Supplementary materials S1

Experimental techniques

The thermal characterization of the polymeric materials (polylactic acid-PLA and polyethylene terephthalate glycol-PETG) selected for Fused Filament Fabrication (FFF) printing, and the study of the thermal and mechanical properties of the respective printed samples, was carried out using the following analytical methodologies:

- DSC analysis (Mettler Toledo DSC1 StareSystem, Milano, Italy) was performed on PLA and PETG filaments and 3D printed bars, to investigate the thermal features of materials, by measuring glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m). The analyses were conducted using a temperature range of 25°C to 200°C, at a heating rate of 10°C/min.
- The Netzsch STA 409 simultaneous thermal analyser (Netzsch, Selb, Germany) was used for thermogravimetric characterisation (TGA) of the two filaments. The samples were heated in the range of 20°C to 700°C, heating rate of 10°C/min in air.
- 3D samples used for mechanical tests were printed using the Creality CP-01 printer (Creality, London, UK) and setting the following operating conditions: extrusion temperature 200°C for PLA and 220°C for PETG, printing speed 50 mm/s, infill 20%. The CAD model was created with Fusion 360 software (Autodesk, San Rafael, CA, USA), which was converted to an .STL file using Cura software (Ultimaker B.V., Utrecht, The Netherlands).
- According to the ISO178(2014) standard, flexural tests were performed on all 3D printed bars using a Lloyd LR5K dynamometer (Lloyd Instruments Ltd., Bognor Regis, UK), with a test speed of 2 mm/min and a specimen support spacing of 64 mm. Finally, tensile tests were performed on the 3D printed samples, of dimensions of 60 mm x 13.2 mm x 0.7 mm, using the same dynamometer. Six replicates for each mechanical measurement were performed, in order to obtain statistically relevant results.

Results

A careful study of the thermal properties and stability of the PLA and PETG was carried out, in order to confirm the literature data and to select the most suitable material for 3D printing. DSC analysis was performed to verify the difference in the crystal structure of the two filaments. The glass transition temperature (T_g) was calculated by inflection point method, and T_g coincides with the point where the second derivative is zero. As expected, the DSC curves (Figure S1A) of the two polymers are very different, like the thermal properties, crystal structure, molecular weight and mobility of the polymer chains. The glass transition temperature values T_g measured for PLA and PETG are 56.5°C and 71.0°C (Figure S1B), respectively, comparable to those reported in the literature [1–5]. A higher degree of crystallinity and a proximity of the polymer chains to the crystallites corresponds to a higher glass transition temperature, as can be seen for PETG [6,7]; the mechanism of polymer crystallization also depends on the type of fillers, fibers and plasticizers possibly used, as well as, the induced nucleation [7,8], information not known from the manufacturers' data sheets. For example, Cano-Vicent et al. [3] reported a value of T_g approximately 74°C for PETG. Shi et al. [9] reported variations in the T_g value between 70°C and 90°C for PETG, depending on different thermal and degradation conditions, while Quintana et al. [8] reported a value of glass transition of 77.5°C for neat PETG and 75.9°C for PETG with added glass fibres (GF). Marković et al. [10] report a glass transition temperature range for PETG filaments between 73°C and 75°C, for pure PETG or related titanium dioxide (TiO_2) and carbon nanotube (CNT)-based composites. Also for PLA, for example Carrasco et al. [11] report in their study variations of T_g from 60°C up to 68°C, depending on the different conditions of extrusion and injection of the polymer, or Esposito Corcione et al. [12] report an increase of T_g until to 66°C

with the addition of inorganic filler (limestone), while Fico et al. [13] indicate a reduction of the T_g until to 51.3°C with the addition of wood particles to matrix. The crystallization of PLA starts at lower temperatures (T_c=95.5°C) than PETG (T_c=117.6°C), as does the melting process (T_m of PLA equal to 168.1°C, of PETG equal to 253.8°C); also for this reason, in addition to biodegradability, polylactic acid is often preferred for 3D printing. The curves related to the TGA analysis performed on both filaments are shown in Figure S1D. The results indicate a reduction in thermal stability for PLA at temperatures above 300°C, while the data highlight a greater range of thermal stability for PETG, which degrades above 400°C. Table S1 shows additional information obtained from the TGS curves of the filaments.

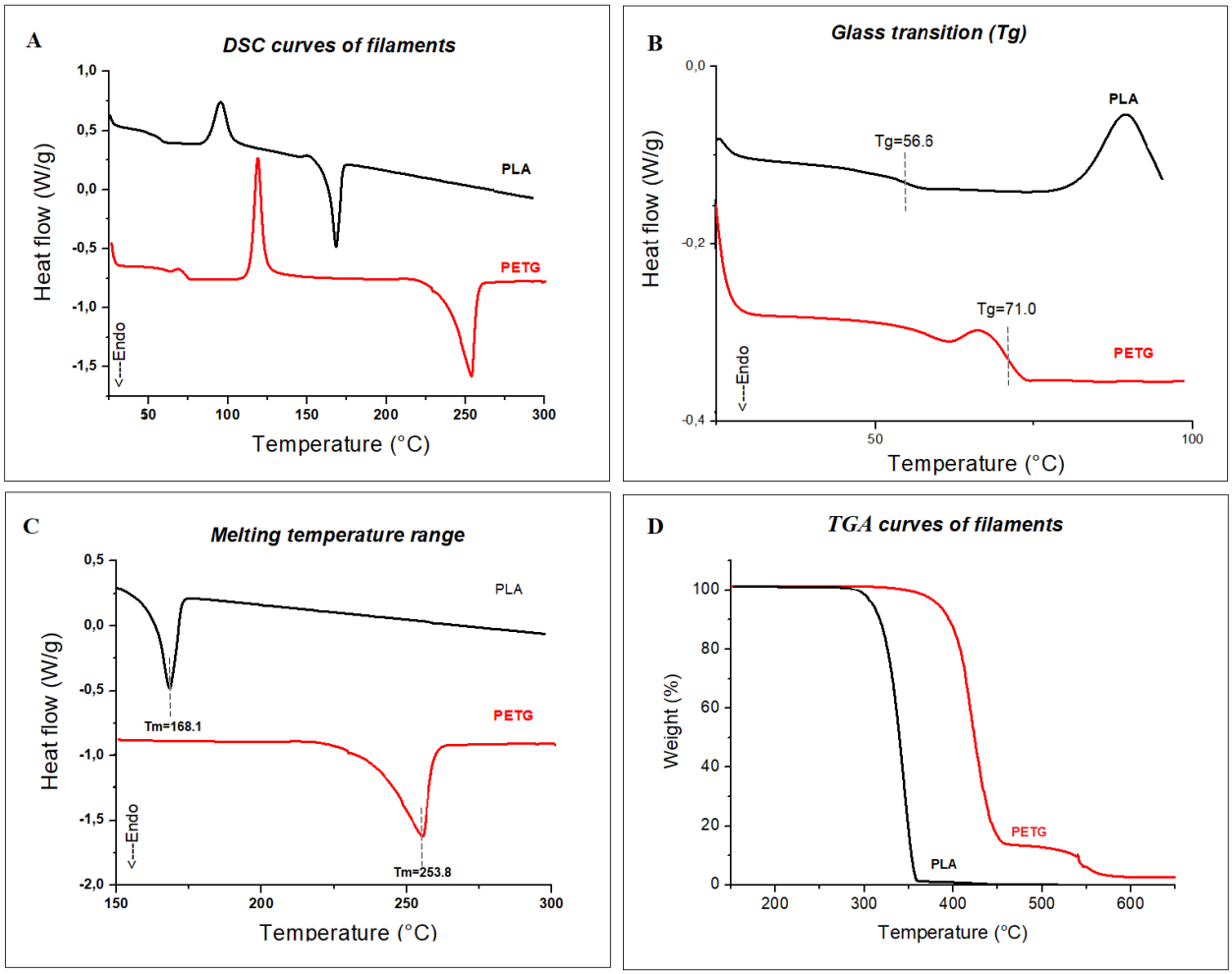

Figure S1. DSC analysis of filaments (A), Glass transition (B), Melting temperature range (C) and TGA curves on filaments (D).

Table S1. T_{onset} (°C) and Solid Residue (%) of filaments from TGA curves.

Sample	T_{ONSET} (°C)	$T_{95\%\ weight\ loss}$(°C)	Solid Residue (%)
PLA	283.1	401.0	0.4 ± 0.1
PETG	351.6	584.1	2.9 ± 0.3

Finally, thermal analysis and mechanical tests were performed on printed PLA and PET samples (labeled PLA 3D and PETG 3D). The overall results are shown in Table S2. As expected, the FFF printing process, and thus the melting of the materials, changes the molecular structure and length of the polymer chains of the materials. Materials are usually subjected to thermo-mechanical degradation during the printing process,

which results in a reduction in molecular weight, in the respective glass transition temperatures and an increase in crystallinity. In this specific case, the DSC analysis performed on the 3D-printed bars does not show any significant changes in the thermal properties, and therefore there were no evident structural changes in the PLA and PETG materials. Mechanical test data show a different behavior of the two materials at different stresses. However, the results are comparable with those reported in the scientific literature [1,2,13,14]. Overall, Table S2 shows a higher strength of PETG than PLA, especially at tensile stress. For all these reasons, PETG was selected as the most suitable material for the realization of the 3D copy of the column.

Table S2. Thermal and mechanical properties of PLA 3D and PETG 3D bars.

Sample	Thermal properties		Tensile properties			Flexural properties		
	T_g(°C)	T_m (°C)	E (GPa)	ε (%)	σ (MPa)	E (GPa)	ε (%)	σ (MPa)
PLA 3D	56.5	166.1	1.1 ± 0.2	3.6 ± 0.4	38.2 ± 5.1	2.9 ± 0.1	3.3 ± 0.3	66.9 ± 4.1
PETG 3D	70.8	254.0	1.7 ± 0.3	5.2 ± 0.9	40.9 ± 6.2	1.4 ± 0.1	3.6 ± 0.5	67.1 ± 1.9

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