

# Assessment of Recycled PLA-Based Filament for 3D Printing <sup>†</sup>

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<sup>†</sup> Presented at the 2nd International Online Conference on Polymer Science—Polymers and Nanotechnology for Industry 4.0, 1–15 November 2021; Available online: <https://iocps2021.sciforum.net/>.

**Abstract:** This study investigated the possibility of replacing virgin matrices with recycled polymers in additive manufacturing (AM). In this regard, two commercial filaments, made from polylactide acid (PLA)—the second (here referred to as recycled) obtained from the recovery of waste production of the first one (here referred to as virgin)—were initially characterized using infrared (IR) spectroscopy, thermogravimetric analysis (TGA) and dynamic rheology. Then, filaments were extruded in a 3D printer and characterized by dynamic mechanical analysis (DMA). Despite a small reduction in the intensity of correspondence of typical absorption bands of the PLA polymer, in the case of the recycled material compared to the virgin one (as attested by IR spectra), the thermal-mechanical results allow us to attest the very similar characteristics of recycled and neat filaments. The onset of thermal degradation was found at around 315 °C in both systems. Both materials exhibited the same frequency- and time-dependent trends of the complex viscosity, with a reduction of approximately 30% after 10 min of testing. When samples were dried at 80 °C under vacuum for 10 h, the stabilization of rheological features against time was improved. There was no significant difference in the storage modulus ( $E'$ ) and dissipation factor ( $\tan \delta$ ) of 3D printed parts made with different types of PLA-based filaments.

**Keywords:** poly(lactide) acid; 3D printing; recycling; thermo-mechanical properties; rheological characterization



**Citation:** Patti, A.; Acierno, S.; Cicala, G.; Zarrelli, M.; Acierno, D. Assessment of Recycled PLA-Based Filament for 3D Printing. *Mater. Proc.* **2021**, *7*, 16. <https://doi.org/10.3390/IOCP2021-11209>

Academic Editor: Francesca Lionetto

Published: 20 October 2021

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## 1. Introduction

Plastics are extremely useful for a wide range of applications due to their mechanical and chemical properties, as well as their ease of manipulation [1]. Yet, not being biodegradable, plastic materials pose a serious environmental problem due to the accumulation of products in nature [2]. This aspect has become particularly relevant in the sustainable development of industrial production [3].

Nonetheless, additive manufacturing (AM), well known as 3D printing, is emerging as a crucial industrial technology for rapid prototyping, in order to convert a numerical model into material deposition and 3D printed parts [4]. During this cycle, a huge amount of waste products is developed. In order to reduce plastic waste [5] and limit the environmental impact of the AM process [6], bio-based and recycled polymers have been considered as alternatives to conventional raw materials.

Poly(lactide) acid (PLA), an aliphatic polyester derived from 100% renewable resources, represents a common thermoplastic polymer most often utilized in the AM field, taking into account its excellent biocompatibility and environmental sustainability, absence of

unpleasant odors during handling and realization of final products with fair precision tolerance [5].

Although PLA is considered one of the most promising bio-based alternatives to common non-biodegradable polymers from petroleum [6], its massive use could generate an important waste accumulation [7]. End-of-life disposal of such materials should be carefully considered in order to facilitate the transition to a circular economy for plastics [8]. Mechanical recycling of PLA is a process consisting of the collection, washing and reprocessing of thermoplastic materials, usually achieved thermally, with the main purpose of preserving the original properties [9]. This recycling method has received a significant amount of attention because it is relatively simple, requires little investment and its technological parameters are controlled [10]. During recycling, the major problem is the thermal stability of PLA and the slight decrease in mechanical properties after several extrusion processes [7].

In this framework, this study was focused on improving the sustainability aspects of the AM technology by verifying the thermal and mechanical characteristics of recycled polymers, coming from waste products, in comparison with virgin matrices, for developing 3D printed parts.

## 2. Materials and Methods

This experiment used commercially available filaments made from a poly(lactide) acid (PLA)-based polymer. In particular, a basic PLA, here referred to as virgin PLA (cod. Ingeo™ 4043D, density of 1.24 g/cc ASTM D792, MFR of 6 g/10 min ASTM D1238, a product from NatureWorks LLC, Minnetonka, MN, USA), and a recycled filament derived from the production waste of the first filament, here referred to as recycled PLA, were supplied by EUMAKERS (Barletta, Italy).

On these filaments, preliminary characterization was conducted through thermogravimetric analysis (TGA) to establish the degradation temperature; infrared (IR) spectroscopy to gain information on the main constituents; and rotational rheology to understand the thermal stability over time at a given temperature. Samples to be tested through dynamic mechanical analysis (DMA) were obtained by a 3D printing machine at a temperature of 210 °C, by setting, as design parameters: an infill density equal to 70%, a layer thickness of 0.19 mm and a linear pattern.

Thermogravimetric measurements were performed using a Q500 TGA (TA Instruments, NewCastle, DE, USA). Tests were conducted by heating a piece of material (about 10 mg) at a rate of 20 °C/min from room temperature to 600 °C in an inert nitrogen atmosphere (purge gas flow of 50 mL/min).

Infrared spectroscopy was conducted in attenuated total reflectance (ATR) mode, using a spectrometer (model Spectrum 65 FT IR), produced by Perkin Elmer (Waltham, MA, USA), endowed with a diamond crystal. A wavenumber range of 400–4000 cm<sup>-1</sup>, a resolution of 4 cm<sup>-1</sup> and a number of scans equal to 16 were adopted. This analysis was carried out on surfaces of as-received filaments.

To characterize viscoelastic properties of molten polymers, and verify the thermal stability of materials, time sweep tests were performed through a rotational rheometer (model ARES), produced by TA Instruments (New Castle, DE, USA). Parallel plates 25 mm in diameter and a gap of 1 mm were adopted for the investigation. Materials were subjected to small-amplitude oscillations at a frequency of 1 rad/s and a strain amplitude of 1% for 10 min at 210 °C in an inert nitrogen atmosphere. Both samples were tested after being dried at 80 °C in a vacuum oven for 10 h and without being dried. The rheological characterization was then continued with oscillatory tests performed at a variable frequency in a range from 100 to 0.01 rad/s, keeping the amplitude equal to 1%, and the temperature at 210 °C, on dried samples.

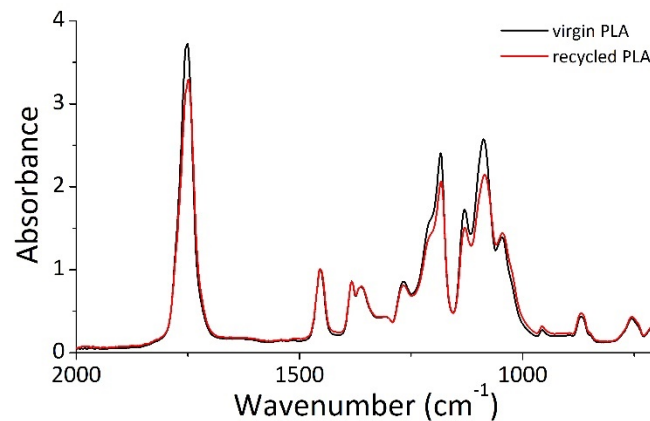
The dynamic mechanical properties (DMA) of PLA filaments were examined using a Triton Technology Ltd. (Leicestershire, UK) instrument (model Tritec 2000). Rectangular

specimens of 2 mm × 5 mm × 25 mm were investigated in single cantilever mode at frequencies of 1 Hz from room temperature to 80 °C, at a heating rate of 2 °C/min.

### 3. Results

#### 3.1. Infrared Spectroscopy

The results of IR spectroscopy are shown in Figure 1, for pristine (black curve) and recycled (red curve) PLA filaments. The absorbance values were normalized in relation to an internal standard for the PLA polymer (1455 cm<sup>-1</sup> peak [11]).

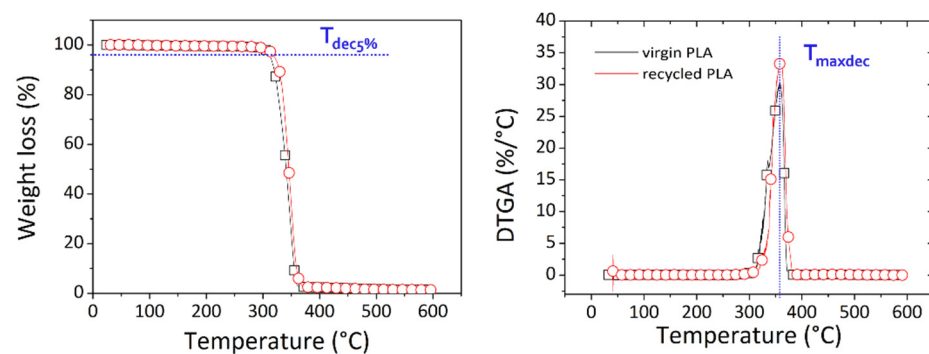


**Figure 1.** ATR spectra of PLA-based materials: virgin PLA (black line) and recycled PLA (red curve). Normalized peak at 1455 cm<sup>-1</sup>.

PLA's characteristic peaks of the occurrence of oxidation and decomposition phenomena could be identified in both filaments: (i) 1750 cm<sup>-1</sup>, linked to carbonyl (C=O) stretching; (ii) 1183 cm<sup>-1</sup> and 1085 cm<sup>-1</sup>, attributed to the asymmetric vibration of the ester group (C-O-C) [12]. In the case of the recycled material compared to the virgin one, a small reduction in the intensity of the correspondence of typical absorption bands of the PLA polymer was verified. This was interpreted a sign of weak thermal degradation of the PLA polymer [13] caused by exposure of the material to high temperatures during melt reprocessing and recycling operations. However, differences between spectra of pristine and processed PLA were not so substantial by displaying similar patterns of absorption. Therefore, it was excluded that a significant change in molecular structure took place upon reprocessing [14].

#### 3.2. Thermogravimetric Analysis

During heating in the thermogravimetric analysis (Figure 2), one step of PLA degradation was shown in both samples. This trend was due to the loss of the ester group [15] that started at about 310 °C.



**Figure 2.** TGA thermograms of virgin and recycled filaments and their respective DTG (derivative thermogravimetric) curves.

In Table 1, the initial decomposition temperature ( $T_{\text{dec}5\%}$ ), the temperature corresponding to the maximum rate of degradation ( $T_{\text{maxdec}}$ ) and the final residue at 600 °C are reported for two analyzed samples.

**Table 1.** Initial decomposition temperature ( $T_{\text{dec}5\%}$ ), temperature of maximum rate of decomposition ( $T_{\text{maxdec}}$ ) and residue at a temperature of 600 °C.

	$T_{\text{dec}5\%}$	$T_{\text{maxdec}}$	Residue
Virgin PLA	315 °C	357 °C	1.5%
Recycled PLA	319 °C	360 °C	1.4%

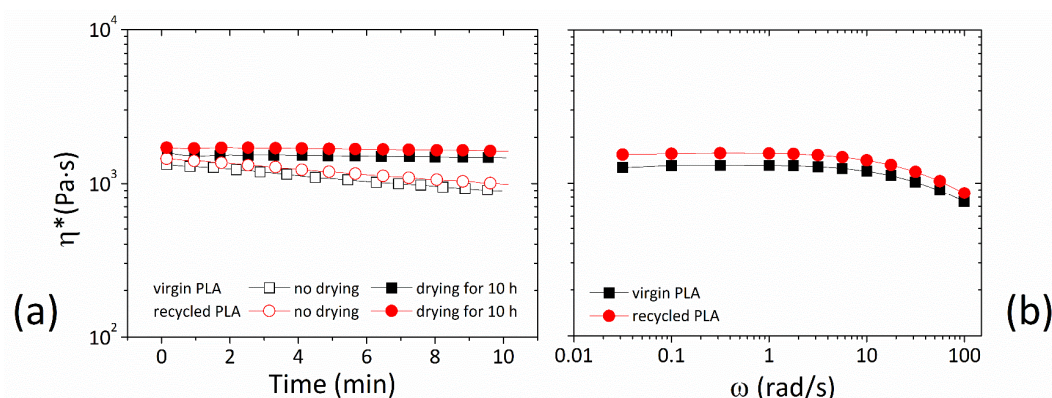
For both polymers, the temperature at 5% of weight loss was recorded at around 320 °C, the maximum rate of thermal degradation was found at around 360 °C and a final residue of 1.5% remained. These data were compared with the TGA analysis on pellets of the same polymer (Ingeo 4043D by Naturework) reported in the literature. According to the study of da Cruz Faria et al. [16], neat PLA (Ingeo 4043D by Naturework) showed an onset temperature of mass loss of 300 °C, a temperature of the maximum mass loss rate  $T_{\text{peak}}$  of 348 °C and a final residue of about 1% after 600 °C. The author concluded that this grade of commercial PLA was endowed with a high degree of purity, with TGA data in the expected range [13,17,18].

### 3.3. Rotational Rheology

Figure 3 depicts the experimental results of time and frequency sweep tests in terms of complex viscosity (Pa·s) over time (10 min) (Figure 3a), and complex viscosity (Pa·s) over angular frequency (Figure 3b), for the investigated systems.

Similar to other polyester polymers, PLA is sensitive to hydrolysis under melt processing conditions in the presence of a small amount of water [19]. In fact, as verified from the data in Figure 3a, a reduction in the rheological signal was attested, up to 30%, in 10 min when non-dried materials were analyzed. On the contrary, stabilization of the complex viscosity over time at a temperature of 210 °C was obtained through sample drying.

At a temperature of 210 °C, the complex viscosity trend as a function of the angular frequency (Figure 3b) displayed a Newtonian behavior for both polymers at low angular frequencies up to 10 rad/s, during which the value remained almost constant around  $2\text{--}3 \times 10^3$  Pa s. Then, a shear thinning behavior followed for frequencies over 10 rad/s, during which the complex viscosity decreased.



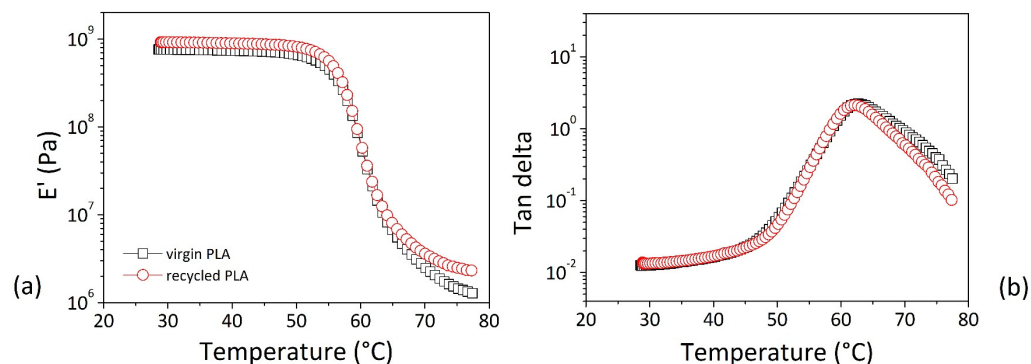
**Figure 3.** (a) Complex viscosity as a function of time for dried and non-dried specimens; (b) complex viscosity as a function of angular frequency for dried specimens.

In general, the main problem of PLA recycling is the polymer thermal instability attributed to the presence of moisture, lactic acid residues and metal catalysis that favor thermal degradation by leading to a reduction in the molecular weight and, consequently,

the material viscosity [20]. In this case, no strong difference was observed between the complex viscosities of virgin and recycled PLA. This result highlights the negligible effects of recycling on the physico-chemical properties of resin.

### 3.4. Dynamic Mechanical Analysis (DMA)

The experimental results of DMA on 3D printed parts made from virgin and recycled filaments are shown in Figure 4 in terms of the storage modulus ( $E'$ ) (Figure 4a) and dissipation factor ( $\tan \delta$ ) (Figure 4b) as a function of the temperature. In both cases, storage modulus curves underwent the typical sharp decline from 30 °C to 80 °C, related to glassy-to-rubbery state transition [12]. This behavior was usually attributed to an increase in the molecular mobility of polymer chains as the temperature was increased [21]. The dissipation factor ( $\tan \delta$ ) provided the damping ability of the overall system, and the value of the glass transition temperature ( $T_g$ ) corresponded to its maximum point [12]. According to the work of Pillin et al. [20], PLA possessed a glass temperature of 66.2 °C that decreased to 56.5 °C after seven injection molding processes. The authors concluded that a higher mobility of polymer chains attributed to a chain scission occurred during the reprocessing and recycling. From our data,  $E'$  and  $\tan \delta$  curves corresponding to virgin (black square points) and recycled samples (red circle points) roughly overlapped with almost comparable values across the entire temperature range. The value of the glass transition temperature in both cases was around 62 °C. Therefore, also through DMA analysis, it was confirmed that if a possible polymer degradation occurred during recycling, this phenomenon was mild and did not involve an alteration in the thermo-mechanical properties.



**Figure 4.** (a) Storage modulus ( $E'$ ) and (b) dissipation factor ( $\tan \delta$ ) against temperature for 3D printed parts made from virgin and recycled filaments.

## 4. Conclusions

This was a preliminary study devoted to understanding the applicability of recycled matrices instead of virgin polymers for the 3D printing process. From the data, despite a small reduction in the ATR spectra, in correspondence with the PLA characteristic peaks of thermal degradation, no substantial differences could be highlighted in terms of thermal degradation, rheological behavior and thermo-mechanical properties. In fact, for both materials, the initial degradation temperature was measured at around 310 °C, the glass transition temperature was around 62 °C and the stability of the complex viscosity over time was achieved through sample pre-drying. The complex viscosity as a function of the angular frequency and the storage modulus of 3D printed parts made from recycled matrices were very comparable with those of the virgin matrices.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/IOCP2021-11209/s1>.



**Author Contributions:** Conceptualization, A.P. and D.A.; validation, G.C.; data curation, S.A. and M.Z.; writing—original draft preparation, A.P.; writing—review and editing, S.A. and G.C.; supervision, D.A. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Acknowledgments:** A. Patti wishes to thank the Italian Ministry of Education, Universities and Research (MIUR) in the framework of Action 1.2 “Researcher Mobility” of The Axis I of PON R&I 2014–2020 under the call “AIM- Attrazione e Mobilità Internazionale”. S. Acierno and G. Cicala acknowledge the support of the Italian Ministry of University, project PRIN 2017, 20179SWLKA “Multiple Advanced Materials Manufactured by Additive technologies (MAMMA)”.

**Conflicts of Interest:** The authors declare no conflict of interest.

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