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# Direct Ink Write and Processing of Complex 3D Marine Compatible Structures with Calcium Carbonate Slurries

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# Direct Ink Write and Processing of Complex 3D Marine Compatible Structures with Calcium Carbonate Slurries

Laurie Jin, Bruce Yang, Beck Walton, Rick Hynes, Xavier Mayali

## Abstract

Ocean acidification heavily impacts marine ecosystems by reducing calcification. Many coral-algae symbiotic relationships are in jeopardy due to the destruction of coral reefs. Here, a ceramic ink compatible with the direct ink write additive manufacturing technique was formulated and used to print marine compatible structures that could grow algae and restore that relationship. A diacrylate polymer was mixed with calcium carbonate, a material that comprises a coral skeleton, to create a slurry with shear thinning properties. Rheology studies were conducted to confirm printing properties and characterize the slurry. Printed parts demonstrated strong control over print features, including size and infill design. Various infill patterns and percentages were attempted to optimize printability and potential algae growth. Thermogravimetric analysis helped determine a logical burnout and sintering procedure to avoid large cracking. This project developed a printable and sinter-able calcium carbonate ceramic slurry for complex marine-compatible structures and algae growth. This research was conducted in the support of the Eco Reef project.

## 1. Introduction

Coral reefs play an integral part in marine ecosystems. They serve as a habitat for marine animals and protect coastlines from strong waves, reducing the impact of storms and erosion. Over the past 25 years, climate change has killed off many coral ecosystems, including over 80% of the Caribbean's coral ecosystem and 50% of Australia's Great Barrier Reef.[1] Ocean acidification has significantly reduced calcification—the process where corals build up their skeletons using calcium carbonate ($CaCO_3$)—by 40%. Acidification has also weakened many mollusks, crustaceans, and echinoderms.[2] This destroys ecosystems and cohabitating relationships, including the symbiotic relationship between coral and algae. Corals provide a protective environment that allows algae to photosynthesize, and algae provide coral with food and oxygen.[3] Research in combating the impact of climate change on marine animals is vital to preserve current marine ecosystems.

The direct ink writing (DIW) printing technique allows for a multitude of materials (ceramics, polymers, food, etc) to be 3D printed into complex shapes by dispensing material onto a build plate layer by layer. These printing systems can print structures made up of $CaCO_3$ that support algae growth. Fabricating complex calcium carbonate structures can help revive marine ecosystems by introducing healthy algae growth into the system, subsequently promoting coral growth in these areas.

Previous research explored the feasibility and advantages of creating an artificial reef using various printing techniques.[5,6] The printed systems create a viable habitat for many reef-dependent species. However, most studies use FDM printing with PLA or other materials that do not degrade well in the natural environment.[5] Printing corals with biomimetic material has only been done on a single digit millimeter scale.[7] We developed a replicable biodegradable ink formula, printing technique, and post processing procedure to create coral-like structures that can help restore dying reef ecosystems.

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## 2. Methods

### *2.1 Ink Formulation*

Printing ink primarily comprises of a mixture of fine (9-40 nm) and coarse (≤ 50 um) $CaCO_3$. Scanning Electron Microscopy (SEM) verified the reported particle size of the ceramic powders. A 1:1 ratio of fine to coarse $CaCO_3$ was used to maintain surface roughness while mitigating clogging risk. Previous studies have found that poly(ethylene glycol) diacrylate (PEGDA) is an effective biocompatible binder for printable slurries.[8] Ceramics were mixed with PEGDA at 42 vol %. Luperox (L231) thermal initiator and lithium fluoride (LiF) were added at 1.4 vol% and .7 vol% respectively to help the process the printed ceramics. A separate formulation with UV curing properties also includes .5 vol% of Speedcure TPO-L photo initiator. All products were purchased from Sigma Aldrich, except the nano $CaCO_3$ and TPO-L, which were from Sky Spring Nanomaterials and Arkema respectively.

Intermediary mixing steps were done with a planetary centrifugal Thinky mixer at 2000 rpm for 30-60 seconds. Extensive milling after mixing the ink components is required to break apart ceramic conglomerates and prevent clogging during printing. A previous ceramic printing study found that using mixing media in an acoustic mixer for 3 hours at 70-g force would be most effective in breaking up agglomerates.[8] The ink was mixed with 4.75mm diameter steel mixing media before being loaded into 30cc Nordson EFD syringes and centrifuged to remove air bubbles.

### *2.2 Ink Characterization*

The ink's rheological properties were measured on a Discovery Hybrid Rheometer (TA Instruments) to understand and verify its printing properties. Inks were pre-sheared at 1 rad/s for 30 seconds and soaked for 100 seconds prior to measurement. The ink viscosity was measured against shear rate ramping from 1 to 100 $s^{-1}$. Oscillatory amplitude sweeps were used to measure the storage and loss modulus of the ink; the main point of interest being the crossover yield stress point. Stress measurements were taken between 0.001 and 200 strain %. Both sweeps were conducted with a 400 um gap between 25mm parallel plates.

### *2.3 Direct Ink Writing*

Printing was done with a custom gantry system with a volumetric extrusion system. A stepper motor-controlled screw attached to the piston at the top of the syringe. The syringe was loaded into a metal sleeve and connected to clear PVC tubing with a 1/16 in inner diameter using luer lock connectors. The other end of the tube connected with the printing tip that clamped into the gantry's single-material configuration. 18 and 20 gauge (.84mm and .61mm inner diameter) Nordson EFD SmoothFlow Tapered Dispense Tips and General Purpose tips were used during printing depending on structure size and desired precision. Bed movement speed ranged from 10-20 mm/s depending on part complexity and UV curing. Ramp rate and acceleration limits ranged from 50-300 $mm/s^2$ and 100-700 $mm/s^2$ respectively depending on part complexity. The printer extruded onto alumina or glass bed plates, nonporous materials that prevent drying mid-print. G-code for the structures was either hand written or sliced with Cura Slicer.

During printing experiments with heat curing, a heat gun was held 3-6 inches away from the print bed and set to heat at approximately 200°C. During printing experiments with UV curing, three lights were attached to the printer and shined 365 nm waves towards the end of the nozzle.

A rubber casing was attached to the nozzle to prevent curing inside of the plastic section of the nozzle. The following shapes were printed: lattice structure cubes, varied gyroid infill cubes, 100% concentric infill corals, varied lines infill corals. Infill patterns depended on likelihood of algae growth in the structure; factors considered include effective sunlight penetration, structural strength against the ocean, and protection offered to organisms.

### *2.4 Post Processing*

Ceramics must be cured, burned out, and sintered to remove all organics and other contaminants. Printed structures were cured at a ramp rate of 1°C/min to 150°C and held for one hour in a Vulcan Oven. Thermogravimetric analysis (TGA) of cured samples on a was used to determine a logical procedure for burn out and sintering. Samples were heated from room temperature to 550°C at 5°C/min and held for 100 minutes before cooling. Additionally, various post processing ramp rates and holding times were attempted to hone the best procedure that avoids significant cracking.

## 3. Results and discussion

### *3.1 Ink Rheology*

The viscosity of the ink decreases as the shear rate increases, indicating shear thinning properties. This allows material to flow smoothly it is pushed through the print nozzle under high shear stress. Once the material is laid down, it will maintain its shape on the build bed in the absence of shear. Shear thinning properties are key to creating successful prints with direct ink writing systems. The storage and loss moduli of the ink offered more insight into the elastic and viscous behavior of the material. The crossover point (or yield stress) is approximately 1200 Pa. Some small agglomerates were still present after the pre-shear procedure, resulting in an irregular modulus curve.

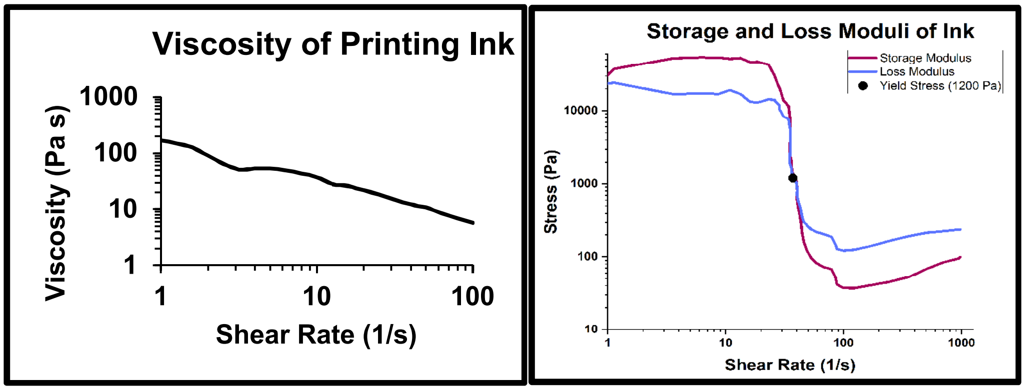

*Figure 1: Viscosity (left) and Moduli (right) measurements of CaCO$_3$ ink.*

### *3.2 Direct Ink Writing*

Initial printing attempts faced issues with poor layer adhesion and sagging or collapse of overhang parts due to sudden bed movements from acceleration. Tapered tips prevented clogging risk. Ink used did not include photo initiator. Ramp rate and acceleration limits were originally set to their defaults at 300 and 700 mm/s$^2$. Decreasing the acceleration limits and ramp rates to 100 and 150 mm/s$^2$ respectively reduced shaking and allowed for more stability. However, this also resulted in over extrusion of ink, especially at curved points of a print. Additionally, large uncured prints sagged after printing and were extremely difficult to transport without shifting the sample.

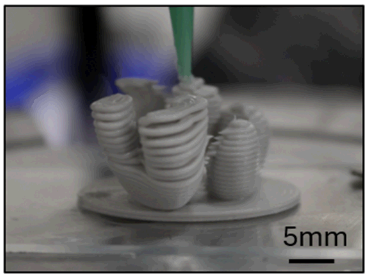

*Figure 2: Layer adhesion issues.*

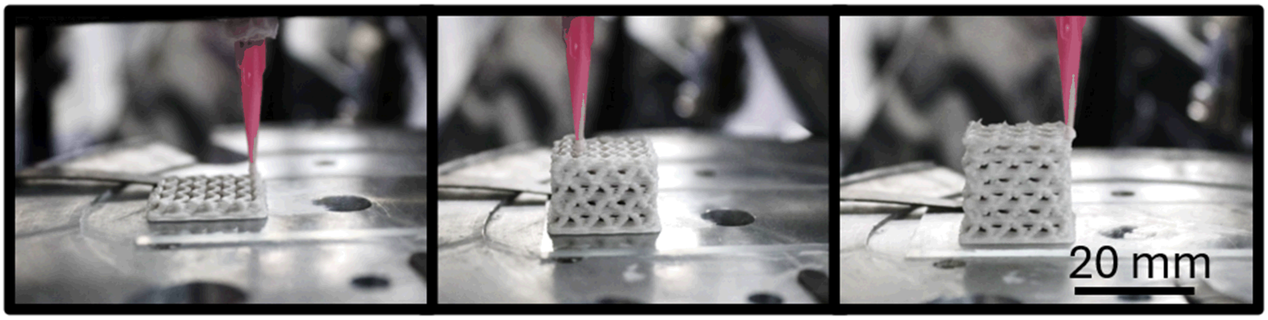

*Figure 3: Progression of printing; intermediary UV curing by hand stabilized the print.*

To increase stability with the ink properties available, a heat gun was used to partially cure material in situ. The heat gun was pointed approximately 3-6 inches away from the print plate depending on location and size of the print. It heated the bed at 200°C. While this solution significantly reduced overhang sagging, it required a lot of human precision. The heat gun had a 2 inch outlet; too much upward heat could warp the plastic nozzle; uneven curing resulted in parts shifting during the print. This was not a permanent solution.

A more permanent solution offered was UV curing. Three 365 nm wavelength lights were pointed towards the bottom of the nozzle. General purpose dispensing tips replaced the tapered ones as the metal prevented ink from being cured too early. A rubber sleeve protected the plastic component of the nozzle. Printing attempts with photo-initiable ink determined that 2-3% intensity would be suitable to sustain long prints. Curing occurred 5-10 seconds after extrusion and acceleration limits were reverted back to their default numbers to remove over extrusion issues.

*Figure 4: DIW prints with (left to right) in situ UV cure, in situ heat cure, no in situ curing. Uneven heating of part resulted in print shifting.*

### *3.3 Post Processing*

Thermogravimetric analysis determined that the largest mass loss of cured samples is between 250 and 390°C, with an additional 5% drop from 420-450°C. Samples burned out at

1°C/min to 250°C at a 2 hour hold and then .2°C/min to 450°C at a 4 hour hold. Two burnout steps were required to avoid sudden mass loss that could result in cracking. Samples sintered at .5°C/min to 550°C at a 4 hour hold. Cracking significance varied depending on part porosity. Coral shapes printed with 100% infill required a much slower post processing procedure than cubes with 30% gyroid infill as there is more material to burn out and less surface area in the part. Samples shrunk linearly by about 30% during the procedure, with a majority of shrinkage occurring during the sintering process.

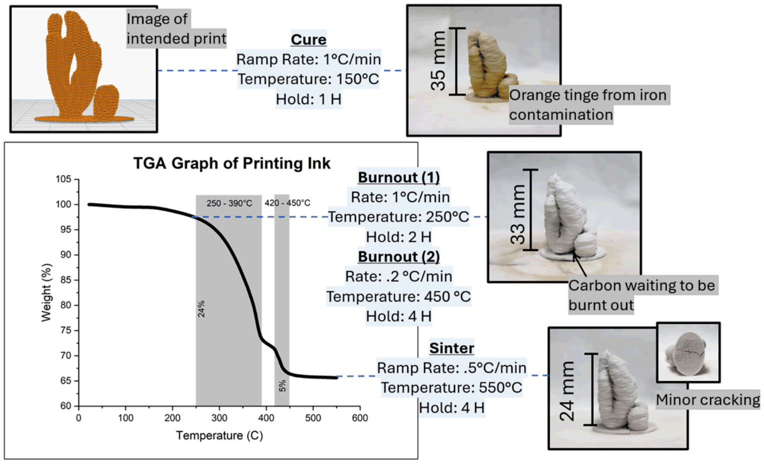

*Figure 5: TGA data and post processing procedures graphic.*

## 4. Conclusion

Direct ink writing of calcium carbonate slurries is a reliable way to produce structures that have capabilities to grow and house algae. All printed results are easily replicable with other direct ink writing systems with UV light curing capabilities. Calcium carbonate slurries are printable at 42 vol% loading with PEGDA. The printed structures demonstrate effective control of part features. Burnout of $CaCO_3$ parts occur between 250 and 450°C. Sintering occurs at 550°C. Direct ink write of $CaCO_3$ is best done with UV curing at 2-3% intensity.

More work should be done to continue optimizing DIW of $CaCO_3$ for marine applications. Minor material build up at the nozzle tip can interrupt ink flow and damage infill patterns. Printed structures are also too small to create a significant impact on most reef ecosystems. Additionally, the material has not been tested and verified to be ocean safe. Next steps include printing more complex geometries with varied infill patterns and experimenting with various z-heights to remove build up issues while maintaining structural integrity. While thermogravimetric analysis confirmed that there are no more burnable organics after the sintering process, x-ray diffraction should be conducted to determine the makeup of final parts. This will ensure that there are no marine-toxic materials remaining in the sample. Additionally, it may be beneficial to explore formulations with bio-based or biodegradable binders and initiators as an eco friendly alternative to the current organics, especially Luperox and TPO-L.

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