PHMSA
Pipeline and Hazardous Materials
Safety Administration

Development of New Multifunctional Composite Coatings for Preventing and Mitigating Internal Pipeline Corrosion

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Acknowledgment

- **Sponsor**

US Department of Transportation-CAAP

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USDOT CAAP program director, Joshua Arnold, Zhongquan Zhou, and the other project committee members for the valuable guidance and support.

- **Group members**

Graduate students: Mingli Li, Matthew Pearson, Zi Zhang, Hong Pan

Undergraduate students: Devin Neubeck, Wyatt Schirrick, Arianna Christian

High school students: Over eight high students from different schools in North Dakota State through past years

Summary of Accomplishments

- **Technical Accomplishments**
  - ❖ Three patent pending
  - ❖ One invited talk and one keynote for internal conferences
  - ❖ Publications, including 12 top-notched journal papers, and over 15 conference papers/posters
  - ❖ Awards, PI Zhibin Lin received Research of the Year in 2018, College of Engineering, NDSU
    PhD student Xingyu Wang received Graduate Researcher of the Year in 2020
- **Education Accomplishments**
  - ❖ Student Recruitment: Xingyu Wang (doctoral dissertation), Matthew Pearson (M.S. thesis)
    Over five PhD and M.S. students participating in this project
  - ❖ Outreach activities: Mentoring over eight high-school students working on related research for ND Governor high school summer program | 2016-2019

Outline

- 1. Background
- 2. Proposed Concept
- 3. Coating Synthesis
- 4. Evaluation of Performance of the New Coatings
- 5. Enhancement of the Coatings
- 6. High-Performance Coatings for Pipeline Application
- 7. Summary
- 8. Education and Outreach Activities

1. Background

Incidents experienced in onshore oil/gas metallic pipelines

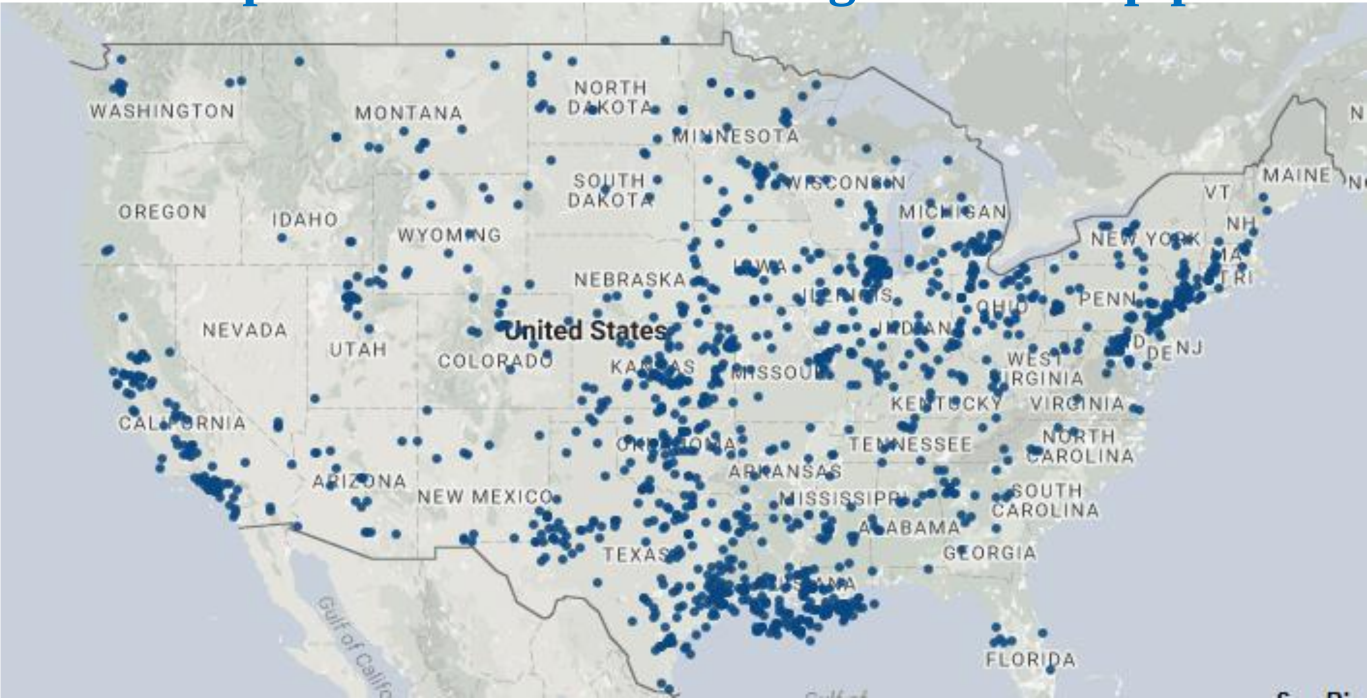

Fig. 1 Pipeline incident in the United State

Photos from http://projects.propublica.org/pipelines/

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1. Background

Corrosion is the leading causes for incidents in oil/gas metallic pipelines

Table 1. Pipeline incidents in recent years at North Dakota (Pan et al., 2017[1]).

Accident	Location	Year	Loss
Pipeline spill	Tioga	2014	One gas pipeline exploded and burned
Pipeline spill	Tioga	2013	**865,000 gallons (<u>one of the largest to happen onshore in U.S. history</u>)**
Pipeline spill	Sargent County	2011	Spilling 400 barrels of crude oil
Pipeline spill	Neche	2010	Releasing 3,784 barrels of crude oil
Pipeline spill	Mantador	2004	Residents were evacuated, and a rail line was shut down
Pipeline spill	Barnes County	2003	Releasing 9,000 barrels of propane
Pipeline ruptured	Bottineau	2001	1.1 million US gallons (4,200 m^3) of gasoline burned
Pipeline spill	Harwood	2001	Spilling 40 barrels of fuel oil

Pipeline spill (North Dakota, 2013)

Pipeline explosion (West Virginia, 2012)

[1]. Pan, H. et al. 2017.

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1. Background

Internal corrosion of oil/gas metallic pipelines is a big challenge

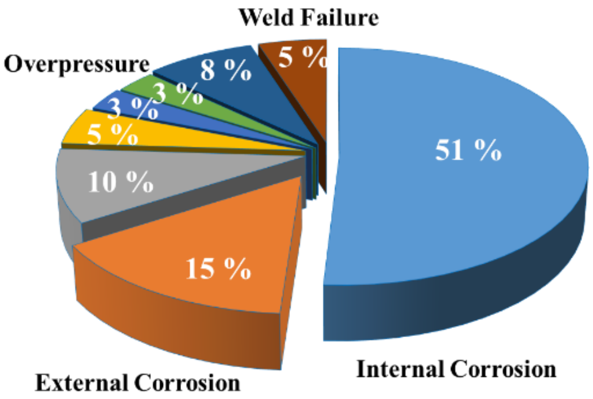

Fig. 1 Dominant internal pipe corrosion[1]

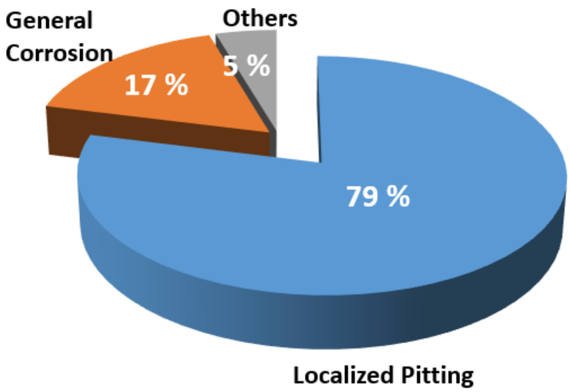

Fig. 2 Detailing in pipeline corrosion[2]

Fig. 3 Internal corrosion: a) localized pits[3], b) fouling[4] and c) wear-erosion[5]

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[1]. Data from Nalli, 2012
[2]. Data from PHMSA 2010-present
[3]. Photos from http:--www.flickriver.com-photos-59127492@N07-5416927808-
[4]. Photos from http:--www.icorr.org-news-180-index.phtml
[5]. Photos from https:--sites.google.com-site-metropolitanforensics-root-causes-andcontributing-factors-of-gas-and-liquid-pipeline-failures

1. Background

Protective coatings for internal corrosion of oil/gas metallic pipelines

- Have a wide variety of types for internal corrosion control.
- Act as barriers between the steel substrate and the environment in order to resist the transport of water, oxygen, ions and other aggressive species to the coating metal interface.

Defects often experienced in existing protective coatings

- As typically observed, the percolation of afore mentioned aggressive species leads to coating delamination and under-film corrosion, and the loss of corrosion protective function.
- Therefore, lessons from major failure modes of coating systems in pipelines can attribute to valuable information for selection of suitable coating systems.

1. Background

Limitations of existing protective coatings for internal corrosion

1) Low mechanical and damage tolerance.

2) Low long-term durability.

3) Low anti-fouling resistance.

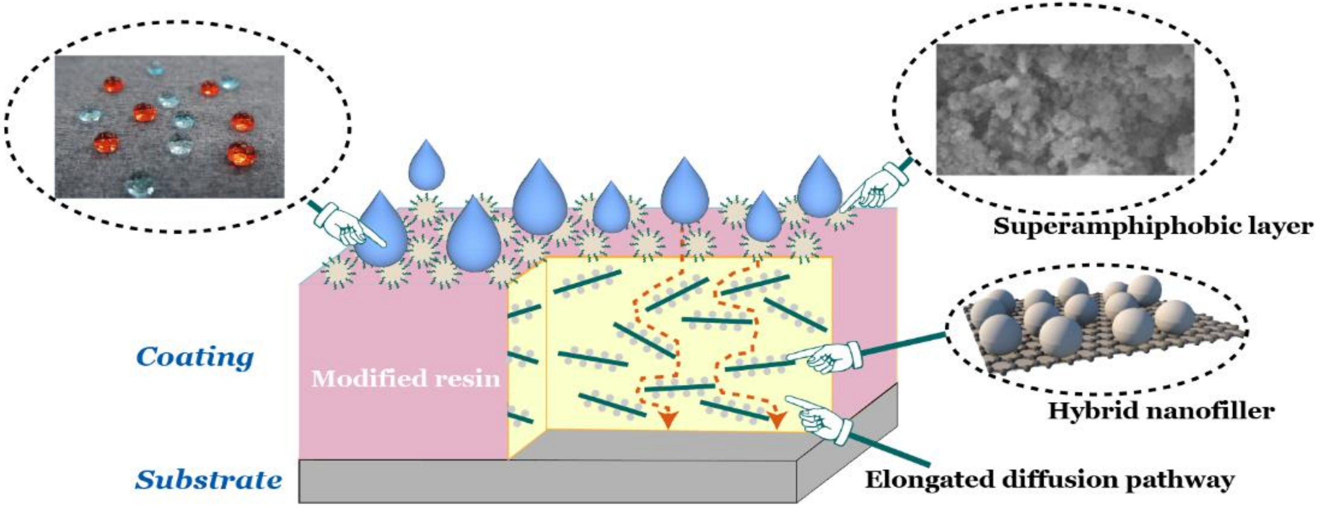
4) Low resistance to combined effects of corrosion, fouling, and wear.

As such, a high-performance coating is expected that enables providing multifunctional protection against corrosion as well as fouling-wear issues.

2. Proposed Concept

High-performance composite coatings:

Propose to use nanomodified high-performance composite as protective coatings to mitigate corrosion issue in oil/gas metallic pipelines.



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**Note: the information has patent protection in the United States.*

2. Proposed Concept

High-performance composite coatings:

Due to the unique properties that provided by nanomaterials, nanofiller-polymer composites are expected to have superior performance and offer opportunities to fabricate new high-performance composites.

New composite coatings:

- Excellent corrosion resistance
- Excellent abrasion resistance and antifouling protection properties
- Excellent long-term durability and damage tolerance
- Environment-friendly

2. Proposed Concept

Objectives of this study:

- Polymer screening process for nanocomposite coatings
- Nanoparticle reinforcement for nanocomposite coatings
- Evaluate the overall performance of the hybrid nanofiller coatings
- Enhancement of the selected nanocomposite coatings
- High-performance multifunctional coatings for pipeline applications
- Summary the education and outreach activities associated with this project

3. Coating Synthesis

Polymer screening process for nanocomposite coatings:

Table. 2 Selected coatings during the polymer screening process

Mixture	Type	
Epon 828 / Epikure 3175	Epoxy / Polyamine	Excellent long-term corrosion resistance and chemical resistance
Epon 828 / Epikure 3164	Epoxy / Polyamine	High degree of toughness and flexibility
Lumiflon 910 / Desmodur N 3600	FEVE / Polyisocyanate	Polyisocyanate is harmful if inhaled, may cause respiratory irritation
EPI-REZ 7510-W-60 / Epikure 8535-w-50	Waterborne Epoxy	Weak mechanical properties and durability
EPI-REZ 7520-WD-52 / Epikure 6870-w-53	Waterborne Epoxy	Weak mechanical properties and durability
Epon 828 /Baxxodur EC 302	Epoxy / Polyether-amine	Polyether-amine is harmful in contact with skin, causes severe skin burns and eye damage
Epon 828 /Baxxodur EC 310	Epoxy / Polyether-amine	Polyether-amine is harmful in contact with skin, causes severe skin burns and eye damage

Note: During the screening process, the abrasion resistance, fouling resistance, and corrosion resistance was characterized for each polymeric coatings.

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Selection of polymer:
Epon 828 / Epikure 3175

3. Coating Synthesis

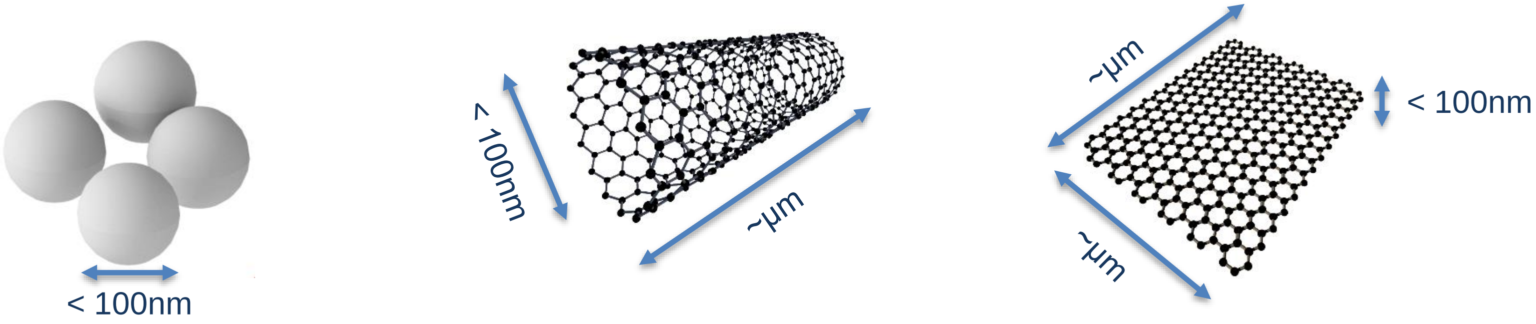
Nanoparticle screening process for nanocomposite coatings:

Size ranges from 1 to 100 nm

- 0-dimensional
- 1-dimensional
- 2-dimensional

} nanomaterials

Example: Nano-silica (NS), Carbon nanotubes (CNT), graphene nanoplatelets (GNP)



a) Spherical structure   b) Cylindrical structure   c) Planar structure

Fig. 7 Classification of nanoparticle by dimensions

3. Coating Synthesis

Nanoparticle screening process for nanocomposite coatings:

- Carbon nanotubes (1D), graphene nanoplatelets (2D), and nano-silica (0D)

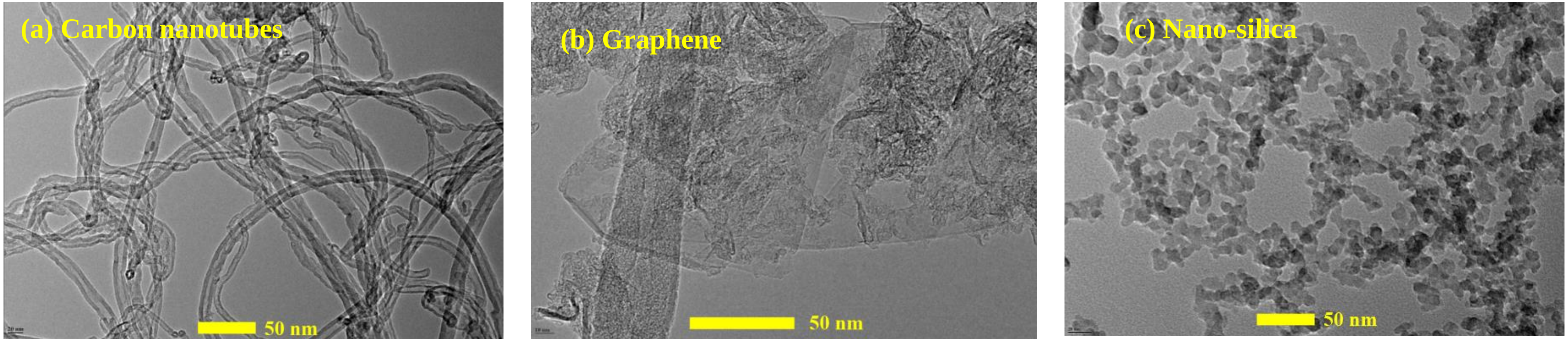


Fig. 10 Transmission electron microscopy (TEM) photograph of nanoparticles

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3. Coating Synthesis

Dispersion of nanomaterials:

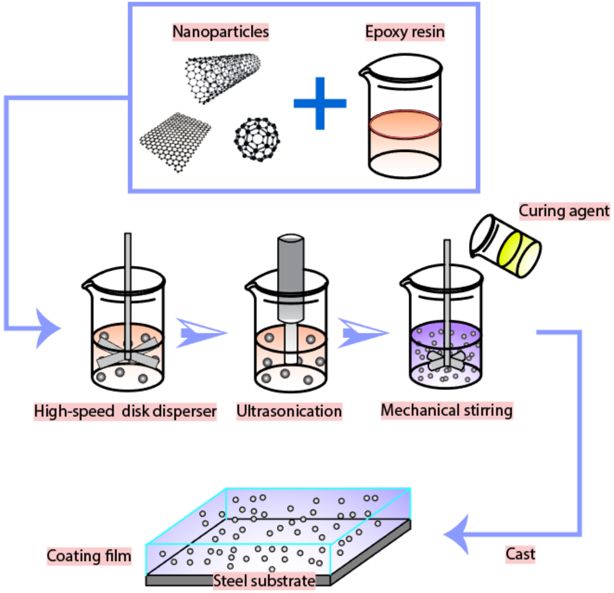


Fig. 8 Schematic of the fabrication process

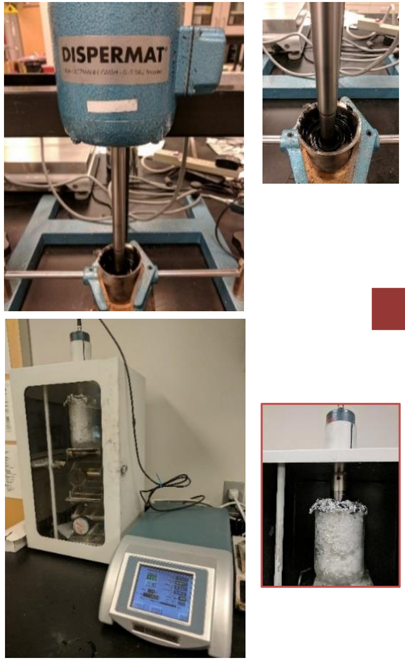


Fig. 9 GNP-epoxy composite with and without proper dispersion procedure

3. Coating Synthesis

Test of the new developed coatings:

(a) Corrosion protection (b) Taber abraser (c) Coupon tensile (d) Contact angle (e) Adhesion

Fig. 11 Schematic of test setup

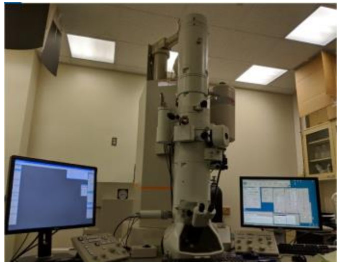
Characterization of the new developed coatings:

Particle size distribution

Transmission electron microscopy (TEM)

Powder X-Ray diffraction (XRD)

Fourier-transform infrared spectroscopy (FTIR)



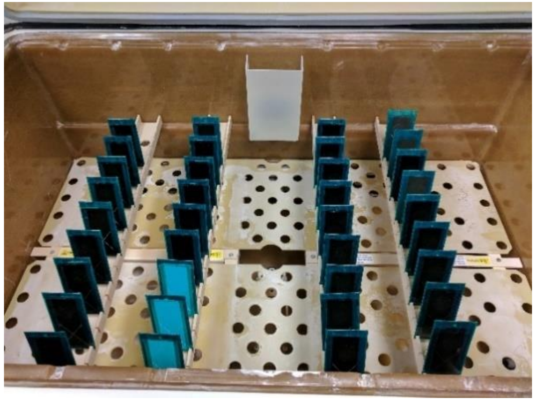
4. Evaluation of Performance of the New Coatings

Test Matrix:

- Three types of hybrid nanofillers were examined, which included CNT/NS, GNP/NS, and CNT/GNP.
- Total concentration was fixed at 1.0 wt.%

Test Setup:

- Corrosion protection
- Taber abraser
- Coupon tensile
- Contact Adhesion
- Salt fog test



4. Evaluation of Performance of the New Coatings

Corrosion resistance:

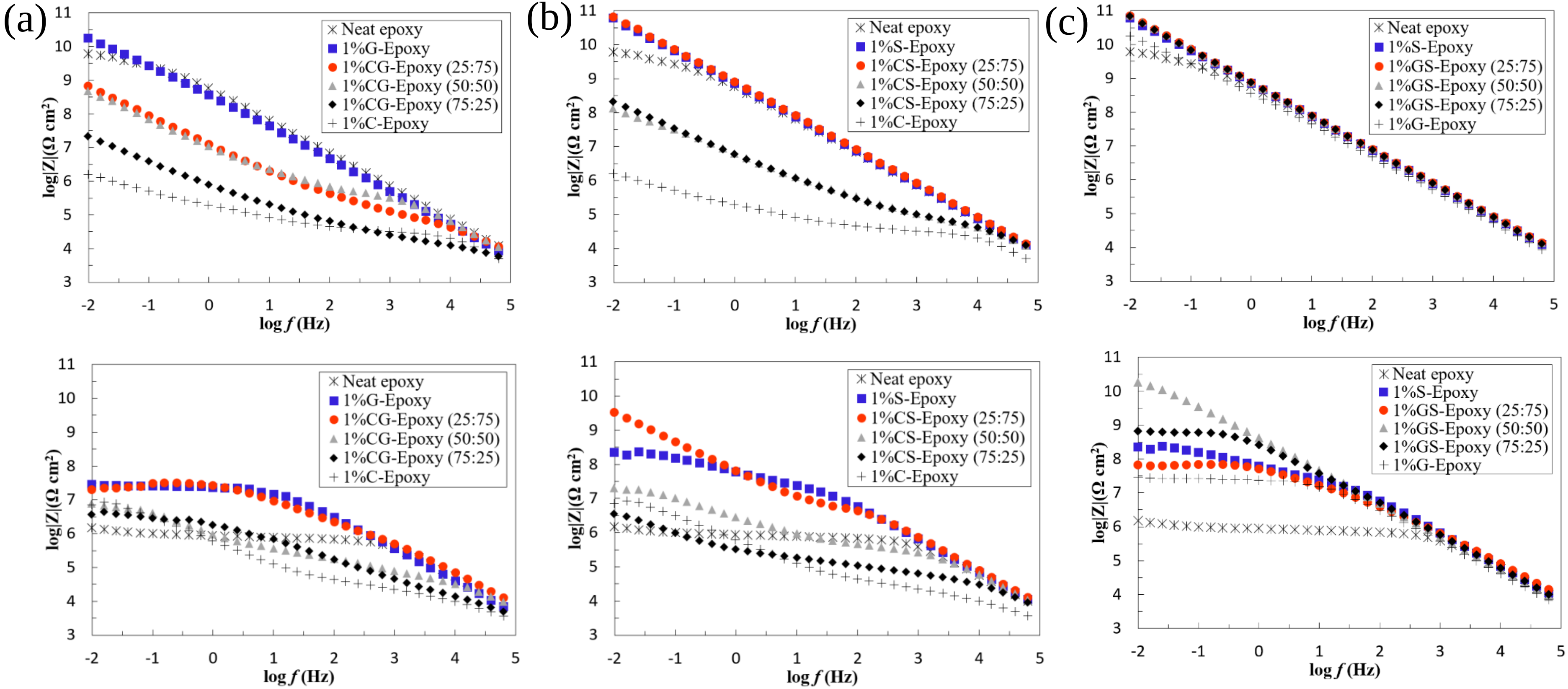


Fig. 17 EIS result of nanocomposites before and after exposure (a) CNT+GNP/epoxy, (b) CNT+NS/epoxy , (c) GNP+NS/epoxy

4. Evaluation of Performance of the New Coatings

Abrasion resistance:

- Mass loss after abrasion

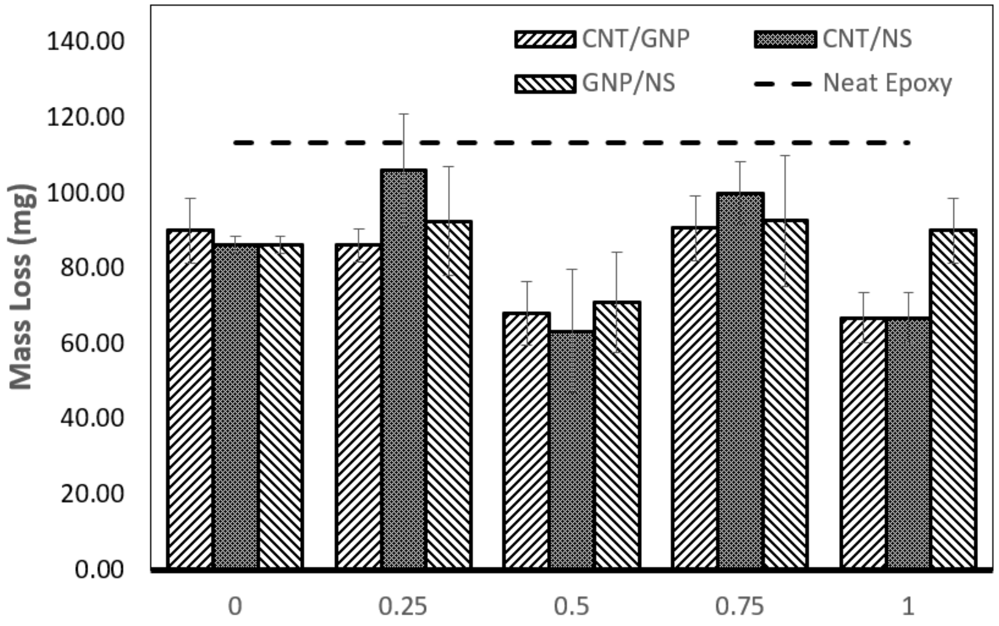


Fig. 18 Mass loss of nanocomposites

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4. Evaluation of Performance of the New Coatings

Tensile properties:

- Tensile strength
- Ultimate strain
- Young’s modulus

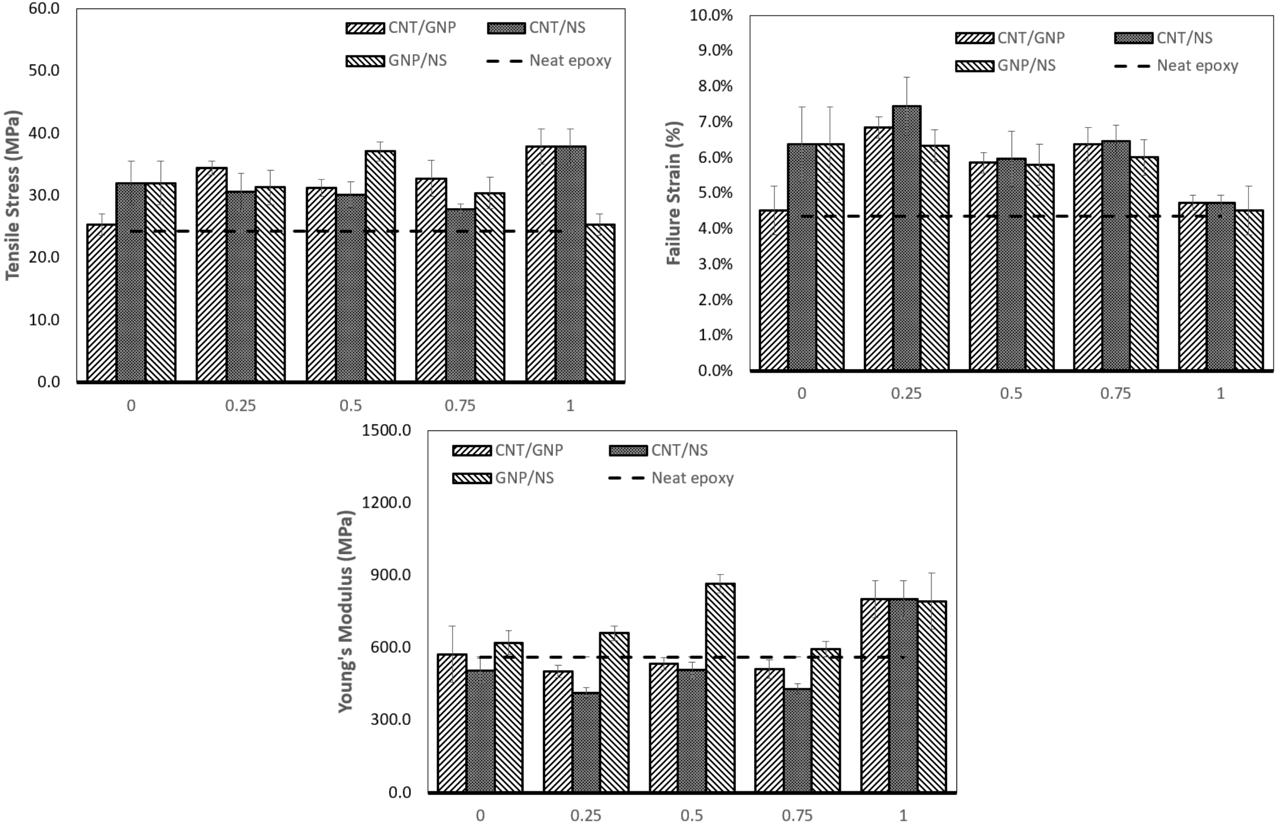

Fig. 19 Tensile properties of nanocomposites

4. Evaluation of Performance of the New Coatings

- The 1%GS-Epoxy group has excellent properties compared with others.
- To further investigate GNP/NS nanofiller systems, nanocomposites with different weight contents of hybrid filler were also examined.

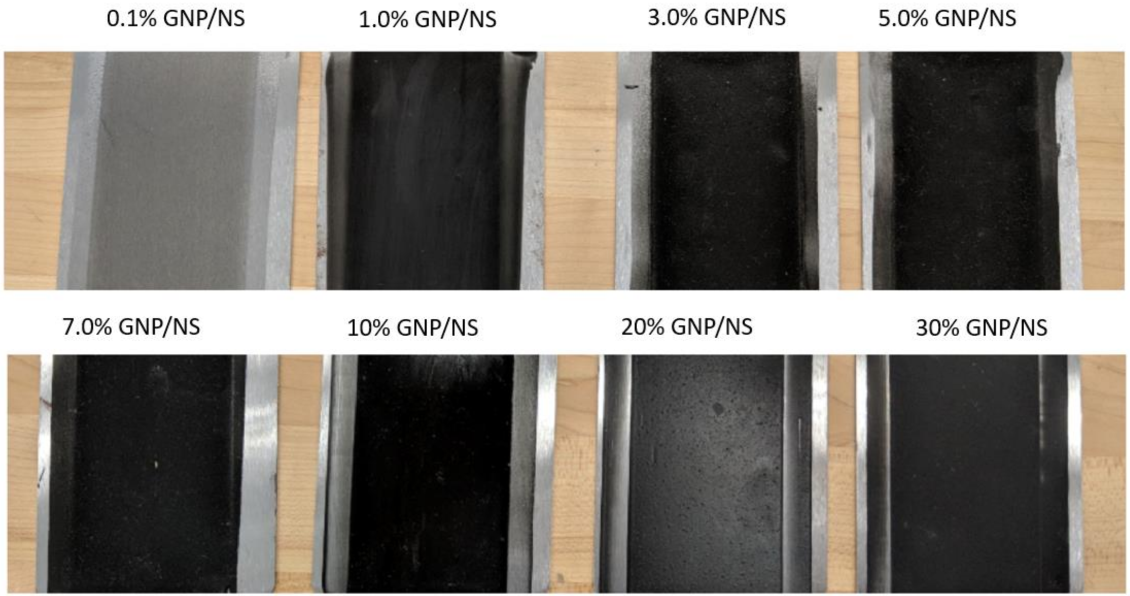

Fig. 20 GNP/NS epoxy nanocomposites with varied filler concentration

Selection of Nanofiller Reinforcement:
1.0%GS-Epoxy

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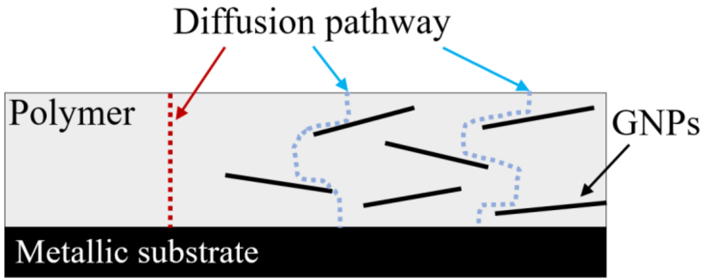
**Note: the information has patent protection in the United States.*

4. Evaluation of Performance of the New Coatings

Strengthening mechanisms of nanocomposite

- Interaction between nanofiller and polymer
- Interphase region surrounding nanofiller
- Intrinsic properties of nanofiller



Diffusion pathways in nanocomposite

Fig. 31 Strengthening mechanisms of nanoparticles

4. Evaluation of Performance of the New Coatings

Strengthening mechanisms of nanocomposite

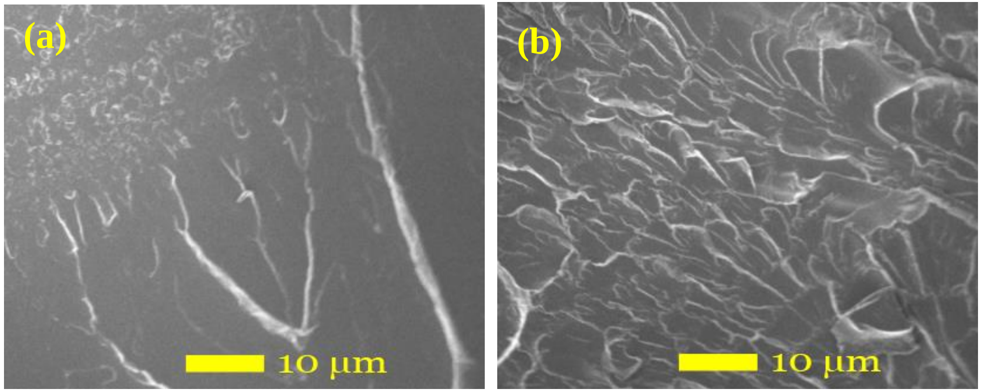


Fig. 32 SEM image of fracture surface (a) neat epoxy, (b) nanocomposite

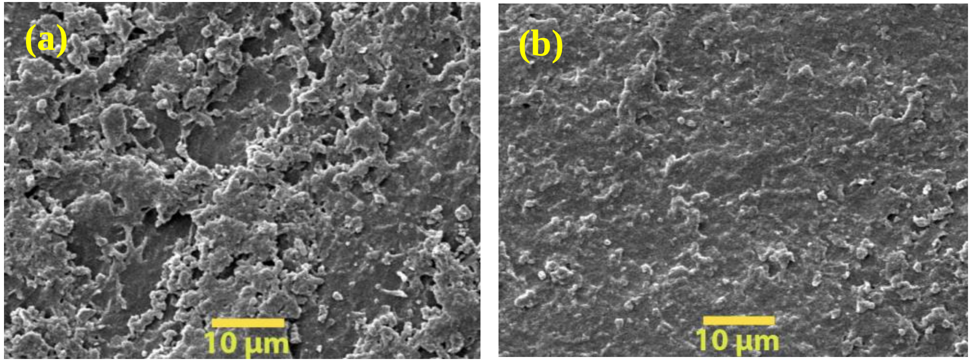


Fig. 33 SEM image of abraded surface (a) neat epoxy, (b) nanocomposite

4. Evaluation of Performance of the New Coatings

Hybrid nanoparticle reinforcement:

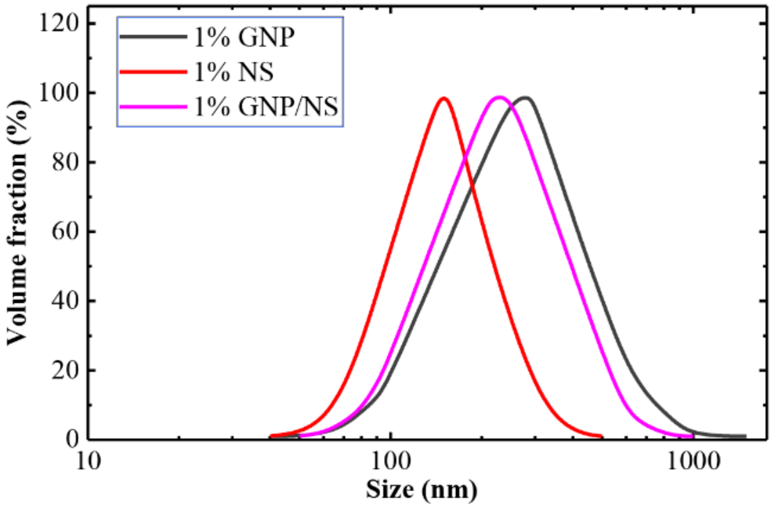


Fig. 34 Particle size distribution of GNP/NS hybrid filler

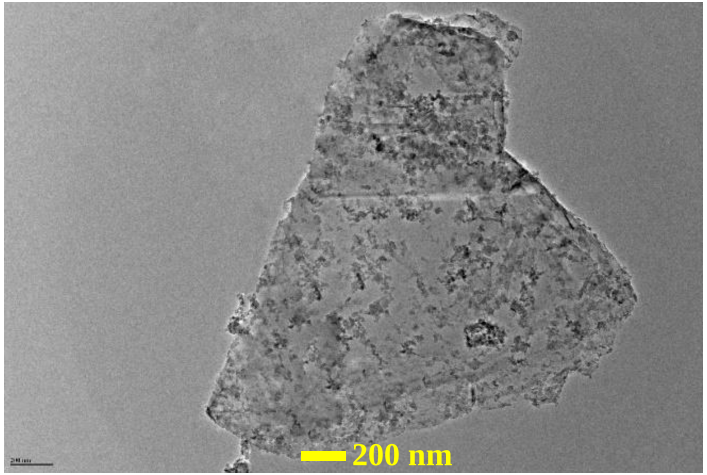


Fig. 35 TEM photograph of GNP/NS hybrid filler

4. Evaluation of Performance of the New Coatings

Hybrid nanoparticle reinforcement:

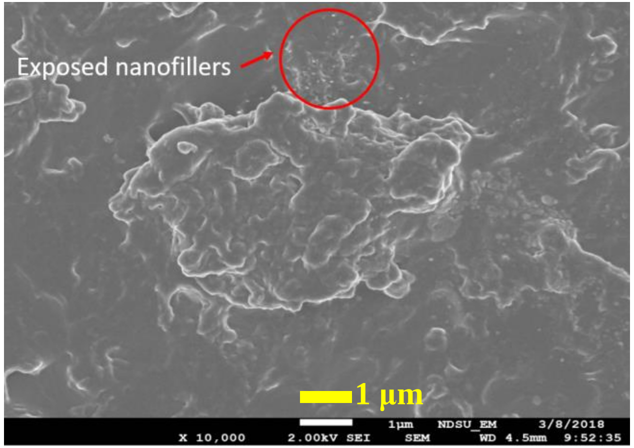


Fig. 36 SEM images of nanocomposite coating surface after surface damage

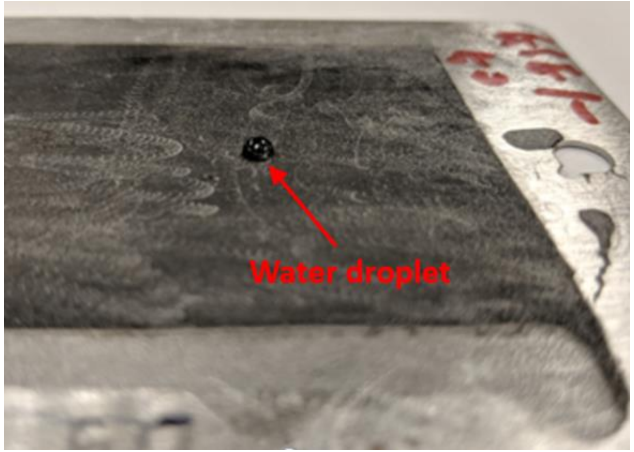


Fig. 37 Water contact angle of 1.0%GS-Epoxy sample after surface modification

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4. Evaluation of Performance of the New Coatings

Hybrid nanoparticle reinforcement:

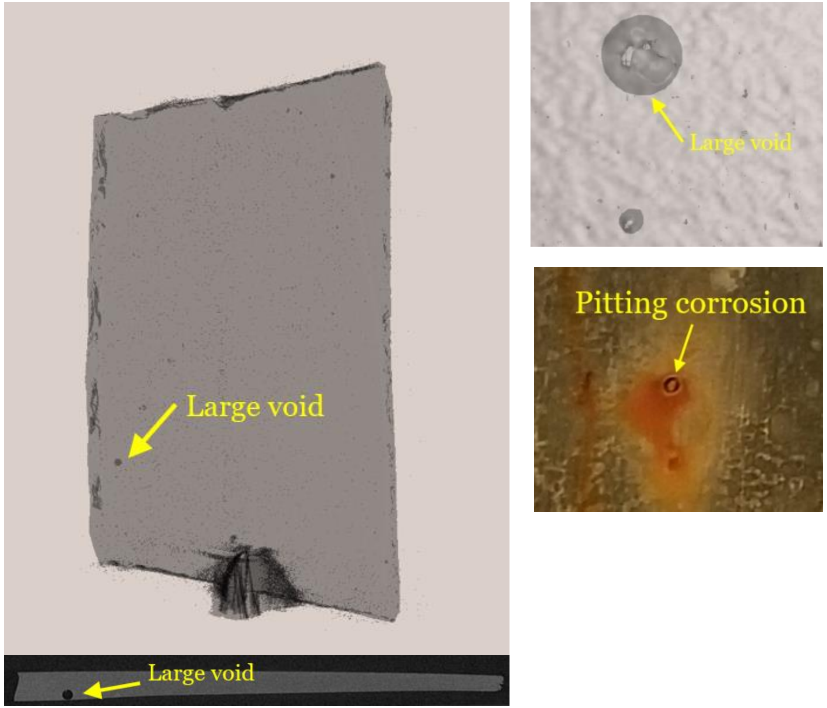

Fig. 38 Defects and pitting corrosion in the neat epoxy coating

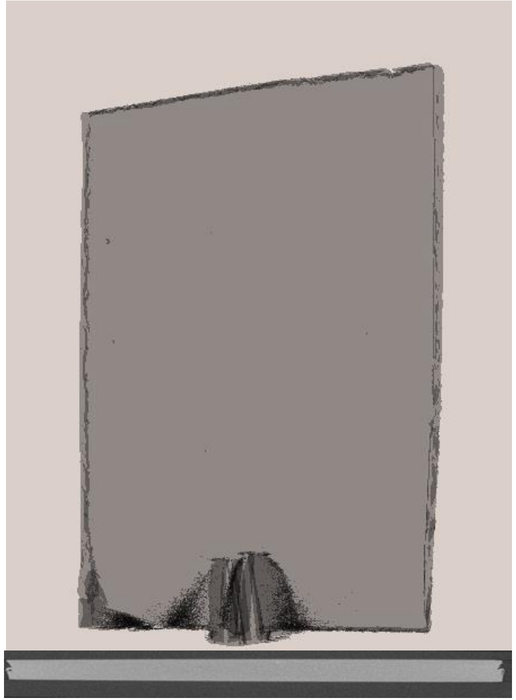

Fig. 39 Micro-CT scan of nanocomposite

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5. Enhancement of the Coatings

Proposed approach for the remained challenges:

Polydimethylsiloxane was introduced to modified epoxy resin, as the intercalation will result in a hydrophobic surface, which leads to an increase in contact angle.

Test Matrix:

Different weight contents of PDMS were used, and the modified resins have incorporated with GNP/NS hybrid filler.

**Note: the information has patent protection in the United States.*

5. Enhancement of the Coatings

Hydrophobicity, before and after abrasion

Group	Contact Angle (°)	
	before	after
Neat epoxy	51	50
1%GS-Epoxy (50:50)	26	95
1%GS-PDEP (10:90)	106	119
1%GS-PDEP (30:70)	109	115

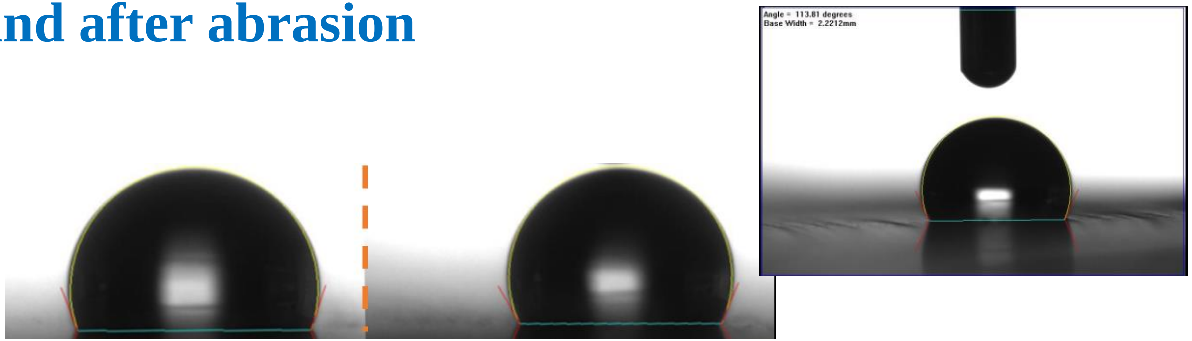
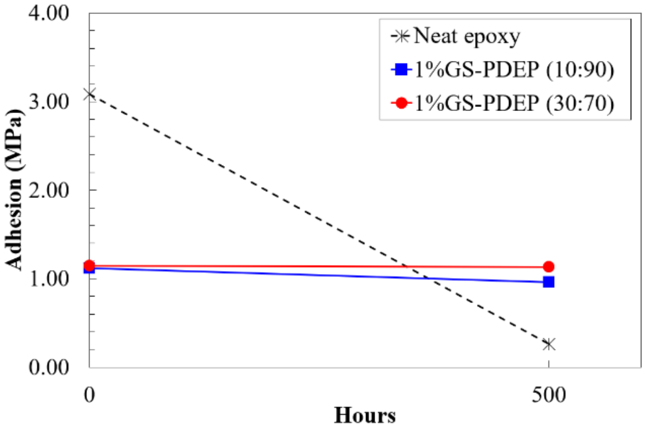


Fig. 23 Contact angle before and after abrasion for the and 1%GS-PD/EP (10:90) samples

Adhesion after durability test



**Note: the information has patent protection in the United States.*

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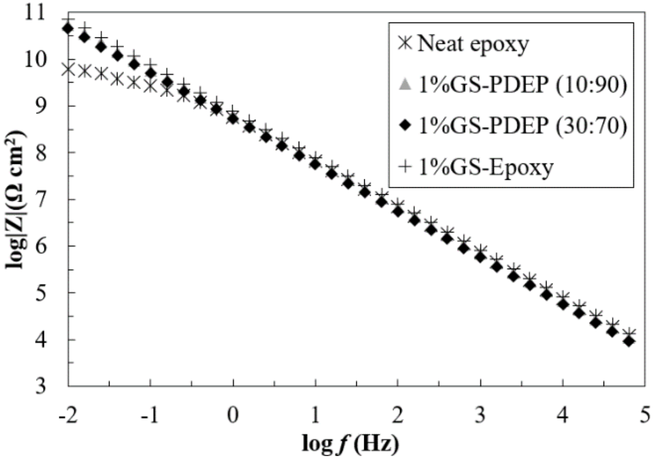
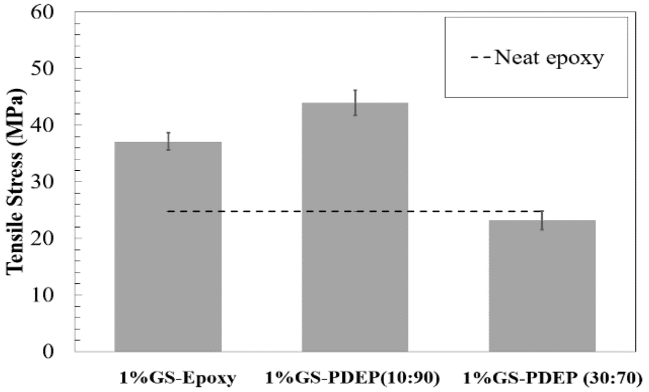
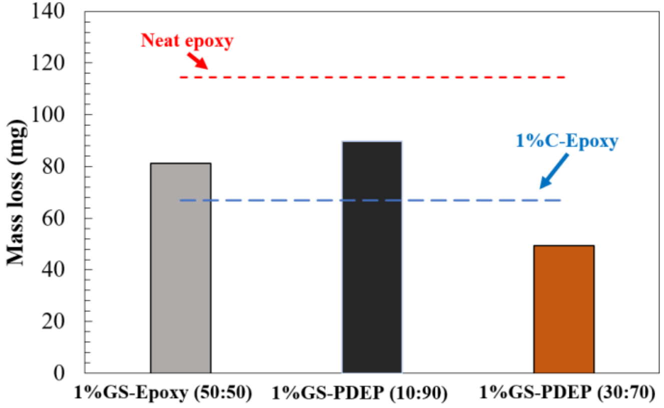
Fig. 24 Pull-off strength of the 1%GS-PDEP coatings after exposure

5. Enhancement of the Coatings

Other protection properties:







More requested feature: Oil repellency?

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Selection: 1**%GS-PDEP (10:90)**

**Note: the information has patent protection in the United States.*

6. High-Performance Coatings for Pipeline Application

The proposed high-performance multifunctional coating includes:

1) hybrid nanofiller reinforcement
2) superamphiphobic layer
3) modified resin

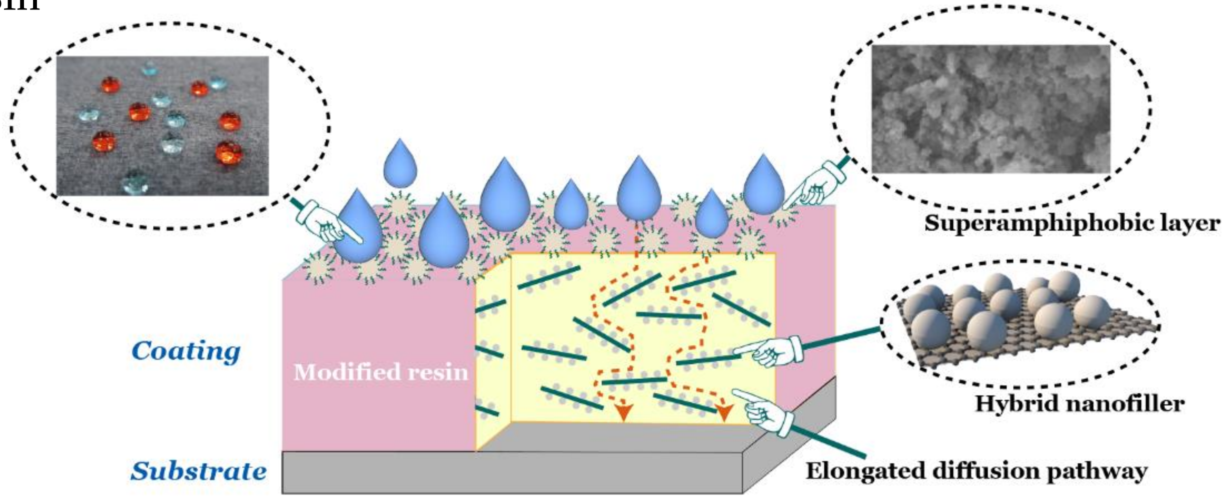

Fig. 25 Proposed high-performance multifunctional coating

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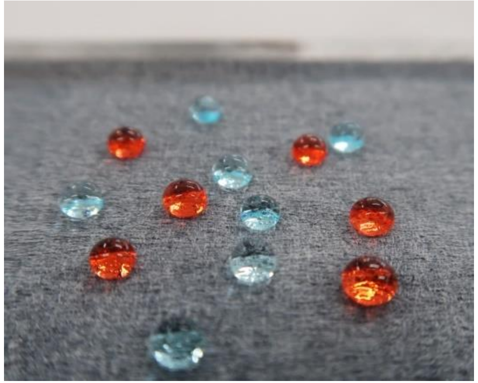
**Note: the information has patent protection in the United States.*

6. High-Performance Coatings for Pipeline Application

Superamphiphobic surface:

Table 3. Contact angle of the high-performance coating

Group	Contact Angle (°)	
Neat epoxy	Water	51
	Hexadecane	13
1%GS-PEDP (10:90) MS	Water	162
	Hexadecane	146



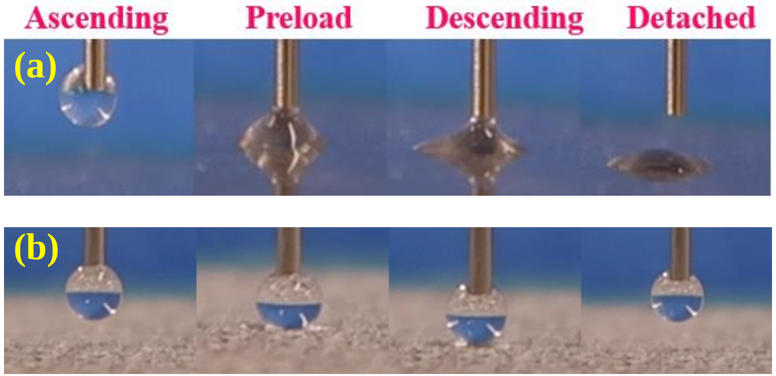


Fig. 26 Water droplet ascending and descending of (a) neat epoxy, (b) high-performance coating

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**Note: the information has patent protection in the United States.*

6. High-Performance Coatings for Pipeline Application

Long-term durability:

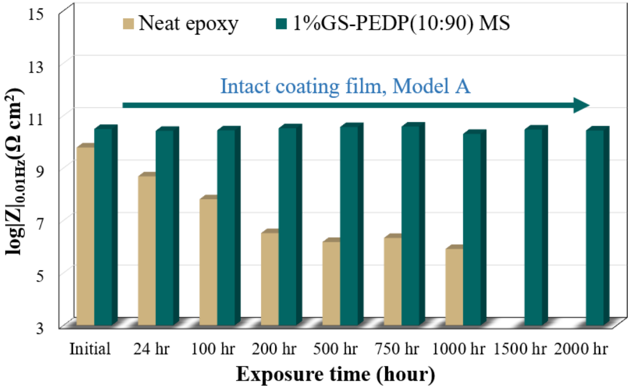

Fig. 27 Corrosion protection of the high-performance coating after exposure

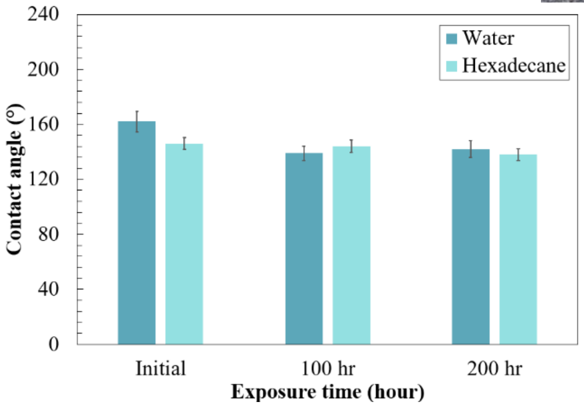

Fig. 28 Contact angle of the high-performance coating after exposure

**Note: the information has patent protection in the United States.*

6. High-Performance Coatings for Pipeline Application

Long-term durability:

Fig. 29 Simulated long-term test of the developed coatings under flow condition

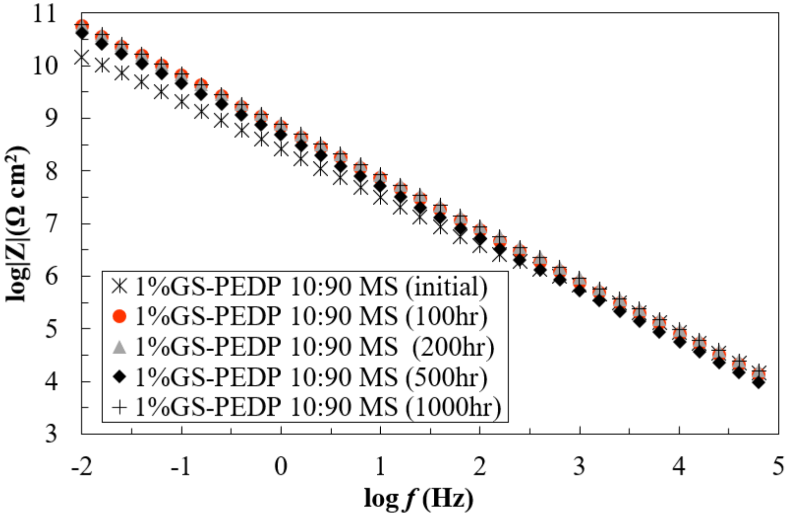

Fig. 30 Corrosion protection properties of the high-performance coating after flow test

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**Note: the information has patent protection in the United States.*

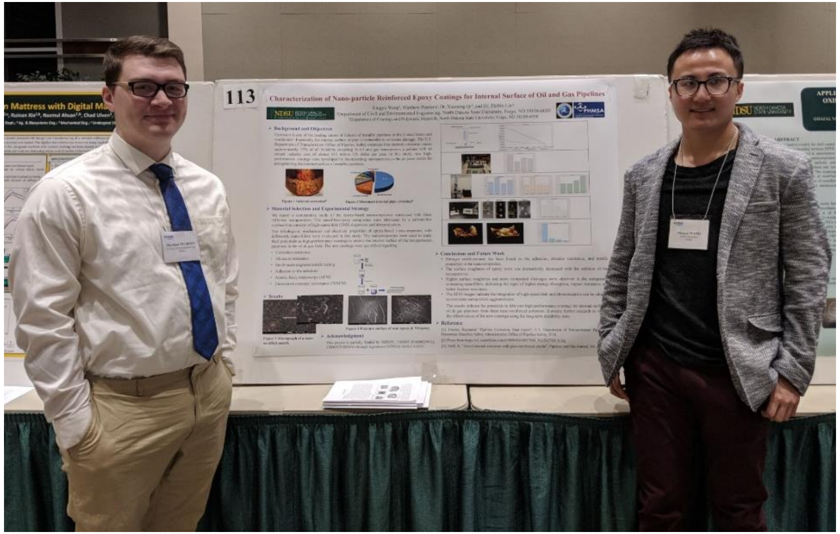
7. Summary

This project provided a comprehensive investigation of the new high-performance coatings, from fabrication, characterization, to overall performance, striving for superior protective coatings for internal corrosion mitigation of oil/gas pipelines. The project proofs the proposed concept, and fulfills the targeted outcomes:

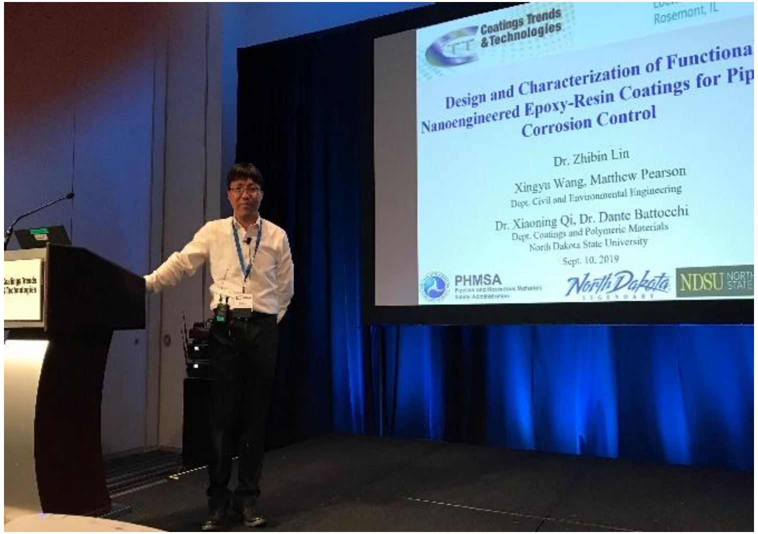
- Excellent corrosion resistance
- Significant improvement on mechanical properties
- High anti-fouling capacity
- The results obtained during the accelerated corrosion test revealed the proposed coating was durable, as its excellent corrosion resistance and superamphiphobicity remained undamaged after exposure.

8. Education and Outreach Activities

Dissemination of the research findings:



MS student Matthew Pearson (left) and PhD student Xingyu Wang (right) attended and presented their US DOT CAAP project in poster session in ND EPSCoR 2018 State Conference in Grand Forks, April 17th, 2018



Dr. Lin gave an invited talk on the national coating conference in Rosemont, IL, on Sept. 10th, 2019

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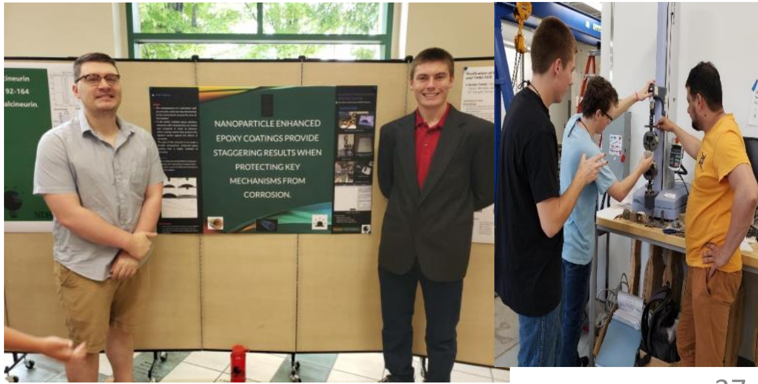
8. Education and Outreach Activities

Dissemination of the research findings:

Four high school students with the graduate student (from left to right: Julia Bauroth, Josh Gronneberg, Xingyu Wang, Olivia Svanes and Natlie Lemnus) for preparing coating samples and performing tests in 2018

High school students working in the project in 2017



High school students working in the project in 2019

Questions?

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