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3D PRINTING OF ACRYLATE EPOXIDIZED SOYBEAN OIL [AESO]-BASED COMPOSITES CONTAINING LIGNIN

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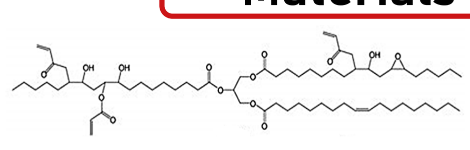
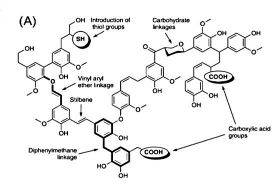
Introduction

Bio-based polymers from renewable sources are emerging as alternatives to fossil-based plastics due to their ease of processing, durability, biodegradability, lower cost, and reduced environmental impact. At the same time, 3D printing (3DP) is attracting attention as a greener alternative to polymeric material production. 3DP offers high precision, minimal material waste, and allows for complex geometries with good dimensional stability. Among 3DP polymerization methods, vat photopolymerization (VPP) achieves the highest resolution and complexity, but is limited by the scarcity of commercially available sustainable photopolymer resins. The composites were printed by using a 60:40 wt% blend of acrylate epoxidized soybean oil (AESO) and tetrahydrofurfuryl acrylate (THFA) as a reactive diluent. Phenyl bis[2,4,6-trimethylbenzoyl] phosphine oxide (BAPO) 2 wt% was chosen as the radical photoinitiator, all sourced from Merck (Italy). UPM BioPiva™ 395 lignin, sourced from Metal Tech (Spain) was added at 5 and 7.5 phr as a bio-filler. Firstly, the viscosity and printability of the formulation were evaluated, and the printing parameters were optimized. Then, the properties of the lignin powders were analyzed by thermogravimetry (TGA), particle size distribution (PSD) and scanning electron microscopy (SEM) characterizations. Subsequently, photopolymerization kinetic and conversion were monitored by Fourier-transform infrared (FTIR) spectroscopy. Finally, morphological, thermal, and mechanical properties were evaluated on photocured samples. The resulting 3D printed components demonstrated good dimensional accuracy and increasing geometric complexity.

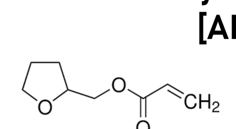
Materials



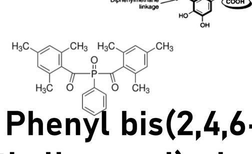
Acrylate Epoxidized Soybean Oil [AESO]



KRAFT LIGNIN



Tetrahydrofurfuryl acrylate [THFA]

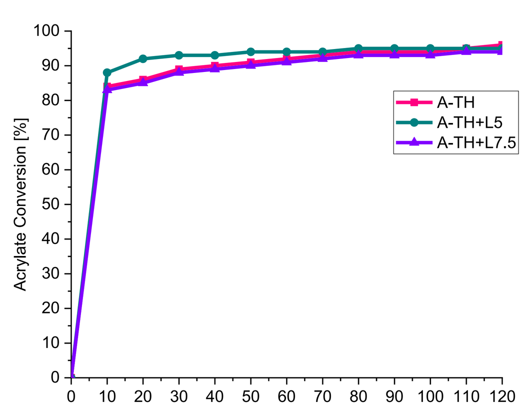


Phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide [BAPO]

Photocurable formulations characterization

SAMPLE	VISCOSITY [mPa·s]
A-TH	347
A-TH+L5	364
A-TH+L7.5	433

η_0 evaluated at a steady-state shear rate of 398 1/s.



3DP

LCD VAT PHOTOPOLYMERIZATION 3D PRINTER

Phrozen Sonic Mini 8K by Phrozen

WASHING AND POST-CURING SYSTEM

Wash & Cure Plus by Anycubic

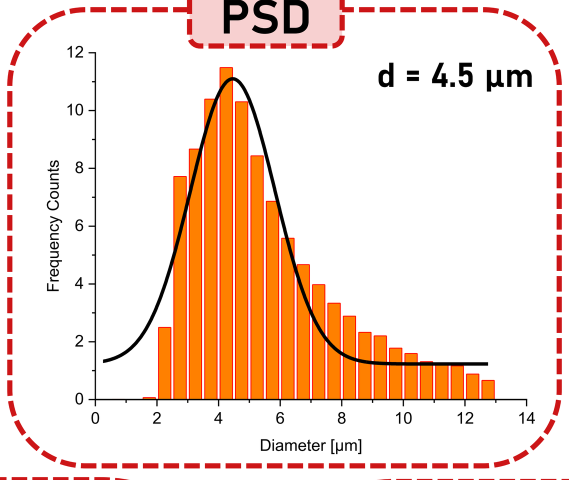
PARAMETER	A-TH	A-TH+L5	A-TH+L7.5
Layerheight [mm]	0.1	0.1	0.1
Exposure time [s]	18	25	28
Bottom exposure time [s]	40	360	400
Bottom lift speed [mm/min]	90	70	70
Lifting speed [mm/min]	90	70	70
Bottom retract speed [mm/min]	170	150	150
Retract speed [mm/min]	170	150	150

POST TREATMENTS on samples:

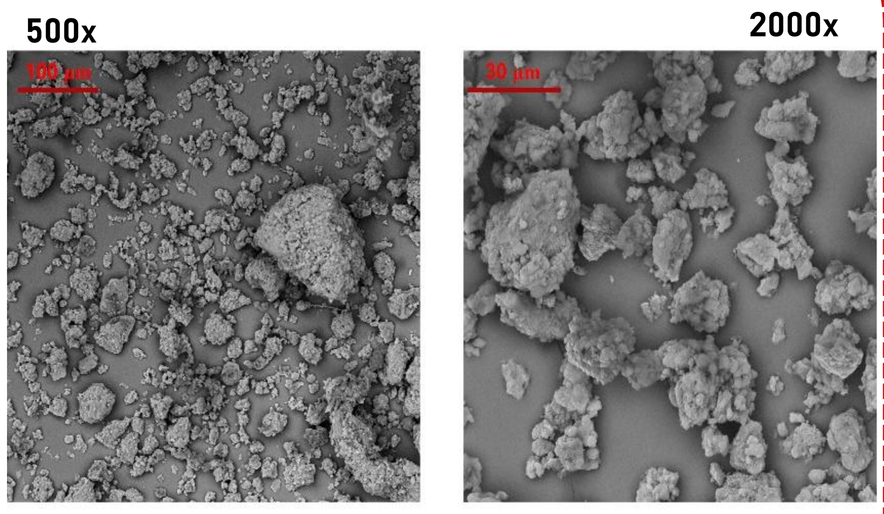
1. Wash with 1-butanol Merck (Italy) for 15 minutes.
2. UV post-cured for 30 minutes.

Powders characterizations

PSD



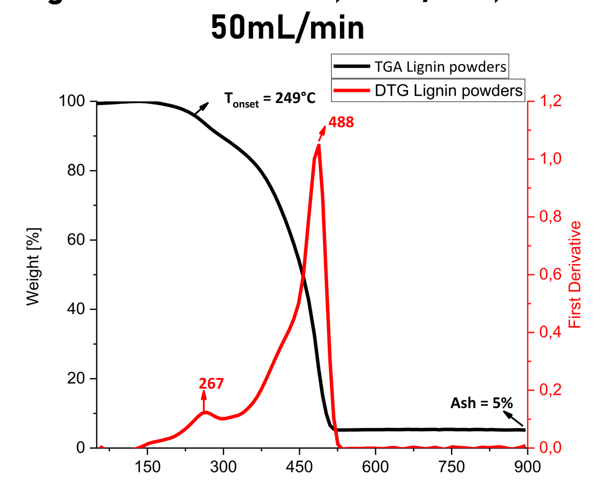
SEM



- SEM micrographs reveal that lignin powder consists of irregular, tiny sheet-like particles measuring less than 10 microns, which readily tend to form aggregates.

TGA

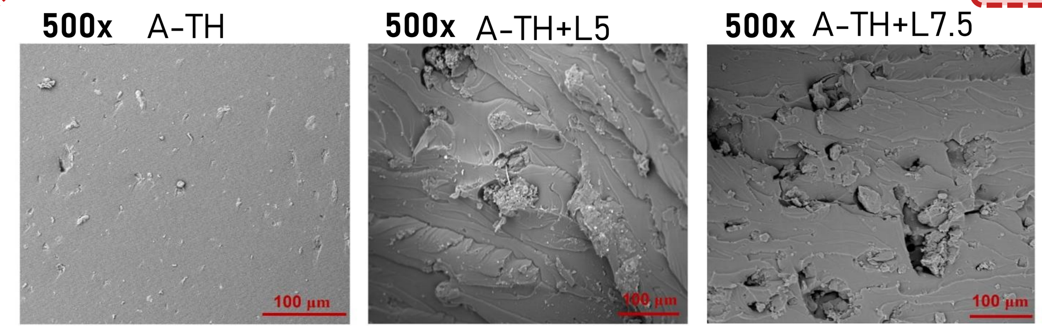
Heating from 25 to 900°C, 10°C/min, air flow 50mL/min



- 2 degradation stages:
  - ❑ The first begins at 180°C and first peak at 267°C (formic acid, formaldehyde, carbon dioxide, sulfur dioxide and water).
  - ❑ The second at 488°C, linked to the decomposition of residual carbohydrates.

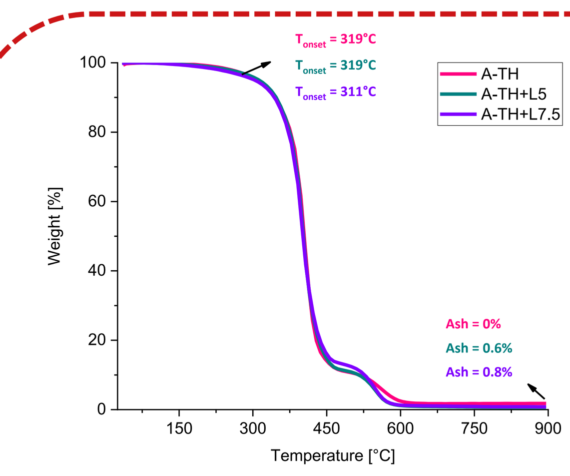
Photocured samples characterizations

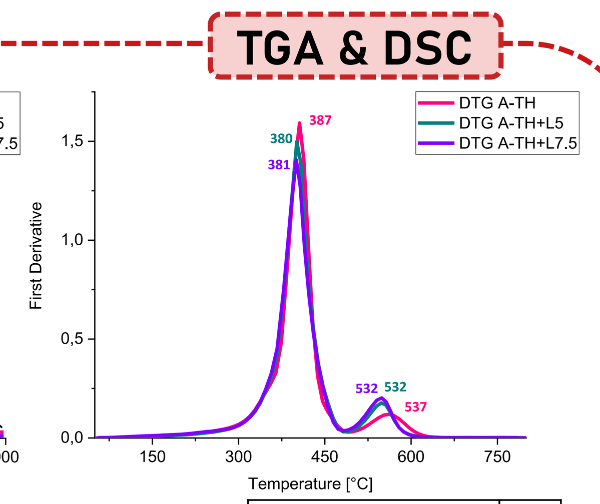
SEM



- SEM analysis showed uniform lignin dispersion in the matrix; some agglomerates are visible.

TGA & DSC





Conditions:

- ❑ **TGA: Heating from 25 to 900°C, 10°C/min, air flow 50mL/min**
- ❑ **DSC: Heatinh from 25 to 250°C, 10°C/min, nitrogen flow 40mL/min**

SAMPLE	T_g [°C]
A-TH	5
A-TH+L5	10
A-TH+L7.5	13

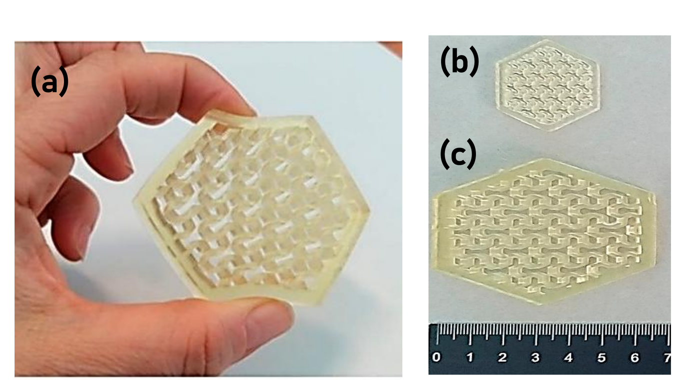
Gel Content & Tensile Test

SAMPLE	Gel Content [%]	Young's modulus [MPa]	Elongation at break [%]	Ultimate tensile strength [MPa]
A-TH	99.2	15.0 ± 1.0	22.0 ± 9.0	3.0 ± 1.0
A-TH+L5	99.5	12.0 ± 0.4	6.2 ± 1.3	0.7 ± 0.2
A-TH+L7.5	99.2	13.0 ± 0.5	7.1 ± 0.8	0.9 ± 0.1

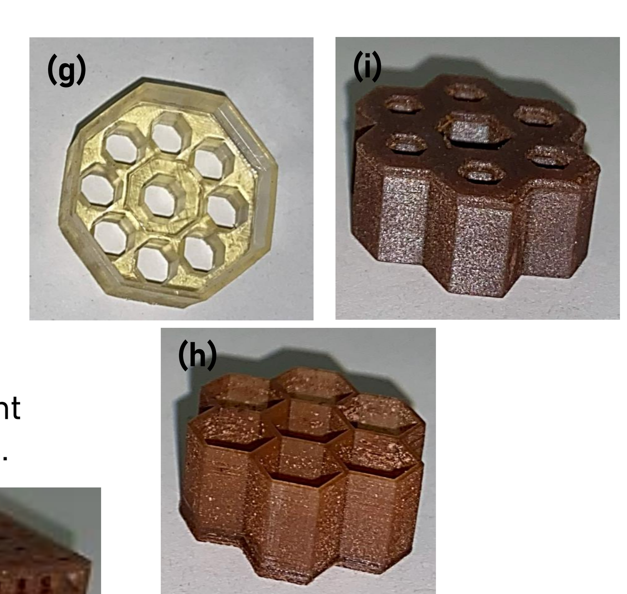
- No significant impact on thermal stability (TGA in air) or glass transition temperature (T_g) (DSC).A slight decrease in onset degradation temperature (5 wt.% weight loss) was observed in lignin-containing samples, attributed to reduced curing efficiency due to higher lignin content. Increased lignin also led to higher ash content.
- The gel content remains high and similar in all samples, indicating that crosslinking is not significantly influenced by the presence of lignin.
- Tensile test results indicate that lignin addition slightly reduced Young's modulus, tensile strength and elongation at break.

This may be due to poor compatibility between lignin and the matrix, which could cause defects or a weak interface.

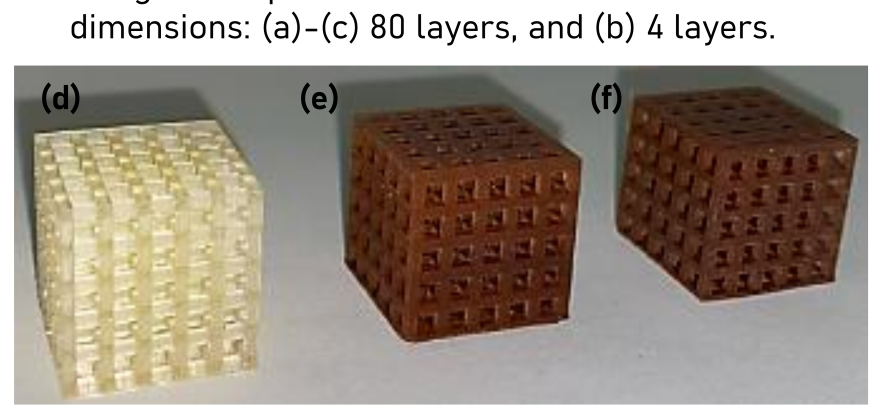
3D Printed AESO-based objects



Hexagons 3D printed AESO-THFA with different dimensions: (a)-(c) 80 layers, and (b) 4 layers.



Intricate geometry 3D printed objects with same numbers of layers (100 layers): (g) A-TH, (h) A-TH+L5, and (i) A-TH+L7.5



Cubes 3D printed with same numbers of layers (200 layers): (d) A-TH, (e) A-TH+L5, and (f) A-TH+L7.5

Different 3D printed components using LCD VPP have been successfully produced, showing high resolution, precision and well-detailed geometries.

Funding

The present work was supported by MICS (Made in Italy – Circular and Sustainable) Extended Partnership and the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 – D.D. 1551.11-10-2022, PE00000004).

MICS Made in Italy Circolare e Sostenibile

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