From Brown Tides to 3D Printers: Additive Manufacturing of Novel Algae-Based Polymer Composites

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ABSTRACT

As a direct effect of ocean warming and nutrient enrichment, tones of a brown macroalgae known as Sargassum, have been accumulating on shores throughout the Caribbean region since 2011. These unprecedented annual events have been detrimental to marine ecosystems, human health, and economy of coastal communities.

In the search for new applications of Sargassum biomass, the present work aimed to explore the use of this seaweed as a raw material for the fabrication of renewable powder that was incorporated into polylactic acid (PLA) composite filaments to 3D print different specimens. The mechanical properties of the resulting structures were evaluated via tensile tests, while studies of biodegradability were performed using burial tests.

The results indicate that it is possible to fabricate filaments with Sargassum powder contents up to 30 wt%. However, the required extrusion temperatures and the brittleness of the filaments increase with the Sargassum content. Also, 3D printing of these composite materials required nozzles with sizes ≥1 mm to avoid clogging.

Regarding the mechanical properties of the specimens, both the elastic modulus and yield strength exhibit a declining trend as the Sargassum content into the PLA polymer matrix increase.

As expected, preliminary studies of biodegradability suggest that the composite degradation increases significantly with the Sargassum content. Samples having 30 wt% of Sargassum exhibited weight loss % of 25.6, after 60 days of being buried into a compost at ambient temperature. Additional experiments are required to gain evidence of accelerated biodegradation at ambient conditions of the PLA conforming the 3D printed structures.

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!

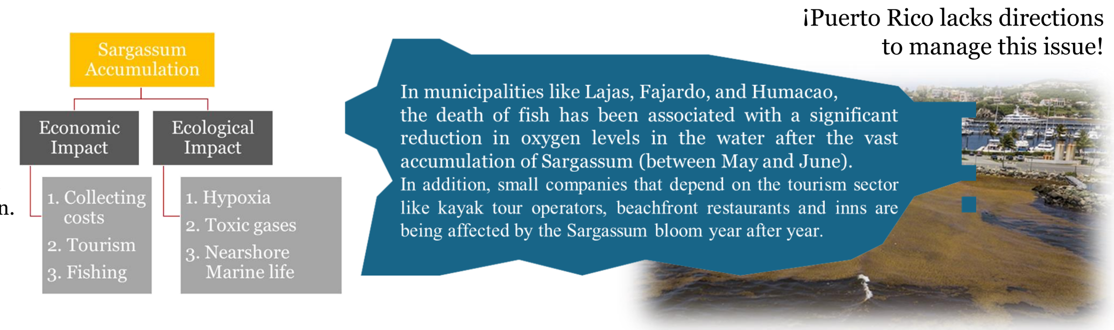

Figure 2. The brown tides impact on the region.

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.

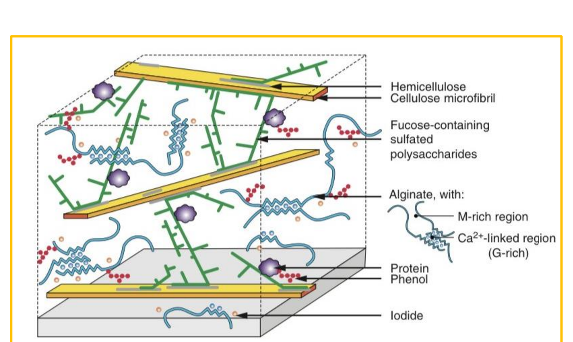

Figure 3. Cell wall model for Sargassum.[6]

Sustainable & innovative approach

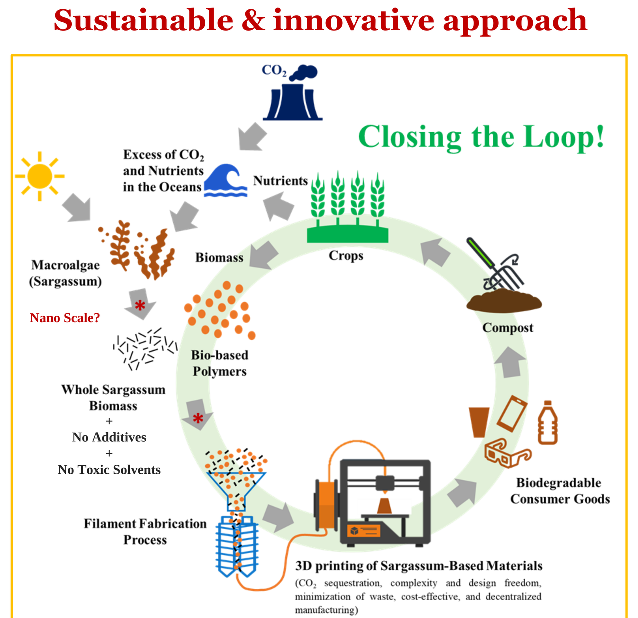

Figure 4. Proposed approach.

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.

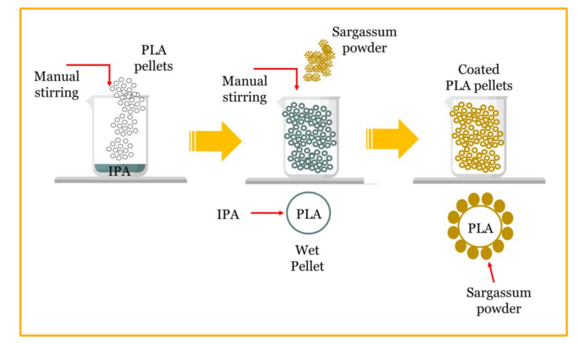

Figure 6. Coated PLA pellet fabrication process.

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.

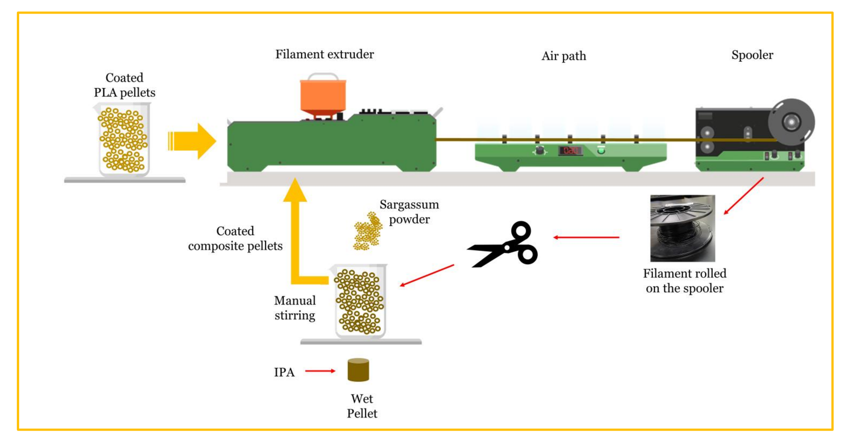

Figure 7. PLA/Sargassum composite filament fabrication process.

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 standards. TGA/DSC and SEM analysis were run at Rutgers University – Camden.

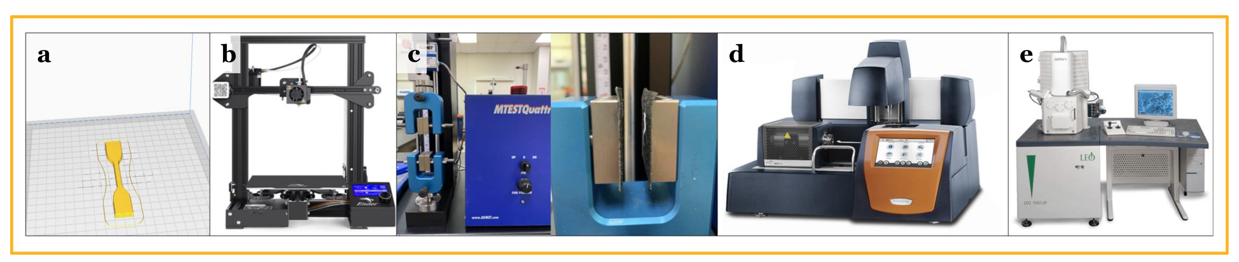

Figure 8. (a) Ultimaker Cura® software showing the created model, (b) Ender-3 Pro 3D Printer from Creality®, (c) tensile test machine with sandpaper attached to the grip surface to avoid slippage, (d) Discovery TA Series TGA and DSC, and (e) LEO scanning electron microscope (SEM) with X-ray for elemental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

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 10. (a) Images of some of the fabricated PLA/Sargassum filaments.

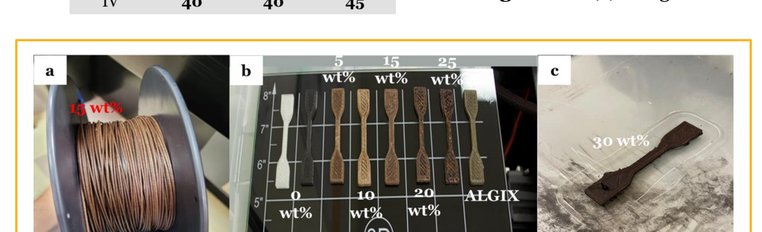

Figure 11. Images of (a) a fabricated filament, (b and c) different dog- bone-shaped specimens for the tensile tests.

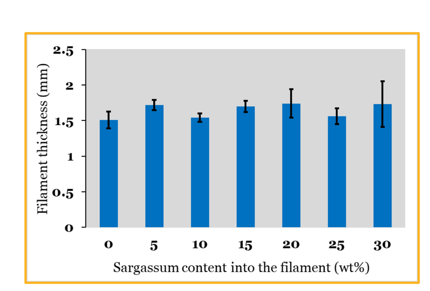

Figure 12. Thickness of the fabricated filaments.

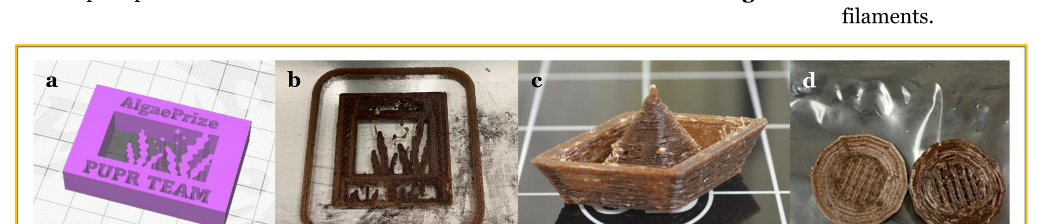

Figure 13. Structures fabricated with the filaments: (a and b) 3D model designed by computer and its corresponding 3D printed structure, (c) 3D printed origami boat, and (d) 3D printed coin-shaped specimens for burial tests.

RESULTS (Cont.)

Mechanical properties of the 3D printed specimens

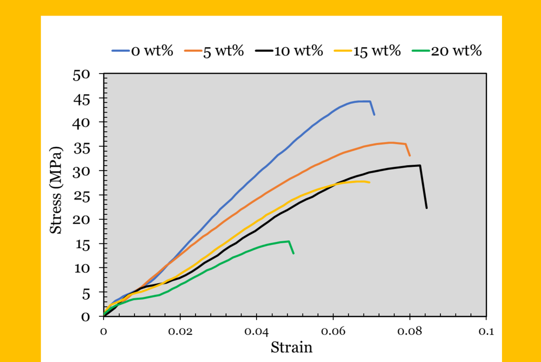

Figure 14. Stress-strain curves for specimens with different Sargassum contents (wt%).

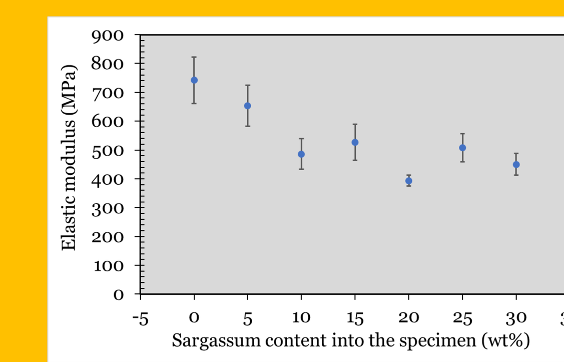

Figure 15. Elastic modulus as a function of Sargassum contents (wt%) into the specimen.

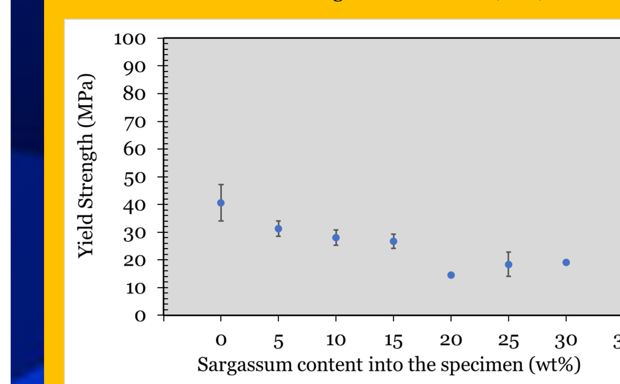

Figure 16. Yield strength as a function of Sargassum content (wt%) into the specimen.

The mechanical properties of the fabricated composites exhibit a declining trend as the filler content increases, probably because:

- Aggregation of Sargassum particles, which could create voids and defects into the sample.
- The variability of the filament thickness at high Sargassum contents could result in printed layers with a rougher surface and, which promotes the formation of undesired air gaps into the specimens. Further analysis is required (SEM).

Biodegradability of the 3D printed specimens

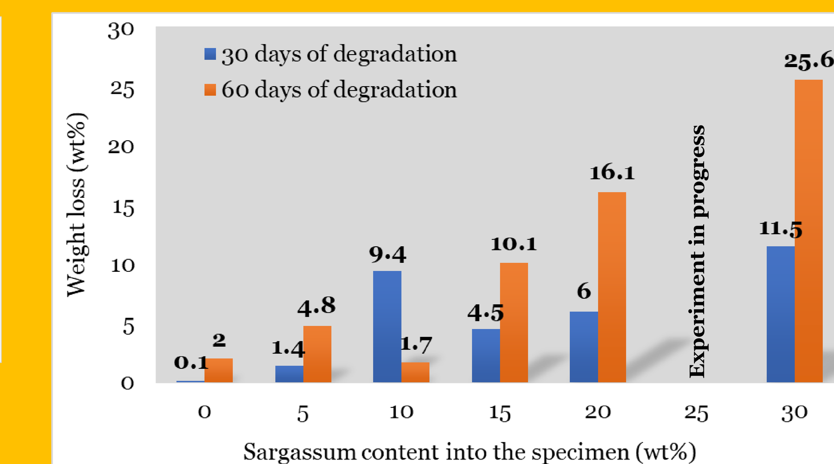

Figure 17. Specimen weight loss (%) as a function of the Sargassum content into the specimen (wt%) at different continuous degradation times (in days).

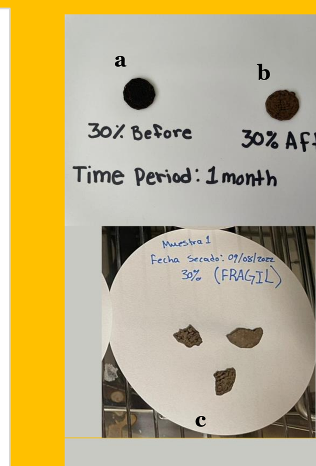

Figure 18. 3D printed specimen at 30 wt% of Sargssum at different degradation times: (a) 0 days, (b) 30 days, and (c) reburied for 30 additional days.

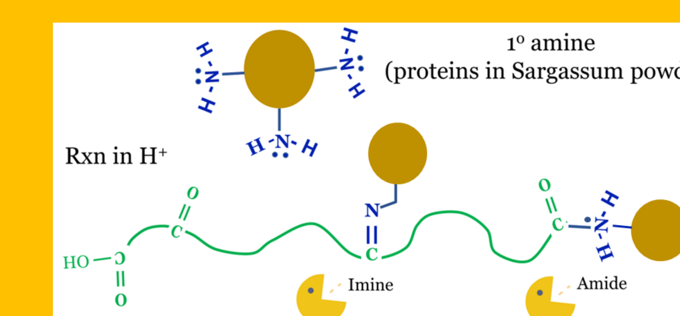

Figure 19. Proposed biodegradation mechanism. The green chain represents PLA polymer.

OUTREACH ACTIVITIES

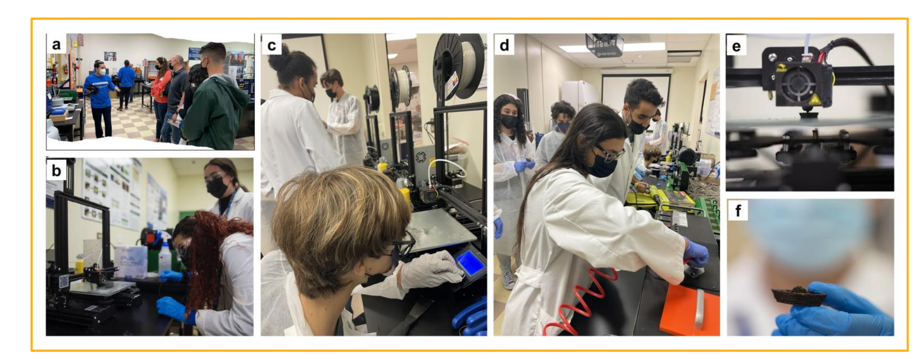

Figure 20. Outreach activities performed for the PUPR research scholars.

Figure 20 shows some PUPR research scholars and AlgaePrize team members interacting with students and parents during the 2022 PUPR Chemical Engineering Summer Camp. (a) algal innovators talking to a family attending one of the sections, (b) research scholars supervising a 3D printing process performed by a participant, (c) high schooler using the fabricated filaments to 3D print structures, (d) research scholars assisting the high schoolers to fabricate Sargassum-based filaments, (e) origami boat printing process performed during the camp, and (f) one of the students presenting his final product.

ONGOING & FUTURE WORK

- Complete the burial tests (four additional months) and repeat some tensile test experiments.
- Study the thermal behavior of the fabricated materials using TGA/DSC analysis.
- Study the microstructure and quality of the fabricated specimens via Scanning Electron Microscopy (SEM).
- Measure the melt flow rate index of the fabricated filaments (XNR-400B Tester for polymer plastics).
- Stablish the relationship between processing, microstructure, and materials properties of 3D printed specimens made from Sargassum-based filaments

CONCLUSIONS

- Sargassum processed via ball milling exhibited fine particles. However, it is necessary to evaluate the material via SEM to confirm the presence of nanopowder.
- 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 this novel composites, since the filaments were extruded three times.
- Filament thickness variability increased with the biomass content, which could have effects on the mechanical properties of the 3D printed specimens.
- 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. SEM analysis is required to confirm defects and Sargassum aggregation into the polymer matrix.
- Preliminary results of the burial test suggest that biodegradability increases significantly with the biomass content, which could represent a significant contribution toward a more sustainable additive manufacturing field.

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.
- Implement the use Pellets 3D printing machines to fabricate specimens with higher contents of Sargassum (up to 70 wt%).
- Modify the surface of the Sargassum particles to make this material more compatible with PLA.
- Implement the use of biodegradable compatibilizer to enhance the interaction between Sargassum and 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.

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ACKNOWLEDGMENTS

We would like to thank:

- URP-HS for providing the required funding (title III award P031S210139).
- Dr. David Salas for contributing to this research project with SEM and TGA/DSC analysis.
- SSMART LAB former students: Nelson Rodríguez, Ambar Rivera y Carlos Landrau for the proof-of-concept experiments.
- U.S. Department of energy for: (1) providing the resources to acquire some piece of equipment, and (2) sponsoring the PUPR team's travel to participate as finalists at the AlgaePrize competition to be held at the National Renewable Energy Laboratory (NREL) in Boulder – Colorado in April 2023.