CAAP Annual Report

Date of Report: *October 7, 2019*

Contract Number: *693JK31850009CAAP*

Prepared for: *U.S. DOT Pipeline and Hazardous Materials Safety Administration*

Project Title: New Bio-Inspired 3D Printing Functionalized Lattice Composites for Actively Preventing and Mitigating Internal Corrosion

Prepared by: *North Dakota State University*

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For quarterly period ending: *October 7, 2019*

Business and Activity Section

(a) Generated Commitments

No changes to the existing agreement

Purchase made for the nano-materials, and the 3-D printable polymers

Conference posters: Dr. Lin will attend and present their work on the poster sections for 3D printing lattice structures ("*Wettability properties of 3D printable polymers and 3D printed structures for engineering applications*") in national conference 2019 Defense TechConnect Innovation Summit in National Harbor, MD on Oct. 8-10, 2019

(b) Status Update of Past Quarter Activities

The research activities in the annual report aimed to summarize the work in Tasks 2 and 3 through early reports and additional work in this quarter period, as summarized below.

(c) Cost share activity

Cost share was from the graduate students' tuition waiver.

(d) Summary of detailed work for Tasks 2 and 3

1. Background and objectives in the annual report

The 3rd quarter demonstrated that we screened the current polymers as candidates for 3D printable materials, including acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polyamide (PA), polycarbonate (PC), polyethylene terephthalate (PETG), polypropylene (PP), polyoxymethylene (POM), Thermoplastic Polyurethane (TPU), and high impact polystyrene (HIPS). We characterized their wetting capability using the criteria of the measured contact angle. Clearly, the bulk printed flat surface had the low contact angles of water to the specimens, from 40 to 60 degrees, while the contact angles of hexadecane were even lower, about 0~20 degrees. The 3D printing lattice structures were selected due to its high porosity, controllability of pore size and excellent mechanical property. Clearly, the desirable wettability capability will be controlled and optimized based on the functionalization of the 3-D printed polymeric materials. Thus, this quarter report aimed to address this challenge along two directions.

1.1 Objectives of the report

The objectives of the research work in this report included:

a) Summary of the design, fabrication, and characterization of 3D printing materials and lattice structures.
b) Summary of synthesis of the materials for treatment of 3D printing structures.
c) Different pore sizes and two types of lattice orientations were fabricated.
d) Mechanical property of the lattice structures, including tension and compression behavior, were characterized.
e) New test setup for the 3D printing lattice was fabricated.
f) Further surface modification was investigated.
g) Microstructure of 3D printing lattice structures was investigated.

2. Experimental Program

2.1 Design and fabrication of 3D printing lattice structures

As stated in the 3rd report, this section aimed to summarize the concept of 3D printing and fabrication processes used for lattice structure design and characterization, including the pattern of the lattice structures. Porous cellular or lattice structures have been receiving considerable attention as an alternative solution/culture of lightweight design and new materiality. They possess some exceptional characteristics for instance, light weight, low density, high gas permeability, and large specific surface area making them attractive structural and functional materials for both physical and biomedical applications.

For this report, we designed cubic lattice structure with equidistant filament with rotational pattern where the resolution of the rotational angle determines the pore size and hence the permeability. We use 1 mm raster width and 5$_0$ rotation resolution patterns as shown in **Figs. 1** and **2**.

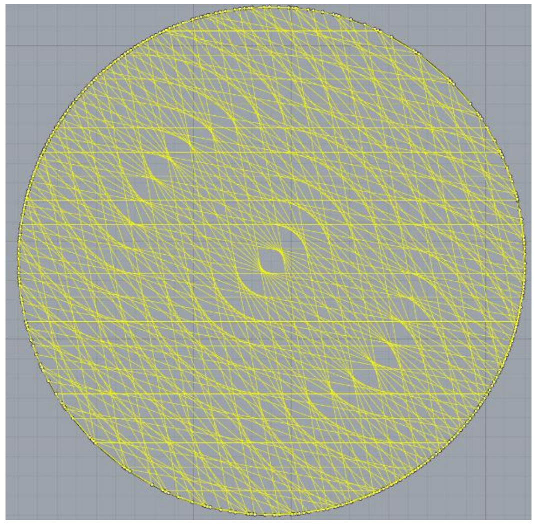


Fig. 1. Design of lattice with pore size control.

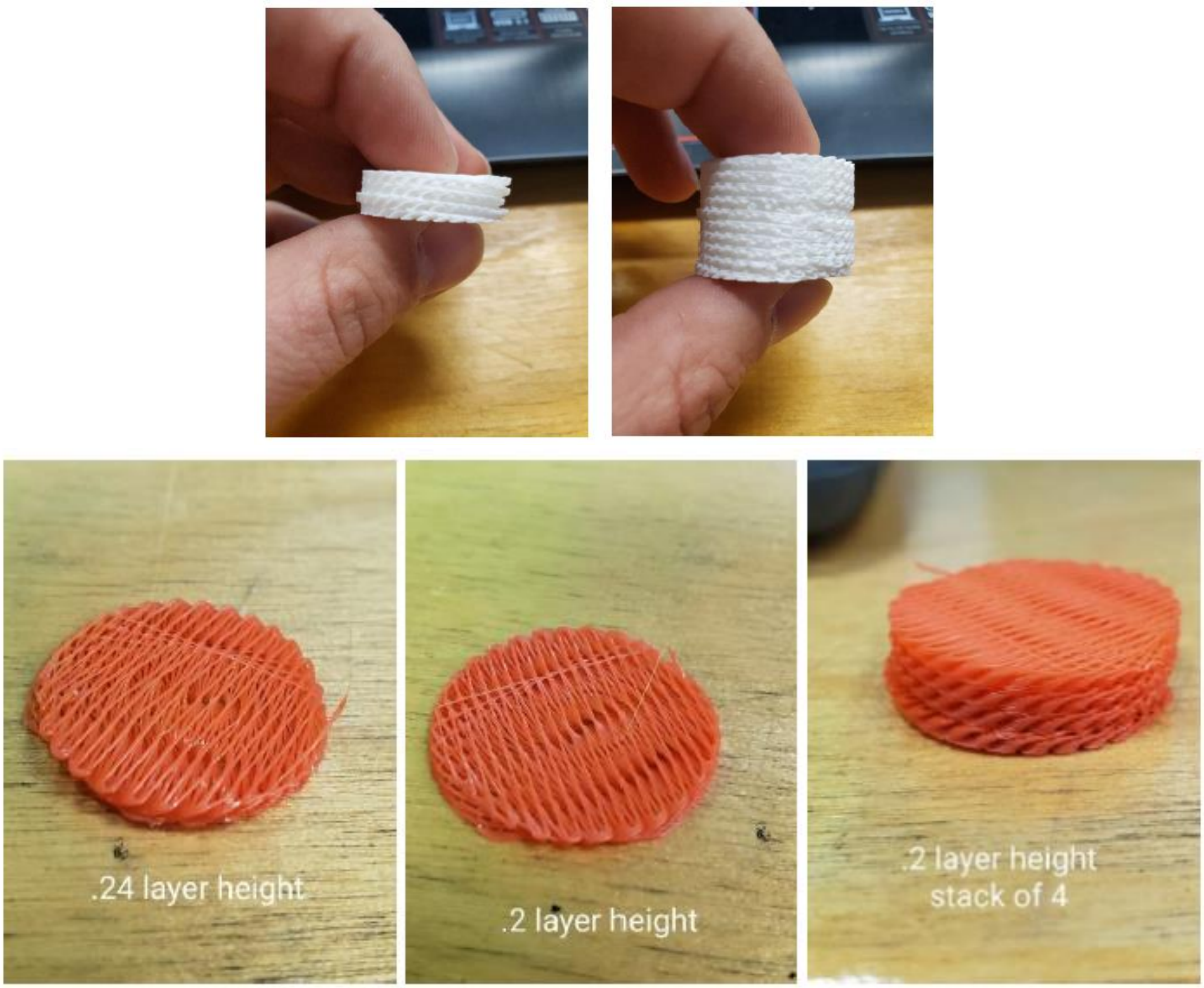


Fig. 2. Typical samples used in the project.

2.2.2 Wettability of untreated single strand and bulk materials

This section aimed to understand wettability of untreated single strand and 3D printing bulk materials.

2.2.2.1 Wettability of untreated 3D printing bulk materials

We selected commercially available 3-D printable polymers, including acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polyamide (PA), polycarbonate (PC), polyethylene terephthalate (PETG), polypropylene (PP), polyoxymethylene (POM), Thermoplastic Polyurethane (TPU), and high impact polystyrene (HIPS). Both pre-spooled polymer filament and raw or granular polymer were purchased from online supplier. Spooled filament came as 2-lb weight and 3-mm diameter, which was fed to the extrusion-based 3D printer used in this research.

ASTM D7334 contact angle test, illustrated in **Fig. 3**, was used, where the specimen was placed in the test plate and a drop of a specific volume of water.

Fig. 3. Equipment used for contact angle test

2.2.2.2 Wettability of untreated sing strand

We fabricated a new test setup to character the wetting of 3D printable polymer materials using the single strand. Note that the contact angle test on the 0.4-mm 3D printing polymer strands is a challenge. To effectively capture such information, a test setup was fabricated to keep a single strand with use of a smaller syringe to allow for a smaller water droplet to be deposited.

2.2.3 Mechanical property of 3D printing lattice structures

This section aimed to understand mechanical behavior of the 3D printing lattice members, including their tensile and compressive strength, striving for their damage tolerance against harsh environment that pipeline could experience in real-world applications. Tensile behavior of the lattice samples was conducted through mounted doubly washers at both sides using a strong glue, as shown in **Figs. 4** and **5**. Due to limitation of contact surface, initial glue as a trial failed at interfacial bond and then the team tried the second strong glue. Note that the initial remaining glue covered in the surface formed a weak layer, which in turn led to weakening the second trial (as shown in Section 3.2.1, where only three out of eleven samples failed by partial tension and remaining failed by interfacial bond). Thus, a further design for direction tension testing of the lattice structures will be refined in the next quarter period.

As compared, compressive behavior of 3D printing lattice structures could be easily achieved by conducting compression testing of the lattice structure using Instron machine, as illustrated in **Fig. 6**.

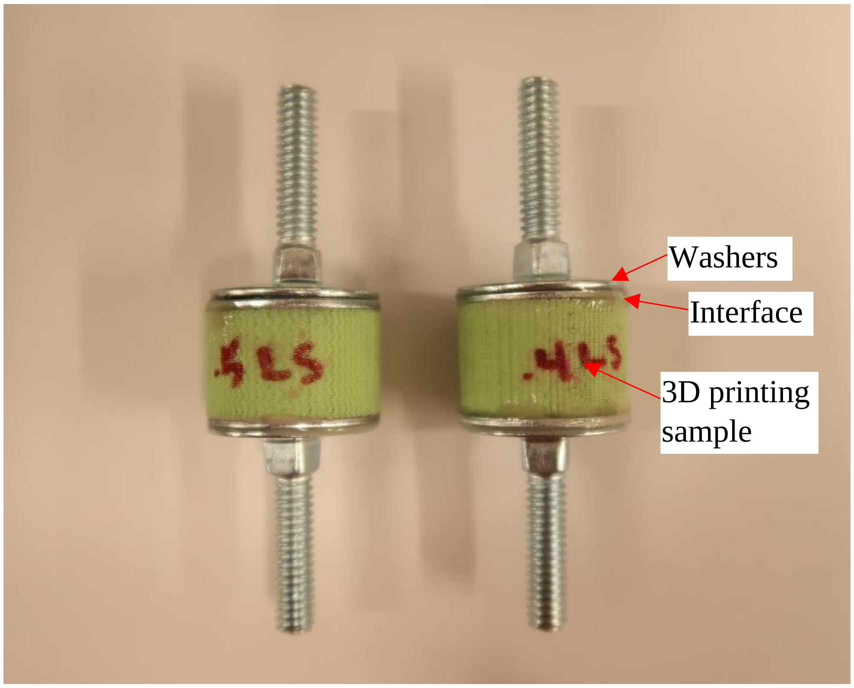


Fig. *4*. Preparation of sample for tension testing

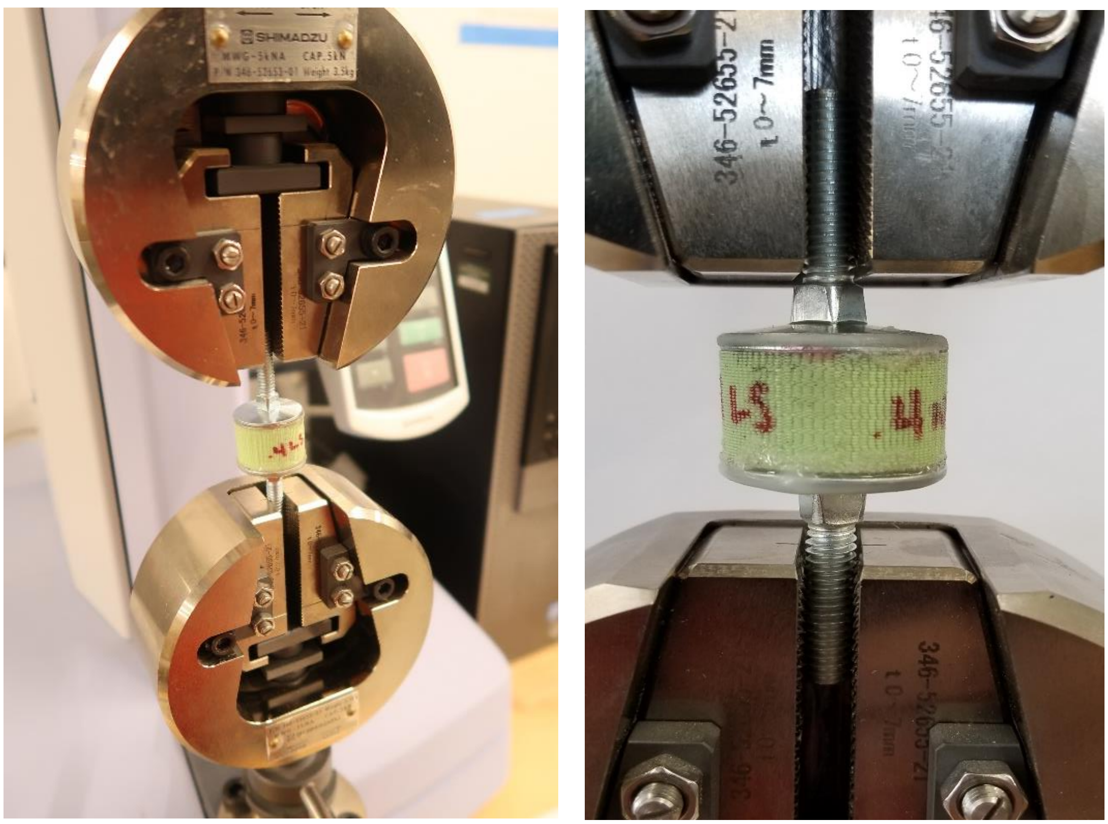


Fig. *5*. Setup of tension testing of the sample

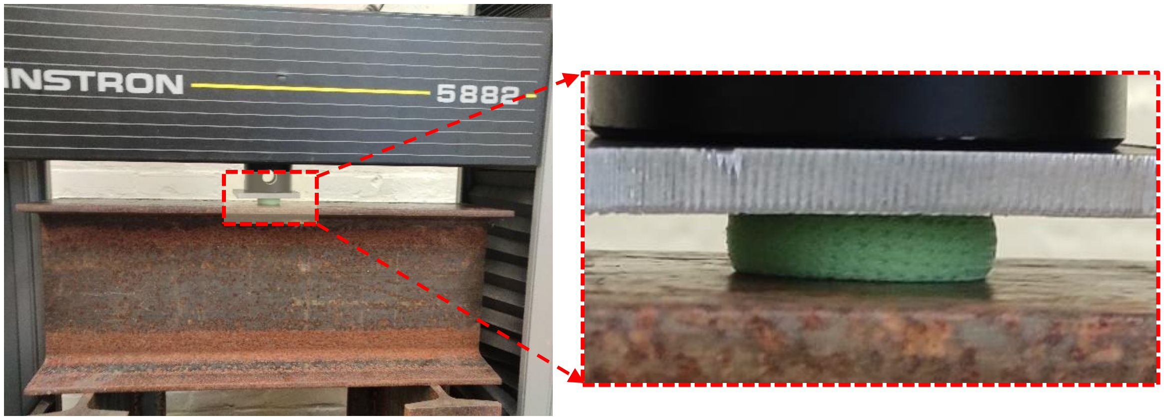


Fig. *6*. Compressive testing of the sample

2.3 Functionalization of 3D printing lattice structures

The second direction herein was to synthesize the materials to functionalize 3-D printable polymer-based lattice structures. The 3D printing lattice structures were functionalized to extract water in the pipeline. Consider that the existing studies on the oil/water separation faced with great challenges, such as easily fouled or even plugged by oils during separation process. Therefore, we screened different material synthesis techniques for identifying the proper performance in air without water.

3. Results and Discussion

3.1 Mechanical behavior of 3D printing lattice structures

3.1.1 Tensile behavior of 3D printing samples

As illustrated in **Figs. 7** and **8**, most of the samples failed without any polymer breaking besides three. Such interfacial failure was mainly because the initial glue used in the face of the samples weakened the loading transfer to washers. Aa a result, although the strong adhesive used in the second time, the failure still initialized localized at the interfaces. As illustrated in **Figs. 8(a)** and **8(b)**, two typical failure modes were observed. Eight out of eleven exhibited interfacial failure (see **Fig. 8(a)**), mainly due to adhesive failure. However, three samples failed by localized layer failure, where partially or near one layer were torn down. Close observation found that these samples were type of LS pattern, suggesting that relatively flat samples with the small pores are preferable to provide better adhesion for direct tension test. In the next quarter period, we will attempt to print heterogeneous layers with dense layers near both ends, in such way that high adhesion force could be achieved to yield the tensile strength of the designed 3D printing lattice structures.

The tensile behavior of the 3D printing lattice structures was plotted in **Fig. 9**, where linear behavior was observed before sudden failure, suggesting it responded for clear interfacial bond failure. The modulus in this stage was about 4.0 MPa, away smaller than that under compression (by 355 MPa). As such, one reason could be due to the fact that low modulus was due to glue used in the interfacial layer, not accounting for actual 3D printing lattice structures.

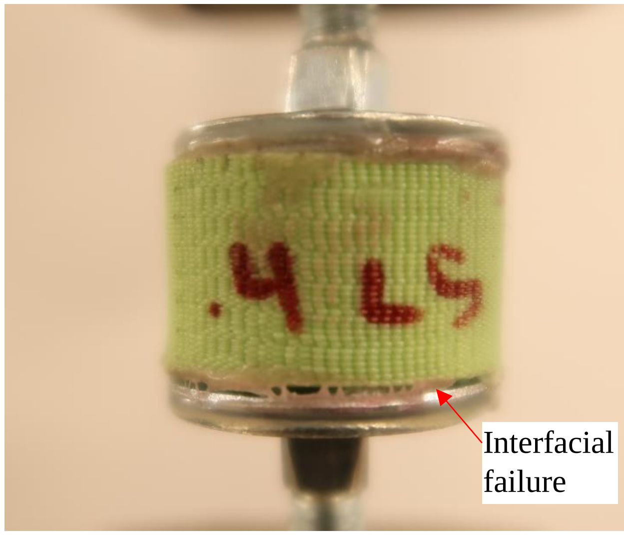
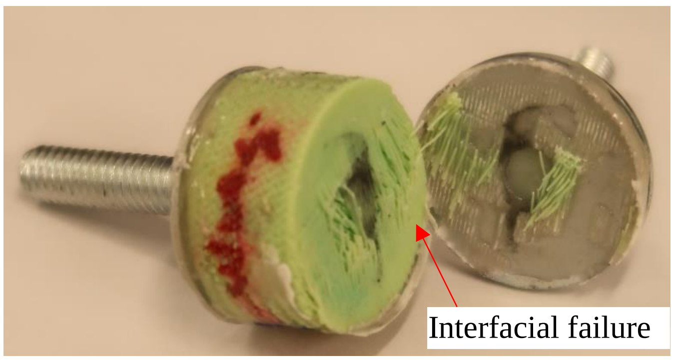
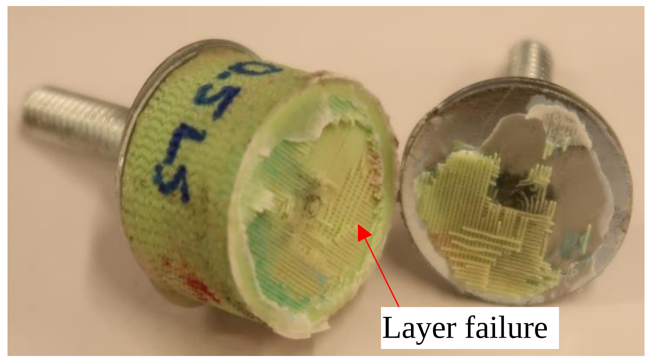


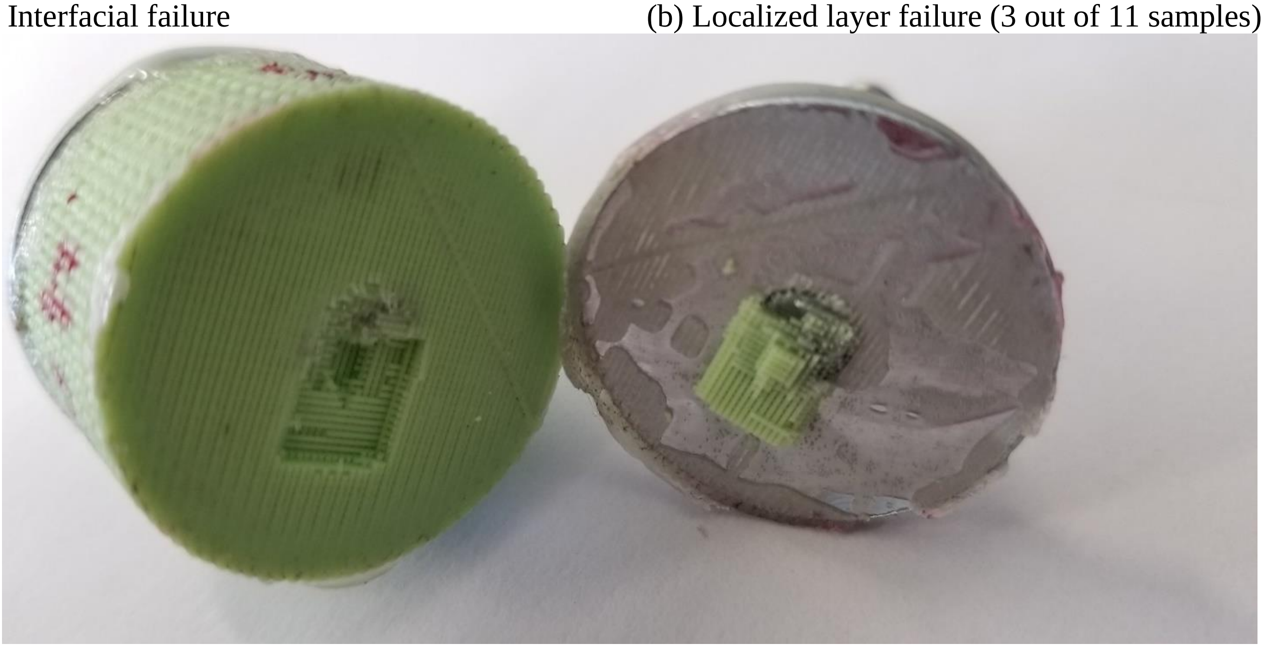
Fig. *7*. Adhesive failure typically found in the tension test



(a) Interfacial failure



(b) Localized layer failure (3 out of 11 samples)



(c) Localized layer failure (3 out of 11 samples)

Fig. *8*. Failure modes observed in the tension test

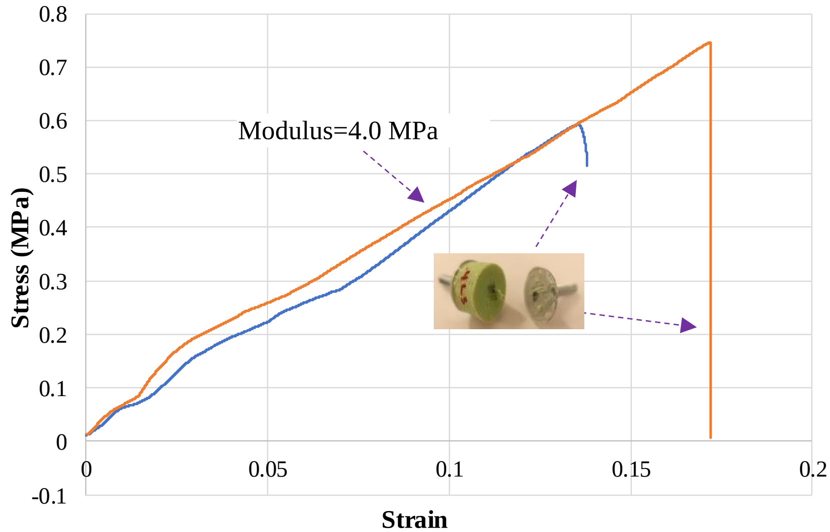


Fig. *9*. Tensile stress-strain curve for the samples

3.1.2 Compressive behavior of 3D printing samples

The compressive behavior of the 3D printing lattice structures was plotted in **Fig. 10**, where three stages were observed: (a) pre-yielding; (b) plateau; and (c) post strain-hardening behavior.

Before yielded, the latticed behaved nearly linear. As such, Young's modulus of three samples, E_{3D}, were generated with an averaged value of 355 MPa and plotted in **Fig. 11**. Polymeric lattice structures started to yielding about 40MPa. After that, the lattice exhibited a plateau mainly due to compression and close of open cell, and then quickly displayed a strain-hardening behavior due to polymer permanent deformation under high pressure, as commonly observed in polymer compression tests.

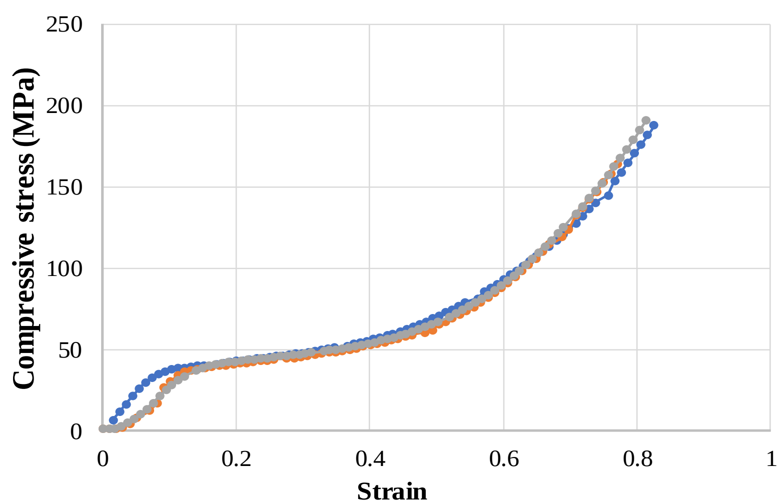


Fig. *10*. Compressive stress-strain curve for three samples

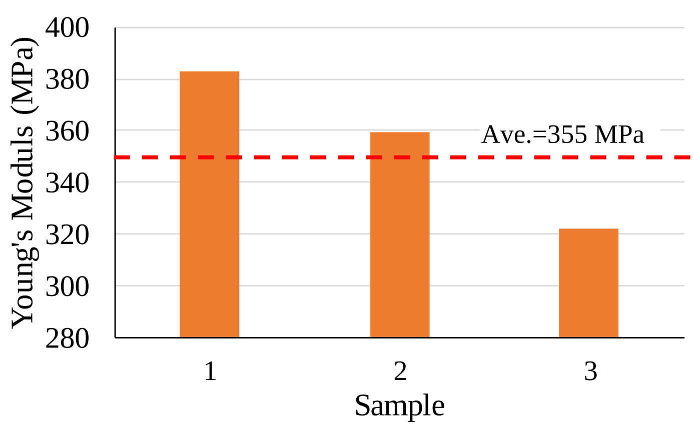
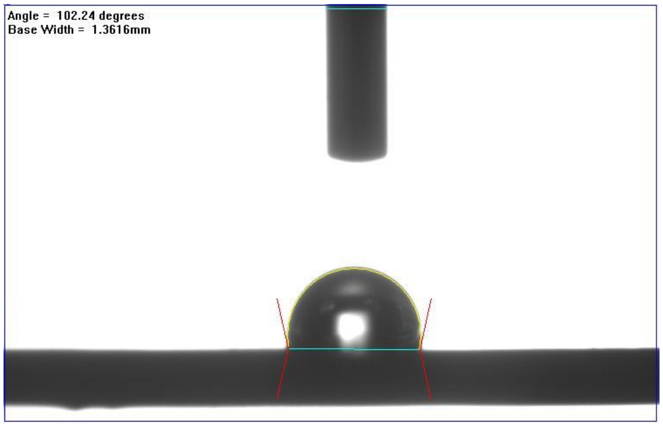


Fig. *11*. Young's modulus of the samples (Compression)

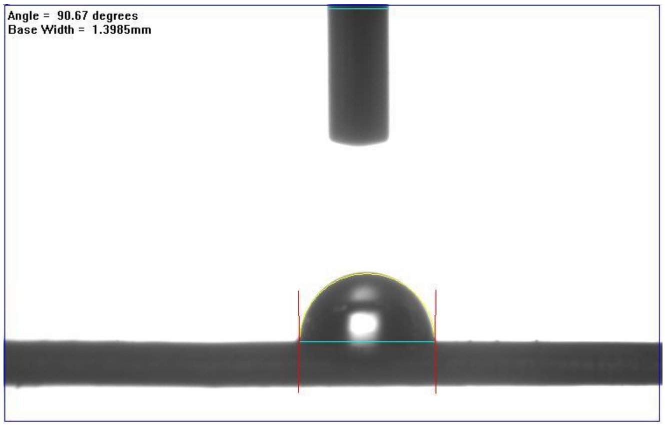
3.3 Wettability of untreated 3D printing single strand and 3D printing bulk materials

3.3.1 3D printing single strand

As shown in **Figs. 12(a)-12(b)**, the water contact angle doesn't appear to differ much between the post-processing polymer strands, narrowly ranging from 80° to 100° as opposed to their theoretical bulk material contact angles which have a much wider range but lower values. The oil substitute (hexadecane) contact angle was close to completely wetting for all the polymer strands. There is an example of a typical oil contact angle when contacting the 3D printing materials, as illustrated in **Fig. 13**.



(a) Water to the ABS surface



(b) Water to the PLA surface

Fig. *12*. Contact angle of the most 3D printing single polymer strand.

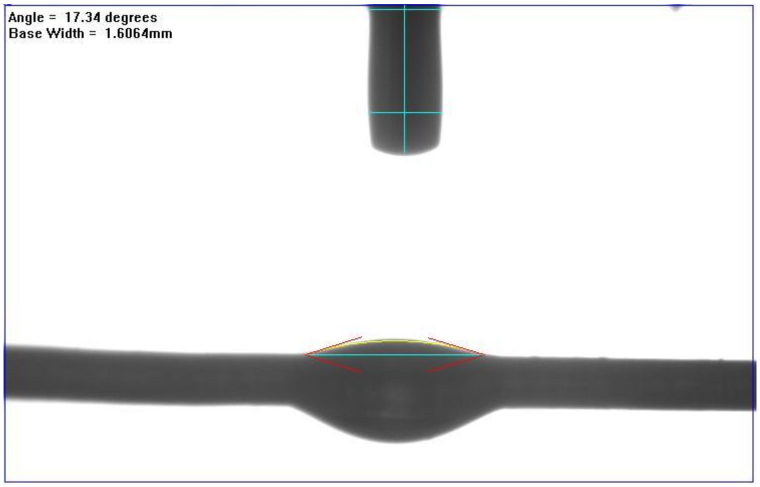
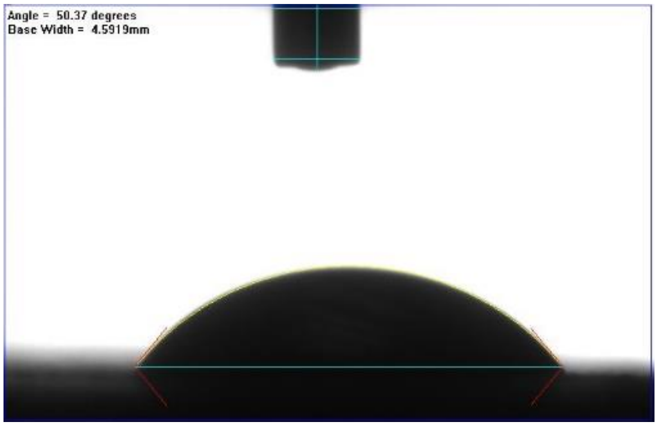


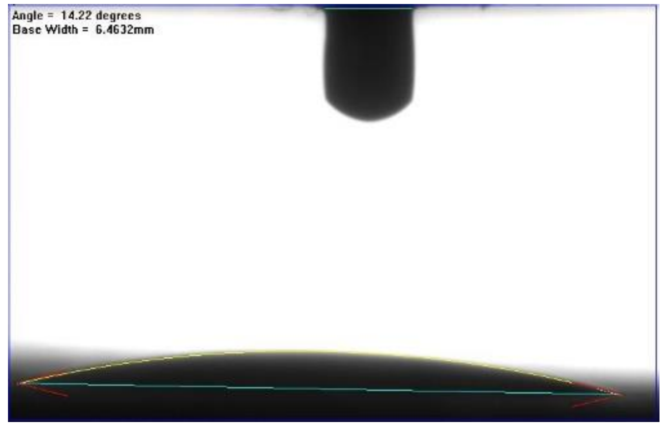
Fig. *13*. One typical contact angle observed at hexadecane to the polymer surface.

3.3.2 3D printing bulk materials

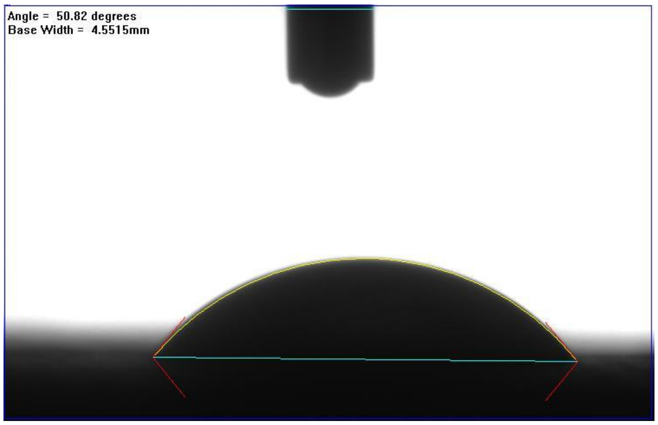
The test results of wettabilty of 3D printing bulk materials were presented in **Fig. 14**. Clearly, the contact angles of water to the specimens ranged from 40 to 60 degrees, while the contact angles of hexadecane were about 10~20 degrees (see **Fig. 14b**) or even complete wetting (see **Fig. 14d**). In summary, the conventional 3-D printed polymeric materials had no favorable properties. Thus, surface treatment is necessary to functionalize the 3-D printable polymer-based lattice structures.



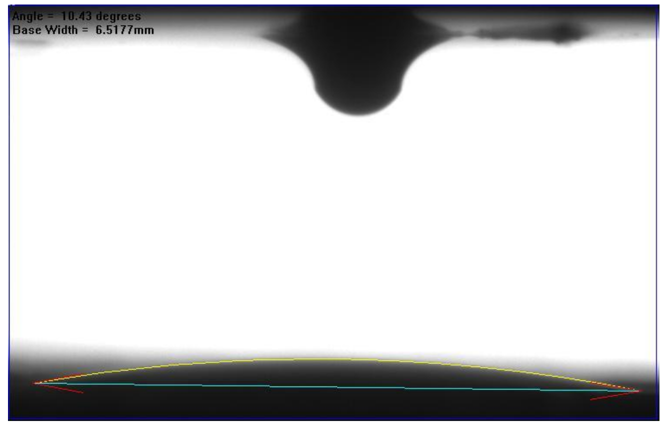
(a) Water to the ABS surface



(b) Hexadecane to the ABS surface



(c) Water to the PLA surface



(d) Hexadecane to the PLA surface

Fig. *14*. Contact angle of the most 3-D printed specimens.

3.4 Summary

3D printing lattice structures were designed and characterized through different pore size and patterns. The wettability behavior of surface-treated 3D printing lattice exhibited behavior as desirable. The results revealed that the performance is responsible for pore size.

There remained several tasks we will refine as stated in the Section (f):

- The most of tension tests failed due to weak interfacial bond, and thus we will refine our setup to ensure a clear direct tension test.
- 3D lattice layers were stacked by a uniform pattern, while a heterogenous stacked layer could achieve better performance.

(e) Description of any Problems/Challenges

No problems are experienced during this report period

(f) Planned Activities for the Next Quarter

The planned activities for next quarter are listed below:

- Design and characterization of heterogenous stacked layers, from various size and patterns, of the 3-D printing lattice structures;
- Characterization of the new 3-D printing lattice structures under multiple levels of nano-, micro- and macro-scales;
- One attempt will start to numerically simulate, identify and optimize the design parameters the capacity required in the pipeline systems;
- Another attempt will start long-term durability tests of the new composite systems.