CAAP Quarterly Report

[03/31/2023]

Project Name: "All-in-One Multifunctional Cured-In-Place Structural Liner for Rehabilitating of Aging Cast Iron Pipelines"

Contract Number: 693JK32250009CAAP

Prime University: North Dakota State University

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Reporting Period: [01/01/2023 – 03/31/2023]

Project Activities for Reporting Period:

In the 1st quarterly report, Task 1 was completed. In this quarter (Quarter 2), the research team has worked on Tasks 2.1, 3.1, 3.3, and 3.4. The summaries for the major activities that were completed during this reporting period are detailed below.

Task 2.1 Preparation of Vitrimer Epoxy Resins, characterization, and optimization of the processing and curing conditions (20%): During this reporting period, the research team (Dr. Long Jiang and Austin Knight, Ph. D. student from NDSU) investigated the reaction mechanisms of the vitrimer epoxy resins and prepared the samples of self-healing epoxy resins as summarized below:

(1) Reaction Mechanisms of Vitrimer Epoxy Resins: Curing epoxy resins with anhydrides requires additives to induce the ring-opening of the anhydride to form a carboxylic acid. This carboxylic acid can then react with the epoxide groups at elevated temperatures, crosslinking the epoxy resin and producing a secondary hydroxyl group. The hydroxyl group produced can then induce the ring-opening of the anhydride, which causes further crosslinking of the epoxy resin. Typically, organic salts or strong bases are used as catalysts to induce ring-opening, which may bring toxicity or cause corrosion of the substrate material. Alternatively, primary hydroxyl groups can induce ring-opening, similar to how the secondary hydroxyl group functions in causing further crosslinking but occurring at relatively lower temperatures. Glycerol and 2-hydroxyethyl acrylate (2-HEA) were used to induce the ring opening of glutaric anhydride (GA) in this study (Figure 1a). Adding acrylate-containing monomers and a photoinitiator to the epoxy-anhydride system allows for an intermediate curing step using UV light. UV curing has the benefits of being much quicker than thermal curing systems and requiring much less energy. A dual UV and thermal curing system can have a reduced thermal curing time and temperature after the initial UV curing compared to just a thermally curing system. Carboxy acrylate monomers, when UV cured, create an acrylate backbone with a high density of carboxylic acid groups, which can be used to thermally cure the epoxide. Multifunctional acrylates can also be added to create crosslinked bridges between carboxylic acid functional chains (Figure 1b). Multifunctional acrylates can also be added on their own to create an interpenetrating polymeric network (IPN) that crosslinks separately to the epoxy-anhydride system to toughen the final polymer.

(2) Procedure and Methods to Prepare Vitrimer Epoxy Resins: Two types of formulations were prepared 1) just glycerol and 2) with a 1:1 primary hydroxyl group ratio of glycerol and 2-HEA. GA was added with a 1:1 ratio of anhydride groups to primary hydroxyl groups. DER-332, bisphenol-A diglycidyl ether (BADGE) with an epoxide equivalent weight (EEW) of 172, was added with a 1:1 ratio of epoxide groups to the theoretical carboxyl groups after the anhydride ring opening. Epoxy resin, anhydride, and primary hydroxyl monomers were added to a container and mixed at room temperature for 10 minutes. Then, the temperature was increased to 130°C and

mixed for 1 hour. After mixing, the sample became clear as the glycerol reacted with the anhydride making it miscible in the epoxy resin (Figure 2a, 2b). Afterward, the multifunctional acrylates (TPMTA, GDGDA) and photoinitiator (TPO-L) were added in formulations that called for them. A mechanical mixer was used to homogenize the mixture at 500 rpm for 5 minutes. Then, the mixtures were placed in a vacuum oven at 110 °C to remove the trapped gas. The resultant mixture is either coated on a metal plates plate (precleaned with acetone) using a film applicator (6 mils) to control the coating thickness (Figure 2c) or poured into a dumbbell or rectangular shape silicon mold (Figure 2d, 2e). For formulations that were UV cured, samples were purged with nitrogen for 5 minutes at a flow rate of 10L/min, then cured for 10 minutes at a flow rate of 2.5L/min (Figure 2f). The resin/gel was then cured at 190°C for 1hr in a convection oven. After curing process, the sample was cooled naturally to room temperature.

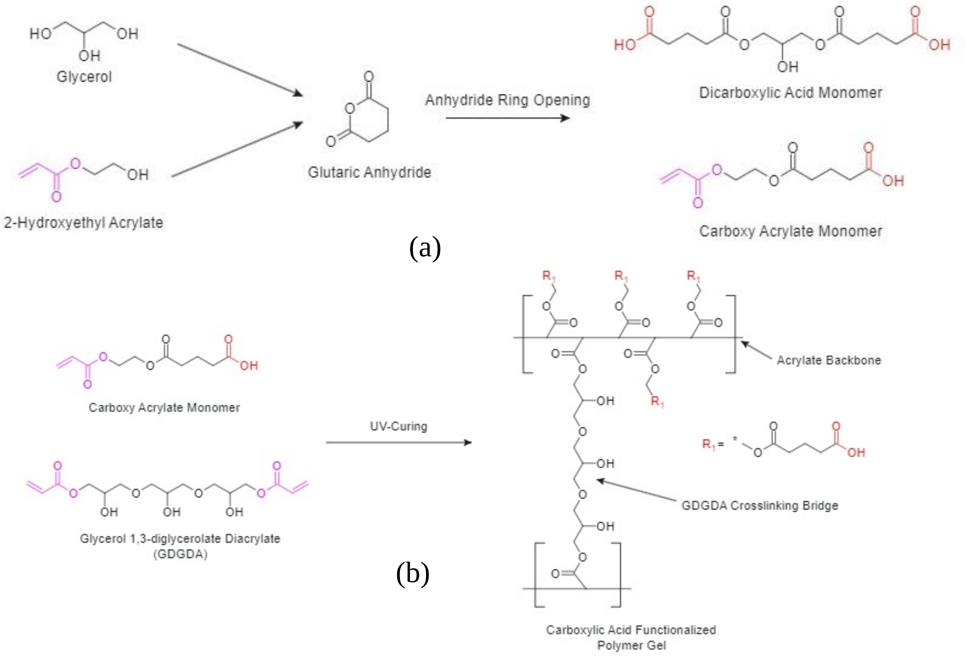

Figure 1. (a) Ring opening of glutaric anhydride using primary hydroxyl-containing monomers and (b) UV-curing of carboxy acrylate monomers and multifunctional acrylates.

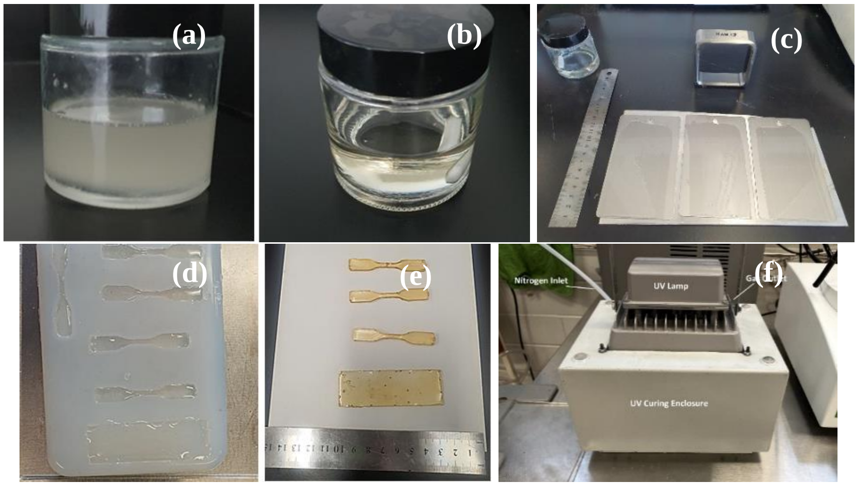

Figure 2. Photos of the resin system (a) before and (b) after heating at 130 °C for 1 h, (c) resin being applied on metal plates, (d) example samples in molds before heat, (e) after heat, and (f) UV curing

Task 3.1 High Mechanical Performance (10%): During this reporting period, the research team (Dr. Ying Huang, Dr. Zhinbin Lin, Dr. Xingyu Wang, Tofatun Jannet, Ph. D. student, Colby Rance and Kathryn Quenettee, sophomore students from NDSU) have performed an experimental study on using nanoparticles to enhance the mechanical performance of the nano-epoxy composite as detailed below:

(1) Materials and Sample Preparations: To investigate the effects of shape and concentration of the nanoparticles, this study focuses on evaluating the influence of nanoparticle morphology, including carbon nanotubes (CNT), graphene nanoplatelets (GNP), and nanodiamonds (ND), on the performance of epoxy-based nanocomposites at concentrations of 0, 0.5, 1.0, and 2.0 wt.%. Commercially commonly used epoxy was employed to study the nano-reinforcement; an undiluted clear difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin, Epon 828, was used to crosslink with a modified polyamide curing agent, Epikure 3175, to formulate high solid ambient cure polymer composite, which offers great overall performance. The nanomaterials were purchased from Skyspring Nanomaterials Inc., and their properties are summarized in Table 1. After the dispersion procedure, which involved a high-shear disperser and ultrasonication, the curing agent was introduced into the mixture in a 1:1 molar ratio with the epoxy resin, and the mixture was subjected to mechanical stirring at 600 rpm for 10 minutes. For all the nanoparticles, three varied concentrations were used, which are 0.5, 1.0, and 2.0 percent by weight. The prepared samples were stored at room temperature for at least seven days before any experiments were conducted, as presented in Figure 3.

Table 1. the properties of the selected nanoparticles

Nanodiamond (ND)	Multi-walled carbon nanotube (MWNT)	Graphene nanoplatelets (GNP)
Purity: > 95% Appearance: Grey nanopowder Morphology: spherical Diameter: 3-4 nm Surface Area: ~282 m^2/g True density: 3.05-3.30 g/cm^3	Purity: > 95% Appearance: Black powder Morphology: fibrous Outside diameter: 50-100 nm Inside diameter: 5-10 nm Length: 5-20 um Surface Area: >60 m^2/g True density: ~2.1 g/cm^3	Purity: 99.5% Appearance: Black powder Morphology: platelets Thickness: 6-8 nm Average Diameter: 15 microns Surface Area: 120-150 m^2/g

Figure 3. Examples of prepared nanocomposite samples

(2) Experiment Design: To characterize the microstructures and the properties of the CNT, GNP, and ND reinforced epoxy resins, as planned in the proposal, various experiments were designed and tested, including a) SEM and TEM image analysis, b) coupon tensile test (Figure 4a), c) abrasion resistance test (Figure 4b), d) adhesion test (figure 4c), and e) water contact angle test (Figure 4d).

(3) Test Results and Discussions: Figures 6a~6l show the testing results for the coupon tensile test, abrasion resistance test, adhesion test, and water contact angle test with epoxy composite reinforced with CNT, GNP, and ND at concentrations of 0.5, 1.0, and 2.0 wt.%. It can be seen from Figure 6 that the optimal concentration for these investigated nanoparticles is between 0.5 to 1.0 wt.%.

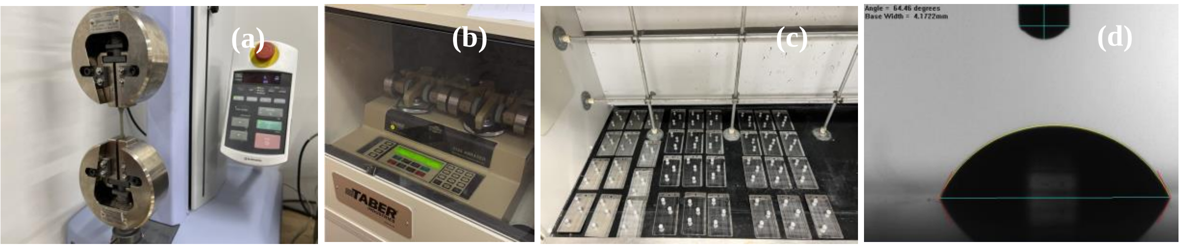

Figure 4. Testing setup for (a) coupon tensile test, (b) abrasion resistance test, (c) adhesion test, and (d) water contact angle test

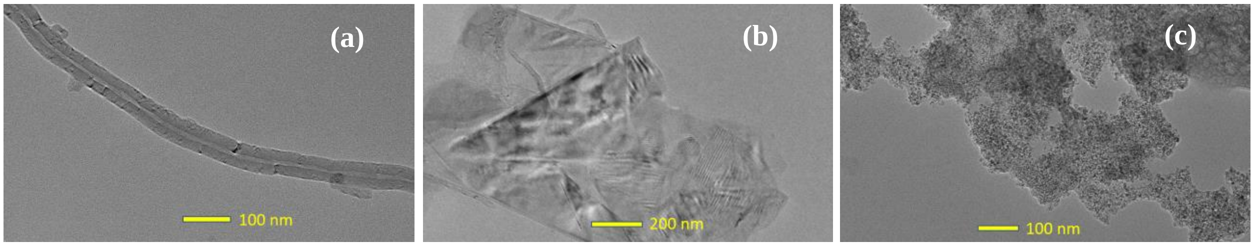

Figure 5. TEM images of (a) CNT, (b) GNP, and (c) ND

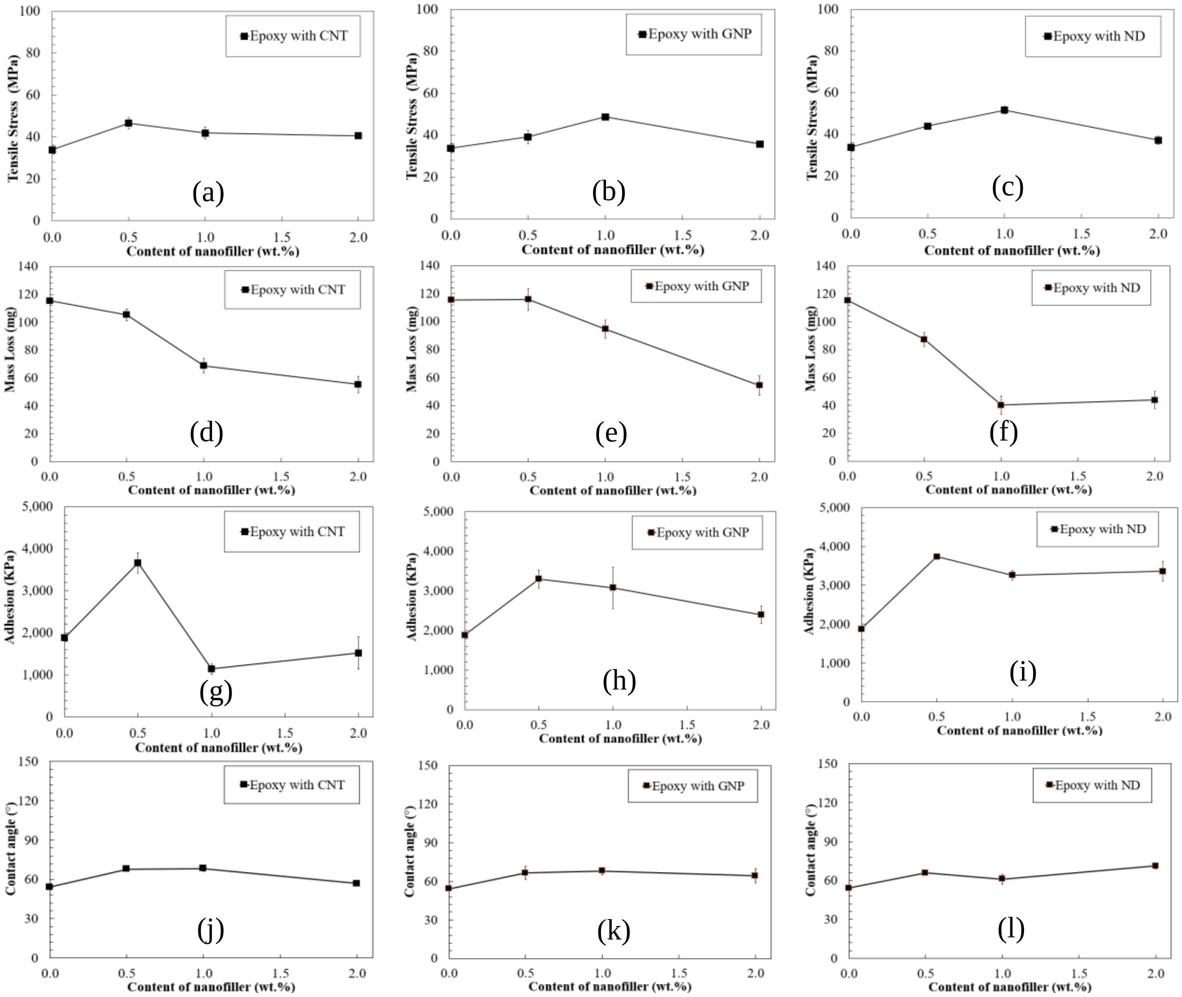

Figure 6. Results for coupon tensile test of epoxy composite with (a) CNT, (b) GNP, (c) ND, abrasion resistance test with (d) CNT, (e) GNP, (f) ND, adhesion test with (g) CNT, (h) GNP, (i) ND, and water contact angle test with (j) CNT, (k) GNP, (l) ND

Task 3.3. Reducing the Permeability and Investigating the Interfacial Bonding Chemical Analysis (15%): During this reporting period, the research team (Dr. Liangliang Huang, Qiuhao Chang, Ph. D. student from University of Oklahoma) have conducted studies on developing computational models for the cast iron/CNT-modified epoxy resin system as detailed below.

(1) Computational Model Setup for Cast Iron/CNT-modified Epoxy Resin System: As summarized in Figure 7a, we performed molecular dynamics (MD) simulations to generate copolymer and covalent adaptable network (CAN) polymer models. The single chains of the copolymer, such as $(A1)_X$-$(T1)_Y$, were constructed with different combinations of X and Y values. Following the initial energy minimization, an annealing procedure was carried out to heat a box of copolymer chains from 300 K to 500 K slowly, and then the system was cooled back to room temperature. Such process was repeated with adjusted initial and final temperatures until the energy of the system no longer changed or the monitored properties (free volume, charge distribution, binding energy) agreed with experiments. Figure 7b shows a Diels-Alder (DA) polymer network that was generated following the model development schematic flow. Specifically, as shown in Figure 8, Furfurylamine and 1,5-bis(maleimido)-2-methyl pentane (MPDBMI) were crosslinked to form the DA-induced network.

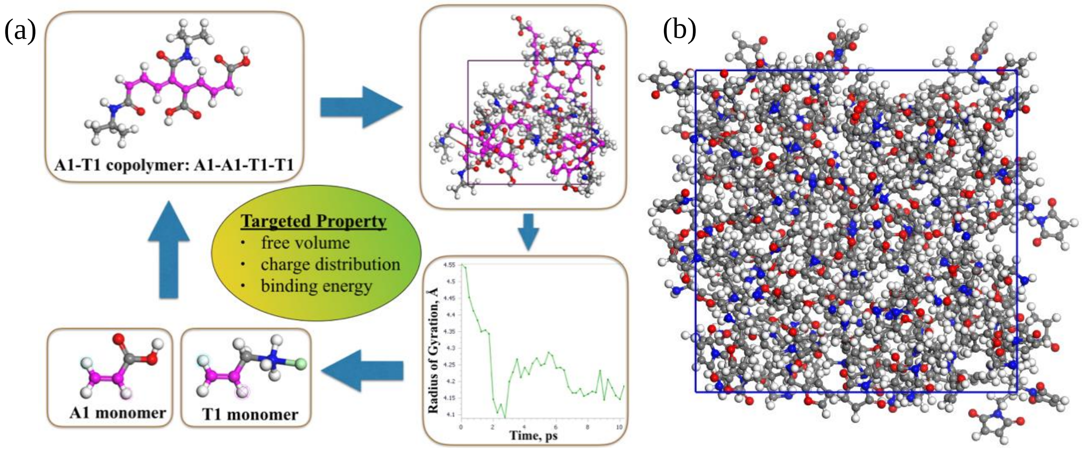

Figure 7. (a) The schematic of copolymer model development and (b) a Diels-Alder (DA) polymer network

Figure 8. Atomistic surface models for Fe (110) (left) and Fe_2O_3 (right). Both literature and our preliminary MD simulation results suggest that epoxy resin has a stronger interaction with the Fe_2O_3 surface.

Task 3.4 Finite Element Numerical Analysis to Guide the Design of the Developed high-performance Healable CIPP Structural Liner (20%): During this reporting period, the research team (Dr. Chengcehng Tao, Xiaoyue Zhang and Junyi Duan, Ph. D. students from Purdue University) have conducted numerical studies on the CIPP pipeline liners as summarized below.

(1) Model Setup: A 3D finite element model (FEM) was set up in ABAQUS software, as shown in Figure 9, to simulate a cast-iron pipe rehabilitated by the CIPP liner buried in a subgrade structure.

Two loading conditions on the FEA model were considered: 1) external subgrade load; 2) internal in-pipe pressure. Table 2 shows the applied material properties for the FEM analysis.

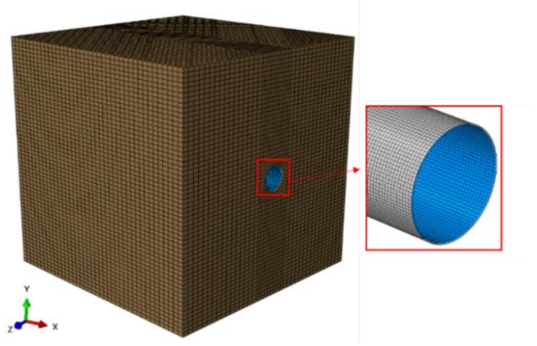

Figure 9. The 3D finite element model with meshes for the subgrade – pipeline – liner system (Brown: subgrade; Silver: cast-iron pipe; Blue: epoxy resin liner).

Table 2. Material properties.

Component	**Parameters**	**Value**
Subgrade	Elastic modulus (MPa)	30
	Poisson's ratio	0.35
	Density (kg/m^3)	1800
	Cohesion (Pa)	8000
	Internal friction angle (deg)	30
	Dilation angle (deg)	0.1
Cast-iron pipe	Elastic modulus (GPa)	148
	Poisson's ratio	0.287
	Density (kg/m^3)	7200
Epoxy resin liner	Elastic modulus (MPa)	8000
	Poisson's ratio	0.3
	Density (kg/m^3)	1200

(2) Preliminary Numerical Simulation Results and Discussions: Figure 10a shows the parametric study results regarding the effect of buried depth and CIPP liner thickness on the cast-iron pipe. The maximum principal stress of the pipe increases with the buried depth, while decreasing with liner thickness. Figure 10b shows the relationship between the maximum principal stress of the pipe and the in-pipe pressure for the bare pipe and the pipe rehabilitated with the 4mm CIPP liner. The maximum principal stress of cast-iron pipe decreases by 6.6% as rehabilitated by CIPP liner. The effects of liner thickness and in-pipe pressure on cast-iron pipe mechanical performance are illustrated in Figure 10c. The maximum principal stress of the pipe decreases as the liner thickness and internal pressure decrease. The pipe stress decreased by 16.5% when the thickness of epoxy resin liner increased to 15 mm.

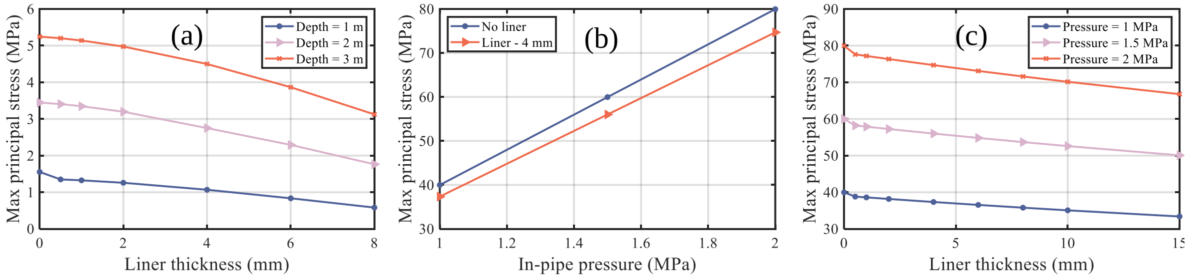

Figure 10. (a) The relationship between maximum principal stress of cast-iron pipe and liner thickness at different buried depths, (b) with and without liner, and (c) with different in-pipe pressure.

Project Financial Activities Incurred during the Reporting Period:

The cost breakdown during the reporting period in each category according to the budget proposal is shown in Table 3.

Table 3. Cost breakdown

Category	Amount spent during Q2
Personnel	
Faculty	$0
Postdoc	$0
Students (RA and UR)	$10,470
Benefits	$9.97
Operating Expenses	
Travel	$0
Materials and Supplies	$19,855.8
Recharge Center Fee	$8,265.83
Consultant Fee	$0
Subcontracts	Subawards issued
Indirect Costs	$39,870

Project Activities with Cost Share Partners:

The Match fund from NDSU for this project is coming from the tuition of the associated graduate students during their work on this project. During the reporting period (Q2), Austin Knight and Tofatun Jannet were hired on the project. The tuition for the two students during Q2 is estimated to be $10,955.52 at a rate of $811.52 per credit.

Project Activities with External Partners:

During this reporting period, the research team established a partnership with two industry companies including PPM and Nuflow. In addition, the research team is hiring a project consultant, George Ragula, the president and CEO of Rauglatech, who has 43 years of service in the gas industry, engineering, operations, construction (including trenchless), R&D and management. George is currently a consultant for Nuflow. The NDA with the consultant is completed and the contract is in progress. In addition, the subawards to the sub-universities were established. The research team meet on a regular basis bi-weekly and the sub-universities have conducted research as planned.

Potential Project Risks:

No potential risks were noticed during this reporting period.

Future Project Work:

In the next quarter, the research team will continue working on Tasks 2.1, 3.1, 3.3, 3.4, and expand the work onto Tasks 2.2 and 3.2 whenever applicable.

Potential Impacts on Pipeline Safety:

The preliminary results on self-healing epoxy and high-performance nano-epoxy composites show the potential of the proposed materials, which can be used to enhance the safety of any pipelines which needs to use epoxy related materials.