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Abstract

Assessment of recycled PLA based filament for 3D printing

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Abstract:. This study investigates the possibility to adopt recycled polymers in the additive manufacturing (AM) technology by replacing virgin matrices. At regards, two commercial filaments, made from polylactide acid (PLA), -the second (recycled) obtained from the production waste of the first one (virgin)-, were initially characterized using infrared (IR) spectroscopy, thermogravimetric analysis (TGA) and dynamic rheology. Then, the filaments were extruded in a 3D printer and characterized by dynamic mechanical analysis (DMA). Despite of a small reduction of intensity in correspondence of typical absorption bands of PLA polyme, in the case of recycled material compared to virgin one (as attested by IR spectra), the thermal-mechanical results allowed to attest very similar characteristics of recycled and neat filaments. The onset of the thermal degradation was found around 315°C in both systems. Both materials exhibited the same time-dependent trend of complex viscosity, with a reduction of approximately 50% after 900 seconds of testing. When the samples were dried at 80°C under vacuum for 10 hours, the stabilization of the rheological features against time was improved. There is no significant difference in the storage modulus (E') of 3D printed parts made with different types of PLA-based filaments.

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

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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, to convert a numerical model into material deposition and 3D printed parts [4]. During this cycle, a huge amount of waste products has been developed. In order to reduce plastic waste [5] and limit the environmental impact of AM process [6], bio based and recycled polymers have been considered as alternative perspective to conventional raw materials.

Polylactic 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 production of final products with fair precision tolerance [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 poly(lactide) acid (PLA)-based polymer. In particular, a basic PLA, here referred as virgin PLA, and a recycled filament derived from the production waste of the same filaments, here referred as recycled PLA, have been supplied by EUMAKERS (Barletta, Italy).

On these filaments, a preliminary characterization was conducted through thermogravimetric analysis (TGA) to establish the degradation temperature, (IR) infrared spectroscopy to gain information on 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 3D printing machine at 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 by using Q500 TGA (TA Instruments, NewCastle-USA). Test were conducted by heating a piece of materials (about 10 mg) at a rate of 10 °C/min from room temperature to 600 °C in inert atmosphere.

Infrared spectroscopy was conducted in attenuated total reflectance (ATR) modality by using a spectrometer (mod. Spectrum 65 FT IR), produced by Perkin Elmer (Waltham, MA, USA) endowed with a diamond crystal. A range of wavenumber of 400-4000 cm^{-1}, a resolution of 4 cm^{-1}, and a number of scan equal to 16, have been adopted.

To characterize the viscoelastic properties of molten polymers, and verify the thermal stability of material, time sweep test have been performed through a rotational rheometer (mod. ARES), produced by TA Instruments, (New Castle, DE, USA). Parallel plates 25 mm in diameter and a gap of 1 mm were chosen during testing. Materials were subjected to small–amplitude oscillations at a frequency of 1 rad/s and a strain amplitude of 1% more than 900 s at 210 °C in inert atmosphere. Both samples were tested after being dried at 80 °C in a vacuum oven for 10 hours and without being dried.

The dynamic-mechanical properties (DMA) of PLA filaments were investigated using a Triton Technology Ltd. (Leicestershire, UK) instrument (mod. Tritec 2000). Rectangular specimens of 2x5x25 mm were investigated in single cantilever mode at frequencies of 1 Hz from room temperature to 70°C.

3. Results

3.1 Infrared spectroscopy

The results of IR spectroscopy are shown in Figure 1, for pristine PLA material (black curve) and waste one (red curve). The absorbance values were normalized in relation to an internal standard for the PLA (1455 cm^{-1} peak [8]).

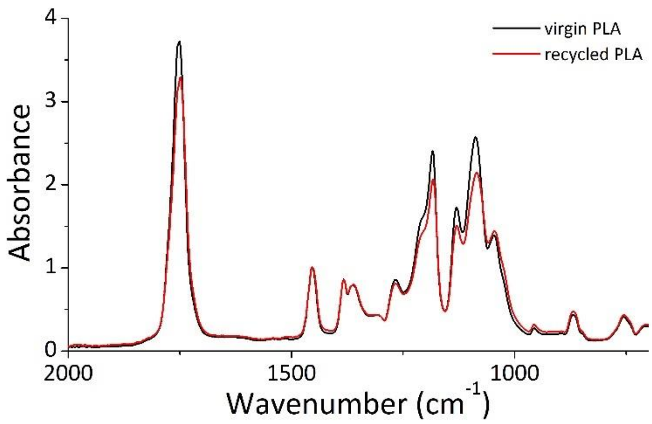

Figure 1. ATR spectra of PLA based materials: virgin PLA (black line) and recycled PLA (red curve). Normalized peak at 1455 cm^{-1}.

PLA's peaks, characteristic of the occurrence of oxidation and decomposition phenomena, could be identified in both filaments: (i) 1750cm^{-1}, linked to carbonyl (C=O) stretching; and (ii) 1183cm^{-1} and 1085cm^{-1}, attributed to the asymmetric vibration of the ester group (C-O-C)[9]. A small reduction of the intensity in correspondence of typical absorption bands of PLA polymer in the case of recycled material compared to virgin one could possible be due to thermal degradation.

3.2 Thermogravimetric Analysis

During the heating of thermogravimetric analysis, one step of PLA degradation was shown in both samples. This trend was due to the loss of ester group[10] that started at about 310 °C. In table 1, the initial decomposition temperature (Tdec 5%), the temperature in correspondence of the maximum rate of degradation (T_{maxdec}) and the final residue at 600°C were reported for the two analyzed samples.

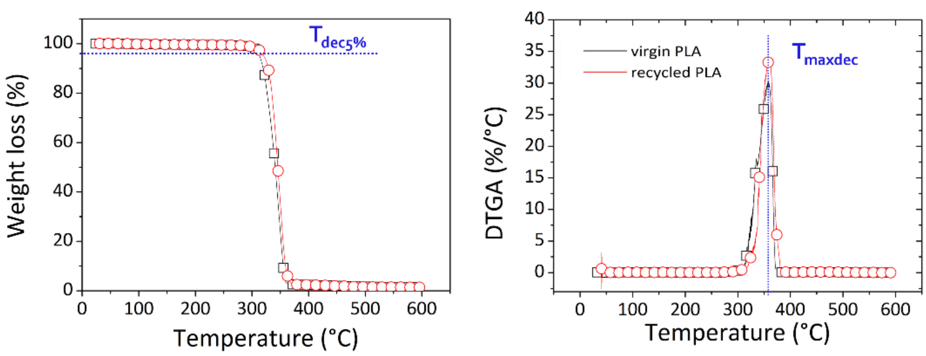

Figure 2. TGA thermograms of virgin and recycled filaments and their respective DTG curves

Table 1. Initial decomposition temperature (Tdec) and temperature of the maximum rate of the decomposition (Tmax) fand residue at temperature of 600°C.

	Tdec5%	Tmaxdec	Residue
Virgin PLA	315°C	357°C	1.5%
Recycled PLA	319°C	360°C	1.4%

3.3 Rotational Rheology

Figure 2 depicts the experimental results of time sweep tests in terms of complex viscosity (Pa*s) over time (> 900 s) for investigated systems. Similar to other polyester polymers, PLA is sensitive to hydrolysis under melt processing conditions in the presence of small amounts of water [11]. In fact, as verified from data in Fig.2, a reduction of the rheological signal was attested during time in the case of non dried material; whereas, the stabilization of the complex viscosity over time at temperature of 210°C for over than 900 s was obtained through sample drying.

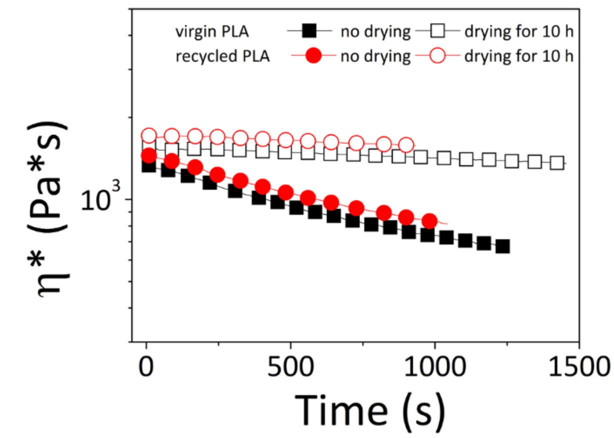

Figure 3. Complex viscosity over time for dried and non-dried specimens.

3.4 Dynamic Mechanical Analysis (DMA)

The experimental results of DMA are shown in Figure 4 in terms of storage modulus (E′) as a function of temperature. From data, the two curves corresponding to virgin (black square points) and recycled samples (red circle points) roughly overlapped with almost comparable values across the entire temperature range.

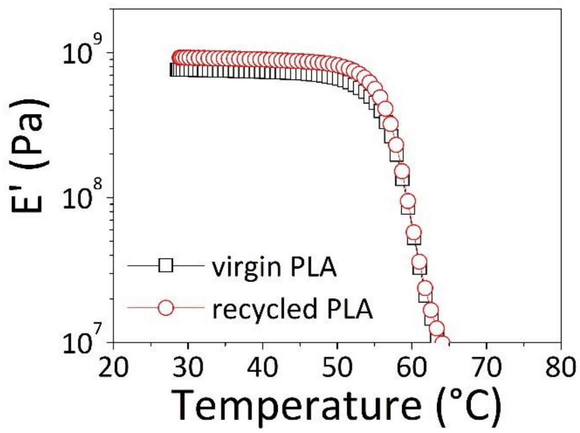

Figure 4. Storage modulus (E′) against temperature for virgin and recycled materials.

4. Conclusions

This was a preliminary study devoted to understand the applicability of recycled matrices instead of virgin polymers for 3D printing process. From data, despite a small reduction in ATR spectra, in correspondence of PLA characteristic peaks of the 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 around 310°C , the stability of complex viscosity over time was achieved through sample pre-drying, and the storage modulus of 3D printed parts made from recycled matrices was very comparable with that of the virgin ones.

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

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Conflicts of Interest: The authors declare no conflict of interest

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