From Brown Tides to 3D Printers: Fabrication & Characterization of Novel Sargassum-Based Polymer Composite Filaments for 3D Printing

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INTRODUCTION & BACKGROUND

Every year, mats of brown algae known as "Sargassum" drift along the seashores of most Caribbean islands. Among all the existing Sargassum species, Sargassum fluitans and Sargassum natans are the two most common in the Caribbean region. In terms of compositions (%w/w), these pelagic species are rich in carbohydrates (~57%), contrasting with microalgae which are rich in proteins (50 – 56 %).[1]

Over the last few years, the volume of floating Sargassum that arrives to the Caribbean beaches has been progressively increasing. In June 2018, researchers at the University of South Florida reported the record high amount of Sargassum (~20 million tons) detected on the surface of the Atlantic Ocean from the west coast of Africa to the Gulf of Mexico. More recently in June 2021, it was reported a Sargassum bloom that essentially had the same size of the record registered in 2018.[2]

What is driving the huge blooms?[3]

- Increment of fertilizer-derived nutrients in the Amazon river.
- Abnormal ocean currents and winds patterns linked to the global climate change.
- Occurrence of massive Sahara dust clouds moving over the Atlantic

Figure 1. Main causes of the algae bloom.

¿What is the impact of these events?[4]

¡Puerto Rico lacks directions to manage this issue!

Figure 2. The brown tides impact on the region.

Potential uses for Sargassum

Sargassum has the potential of being a valuable source for multiple industries including among others, pharmaceuticals, cosmetics, fertilizers, civil construction materials, and bioplastics.[5] However, applications for emerging fields like 3D printing have not been explored.

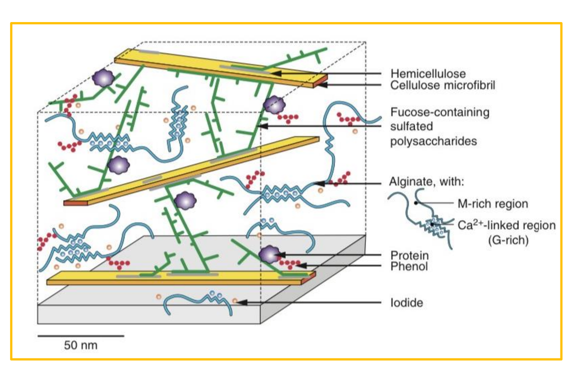

Figure 3. Cell wall model for Sargassum.[6]

Sustainable & innovative approach

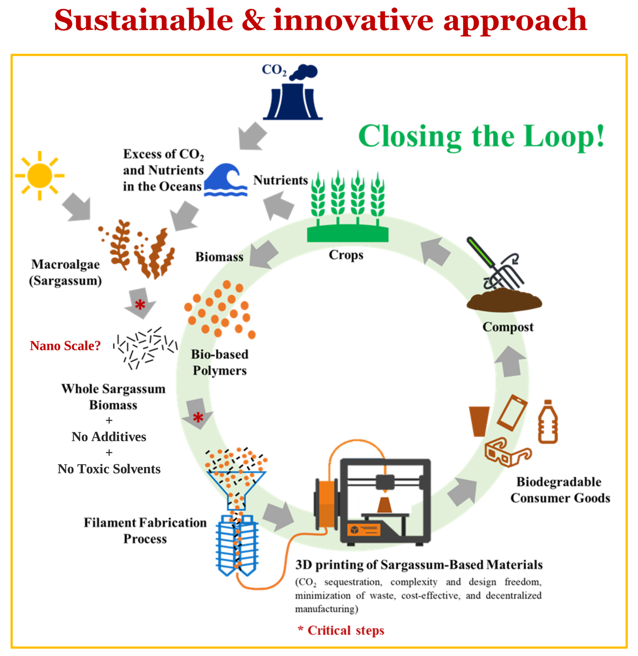

Figure 4. Proposed approach.

OBJECTIVES

This research project has three main objectives:

1. Establish the process conditions to fabricate Sargassum micro- and nano-powder from Sargassum collected from local beaches.
2. Study the effect of the Sargassum weight percent (wt%) on the printability, microstructure, and thermal & mechanical properties of the fabricated polymer composites.
3. Study the effect of the Sargassum weight percent (wt%) on the biodegradability of 3D printed specimens.

METHODOLOGY

Figure 5. Sargassum powder fabrication process.

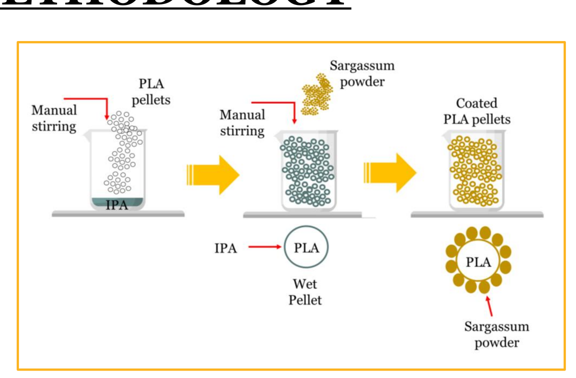

Figure 6. Coated PLA pellet fabrication process.

The temperatures of the extruder (chamber zones) were adjusted to fabricate each filament.

To reprocess the filaments, these were cut into small pieces, coated with additional Sargassum powder and then fed into the extruder to fabricate a new filament. The same process was repeated 2 times.

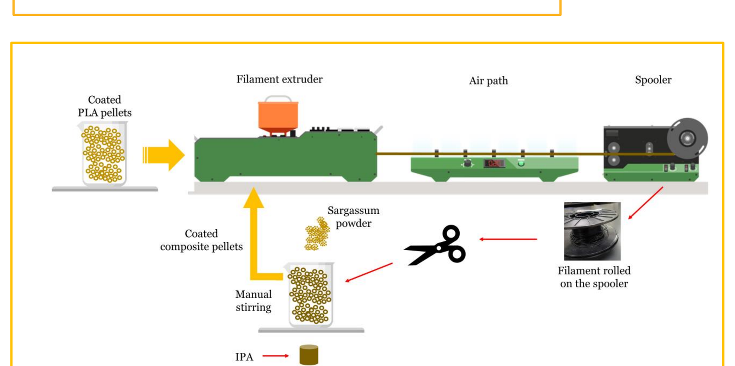

Figure 7. PLA/Sargassum composite filament fabrication process.

METHODOLOGY (Cont.)

The specimens were fabricated using a fused deposition modeling (FDM) 3D printer from Creality® equipped with a 1-mm nozzle set at 220°C, while the plate temperature was set at 60°C. The speed chosen for the 3D printer was 30 mm/s with a line pattern.

The thermal behavior, microstructure, and mechanical properties of the obtained composite materials were evaluated using TGA/DSC, SEM, and tensile test, respectively. To determine the mechanical properties, tensile tests were carried out using the ADMET tensile test machine following a modified ASTM D638-14 standard. TGA/DSC and SEM analysis were run at Rutgers University – Camden.

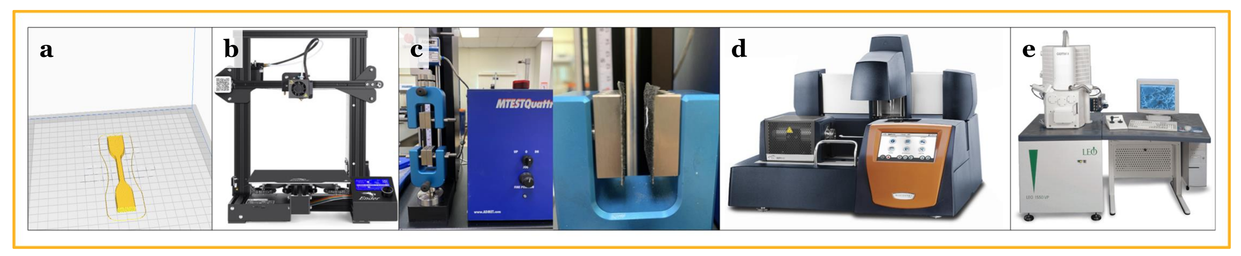

Figure 8. (a) Ultimaker Cura® software showing the created model, (b) Ender-3 Pro 3D Printer from Creality®, (c) tensile test machine with sandpaper attached to the grip surface to avoid slippage, (d) Discovery TA Series TGA and DSC, and (e) LEO scanning electron microscope (SEM) with X-ray for elemental analysis.

Degradation studies were performed via burial tests. In this case, a series of coin-shaped specimens were 3D printed, dried, and weighted before burying them in vases (placed outdoors) containing a suitable amount of homemade compost. 500 mL of water were added onto the surface of each vase weekly to maintain the compost wet. Samples were removed from the compost after 30, 60, 90 and 120 days. After cleaning and drying the samples, these were weighted to calculate the weight losses %.

Figure 9. Images of the burial tests.

RESULTS

Powder morphology and size (SEM Analysis)

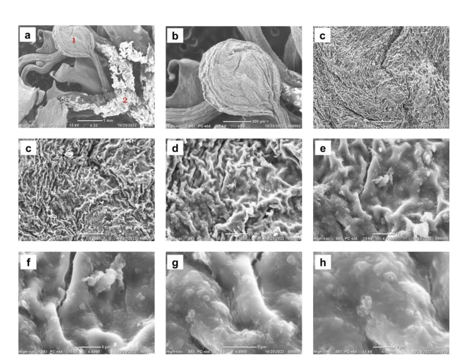

Figure 10. SEM images of dried Sargassum

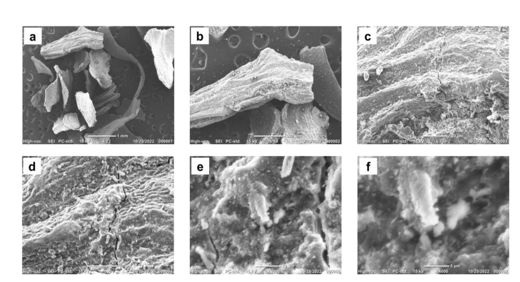

Figure 11. SEM images of dried Sargassum after grinding.

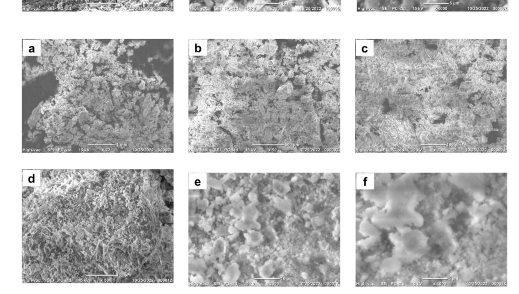

Figure 12. SEM images of dried Sargassum after grinding + ball milling.

Fabricated filaments & specimens

Table 1. Temperatures used to fabricate the filaments via extrusion.

Extruder Heat Zone	Sargassum powder content into the filament		
	0 wt%	5 – 20 wt%	25 – 30 wt%
I	160	160	165
II	170	180	185
III	120	170	175
IV	40	40	45

Figure 13. Images of some of the fabricated PLA/Sargassum filaments.

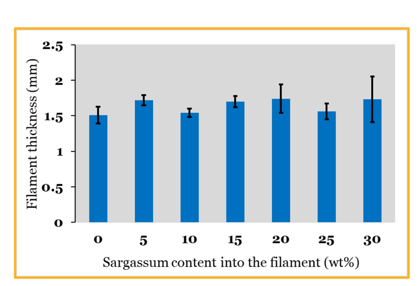

Figure 14. Thickness of the fabricated filaments.

Figure 15. Images of (a) a fabricated filament, (b and c) different dog- bone-shaped specimens for the tensile tests.

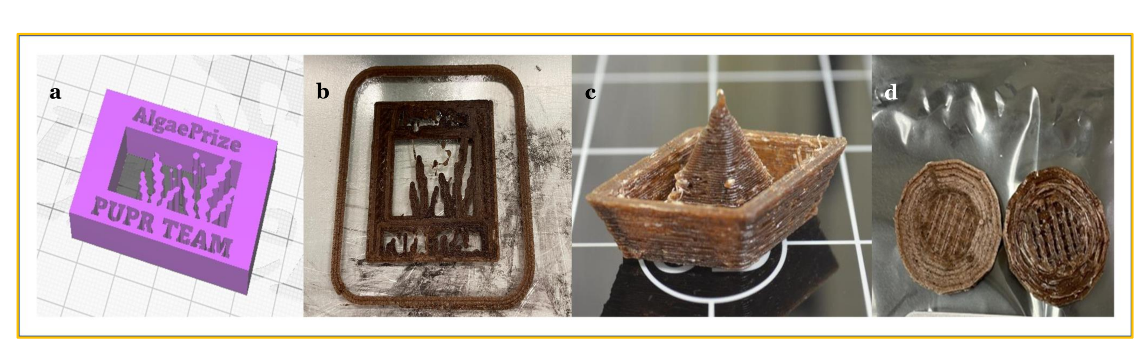

Figure 16. Structures fabricated with the filaments: (a and b) 3D model designed by computer and its corresponding 3D printed structure, (c) 3D printed origami boat, and (d) 3D printed coin-shaped specimens for burial tests.

Thermal analysis (TGA) for Sargassum powders and filaments

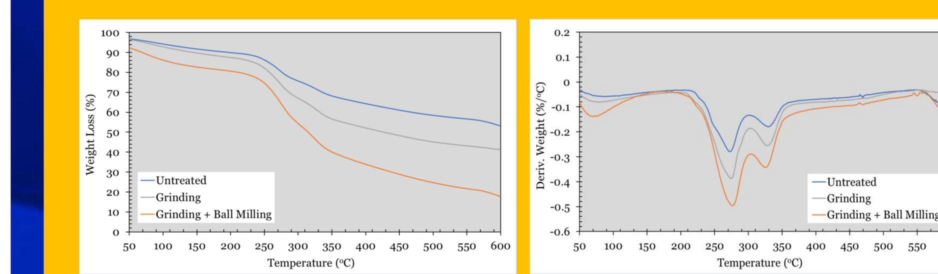

Figure 17. TGA analysis for dried Sargassum, grinded powder, and grinded + ball milled powder.

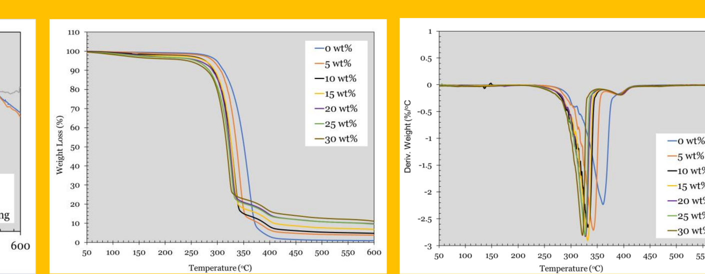

Figure 18. TGA analysis of the composite filaments.

Microstructure of the 3D printed specimens (SEM analysis)

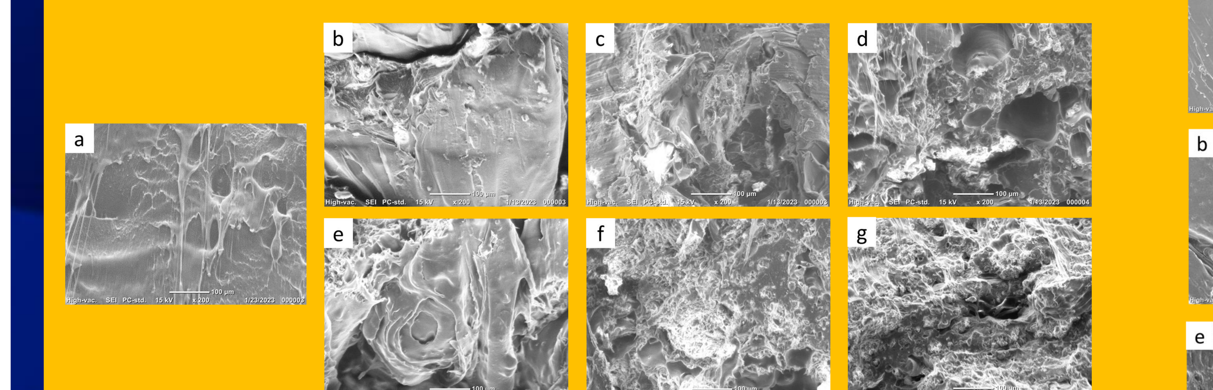

Figure 22. SEM images (fracture views) for 3D printed specimens having Sargassum powder contents of: (a) 0wt%, (b) 5wt%, (c) 10wt%, (d) 15wt%, (e) 20wt%, (f) 25wt%, and (g) 30wt%.

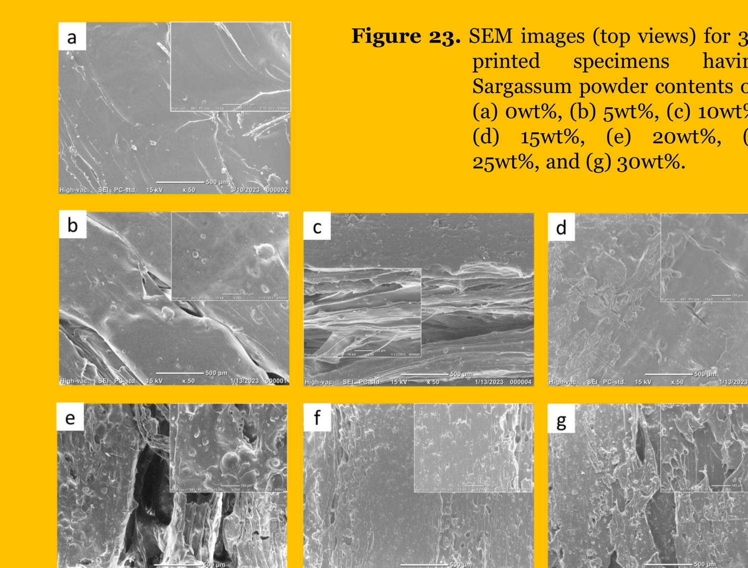

Figure 23. SEM images (top views) for 3D printed specimens having Sargassum powder contents of: (a) 0wt%, (b) 5wt%, (c) 10wt%, (d) 15wt%, (e) 20wt%, (f) 25wt%, and (g) 30wt%.

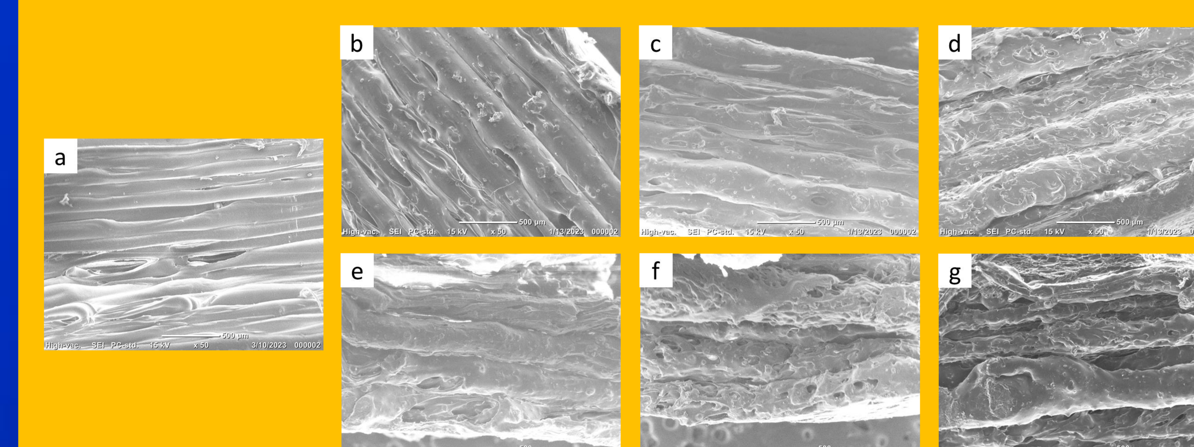

Figure 24. SEM images (side views) for 3D printed specimens having Sargassum powder contents of: (a) 0wt%, (b) 5wt%, (c) 10wt%, (d) 15wt%, (e) 20wt%, (f) 25wt%, and (g) 30wt%.

Mechanical properties of the 3D printed specimens

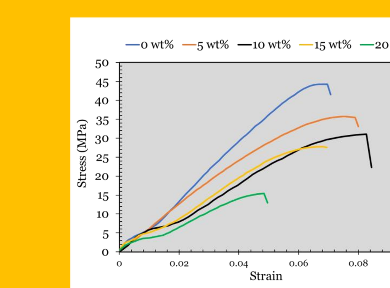

Figure 19. Stress-strain curves for specimens with different Sargassum contents (wt%).

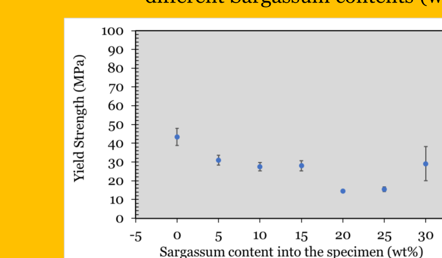

Figure 20. Yield strength as a function of Sargassum contents (wt%) into the specimen.

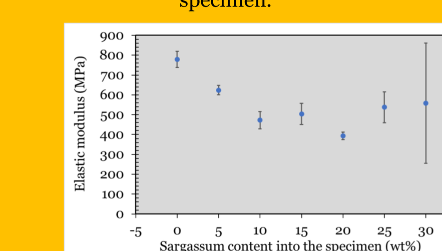

Figure 21. Elastic modulus as a function of Sargassum content (wt%) into the specimen.

Biodegradability of the 3D printed specimens

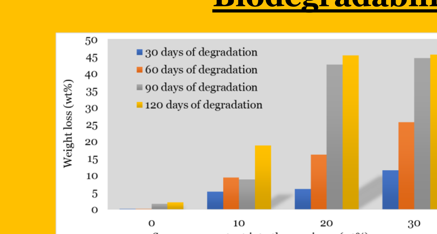

Figure 25. Specimen weight loss (%) as a function of the Sargassum content into the specimen (wt%) at different continuous degradation times (in days).

Figure 26. 3D printed specimen at 30 wt% of Sargassum at different degradation times: (a) 0 days, (b) 30 days, and (c) reburied for 30 additional days.

ONGOING & FUTURE WORK

Challenge: It has been impossible to fabricate consumer goods with filaments having the higher biomass content (30wt%) since these filaments are very brittle.

Proposed solution: Last month, the team received a new 3D printer that works directly with **pellets**. The machine is being used in a new approach that includes:

(1) Cutting the fabricated brittle filaments into pellets

(2) Using the solvent casting approach to fabricate Sargassum-based composite pellets

Fabricated pellets are then fed into the new 3D printer to fabricate consumer goods.

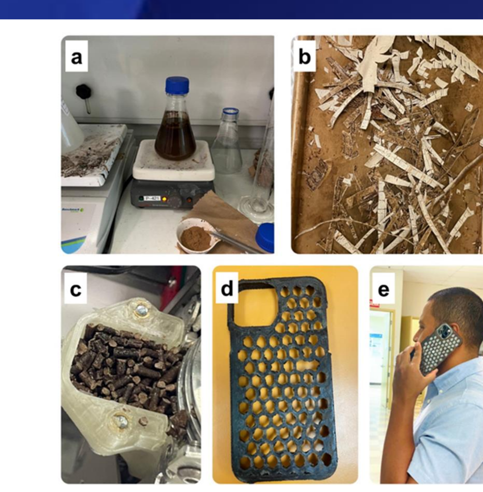

Figure 27. New implemented approach to produce composite pellets. (a,b) solvent casting method experiments, (c) obtained composite pellets having 30wt% Sargassum biomass content, and (d,e) 3D printed SargiCase fabricated with the pellets depicted in image c.

CONCLUSIONS

- Sargassum processed via ball milling exhibited fine particles. However, According to SEM analysis the particle size distribution is very broad (microns). TEM analysis is required to observe the nanosized particles.
- Sargassum powder/PLA composite filaments were fabricated via extrusion. The biomass content varied in the range between 0 wt% (pure PLA) to 30 wt%. Importantly, the results suggest the good reprocessability of these novel composites, since the filaments were extruded three times.
- Filament thickness variability increased with the biomass content, which had effects on the quality of the 3D printed specimens and their mechanical properties.
- The elastic modulus and yield strength of the 3D printed specimens exhibited a declining trend as the Sargassum content into the PLA polymer matrix increased from 0 to 20wt%. These results are supported by the SEM analysis that shows that the number of defects and surface roughness increases with the biomass content. These defects are usually associated with poor mechanical behaviors.
- At higher filler contents the variability in the elastic modulus was significant, making it difficult to draw precise conclusions. This variability is supported by the inhomogeneities, and defects observed in the microstructure of specimens with high Sargassum contents. The yield strength results followed a similar trend.
- Burial test results suggest that the weight loss (wt%) of the fabricated specimens increases ~4.5 times as the biomass content increased from 0 to 30wt% (after 120 days).

RECOMMENDATIONS

- Study the effect of increasing the ball milling time on the sargassum particle sizes and their distribution.
- Study the changes in chemical structure and composition of Sargassum during the powder fabrication process.
- Modify the surface of the Sargassum particles to make this material more compatible with PLA.
- Perform biodegradation experiments in controlled chambers to study the effect of temperature and humidity on the degradation rates of these novel materials. Also, confirm changes in their chemical structures via FTIR.
- Explore the use of different polymer matrices such as Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), Polycaprolactone (PCL), and Acrylonitrile butadiene styrene (ABS).
- Study life cycle environmental impact of these novel 3D printing composite materials.

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