an increase of the Melt Flow Index value [58,102]. And consequently, the more the number of recycling cycles are, the higher the flowability and the subsequent homogenization of the printed part are. A deeper analysis could be made in terms of morphological characterization, and the study of the structural and conformational arrangements of the recycled printed defects, which is beyond the scope of this study.

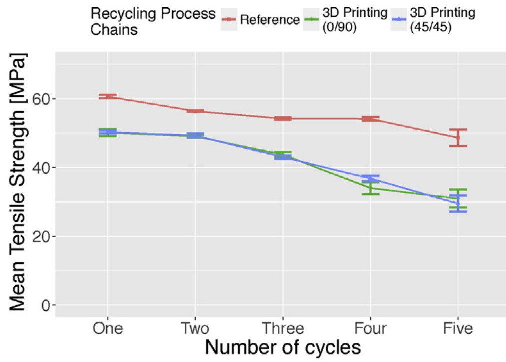
6.2. Tensile strength and tensile strain

Considering the tensile strength and strain, as expected, there is a reduction in the mechanical properties in each recycling process chains as illustrated in Fig. 14.

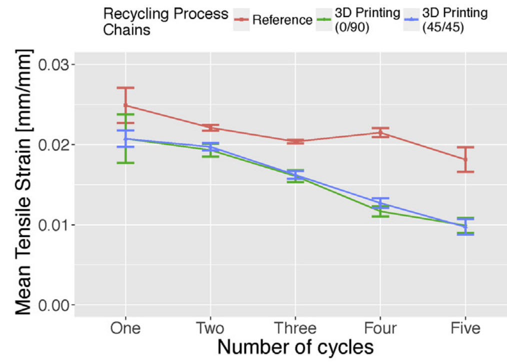
Fig. 14a and b compares the mechanical properties of the *Reference* and *3D printing* process chains. This comparison is made with the purpose of evaluate the mechanical performance of the recycled material between the injected and the printed samples. The *Reference* process chain presented the lowest reduction in mechanical properties with a difference of nearly 10 MPa during the first and second cycles with respect to the *3D printing* process chain. This is in accordance with some previous work by [91,101]. However, if one considers the subsequent recycling cycles, a growing gap in these properties could be observed. The same trend can be seen with regard to the strain values (Fig. 14b) in which there is a constant difference for the first two cycles, but after that, the difference is increased.

Moreover, one can see in Fig. 14c and d that there is a growing difference between the *Feedstock* and the *3D Printing (Reference)* process chains. As remarked previously, in these two processes, for each cycle, there is the same number of extrusion and plastic shredding processes. The only difference between these two process chains is that the *3D printing (Reference)* we have *n* printing processes with *n* the number of cycles. According to Fig. 14c and d, it seems clear that the printing process has an effect on the material degradation as the number of processing cycles increases. One can be see that the material start with a same properties level and systematically the material without 3D printing process (*Feedstock*) is superior to the material that have been printed (*3D printing (Reference)*). This effect has a direct impact on the mechanical properties of the printed samples, as evident in Fig. 14a. Therefore, 3D printing effect is weak for the two first cycles, but increases as the material degradation increases.

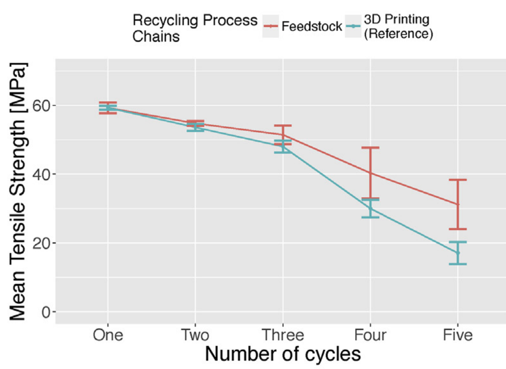
On the other hand, considering the number of cycles three, four and five in Fig. 14, one can observe that the mechanical properties for the *3D printing* process chain (green and blue lines in Fig. 14a and b) are better than the properties of *3D Printing (Reference)* recycling process chain in the same number of cycles (blue line in Fig. 14c and d). This could be explained by two simultaneous opposed effects. First, the 3DP printing process effect which reduces the mechani-



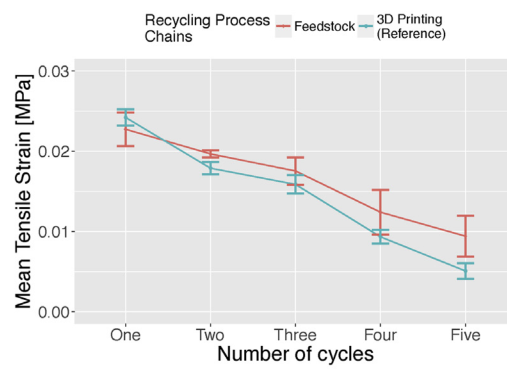
(a) Mean tensile strength values of the *Reference* and *3D printed* recycled samples.



(b) Mean tensile strain values of the *Reference* and *3D printed* recycled samples.



(c) Mean tensile strength values of the *Feedstock* and *3D printed (Reference)* recycled samples.



(d) Mean tensile strain values of the *Feedstock* and *3D printed (Reference)* recycled samples.

Fig. 14. Tensile properties of the recycled samples of the different recycling process chains.

cal properties in each cycle, as remarked previously. However, one consequence of the polymer degradation is the reduction of material viscosity. As said previously in Section 6.1, the material viscosity could be an important parameter in the 3D printing process because it induces better filled printed samples. In this point, it is also recognized that another element that can affect the material degradation is the micro-compounding process, as it is mentioned in Section 5.4.

7. Conclusions and future work

In this study we propose a general methodology to characterize the recycling of polymers used as feedstock for open source 3D printing machines. The proposed methodology was applied to study the conditions for reusing Polylactid Acid (PLA), which is a material widely used in the context of open-source additive manufacturing using the fused filament fabrication (FFF) technique. Four different recycling process chains (*Reference*, *Feedstock*, *3D Printing* and *3D Printing (Reference)* were proposed for the purpose of evaluating the degradation of the mechanical properties after five recycling cycles. Theses recycling process chains enable us to compare the mechanical performance of the material using a standard process and open-source 3D printing process. Moreover, it allows us to evaluate the impact of the printing process on the material degradation. Specific results are summarized as follows (Table 5):

The results showed that the elastic modulus for the samples made using micro injection moulding process presented a virtually constant (or small reduction for the case of *Reference* process chain) value. Nevertheless, for the printed samples, results highlighted a relative and systematic increase in the elastic modulus as the number of recycling cycles increases. The main hypothesis to explain this behavior is related to an appreciable reduction of internal defects (voids, pores) caused by the reduction in the material viscosity, which facilitates the homogenization of the deposited layers in the printing process. An optical microscopy in order to observe the morphology of the cross-section area of the recycled printed samples was performed. We found that there are changes in the geometry and distribution of the internal defects of the printed samples as the number of recycling cycles increase. For samples with one recycling cycle, it is possible to distinguish perimeter and infill zones in the meso-structure. Whereas for samples with five recycling cycles, this distinction is nor clearly defined. Further studies should be addressed in order to characterize the morphology of the recycled samples.

The results of this study are comparable to the literature of PLA recycling using traditional processes. In the same way, the results of the mechanical properties of the printed samples for the first cycle support the idea that 3D printed components from open source 3DP are comparable in tensile strength and elastic modulus to the parts printed on commercial systems [91]. To the authors' knowledge, this is the first study to investigate characterization of the polymer degradation in the context of open-source 3D printing.

Our results from the recycling process provide compelling evidence of the feasibility of using recycled PLA for open-source additive manufacturing. However, as a main result, we highlighted that the 3D printing process reduces the mechanical properties. One has to consider this effect and, in conclusion, one cannot recycle material as many times as in an injection process. Most notably, this finding is promising and it could serve as a basis for the study of recyclability of other industrial polymers in order to establish the viability for use in the 3D printing chain. Eventually, the viability

Table 5
Variation of the mechanical properties afters five recycling cycles.

Recycling process chain	Reduction of the mechanical properties				
	Elastic modulus	Tensile strength	Tensile strength at break	Tensile strain	Nominal strain at break
Reference	−3.7%	−19.81%	−15.95%	−27.31%	−40.65%
3D printing (0/90)	+4.1%	−38.15%	−39.29%	−52.20%	−57.43%
3D printing (45/45)	+4.7%	−41.27%	−40.08%	−53.08%	−56.53%
Feedstock	*Constant*	−47.56%	−42.52%	−58.57%	−70.84%
3D Printing (Reference)	*Constant*	−71.34%	−72.58%	−78.93%	−86.49%

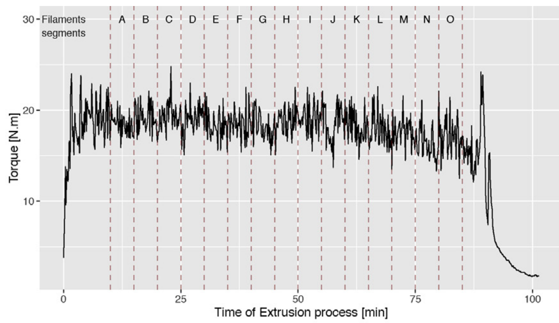
of an industrial sector focused on the polymer waste in 3D printing technology could be a subject of study. Future work should focus on the chemical and thermal degradation of the polymer, as well as the determination of molecular weight reduction and changes in the temperatures of the polymer during the recycling process. Moreover, issues concerning the use of composite materials should be addressed.

Appendix A. Mechanical recycling studies for Polylactic Acid (PLA)

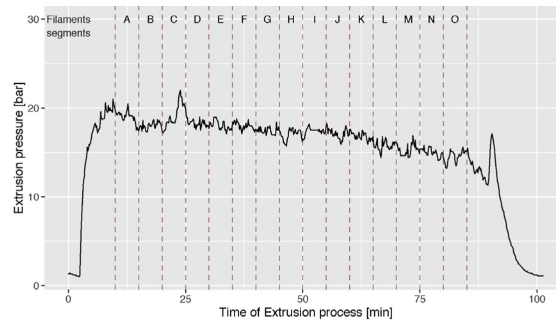
Table 6 presents a short overview concerning the works of mechanical recycling of PLA in the light of the axes of quality assessment of recycled plastics [63,65].

Table 6
Summary of mechanical recycling studies of PLA.

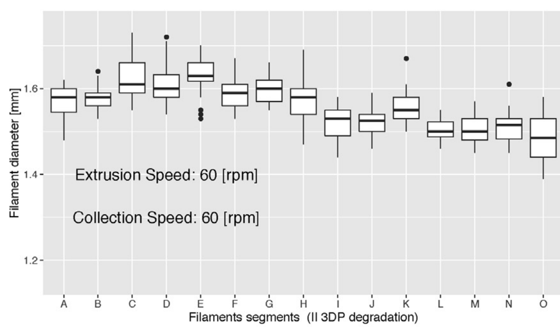
Reference	Material	Recycling process	Evaluation			Comments
			DM	LMWC	DD	
Pillin et al. [94]	PLLA L900	Injection			X	Thermal, mechanical and rheological properties were studied after seven cycles. Oxidative stabilizers were tested in order to evaluate the effect on the recycled material
Le Duigou et al. [107]	PLLA L900 Flax fibres	Injection	X		X	Blends (20% and 30% in weight) were made through a single extruding process. Modification of mechanical, thermal, rheological and molecular properties were investigated after six cycles.
Zenkiewicz et al. [102]	PLA 2002D	Extrusion	X		X	Material was recycled ten times using the extrusion process. Mechanical properties (tensile and impact), melt flow rate, thermal properties and water vapor and oxygen transmission rates were studied
Hamad et al. [108]	PLA (ESUN A-1001) PS (Sabic 125PS)	Extrusion			X	A blend of PLA/PS (50/50) was prepared using a single screw extruding process. Four recycling cycles were performed using the extrusion process. Modification of mechanical and rheological properties were explored
Lopez et al. [96]	PLLA L9000 Mater-Bi TF01U/095R Mater-Bi YI014U/C Cellulosic fibres	Injection	X		X	Recycling process of three commercial bioplastics matrices was conducted. In all cases, the blend was 30 wt%. Mechanical, MFI, and thermal characterization was conducted
Badia et al. [95]	PLA 2002D	Injection	X		X	Characterization of mechanical, thermal properties and segmental dynamics up to five recycling processes was studied.
Stephens et al. [109]	PLA / ABS			X		Measurement of the ultrafine particle (UFP) concentration resulting from the operation of two types of desktop 3D printers.
Kim et al. [110]	PLA / ABS			X		Evaluation of the emission of particulate matter and gaseaous materials during FDM 3D printing
Azimi et al. [111]	PLA/ABS / HIPS/PCTPE / Nylon/PC			X		Quantification of the emission rates of particles and a broad range of speciated volatile organic compounds (VOCs) from five available desktop FFF 3D printers. They explore difference in particle and VOC emissions based on filament material and printer characteristics.
Steinle [112]	PLA/ABS			X		Ultrafine aerosol (UFA) emissions and volatile organic compounds (VOC) were measured from a desktop FFF 3D printer.



(a) Torque in the extrusion process.



(b) Nozzle pressure in the extrusion process.



(c) Diameters of the recycled filament segments

(d) Filaments obtained after extrusion process for use in the OS 3D printer

Fig. 15. Characteristic curves for the control of the recycled filament.

Appendix B. Quality for extrusion process

In order to achieve a regular diameter of the extrudate on every cycle, the filaments were taken after 10 min of transition phase (Fig. 15). Segments of filament were taken every five minutes of the process and were systematically designated with a capital letter. Each segment of filament was measured in order to have a mean value of the diameter, and thus it could be an input parameter for the 3D printing process. Parameters such as torque and the nozzle extrusion pressure were monitored during the extrusion process of the filament. The objective was to obtain steady conditions during the extrusion process, as illustrated by Fig. 15.

Appendix C. Data collection

Table 7
Database of mechanical results used in the experimentation.

Type of information	Parameters	Units	Observations
Identification of material	Initial quantity	(g)	
	Drying	*dd/mm/yyyy*	Date and conditions of drying.
Description of the sample	Sample	1, 2, 3, . . .	
	Recycling process chain	Ref/3DP/ Feed/3DP(Ref)	Type of recycling process chain
	Degradation	One–Five	Number of cycles of the sample
	Thickness	(mm)	
	Width	(mm)	
	Area	(mm^2)	
	Weight	(g)	
Description of the 3DP feedstock	Profile Extrusion		Torque and nozzle pressure profile in the extrusion process.
	Collection Speed		Collection speed used for recollection of the filament
	Diameter measurement	mm	Diameter of filament
	Toolpaths	45/45–0/90	
	Date of sample	*dd/mm/yyyy*	Date of fabrication of printed sample
Description of the test	Date of test	*dd/mm/yyyy*	
	Speed	(mm/min)	
	Pre-stress	(MPa)	
	Validity	Yes / No	
	Comments		

Table 7 (*Continued*)

Type of information	Parameters	Units	Observations
Mechanical properties	Elastic modulus	E (MPa)	
	Tensile load	L (N)	
	Tensile strength	σ_M (MPa)	
	Tensile elongation	Elo (mm)	
	Tensile strain	ϵ_M (mm/mm)	
	Tensile load at break	L_B (N)	
	Tensile stress at break	σ_B (MPa)	
	Tensile elongation at break	Elo_B (mm)	
	Nominal strain at break	ϵ_B (mm/mm)	

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