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3DH-Solutions

Development and characterization of 3D-printed nanocomposites for application in cultural heritage

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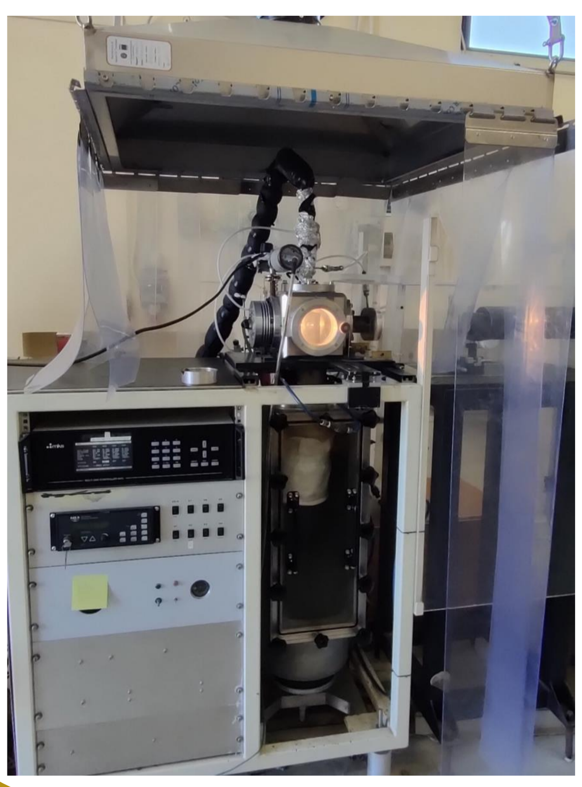
Additive manufacturing coupled with nanotechnologies opens new possibilities and perspectives for application in the field of cultural heritage, from the point of view of preservation, valorisation, communication, and fruition. Advantages of 3D printing technologies are related to the possibility to easily create duplicates of damaged or loss part of artworks for integrative restoration. Employing nanomaterials for 3D printing is a promising approach to obtain innovative and functionalized materials for the artworks element to be recreated.

In the framework of 3DH Solution project, granted by Regione Lazio, innovative nanocomposite materials suitable for 3D printing were prepared and characterized. A commercial PLA filament was additivated with three different ceramic nanoparticles and printed specimens were analysed against their mechanical and hydrophobic properties. TiO_2, SiO_2 and SiC nanoparticles were synthetized by laser pyrolysis technique while nano loaded filament was produced by a co-rotating twin-screw extruder.

Nanoparticles synthesis and nanocomposites production

A CO_2 laser pyrolysis facility was employed for nanoparticles synthesis, the used experimental set-up is LUCIFERO in ENEA Frascati research center.

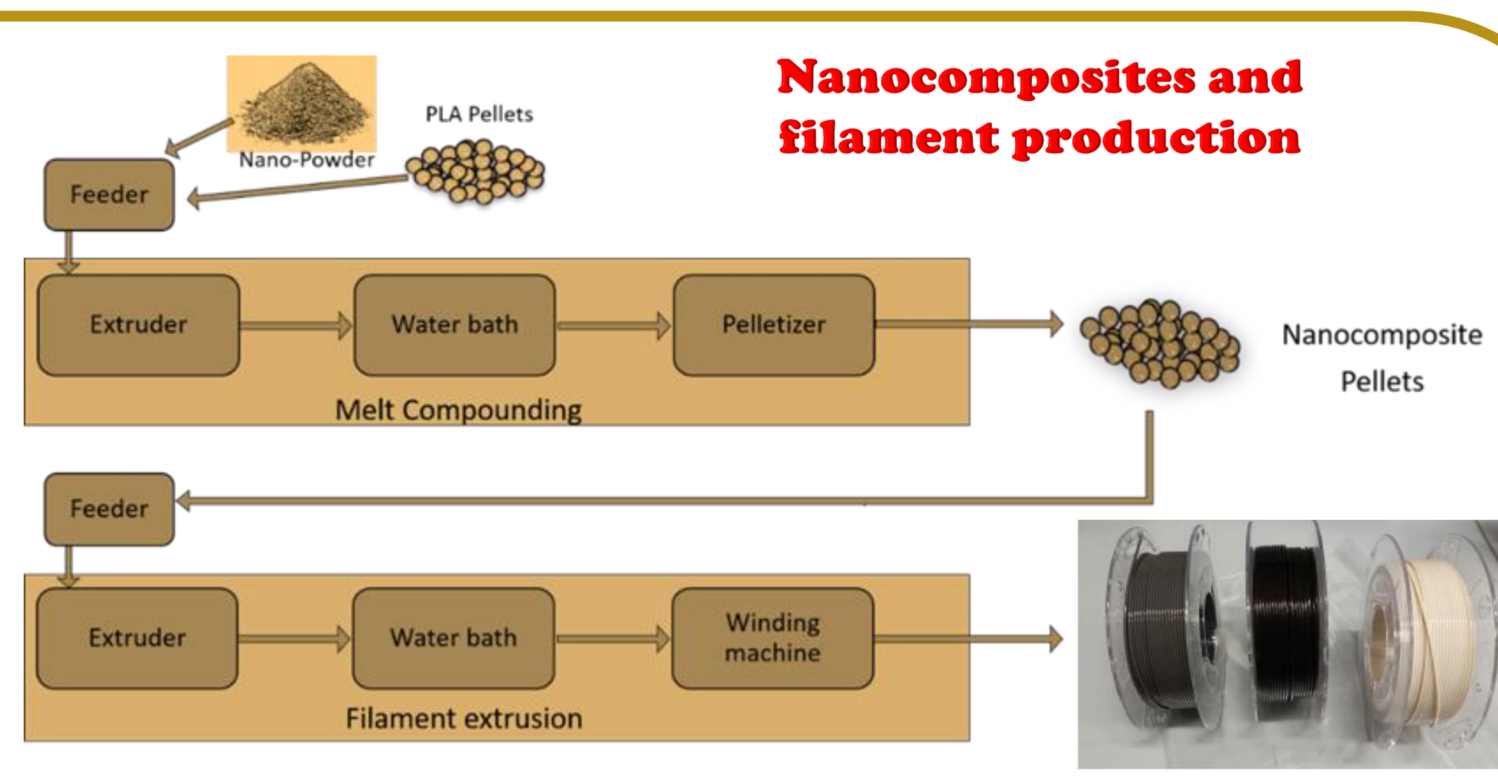


Tested nanoparticles

- Photocatalytic and self-cleaning properties of titanium dioxide (**TiO_2**) nanopowders allow to use nano-TiO_2-based coating on historic architectural stone surfaces
- Silicon dioxide (**SiO_2**) nanoparticles show hydrophobic properties that can be used to give super hydrophobicity to stone surfaces of monuments
- Silicon carbide (**SiC**) nanomaterials show mechanical properties that can be used for nanocomposites coatings with high resistance to aggressive environments

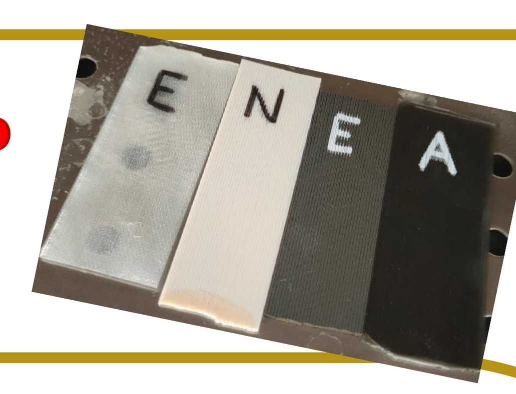
Sample	Productivity (g/h)	Specific surface area (m^2/g)	d (nm)
TiO_2	11	107.3	13
SiO_2	12	221.7	10
SiC	58	75.7	25

Nanocomposites and filament production



Synthesized nanoparticles were used to produce three nanocomposites filament starting by commercial **PLA** and 3% w/w of SiO_2, TiO_2 and SiC nanoparticles. Nanocomposites were manufactured using a Thermo Scientific co-rotating twin-screw extruder (Process 11) equipped with 11 mm screws diameter (ratio length/diameter:40) by a two-step process. In the first step nanopowders and PLA pellets were feed in the extruder and then the nanocomposite pellets were used to produce the filament in the second process step.

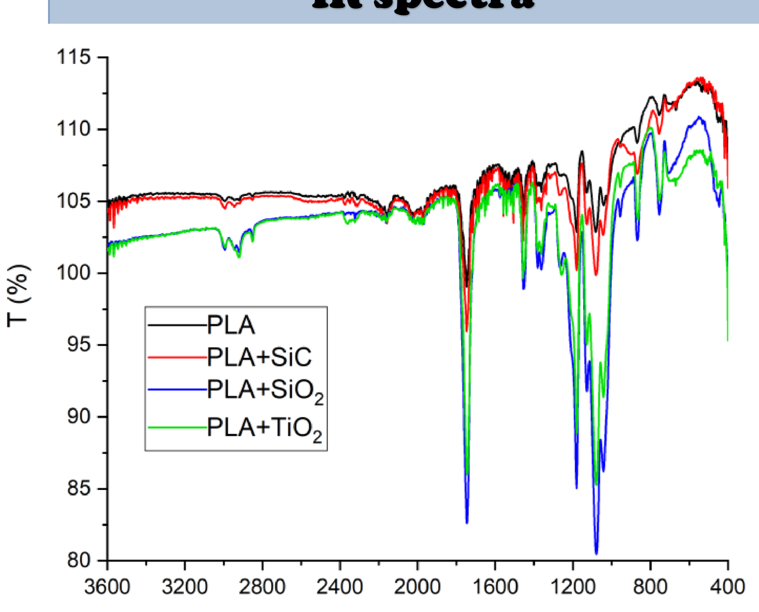
Raw PLA and nanocomposites filaments were used for producing specimens by 3D-printing (by using 3D printer RAISE3D Pro2 Plus) and their chemical and functional properties were tested.



Nanocomposites characterization

Chemical characterization

Raw PLA and nanocomposites IR spectra



IR analyses were performed with a Perkin-Elmer Spectrum100 FTIR spectrophotometer equipped with and ATR module.

The acquired spectra don't show significant changes showing that the PLA chemical structure was not affected by nanopowders presence.

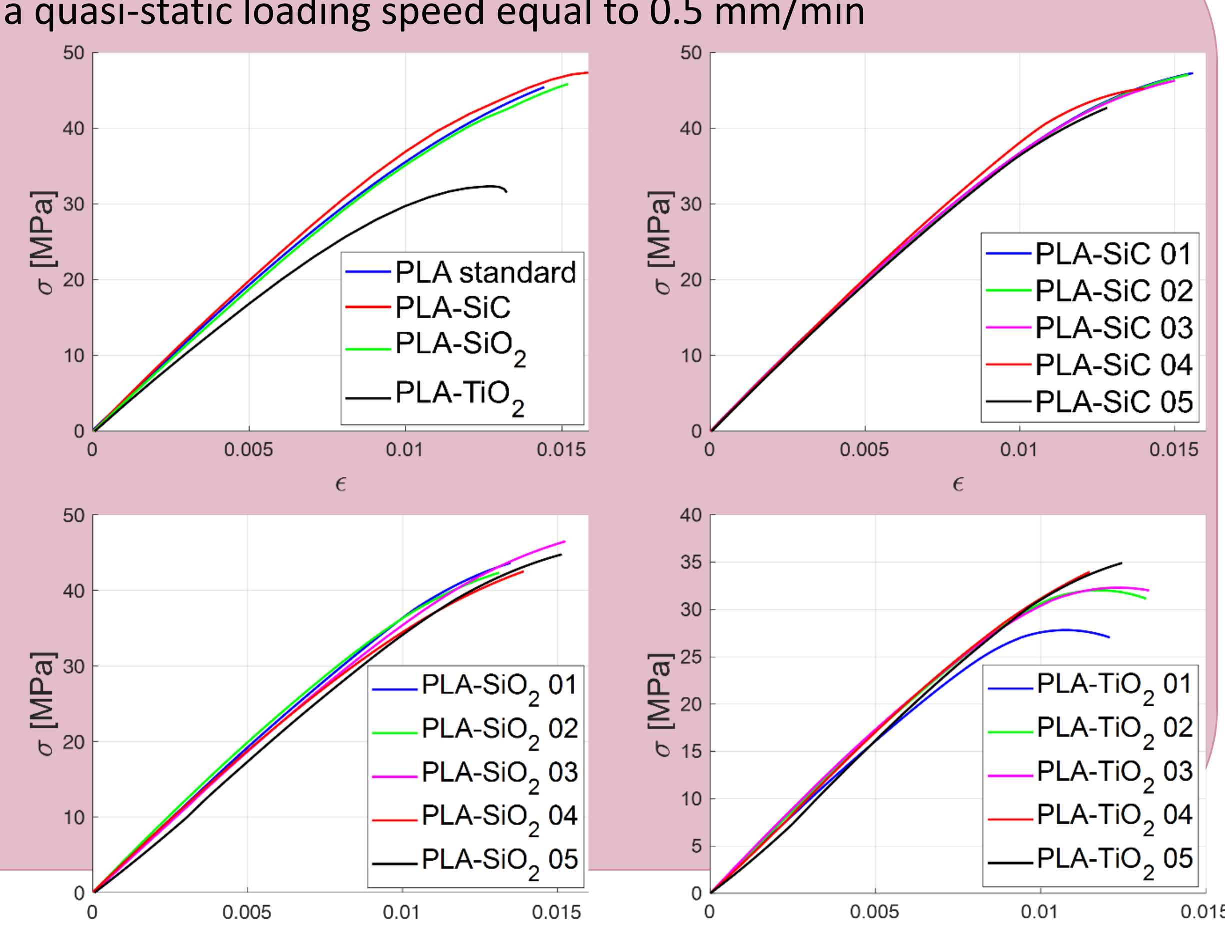
Mechanical characterization

The tensile tests were realized with an MTS machine instrumented with a 100 kN load cell. A displacement control was applied with a quasi-static loading speed equal to 0.5 mm/min

Tensile stress–strain curves and stress-strain curves

SiC and SiO_2 nanoparticles did not significantly affect the elastic stiffness of the sample, with an increase by 3.3% and a decrease by 1.2%, respectively. Thus, the presence of nanoparticles had a positive effect on the mechanical properties of the samples.

TiO_2 nanoparticles determined a decrease in elastic stiffness equal to the 10% and a decrease in the ultimate strain equal to the 8%.

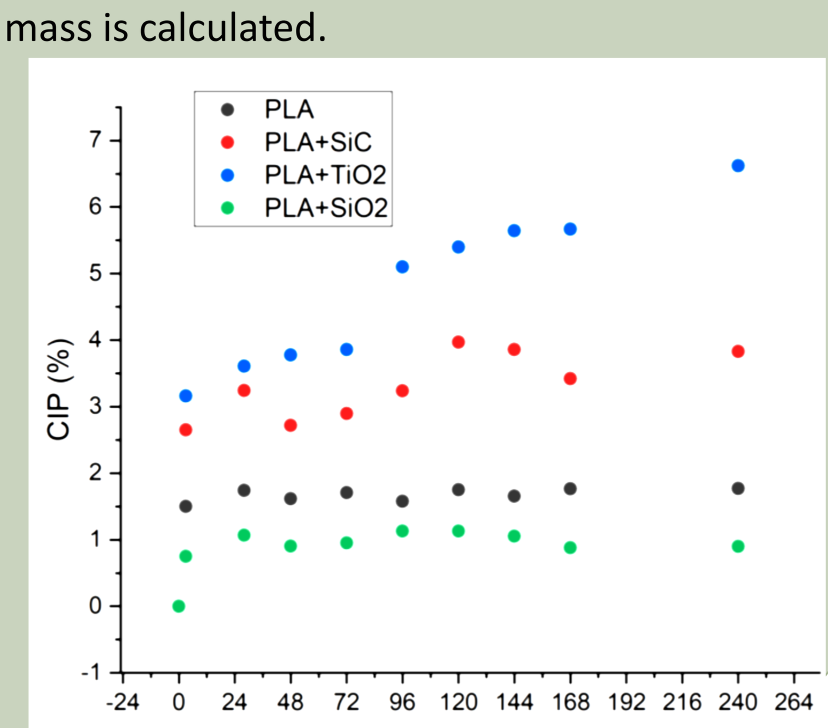


Hydrophobic measurements

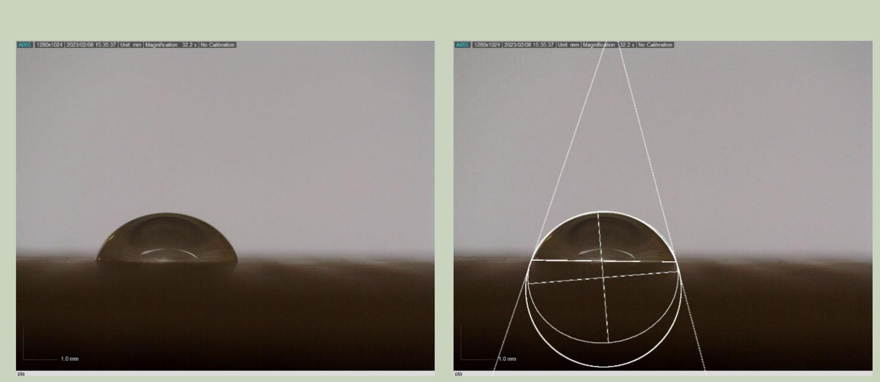
Water absorbtion tests

Water absorption tests were carried out on printed specimens of commercial PLA and three nanocomposites. For each exposure time , the percentage change in mass (CIP) relative to the initial mass is calculated.

A comparison between absorption curves of nanocomposites and PLA shows how nanoparticles affect the material behaviour; it can be evinced as PLA+SiO_2 exhibit more hydrophobic behaviour compared to printed PLA, while PLA+TiO_2 showed an increased hydrophilicity. Also, the SiC presence induce an increasing in the material hydrophilicity.



Contact angle measurement



The wettability properties of the nanocomposite coatings were assessed by static water contact angle measurements to evaluate the local water repellence of the surface specimens.

All the specimens showed a contact angle < 90°, typical of a hydrophilic behaviour. However it can be evinced as the presence of nanopowders slightly induced an increase of contact angle, improving the surface hydrophobicity of tested materials.

Samples	CA (degrees)
PLA	73.2
PLA+TiO_2	74.9
PLA+SiO_2	76.8
PLA+SiC	76.1

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