CAAP Quarterly Report

Date of Report: *July 4th, 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*

Contact Information: *Mr. Yiming Bu, PhD student, Email: Yiming.bu@ndsu.edu, Phone: 701-231-7204; Mr. Muhammad Naveed Metla, PhD student, Email: muhammadnaveed.metla@ndsu.edu, Phone: 701-231-7204; Mr. Matthew Pearson, M.S. student, Email: matthew.pearson@ndsu.edu, Phone: 701-231-7204; Dr. Zhibin Lin, Email:zhibin.lin@ndsu.edu, Phone: 717-231-7204; Dr. Bashir Khoda, Email: bashir.khoda @ndsu.edu, Phone: 701-231-7195*

For quarterly period ending: *July 7th, 2019*

Business and Activity Section

(a) Contract Activity

Kickoff meeting was held at North Dakota State University on June 11st, 2019

Two high-school students from the ND governor's high school program were recruited and participated in the project of Dr. Lin's group

Chemicals were mainly purchased for synthesizing surface treatment of the lattice structures

(b) Status Update of Past Quarter Activities

The research activities in the 3rd quarter included: (i) a kick-off meeting with the USDOT PHMSA program director; (ii) the continuing efforts by the design and characterization of the 3-D printable polymers in **Task 2**; and (iii) the synthesis of materials in **Task 3**, as summarized in Section d.

(c) Cost share activity

Cost share was from the graduate students' tuition waiver.

(d) Kick-off meeting and summary of detailed work for Tasks 2 and 3

-(i) Kick-off meeting

A kick-off meeting was held at North Dakota State University on June 11st, 2019. The USDOT PHMSA program director, Joshua Arnold, had a one-day NDSU campus visit for the kick-off meeting. The meeting agenda and major activities are shown in Table 1, including meeting with PIs and meeting with the student poster section (see photos shown in Fig. A.1) and the graduate students who are current working on the 3-D printed material (see Fig. A.2), and tours to laboratory and facilities at NDSU (see Fig. A.3). This was a great opportunity for the PIs and gradudate students who have been working in the USDOT sponsored projects to communicate with the program director Joshua. Dr. Lin really appreciated the USDOT PHMSA CAAP program for providing this great opportunity to excchange information and discussed shared concerns for pipeline safety.

Table 1 Kick-off meeting agenda (Tuesday, June 11st, 2019)

Items	**Major Contents**	**Note**
Location	College of Engineering, Dept. of Civil Engineering, Dept. of Coatings and Polymeric Materials, Research One, NDSU, Fargo, ND.	
Objectives	a. Funding activities and expectation of the PHMSA b. Introduction and discussion of the project, objectives and tasks c. Meeting with NDSU personnel (PIs and students*, Dean of College o Engineering, Department chair of Civil Engineering) for current projects and potential future collaboration d. Visit NDSU facilities, labs and facilities associated with the projects and future collaborative work	
Detailed schedules and activities	9:00 – 10:00 AM, Kick off meeting (Dean's conference room 106) 10:00 – 11:00 AM, Meeting with students and poster section (CIE 101) 11:30 – 11:00 AM, Meeting with Associate Dean Dr. Scott Pryor 11:30 – 12:00 AM, Meeting with CEE Chair Dr. David Steward 12:00 AM – 1:30 PM, Lunch with the CEE Chair and Dr. Lin and another two graduate students (Applebee's Restaurant, 19TH street) 1:30 –2:30 PM, Lab tour o Joshua visited the laboratory in the Dept. of Coatings and Polymeric Materials (Fig. A.3). o Joshua also visited the laboratories in the research one center at NDSU (Fig. A.3). 2:30 PM, Joshua headed for the airport.	

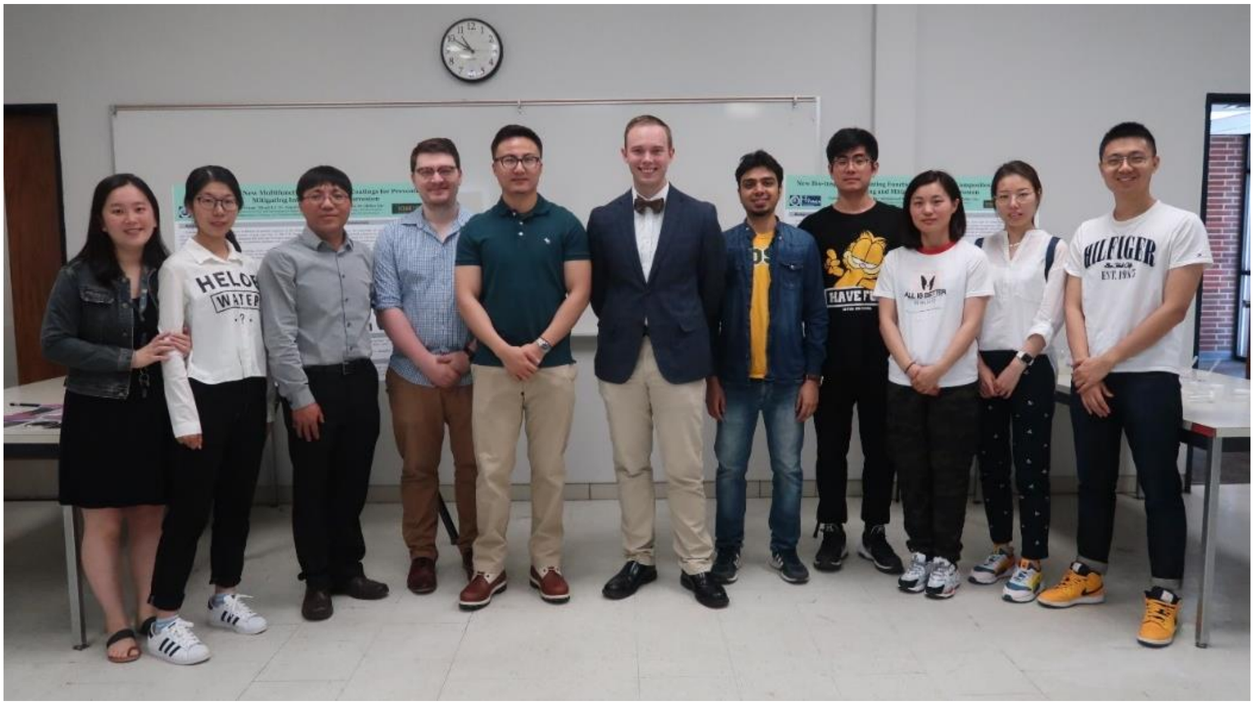


Fig. A.1 PHMSA project director, Joshua Arnold, met with graduate students at NDSU

Fig. A.2 Graduate students, Yiming Bu and Matthew Pearson, demonstrated their work to the PHMSA project director, Joshua Arnold

Fig. A.3 PH MSA project director, Joshua Arnold, had a lab tour at Research one at NDSU

-(ii) **Tasks 2-3: Summary of design and characterization of the 3-D printable polymers and synthesis of surface treatment materials**

1. **Background and Objectives in the 3rd Quarter**

1.1 Background

We have screened the current polymers as candidates for 3-D printable materials. We characterized their wettability capability using the criteria of the measured contact angle (for both water and oil). Clearly, the bulk printed flat surface had the low contact angles of water to the specimens, while the contact angles of hexadecane were even lower. 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.

1.2 Objectives in the 3rd Quarter

The main objectives of the 3rd quarter report aimed to continue our efforts to design/characterize 3-D printed lattice structures along the first direction (in Task 2) and identify the surface treatment for functionalization of the 3-D printed structures along the second parallel direction (in Task 3).

<u>First direction along Task 2</u>

2. **Experimental Program in the 3rd Quarter**

2.1 Design and fabrication of 3D printing lattice structures

we developed a custom multi-material delivery system to print the porously structure with lattice architecture within five-micron spatial accuracy. As well known, periodic cellular structure is the most known man-made cellular structure which are used in the design of light weight sandwich panel structures. We selected the PLA and ABS as our base for printing materials.

3. Results and Discussions

3.1 3D printing lattice structures

3.1.1 PLA-based lattice structures

The lattice structures were printed, while the porosity generated created open cell lattice type architecture, as shown in Fig. 1. To avoid the layer shifting, the more attempts were made to provide the better stable lattice structures by using the thickness of 0.3-in per layer and other types, as shown in Figs. 2 and 3.

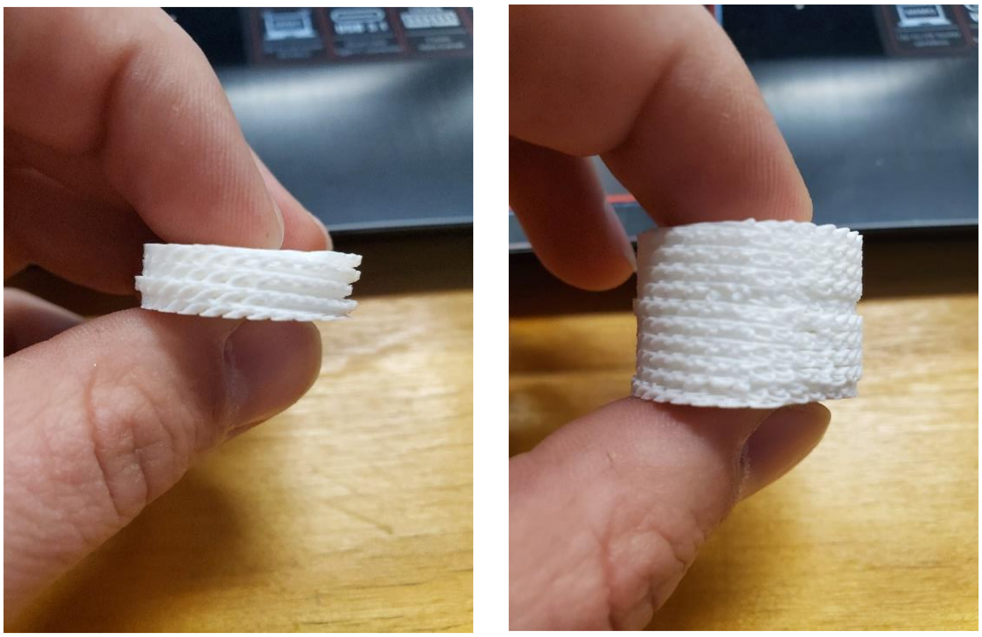


Fig. 1 3-D printed lattice structure.

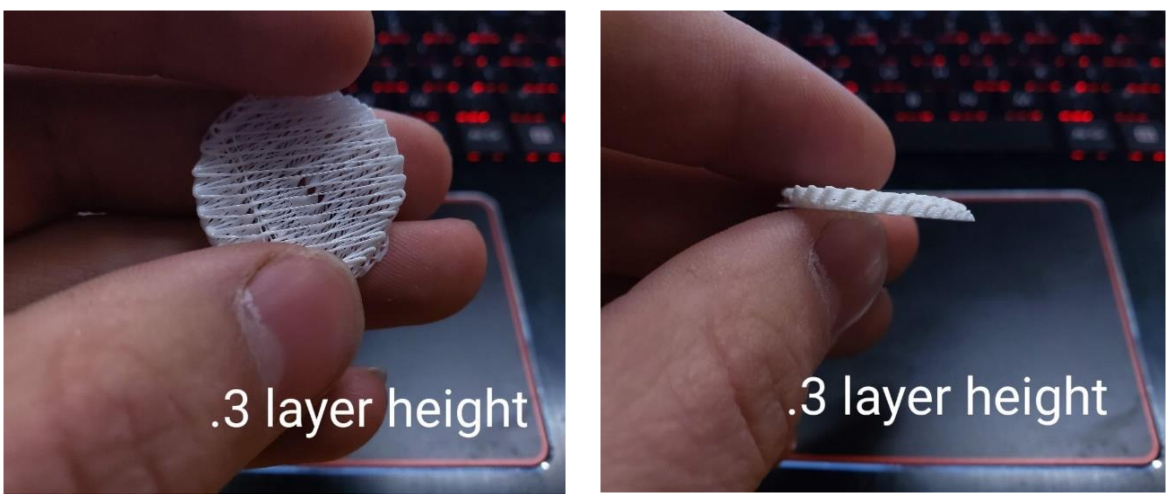


Fig. 2 0.3-in thick PLA lattice structure.

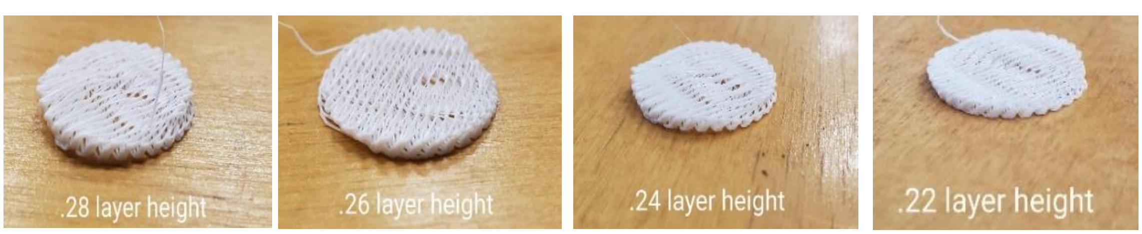


Fig. 3 Different thickness of the lattice structures.

3.1.2 ABS-based lattice structures

By using similar setting, the different printable material, ABS, was selected for the layered structures, as shown in Fig. 4.

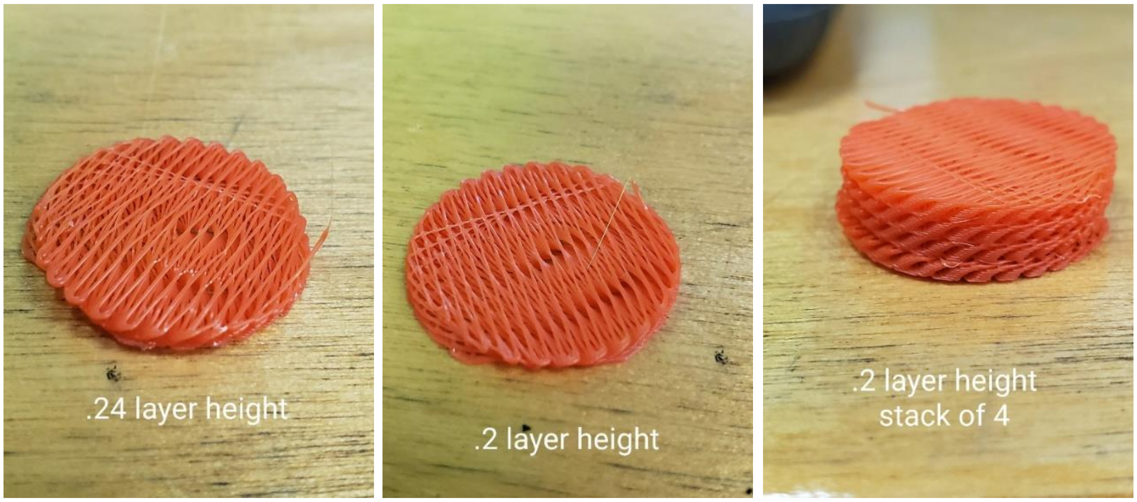
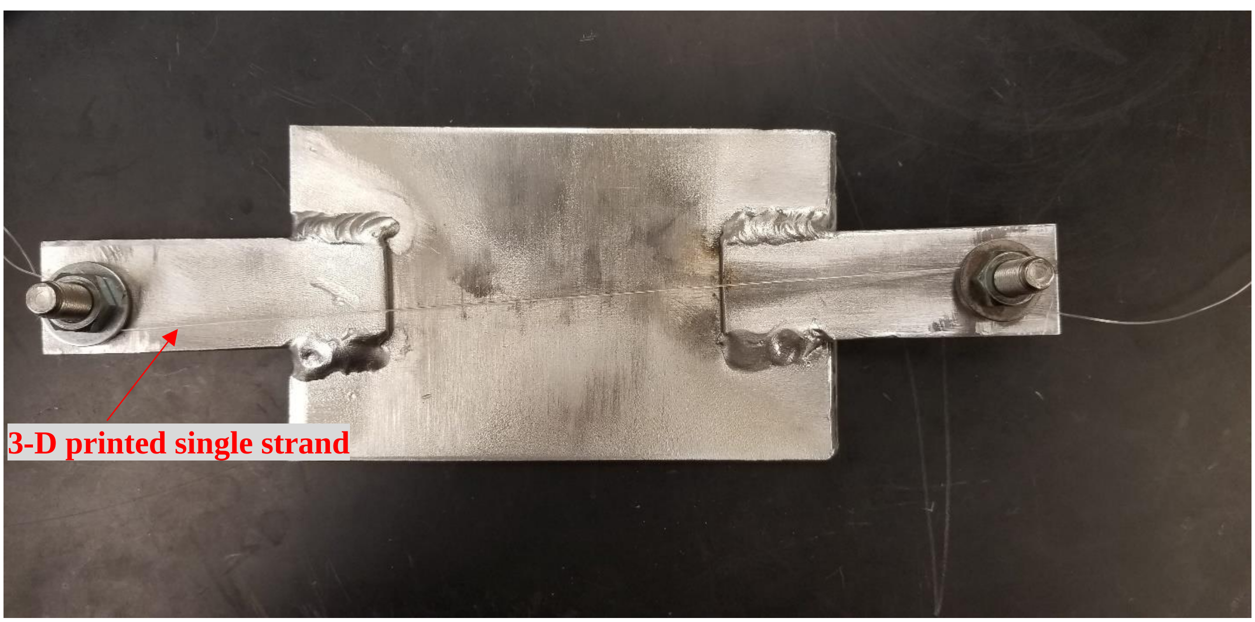


Fig. 4 ABS lattice structure.

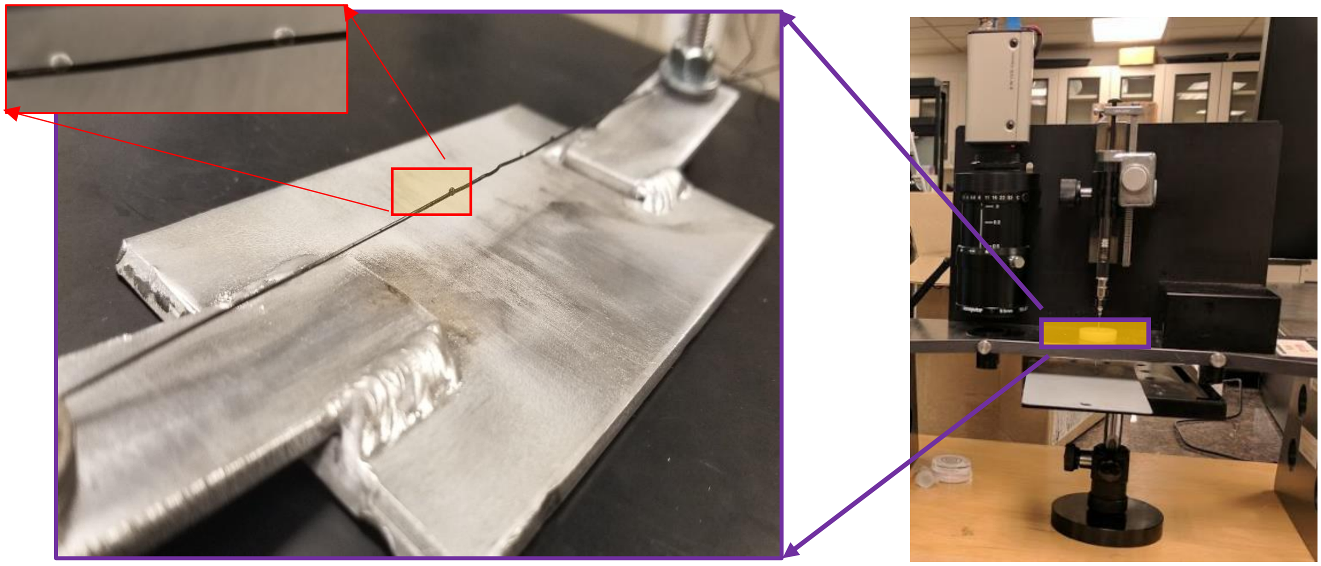
3.2 ***Quantifying wettability of single strand***

3.2.1 Test setup

As stated before, the measurement in the last report was based on the 3D printing bulk plate surface, not individual strand, while the 3D printing lattice structure consists of individual strand as its element. Thus, 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, illustrated in **Fig. 5(a)**, was fabricated to keep a single strand with use of a smaller syringe to allow for a smaller water droplet to be deposited.



(a) Stand for postion of a single 3-D printed polymer strand



(b) Close look of the stand for contact angle test (c) Equipment used for contact angle test

Fig. 5 Refined Contact Angle Tests

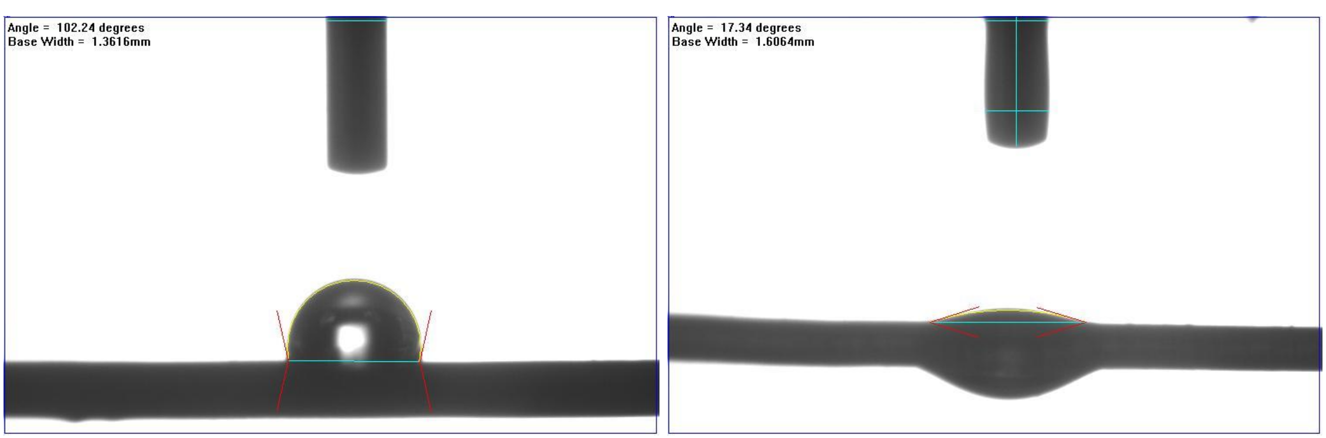
The original 0.5 mL syringe was reduced to a 0.05 mL capacity syringe. This reduced the droplet size from the standard 10 µL down to 1 µL which could consistently sit on top of the polymer strand for easier testing.

The simple cylindrical strands were extruded through a 0.4 mm nozzle on the 3D printer. The strand was suspended in tension using the designed stand (see **Figs. 5(a) and 5(b)**) beneath the syringe on the contact angle machine based on ASTM D7334 contact angle test (see **Fig. 5(c)**), then the water droplet was deposited at different spots along the strand and pictures were taken of the drops to analyze the apparent contact angles seen.

3.2.2 Wettability properties of single strand

As shown in **Figs. 7(a)-7(b)**, the water contact angle doesn't appear to differ much between the post-processing polymer strands as opposed to their theoretical bulk material contact angles which have a much wider range. The oil substitute (hexadecane) contact angle was close to completely wetting for all the polymer strands.

To sum up, the wettability behavior of single strands demonstrated their high hydrophobic and oleophilic properties against the desirable performance.



(a) water to substrate (b) oil to substrate

Fig. 6 Typical contact angles observed at the single strand.

3.3 Summary of the first direction

The 3D printing lattice structures were designed based on the stable aperiodic octet lattice architecture with the thickness of 0.3-in per layer. The wettability properties of these lattice structures presented in Section 6.1 confirmed the pore size is proper for the desirable oil/water separation.

Besides that, there remained information we should gain:

- The current oil/water separation was based on one type of pore size and thus different pore sizes will be fabricated to determine their efficiency.
- The mechanical properties of the lattice structures, including tensile strength or Young's modulus, should be calibrated for the pipeline applications.
- The interfacial bond between the lattice and surface treatment is not clear yet.

Second direction along Task 3: Synthesize, characterize and optimize the materials to functionalize the 3D printing composites

4. Experimental Program in the 3rd Quarter

The second direction herein was to continue to synthesize the materials that will use as the surface treatment to provide the 3-D printable polymer-based lattice structures.

4.1 Screening the materials for functionalization

The 3D printing lattice structures will be 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, it is of great importance to develop anti-oil fouling materials for oil/water separation with high separation capacity.

Therefore, we screened different material synthesis techniques for identifying the proper performance in air without water prewetted for oil/water separation:

a) synthesis I via dip-coating, and the one major material including poly-(diallyldimethylammonium chloride) solution (PDDA, (C8H16ClN)n, 20 wt % in H_2O).

b) synthesis II via dip-coating, and the major material including Chitosan (95% degree of deacetylation, viscosity 100-200 mPa.s).

c) synthesis III via polyphenol chemical method with additional tannic acid for stabilization of interfacial bond.

4.2 Characterization of Wettability of functionalized material surface

The surface-wetting performance of before and after functionalized material surfaces was evaluated by measuring the static oil and water contact angles at room temperature. The filter paper and fabric were first selected as substrate materials (initial trial materials).

5. Results and discussion

5.1 Comparison of Synthesis I and Synthesis II

The surface-treated fabric using Synthesis I exhibited a slight change in the contact angle for both water/oil to the substrates, as compared to initial pristine substrate. The observation revealed that the surface treatment on the surface of fabric using Synthesis I was not stable and quickly lost the functional groups, so that we did not observe the results due to severe degradation of surface treatment, suggesting that the Synthesis I did not result in a stable solution for the proposed study if without further modification.

Differently, the surface-treated fabric using Synthesis II exhibited a significant change in its contact angle for both water/oil to the substrates. The one-week observation revealed that the surface treatment was stable and remained well (and detailed microstructure for the interfacial bond will be carried out for further calibration and verification in the next report).

5.2 Further observation of wettability behavior using Synthesis II

To better qualitatively and quantitively determine the effectiveness of the surface treatment using Synthesis II, the surface-wetting performance of before and after modified filter paper and fabric were evaluated by water and oil contact angle measurement. Clearly, both surface-modified substrates exhibited high oil contact angle with almost wetting for water, as desired.

6. Functionalization of 3D printing latticed structures and characterization

6.1 Wettability of functionalized 3D printing latticed structures

The 3D printing latticed structures that were presented in Section 3.1.1 were functionalized using Synthesis II. After the surface modification, the lattice structures exhibited a higher oil contact angle, the oil droplet can keep spherical.

6.2 Oil/water separation

The separation concept herein was based on the combined of 3-D printed lattice structures. We used them to separate the oil/water mixture after the treatment. The oil/water separation was carried out, as shown in **Fig. 7**. The clear separation was observed, where the water totally penetrated through the lattices and the oil was kept on the top.

(a) initial (b) certain separation (c) final separation

Fig. 7 Process of oil/water separation

6.3 Summary of the second direction

Clearly, the Synthesis II provided a great base for oil/water separation. The new Synthesis III was expected to form the better stable treatment on the basis of the Synthesis II.

There remained several challenges we should overcome:

- The current test attempted to identify the proper synthesis for oil/water separation. As a result, we did not provide a clear flow rate for the separation to quantitively determine their efficiency.
- The stabilization of surface treatment using Synthesis II was not clear (even though one-week observation was carried out).

- The combined layers of polyester non-woven fabric with 3D printing lattice structures were used in the tests.

(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:

Along the first direction:

- Three different pore sizes will be fabricated to identify the proper flow rate of separation.
- The microstructure of 3D printing lattice structures will be investigated using SEM.
- The lattice structures will also be subjected to mechanical testing through tension, indentation, and micro-hardness testing.
- The property characteristics of the lattice structures, such as Young modulus and Poisson ratios in three orthogonal directions, will be calculated.

Along the second direction:

- To improve the efficiency, the further modification of Synthesis II and the Synthesis III will be investigated to provide better separation (using measurement of flow rate) and stabilization.
- The detailed microstructure for the interfacial bond will be carried out for further calibration and verification.
- One reason for the fabric was to seal the plastic tube better to avoid initial leakage of oil/water mixture. The new test setup will be fabricated and as such we could use the designed 3D printing lattice without the fabric layer.