An Exploratory Study on the Development of Algae-Based Biodegradable Polymer Composite Structures Via Selective Laser Sintering

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INTRODUCTION & BACKGROUND

Additive Manufacturing Trends

Over the last 30 years, Additive Manufacturing (AM) techniques have had a consistent and progressive development, and its market value is expected to increase with upcoming years.[1,2] AM allows for versatility by utilizing one machine, and its higher level of design makes it a worthy competitor against traditional manufacturing techniques.[1]

What is Selective Laser Sintering?

Selective Laser Sintering (SLS) is one of the most commonly used AM techniques. SLS uses a laser beam to fuse a powdered raw material over a large area.[3] It has the advantage of not needing supports, reducing processing steps, and can utilize various materials. The process phenomena for SLS is the following [4]:

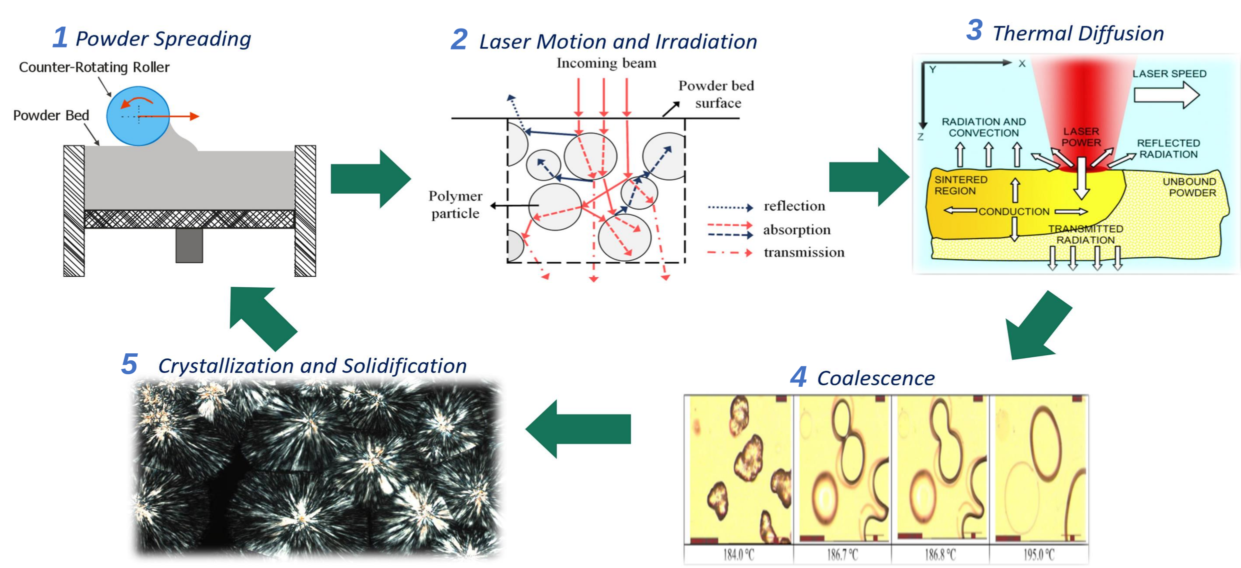

Figure 1. SLS process phenomena cycle

Key Material Parameters for Flowability & Printability in SLS [4]

- ❑ Particle size
- ❑ Particle size distribution
- ❑ Intermolecular forces or Cohesiveness

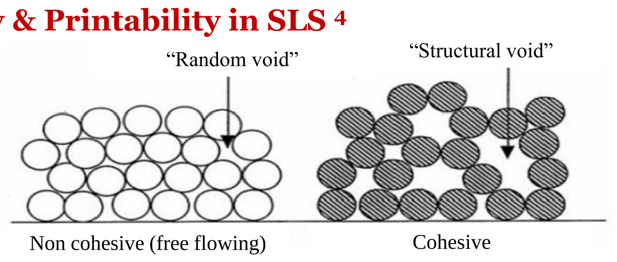

Figure 2. Free-flowing vs. cohesive powders (Micha, 2011).

Figure 3. Sintratec PA12 powder (Sintratec.com, n.d).

PHBV as an Alternative to PA12

Polyamide 12 (PA12) is the standard material for SLS. Due to it being a petroleum-derived polymer, it poses an environmental concern.

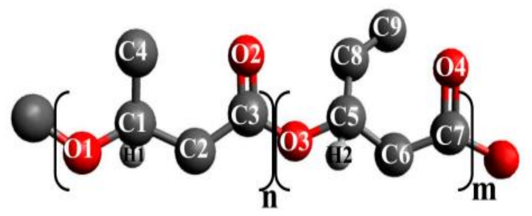

Figure 4. PHBV molecular structure (Ghysels, 2018).

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is synthesized via bacterial fermentation and has excellent biodegradable properties that make it a potential substitute for petroleum-derived polymers. [5]

Using Sargassum for the Fabrication of Biodegrade Composites via SLS

Figure 5. Sargassum in Humacao (Marrero,2022)

Drastic influx of *sargassum* algae have washed up along the Caribbean coastlines, and part of the west coast of Africa, which has caused a negative impact environmentally, economically, and health-wise. [6]

Target: Biodegradable polymer composites with algae biomass contents ≥ 30wt% since these are difficult to be created in form of filaments for FDM.

Proposed Approach to Manufacture Sustainable Bio-composites via SLS

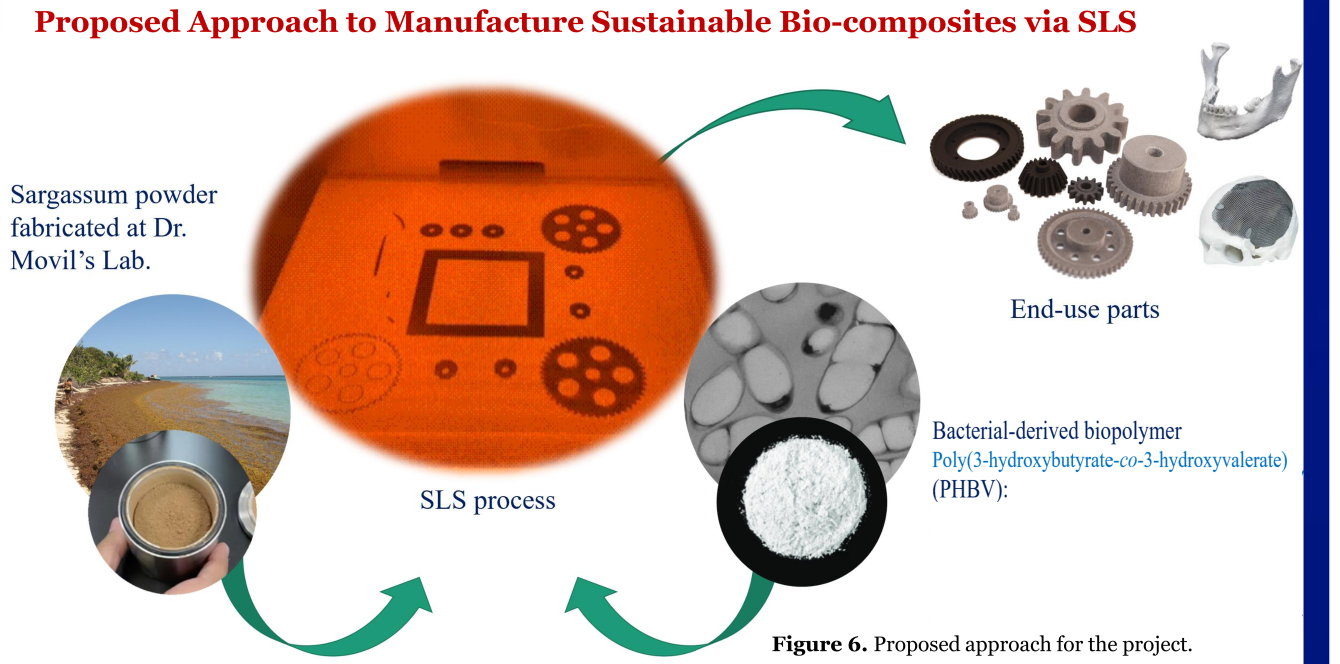

Figure 6. Proposed approach for the project.

GOAL & OBJECTIVES

GOAL: Fabricate mechanically stable Sargassum-based 3D printed parts via SLS

OBJECTIVES:

1. Establish the process conditions to prepare polymer composite granules of Sargassum and PHBV having algal biomass contents ≥ 30wt% and suitable flowability.
2. Establish the process conditions to fabricate printed parts via SLS using polymer composite granules (Sargassum/PHBV) having algal biomass contents ≥ 30wt%
3. Evaluate the microstructure, biodegradability, and mechanical properties of the fabricated parts to establish the relationship between composition, microstructure and materials properties.

METHODOLOGY

Task 1. Assembling, Installing, & Calibrating the SLS equipment

Figure 7. (a) Sintratec Kit core assembly & installation, (b) Sintratec Kit laser calibration, (c) Sintratec Kit fine calibration with PA12

Task 2. Powder Preparation

Figure 8. (a) Dry Sargassum, (b,c) Dry Sargassum is coarsely ground in a commercial blender, (d,e) Sargassum is milled in a PBM – 04 Planetary ball mill

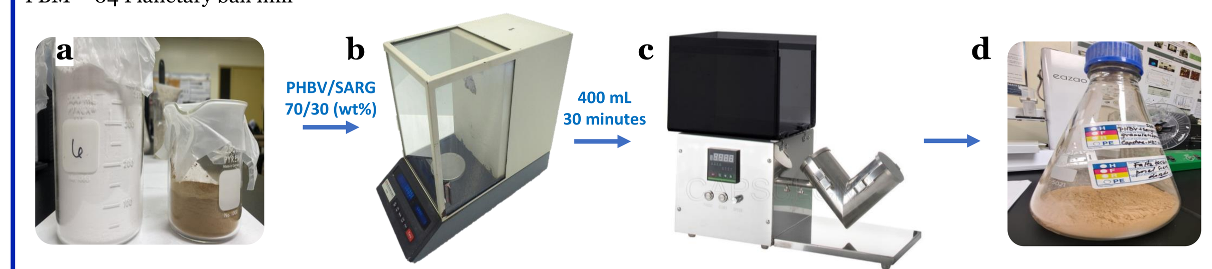

Figure 9. (a) PHBV & Sargassum, (b) weighed in Fischer Scientific Denver Instruments Company (Ebay, n.d.), (c) Mixed in V-Type mini-Mixer (ipharmamachine, n.d), (d) PHBV/SARG 70/30 powder feedstock (wt%).

Task 3. Granulating the PHBV/SARG Powder Feedstock

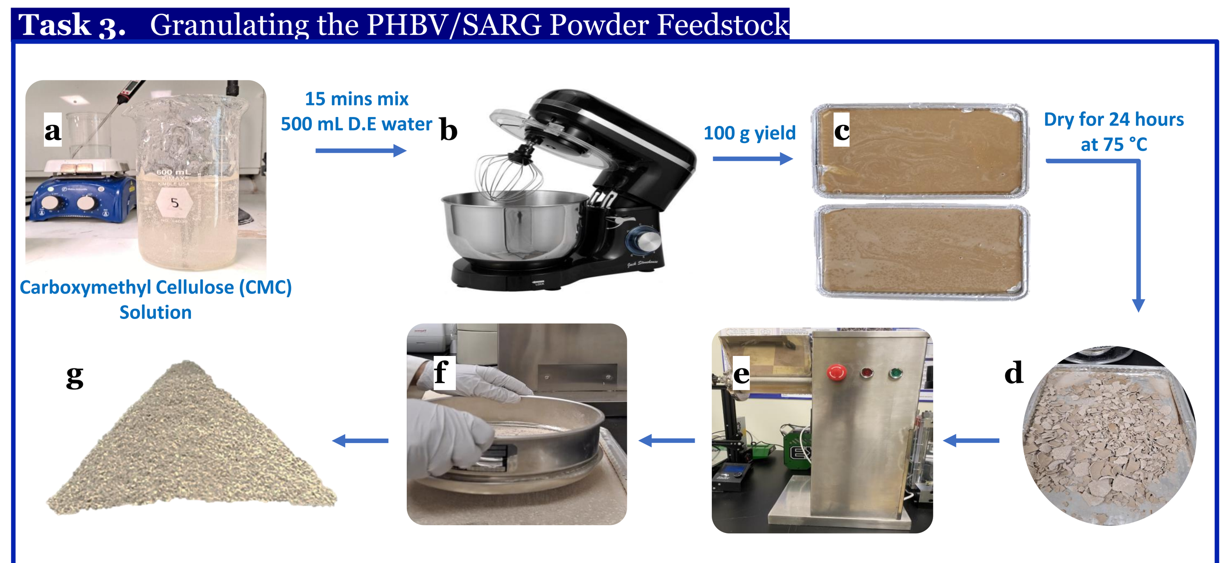

Figure 10. (a) CMC 0.6 (g/mL %) aqueous solution, (b) Jack Stonehouse Planetary Mixer (jackstonehouse,n.d.), (c) PHBV/SARG & binder dispersion, (d) PHBV/SARG granulated feedstock pre-sieving, (e) LFA GR ™ Powder Granulater, (f) Sieving process with Christison Test Sieve, (g) Finalized PHBV/SARG granulated feedstock; (Dr. Movil's Lab, 2022).

Task 4. Powder Characterization

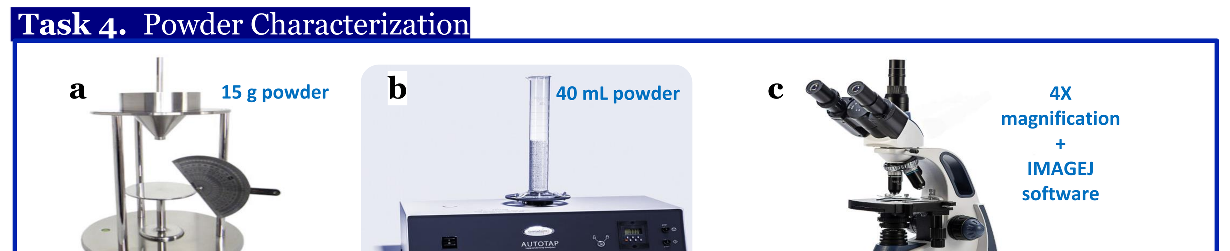

Figure 11. (a) Mitutoyo Precision Measuring Instrument Powder Angle of Repose Tester (amazon, n.d.), (b) Anton Paar Autotap Bulk Density Analyzer (anton-par, n.d.), Swift SW380T microscope (amazon,n.d.).

Task 5. Printability Tests by Manufacturing Specimens via SLS

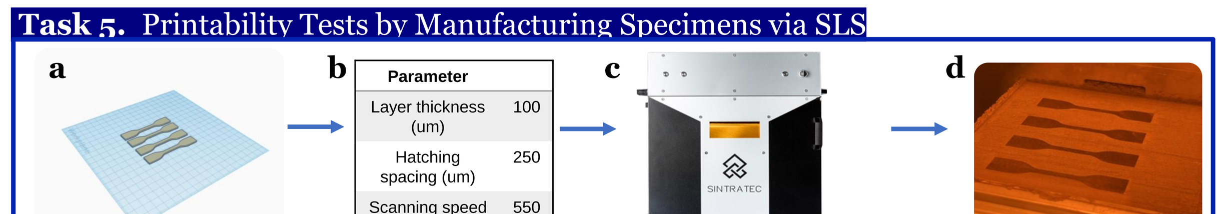

Figure 12. (a) Specimen design in Tinkercad, (b) Default values for parameters of interest, (c) Sintratec Kit SLS equipment, (d) Printing of PA12/SARG specimens.

RESULTS

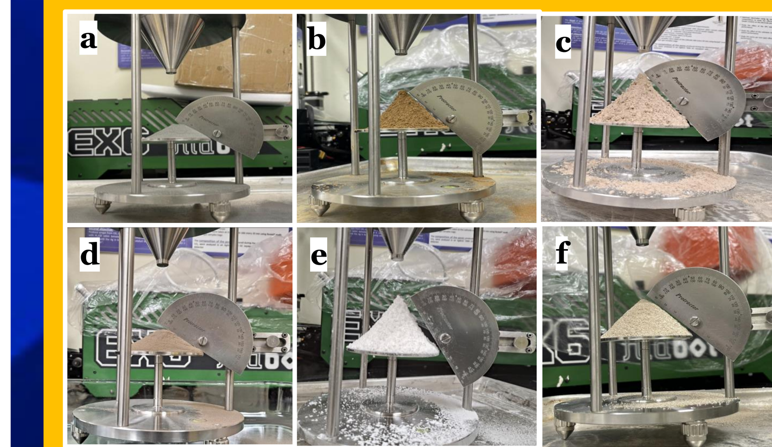

Figure 13. Angle of repose for (a) PA12, (b) sargassum, (c) PHBV/SARG powder feedstock, (d) PA12/SARG, (e) PHBV, (f) PHBV/SARG granulated feedstock.

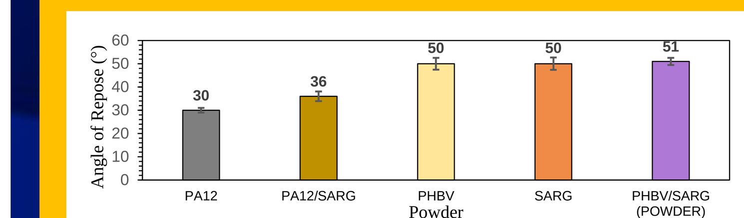

Figure 14. Angle of repose values for powders.

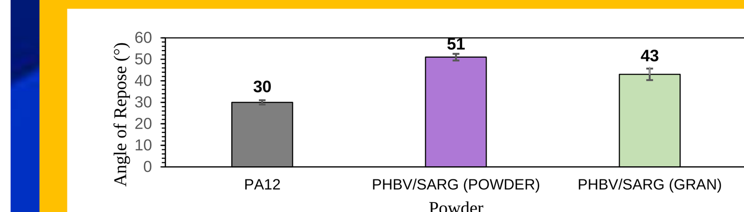

Figure 15. Angle of repose values for PA12 and PHBV/SARG powders, and PHBV/SARG granulated powder.

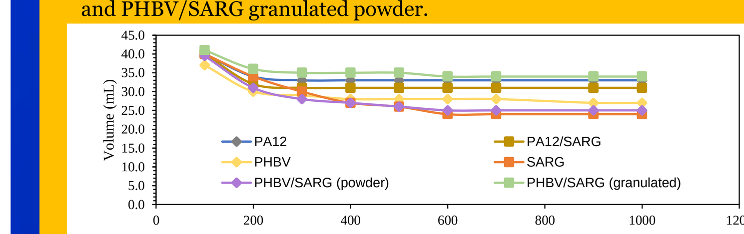

Figure 16. Volume change per 100 taps for all powders.

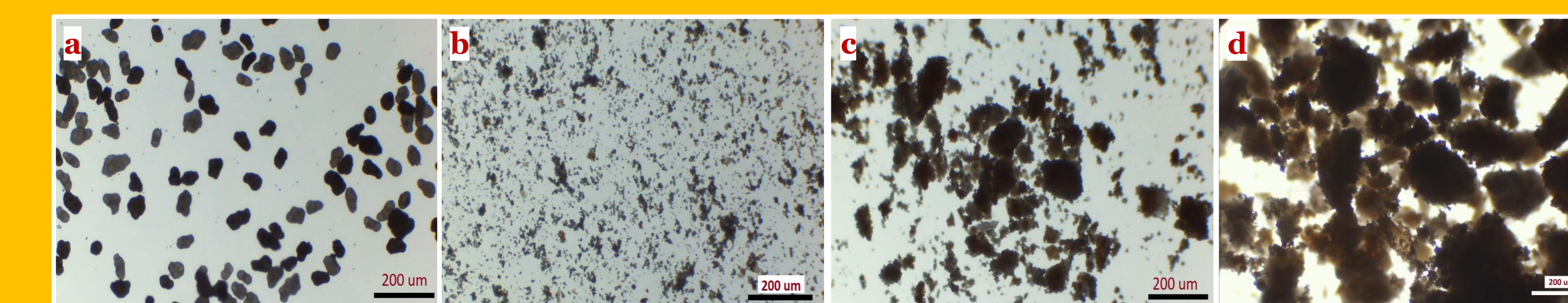

Figure 17. (a) PA12 powder at 4X, (b) PHBV/SARG powder feedstock at 4x, (c,d) PHBV/SARG granulated at 4X.

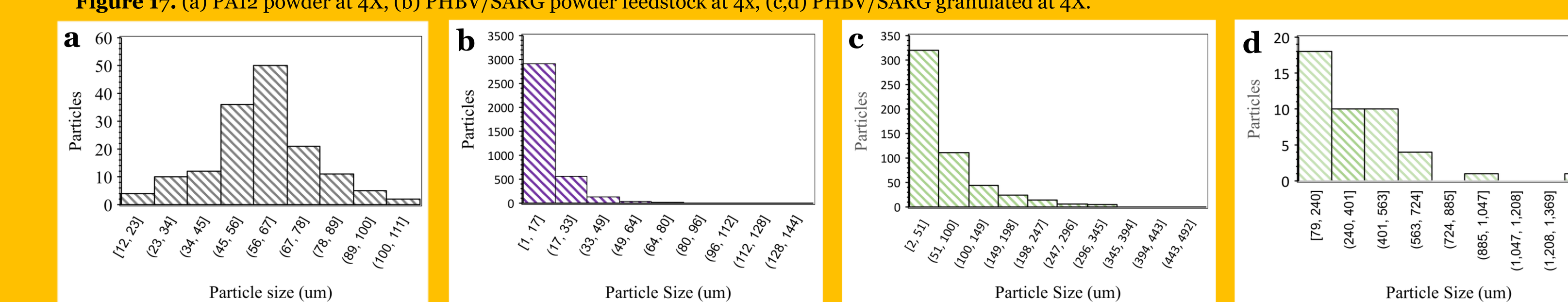

Figure 18. Particle size distribution for (a) PA12, (b) PHBV/SARG powder feedstock, (c) PHBV/SARG granulated feedstock.

Table 1. Angle of repose standard values for flow characterization

Angle of Repose	Flow character
<25	Excellent
25-30	Good
30-40	Passable
>40	Very Poor

Table 2. CRI and HR standard values for flow characterization.

CRI	Flow character	HR
1-10	Excellent	1.00 – 1.11
11-15	Good	1.12 - 1.18
16-20	Fair	1.19- 1.25
21-25	Passable	1.26 – 1.34
26-31	Poor	1.35 – 1.45
32-37	Very Poor	1.46 – 1.59
>38	Very, Very Poor	>1.60

Table 3. CRI and HR values for all powders.

Powder	Carr Compressibility Index (CRI)	Hausner Ratio (HR)
PA12	17.5	1.21
PA12/SARG	22.5	1.29
PHBV/SARG (Granulated)	17.1	1.21
PHBV/SARG (Powder)	36.7	1.58
SARG	40.0	1.67
PHBV	27.0	1.37

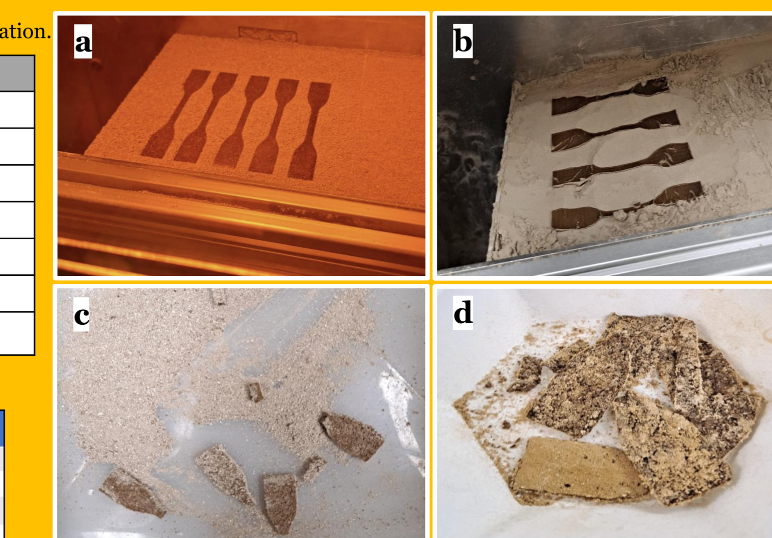

Figure 19. Printing specimens with (a) PHBV/SARG granulated feedstock, (b) PHBV/SARG powder feedstock. (c) Specimens with PHBV/SARG granulated, (d) with PHBV/SARG powder.

ONGOING & FUTURE WORK

- ✓ Determine the optimized equipment processing parameters to increase the sintering to enhance the mechanical stability of the fabricated composite specimens.
- ✓ Conduct annealing treatments on the manufactured specimens.
- ✓ Perform tensile and three-point impact tests on the specimens to characterize the mechanical properties.
- ✓ Examine the microstructure and biodegradability of the specimens via SEM and burial test.
- ✓ Experiment with more complex structures for SLS.

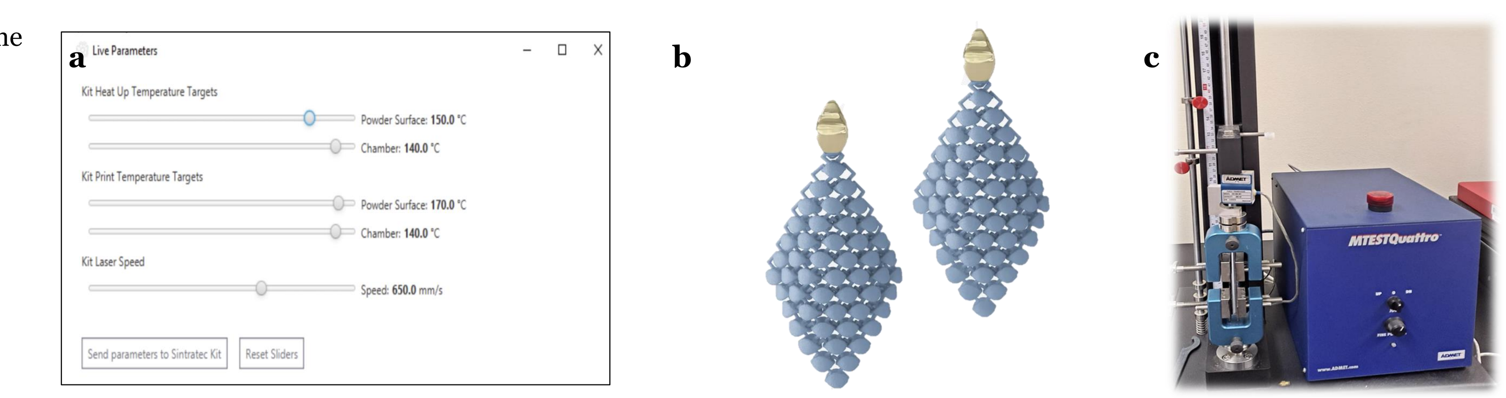

Figure 19. (a) Temperature adjuster from Sintratec software (sintratec.com,n.d.), (b) 3D printed earrings from Evonik (3daept.com, 2023), (c) MTESTQuattro equipment (Dr. Movil's Lab, 2022)

CONCLUSIONS

- ✓ It is necessary to optimize the powder/granule particle size and its distribution since large granule sizes impedes the sintering and fine powders exhibit flowability issues.
- ✓ The PHBV and Sargassum powders had the smallest particle size for all the used SLS feedstocks, which caused printability issues.
- ✓ The PHBV/Sargassum granulated feedstock exhibited features (repose angle, CRI, and HR) similar to PA12 (reference) , which improved both flowability and printability of the granule composites as comparted to the fine powders.
- ✓ A simple and cost-effective method for granulating powder feedstock for SLS was developed. However, it is necessary to optimize it to obtain granulated materials with homogeneous particle size distribution (like PA12).
- ✓ All the above indicate that Sargassum is promising bio-based material for applications in SLS 3D printing.

RECOMMENDATIONS

- ✓ Determine the thermal behavior for all powder feedstock via thermal analysis by TGA/DSC experiments.
- ✓ Examine the thermal heat effects on the flowability and mechanical properties of the powder and specimens, respectively.
- ✓ Controlling the particle size distribution for the PHBV/SARG granulated feedstock via using different binders and granulator meshes.
- ✓ Study the effects of either increasing sargassum content of the PHBV/SARG feedstock and the addition of additives like carbon black on the sintering of these composite granules.
- ✓ Study the biodegradability of these materials via respirometry.

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