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ITALIAN LEATHER RESEARCH INSTITUTE
STAZIONE SPERIMENTALE PER L'INDUSTRIA DELLE PELLI E DELLE MATERIE CONCIANTI

DIRECT PELLET MATERIAL EXTRUSION OF PLA-COLLAGEN COMPOSITES: A CIRCULAR APPROACH TO LEATHER WASTE VALORIZATION

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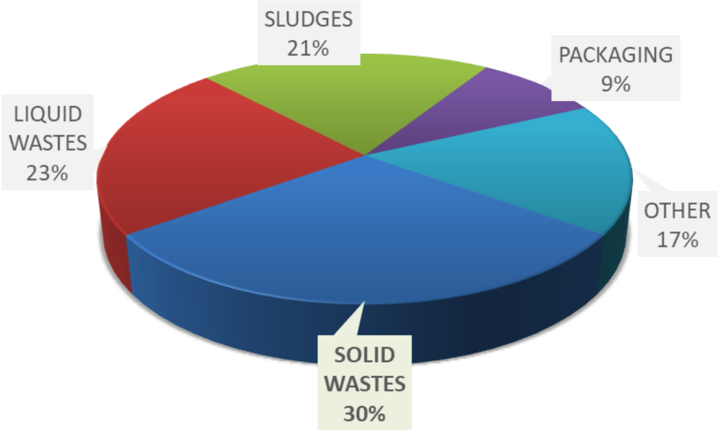
Direct Pellet Material Extrusion of PLA-Collagen composites: a circular approach to leather waste valorization

- Materials and Methods
- Discussion of Results
- Printability Tests

Scope of the Research

Solid wastes related to leather production represent about the **30% of the total** wastes produced.

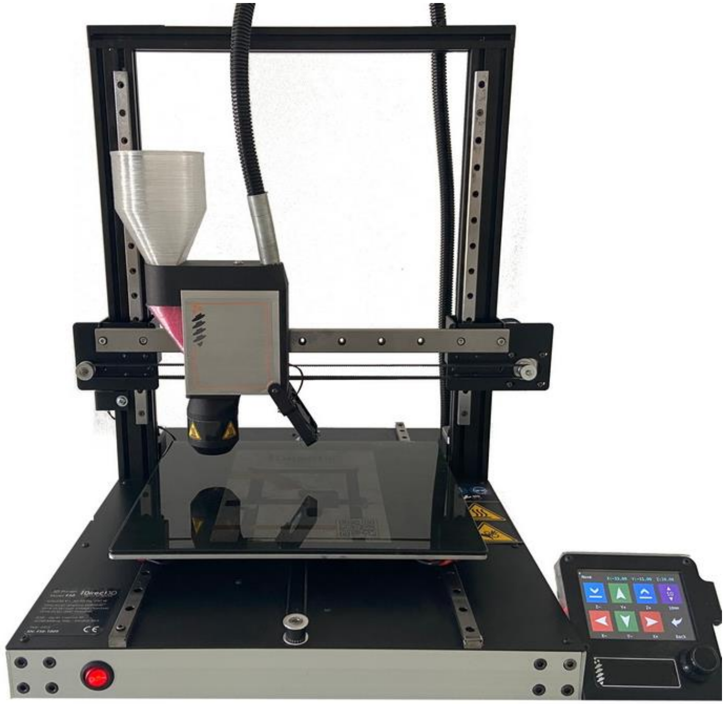


They are made up of residuals from splitting, shaving, finishing, buffing and trimming operations.

Among them, **shaving** residues account 20–25% of the total amount.

To mitigate the environmental impact of solid leather waste generation, it is essential to adopt **circular** strategies for their recovery.

Scope of the Research



In this project circularity paradigm was approached by developing new printable bio-composites from leather wastes for Additive Manufacturing applications.

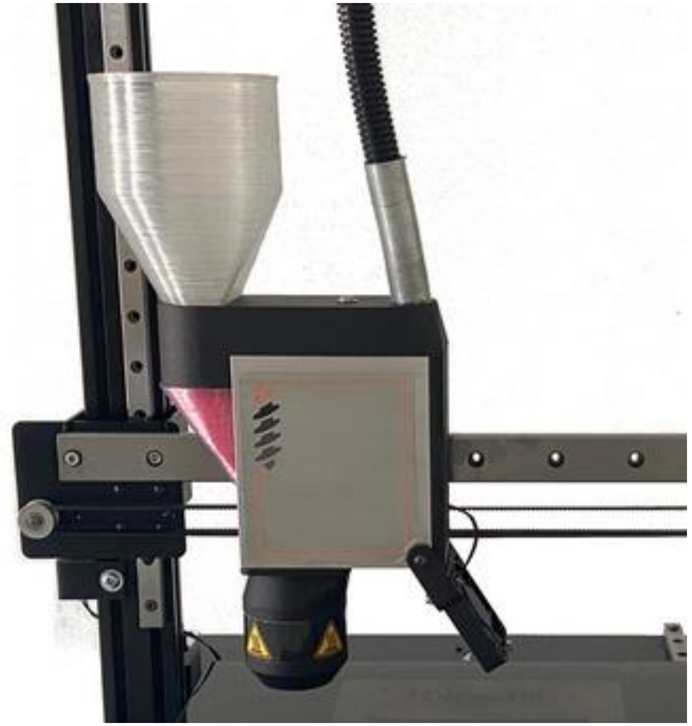
Leather shavings were used as fillers for PLA polymeric matrix for **Direct Pellet Material Extrusion (DME)** techniques.

Scope of the Research

Additive Manufacturing is a layer-by-layer production process able to create components with complex geometries minimizing waste production.

Direct Pellet Material Extrusion (DME) is a technology where pellets are directly melted in a heated nozzle to follow the paths defined during the 3D design phase.

DME is widely used due to **the availability of low costs** and open-source devices.



Direct Pellet Material Extrusion of PLA-Collagen composites: a circular approach to leather waste valorization

Materials and Methods

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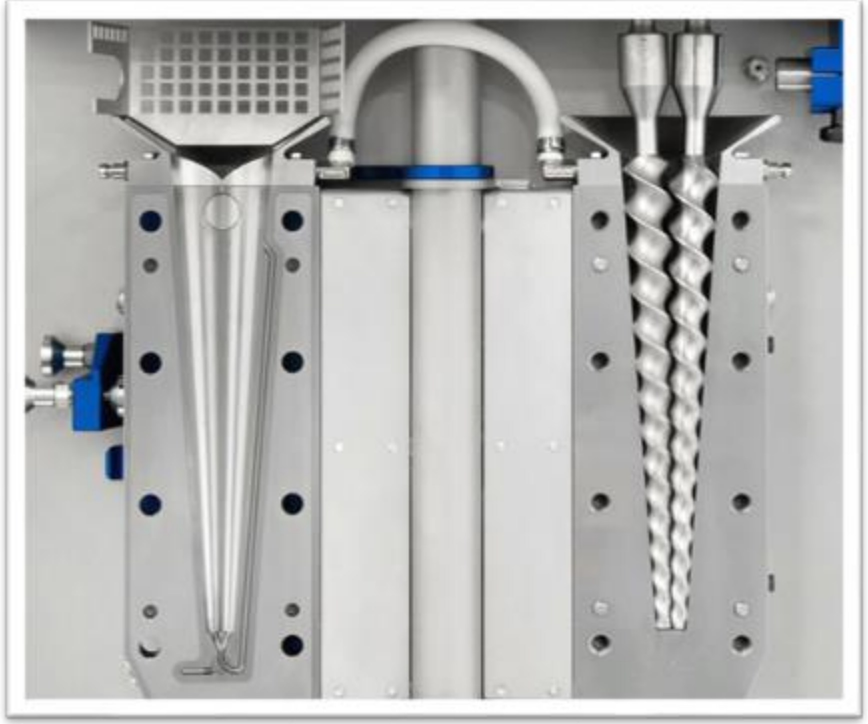
Printability Tests

Materials and Methods

FILLER - Wet-white glutaraldehyde bovine leather shavings were ground using a Pulverisette 19 (Fritsch, Germany) with three different sieve size: **0.5 mm, 1.5 mm and 4.0 mm** to study the particle size dimension effects.



MATRIX - POLYLACTIC ACID (PLA) by Filoalfa 3D was used.

***COMPOSITES PRODUCTION* -** PLA and ground shavings were compounded in a Xplore MC 15 HT **Micro Compounder** for two minutes at 100 rpm and of 180 °C.

Composites in 3 different filler wt % concentrations were prepared: **<u>10 %, 20 %</u>** <u>and</u> **<u>30 %.</u>**

Materials and Methods

Bio-Composites Characterization

Shavings, PLA, and PLA-composites were analyzed to assess the material properties in relation to specific 3D printability aspects:

Morphology of ground shavings ⇨	Particle size distribution ⇨	Clogging of the nozzle
Tensile tests on PLA composites ⇨	Particle size and wt % fraction effects ⇨	Info on mechanical properties of 3D printed object
DSC Analysis ⇨	Melting, glass transition temperature ⇨	Suitability of extrusion and drying temperatures
TGA Analysis ⇨	Denaturation temperature ⇨	Thermal stability at 3D printing temperatures
Rheology on PLA composites ⇨	Change of the viscosity ⇨	Flowability and homogeneity of the melted path

Materials and Methods

Morphology of ground shavings

The morphological characterization of ground shavings was performed by microscopic analysis using an image-based method for **Particle Size Distribution**.

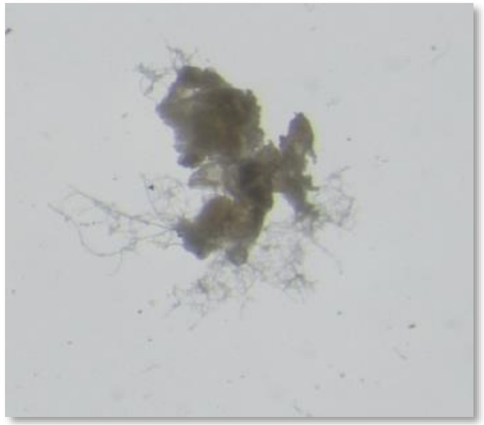
The images were subjected to **digital image processing (DIP)** using the open-source software GIMP (version 3.0.2 rev. 1) for the quantification of 2D particles surface.

SHAVINGS

LEATHER POWDER

MICROSCOPIC ANALYSIS

DIGITAL IMAGE PROCESSING



Materials and Methods

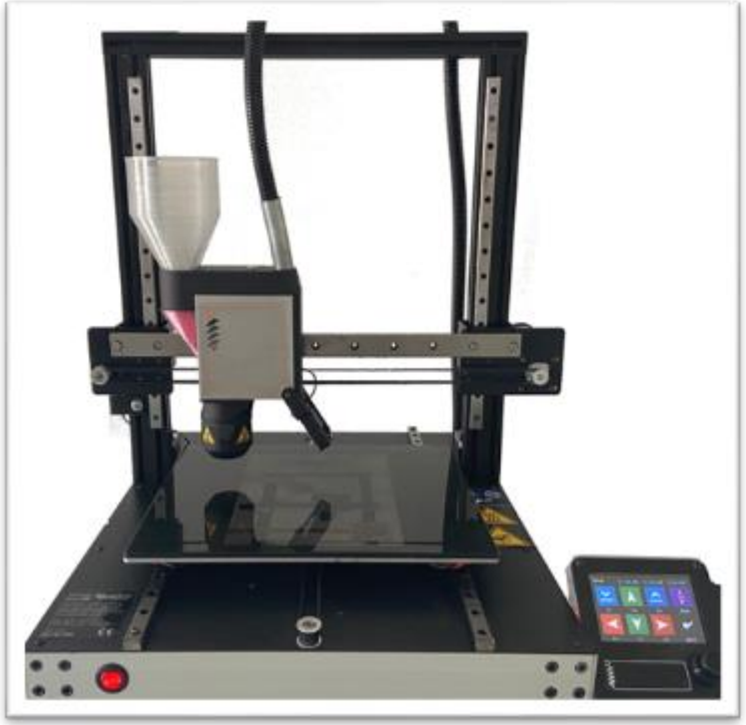
Bio-Composites Characterization

The **following tests** have been carried out on composites materials:

- **TENSILE TESTS** (ISO 527-2:2012) using a Instron 5967 (100 daN load cell) with a crosshead **speed of 1 mm/min**. Young's modulus has been determined in the range from 0.05 % to 0.25%.
- **THERMAL ANALYSIS** (**DSC and TGA**) using TA Instrument STD Q600 **in nitrogen** with a temperature ramp of 5°C/min up to 200 °C for DSC and of 10°C/min **up to 800 °C** for TGA.
- **RHEOLOGICAL TESTS:** carried out using an ARES (Rheometric Scientific) rotational rheometer in nitrogen. Tests were carried out in an **oscillatory regime** (range 0.1 - 100 rad/s) **at 180 °C** using parallel plates with a diameter of 25 mm.

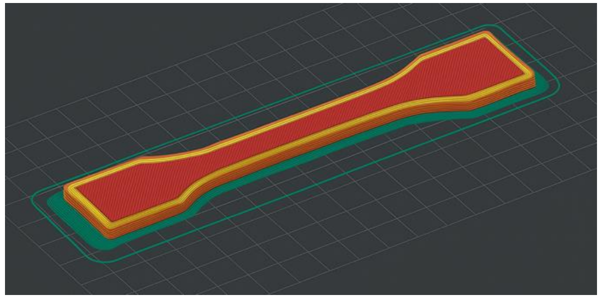
Materials and Methods

Printability tests using DME techniques



For the printability trials the **F30 Pro by Direct3D** has been used.

PrusaSlicer ver. 2.9.2 was used for the generations of the G-Code for printing.



Printability trials were performed by producing **dog-bone specimens** according to ISO 527-2:2012.

In tables the printing set up is shown.

PARAMETER	VALUE
Nozzle diameter	0.8 mm
Nozzle temperature	210 °C
Bed temperature	40 °C
Flow rate	30 000 steps
Print speed	30 mm/s

PARAMETER	VALUE
Layer Height	0.3 mm
Infill Percentage	100%
Infill Strategy	- 45 ° / + 45 °
Wall Layers	2

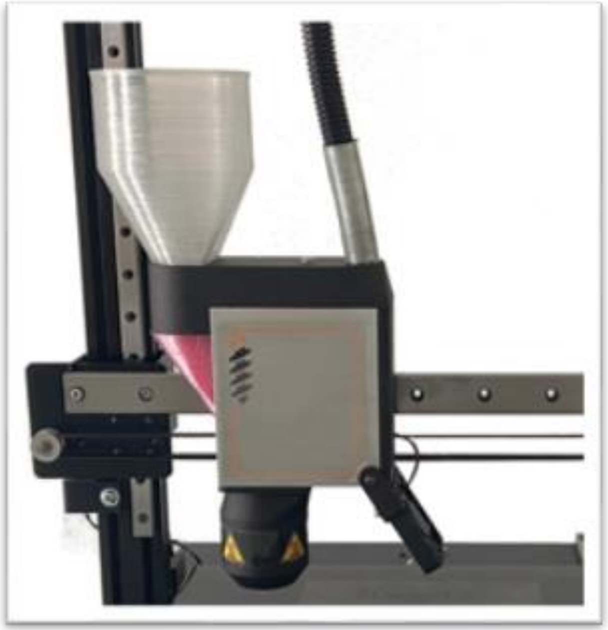
Tests have been carried out at the reference concentration **of 10 wt** %.

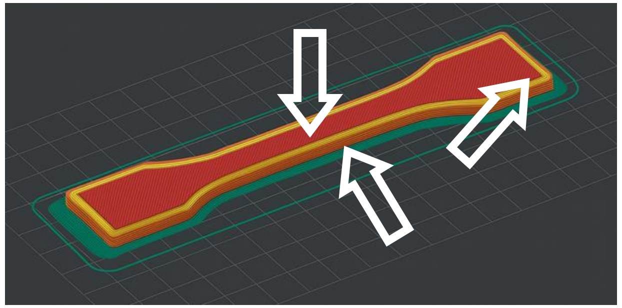
Materials and Methods

Printability tests using DME techniques

Printed test pieces were analysed qualitatively and quantitatively to evaluate printing quality in terms of:

- **Precision of the dimensions** were verified in comparison with the theoretical one defined in the 3D design.
- **Morphological quality** by means Optical analyses using a Digital 3D Microscope (Hirox KH-2000), to verify the inter-layer adhesion, surface uniformity, and geometric accuracy in key areas:
    - the external surface of the gauge section
    - corner transitions in the longitudinal plane
    - the internal microstructure observed in cross-sectional cuts





Direct Pellet Material Extrusion of PLA-Collagen composites: a circular approach to leather waste valorization

Materials and Methods

Discussion of Results

Printability Tests

Discussion of Results

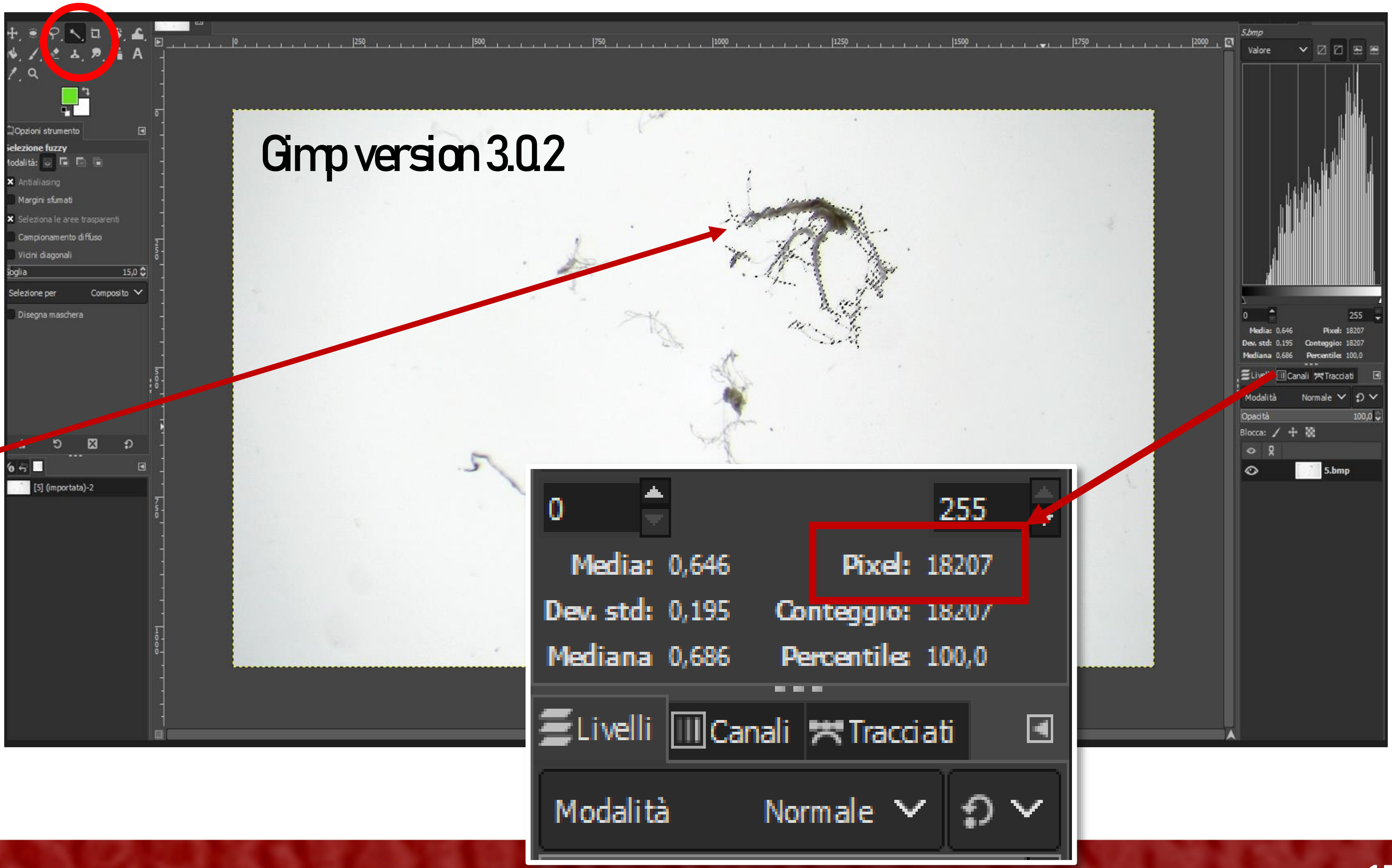
Morphological Characterization powders

For all ground shavings was (0.5, 1.5 and 4.0 mm sieve size) the Particle Size Distribution in terms of surface (2D) were assessed.

Brightness regulation for a white background RGB (100, 100, 0)

Colour selection and identification of pixel numbers for each particle

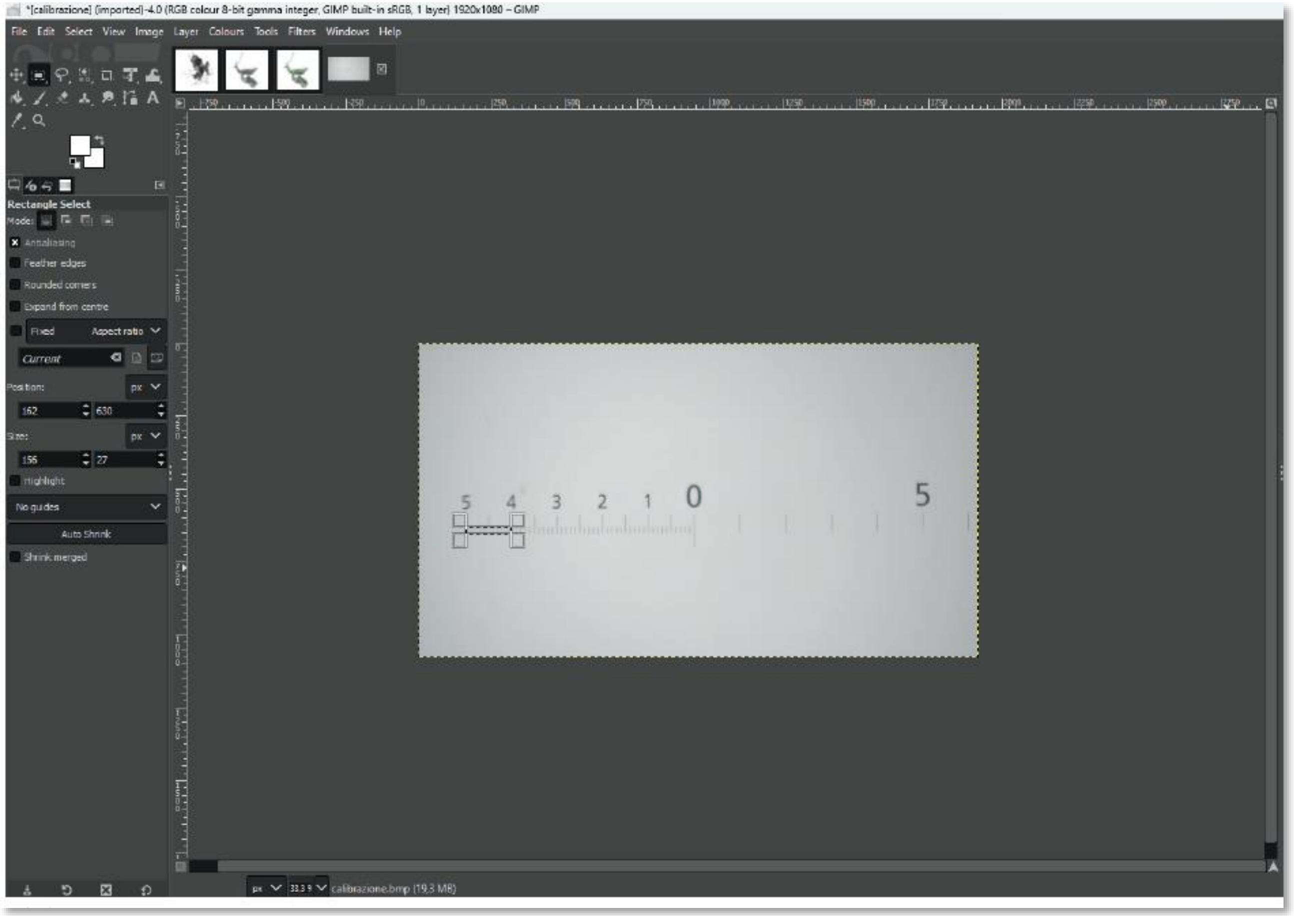
LEATHER POWDER



Discussion of Results

Morphological Characterization powders

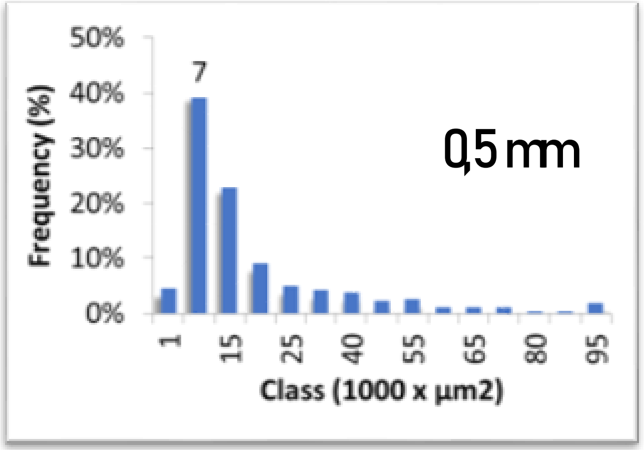
Each particle area in square pixels was converted into square micron using the image of a **calibrated grid** acquired at the same magnification

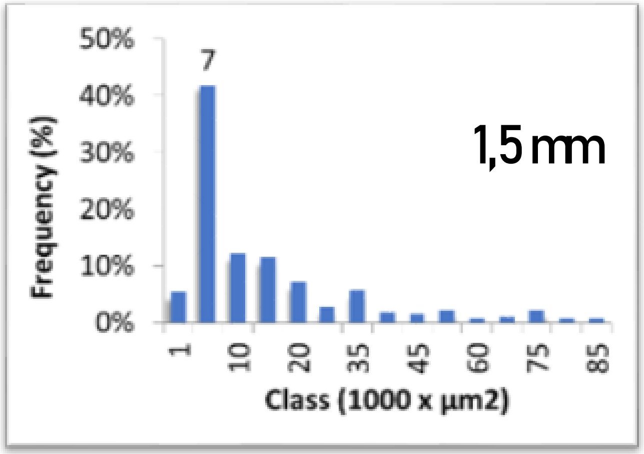


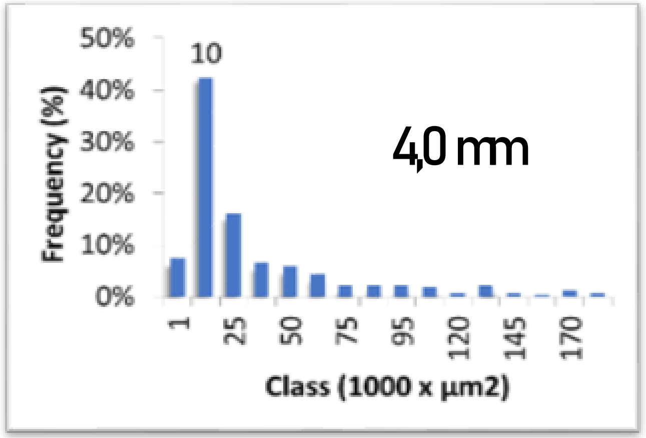
LEATHER POWDER

Morphological Characterization powders

500 particles have been identified for each level. 0.5 mm sieves exhibited surface areas centered around 7,000 μm^2 and a but with reduced dispersion.







In all cases the higher size fraction resulted well above the nozzle area, so that it is minimum the risk of nozzle clogging. However, 0.5 mm sieve was considered as reference filler for the next tests

Discussion of Results

Tensile tests – PLA/Composites

- Tests were carried out on different concentrations **10, 20 and 30 wt %** using **0.5 mm sieve**.
- To verify the **influence** of **particles size**, tests have been carried out on **1.5 mm** and **4.0 mm** too at the reference concentration of 20 wt %.
- **Young Modulus** (MPa) in the linear strain region between 0.05 % and 0.25 %, **tensile stress** in MPa, percentage **elongation** at yield (zero slope) and percentage elongation at break have been assessed.

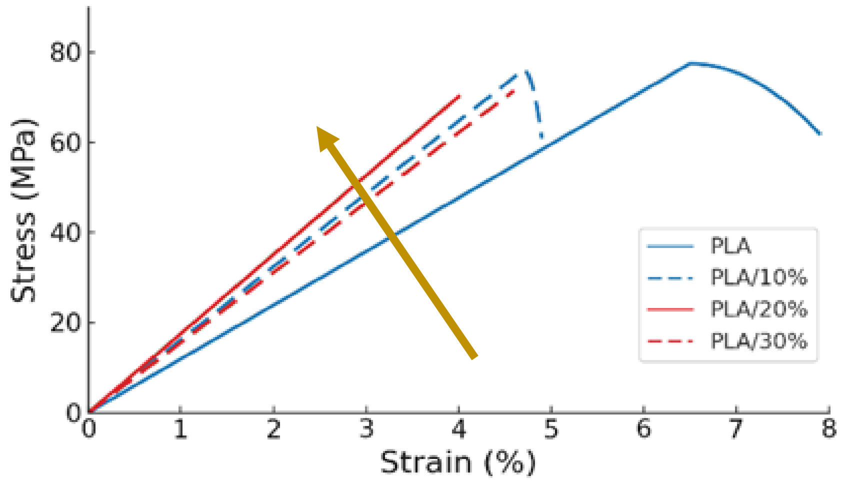
Tensile tests are important to verify the effects of the filler on the mechanical properties of the 3D Printed Objects

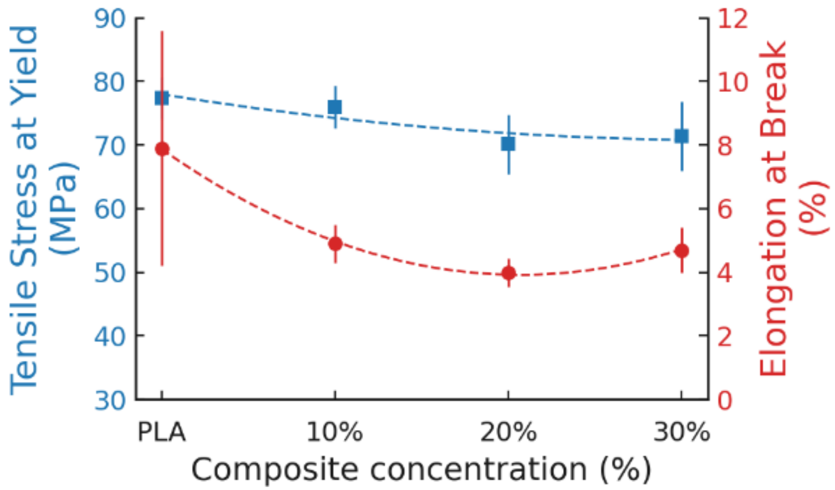
Discussion of Results

Tensile tests

- With **increasing filler content**, the composites become **stiffer** and progressively lose their yielding phase, transitioning toward a more brittle mechanical behaviour

- Increase of the filler concentration determines a relatively low decrease of tensile strength (within the 10 %) and a decrease of elongation at break comprising between 40 % and 50 %.





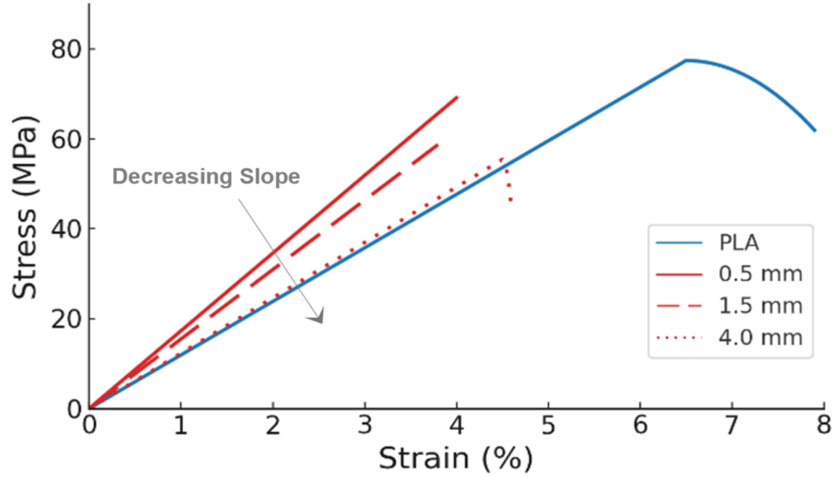
Discussion of Results

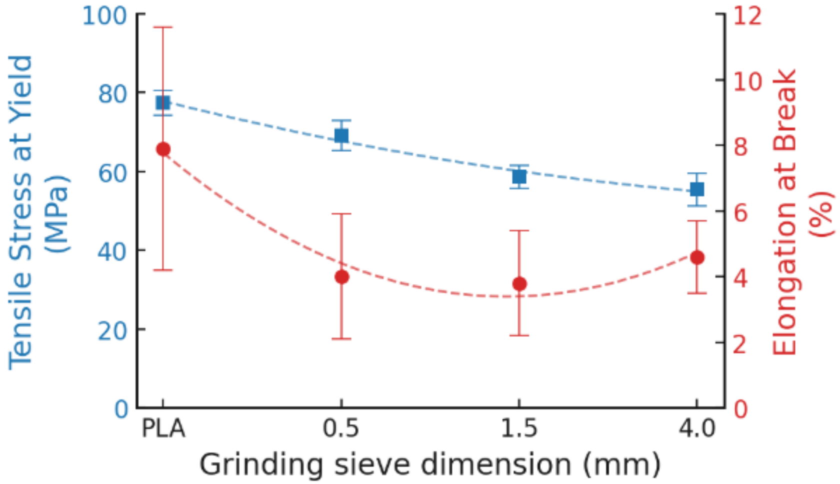
Tensile tests

- With **increasing filler content**, the composites become **stiffer** and progressively lose their yielding phase, transitioning toward a more brittle mechanical behaviour

- Increase of the filler concentration determines a relatively low decrease of tensile strength (within the 10 %) and a decrease of elongation at break comprising between 40 % and 50 %.

- At the reference concentration (20 wt %), increasing the **particle size** of the filler determines a progressive decrease in both tensile strength and elongation at break. This suggests that larger particles act as stress concentrators, weakening the polymer-filler interface





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Discussion of Results

DSC and TGA Analysis

- **DSC analysis** was carried out to identify changes in glass transition temperature (T_g) and melting temperature (T_m) with increasing filler content.

Suitability of extrusion and drying temperatures

- **TGA analysis** was performed to define the degradation temperature (T_{onset}) at increased filler content.

Thermal stability at 3D printing temperatures

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Discussion of Results

DSC and TGA Analysis

SAMPLE	T_g (°C)	T_m (°C)	T_{onset} (°C)
PLA / 0 wt%	60.1 ± 0.8	149.8 ± 0.9	330.1 ± 0.6
PLA / 10 wt%	58.4 ± 0.9	147.2 ± 0.7	326.8 ± 1.3
PLA / 20 wt%	56.9 ± 0.6	144.7 ± 1.2	322.6 ± 0.8
PLA / 30 wt%	55.7 ± 0.2	142.3 ± 1.0	319.3 ± 1.2

- **DSC** analysis shows the decrease in both glass transition temperature (T_g) and melting temperature (T_m) with increasing filler content. This suggests that the filler interferes with the polymer's thermal transitions by reducing molecular mobility and crystalline stability within the PLA matrix.
- **TGA** analysis shows a reduction of thermal stability (T_{onset}) increasing the filler content.

- Drying temperature before printing should be not higher than 40-45°C to avoid the transition in rubbery state
- Melting temperature decreases, so the printing temperature should not be influenced by filler content
- No degradations occurs at extrusion temperatures for compounding and printing

Discussion of Results

Rheological Analysis

The **viscosity** of composites wit increased filler content (0 – 30 wt %) was measured at 180 °C. The results show a slight but consistent decrease in viscosity:

- At 0 wt%, the viscosity is approximately 2300 Pa·s
- At 30 wt% the viscosity decrease to 2150 Pa·s.

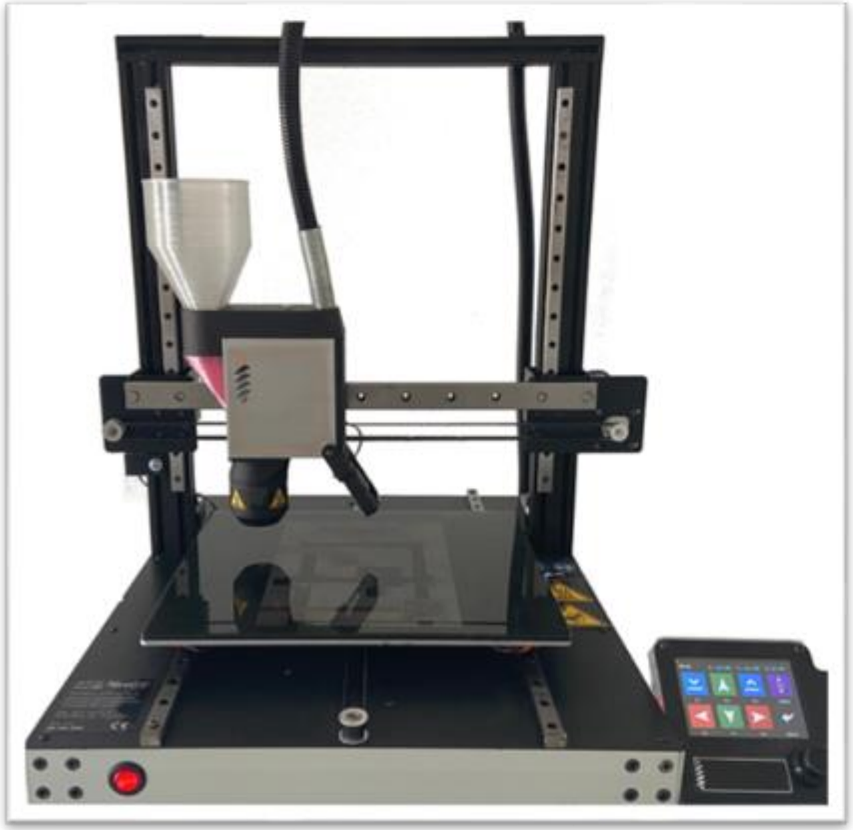
This trend suggests that shaving powders does not significantly hinder the flow of the PLA matrix in the molten state. Instead, its presence appears to have a mild softening effect on the polymer system.

The viscosity varies but remains within the same order of magnitude; therefore, no issues related to melt stability are expected during the printing of the path.

Direct Pellet Material Extrusion of PLA-Collagen composites: a circular approach to leather waste valorization

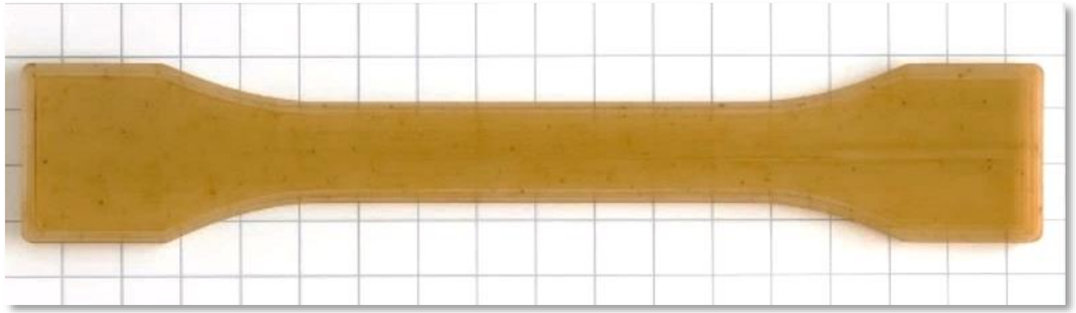
Printability Tests

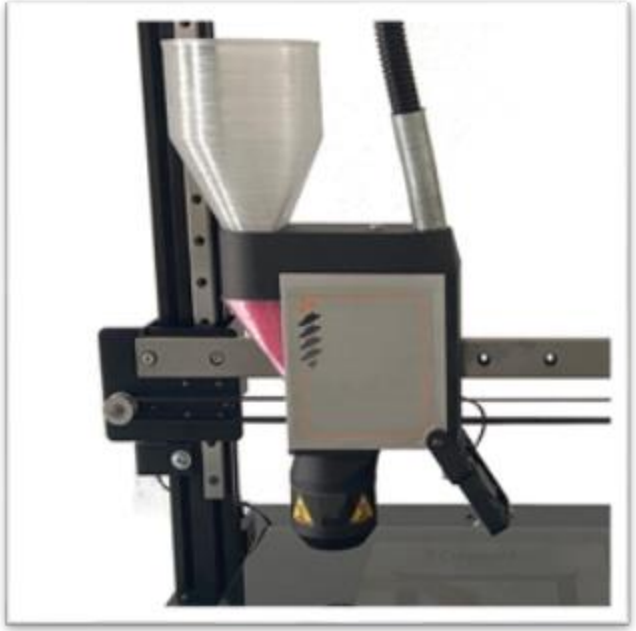
PLA/SHAVING POWDER COMPOSITE PELLETS

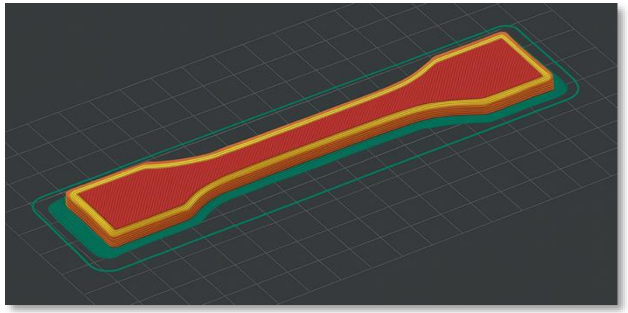


DIRECT PELLET 3D PRINTER

Printability Tests



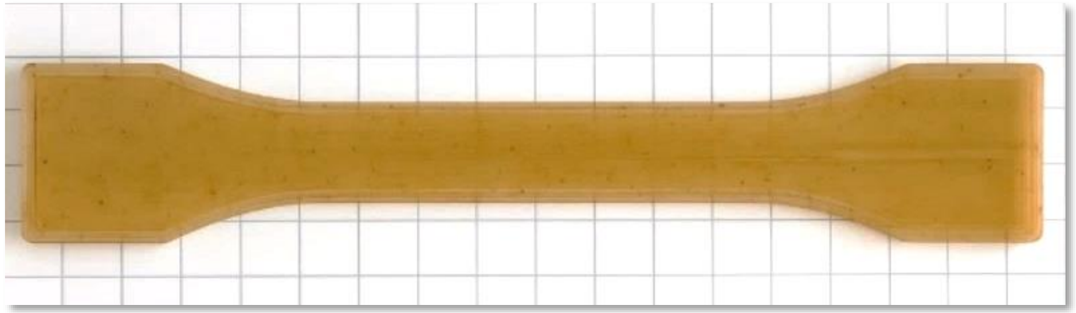


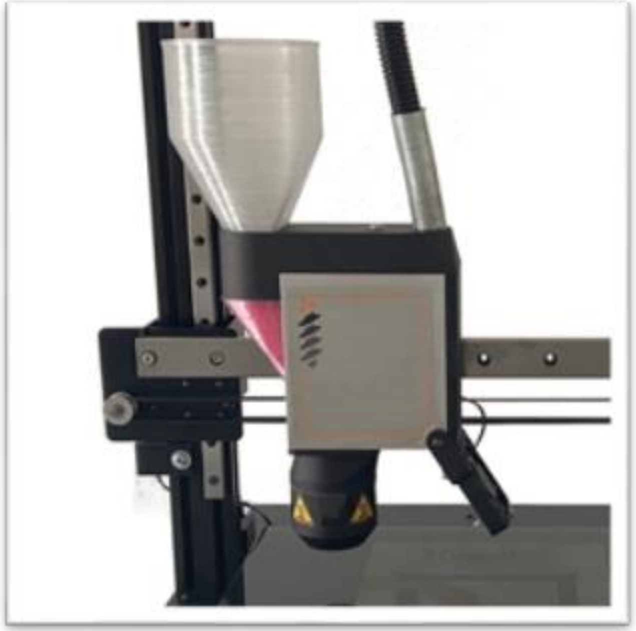


The printability tests demonstrate a stable process without the occurrence of typical FFF-related defects such as:

- **warping** (corners lift from the build plate, causing part deformation),
- **delamination** (layers separate or split apart, weakening the part),
- **porosity** (internal voids or gaps reduce density and strength),
- **ghosting** (repeated patterns or ripples near sharp features),
- **nozzle clogging** (material flow is blocked).

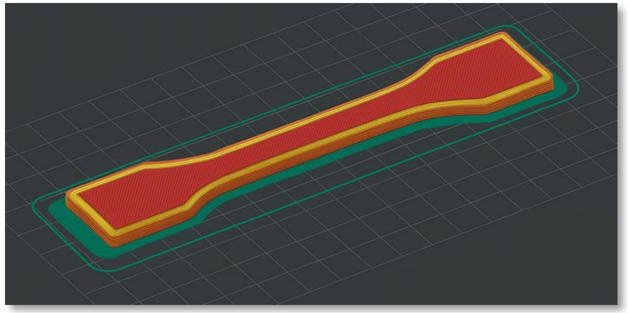
Printability Tests





To check samples accuracy the main dimension of dog bones (total length, width and thickness) was compared to nominal values.

The measurements exhibit high dimensional accuracy, particularly in the Z-direction, where the thickness error is almost negligible (± 0.02 mm).



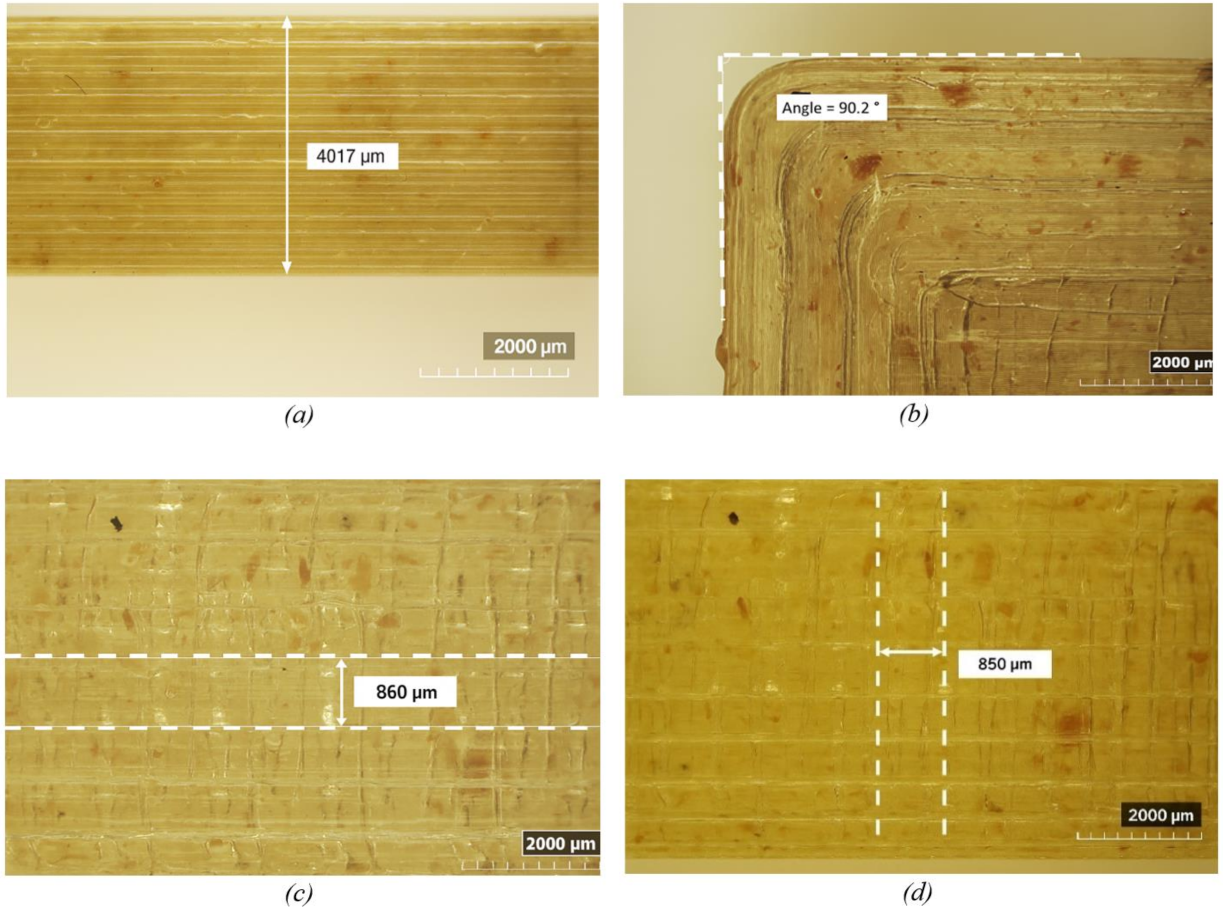
PARAMETER	NOMINAL (MM)	EXPERIMENTAL (MM)
Sample length	150	149 ± 0.4
Sample width	20	20.1 ± 0.2
Sample thickness	4	4 ± 0.02

Printability Tests

Microscopic analysis of the printed dog-bone specimen, highlighting the morphological quality of deposition across critical zones.

Image (a) - clean and homogeneous cross section, indicating uniform material flow and proper layer fusion.

Image (b) - of the top view of the specimen corner shows that no significant warping occurs.



Images (c) and (d) show the well-aligned and regular filament deposition along both the horizontal and vertical directions of the gauge length, further supporting the accuracy of the extrusion process.

Conclusions

DIRECT PELLET MATERIAL EXTRUSION OF

PLA-COLLAGEN COMPOSITES:

A CIRCULAR APPROACH TO LEATHER WASTE VALORIZATION

Conclusions

- In this work, **PLA composites** reinforced using wet-white glutaraldehyde ground leather were studied as novel materials for **Direct Pellet Extrusion** Additive Manufacturing technologies.
- **Different concentrations** of leather waste in bio-composites have been studied (**0 wt% to 30 wt%)** to assess the mechanical, thermal and rheological changes compared with to pure PLA.
- All **grinding processes** of the shavings resulted in particulate with a particle size distribution consistent with the nozzle diameter. The fraction obtained using the 0.5 mm sieve exhibited an average particle size below 7,000 square μm and a more homogeneous distribution.
- **Tensile tests** showed the embrittlement of PLA composites increasing the wt % of the filler, not significant reduction of tensile strength and a reduction of elongation at break, with consequent changes in the mechanical properties of the printed objects.

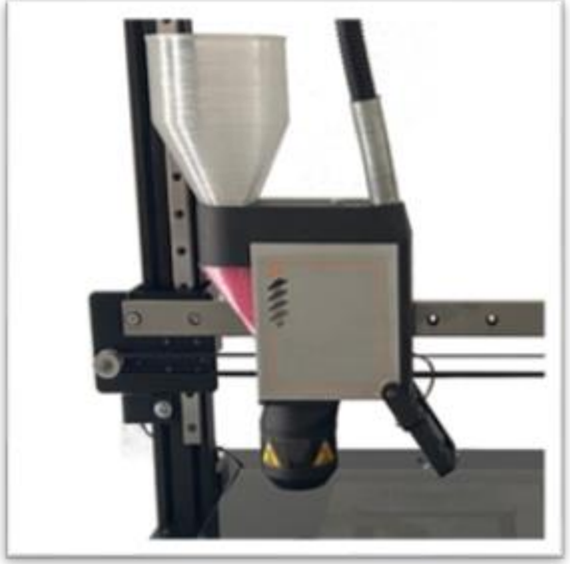
Conclusions

- **Tensile tests** at reference concentration of 20 wt % showed that mechanical properties are affected by the dimension of the particulate.
- **DCS** Analysis highlighted the reduction of glass transition temperature and melting temperature that shall be taken into account in the drying process before printing and during the extrusion.
- **TGA** Analysis showed a reduction of the onset temperature of degradation of composites and that no degradations occurs at the printing temperatures
- **Rheological Analysis** highlighted a reduction of PLA composites viscosity with the increase of filler content that does not affect the flowability during the printing

Conclusions

Printability tests showed:

- **a stable process** without the occurrence of typical FFF-related defects as warping, delamination, porosity, ghosting and nozzle clogging,
- a high **dimensional accuracy** of the printed objects,
- a good **morphological quality** of deposition in critical zones.



Composites of PLA reinforced with shavings of glutaraldehyde leathers can be potential new materials for Additive Manufacturing Direct Pellet Material Extrusion (DME)

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THANK YOU FOR YOUR ATTENTION

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