BOND BEHAVIOR OF NANO-ENHANCED POLYMER CONCRETE FOR BRIDGE DECK OVERLAYS

Quarterly Progress Report

For the period ending June 30, 2023

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1. Background and Introduction

Considering the nation's bridges, 42% of all bridges are at least 50 years old, and 7.5% of the nation's bridges, are considered structurally deficient, meaning they are in "poor" condition. Without improvement in current techniques and materials for better durability and life, the number of deficient bridges will increase, and move into becoming fracture critical infrastructure. In particular, there is an urgent need for effective and durable rehabilitation solutions for deteriorated highway bridge decks. Deck deterioration is commonly caused by a combination of vehicle loading, freeze–thaw degradation, cracking, delamination of cover concrete, and/or corrosion of internal reinforcement. Bridge deck overlays should be able to protect the underlying deck and reinforcement from contaminates, providing additional strength and stiffness to the deck system, and extending the service life of the overall structure. Polymer concrete overlays have proven to be a suitable system for accelerated bridge construction due to their rapid cure, light weight, and small thickness. This project investigates the effect of nanomodification of polymer resin in the concrete on their bond behaviour in an effort to develop a strong bond with the base structure offering improved chemical resistance and wearability extending life of the bridge systems.

2. Problem Statement

Polymer concrete overlays are light weight, wear resistant, skid resistant and waterproofing characteristics make them an intelligent and durable decision for new construction, maintenance, rehabilitation and preservation of bridges. A polymer concrete overlay also minimizes traffic disruption. It's generally applied at a total thickness of only one-half to three-quarter inch. Their rapid cure (open to traffic within 3 hours) characteristic is highly suitable for accelerated bridge construction applications. In some cases, workers can place the overlay at night then open it to traffic the next day. Moreover, these overlays are corrosion resistant, providing a barrier between the dissimilar materials to minimize galvanic corrosion, saving the expense of applying additional corrosion-resistant primers to the steel reinforcement; have very good cracking resistance and have superior durability [1]. When bridge deck overlays are considered, a strong bond to the existing concrete surface and/or reinforcement is required. The properties discussed above make polymer-based materials a favorable material for bridge deck overlays [2] but improving the bond strength of polymer concrete is heavily unexplored and can bring significant benefit in accelerated bridge construction. Polymer-based overlays show no delamination with the substrate concrete beams after 2 million cycles of fatigue loading [3]. It is important for the bonded joint to be able to sustain all expected in-service loads and environmental conditions, which can vary considerably.

3. Objectives and Research Approach

This project proposes to investigate the bond behaviour of polymer concrete for bridge deck overlays modified at the material level using functionalized carbon nanotubes. Over the last fifteen years, researchers have examined the use of nanomaterials to alter a materials' behaviour. The association of CNTs in cementitious composites is well known for improvement of material, elastic, and mechanical properties of cement [4-6]. The incorporation of CNTs in polymer concrete mixes, however, is heavily unexplored and their effect of bond strength of polymer concrete mix has not been investigated. Therefore, the objectives of this research are (a) To assess and compare bond performance of nanomodified polymer overlay systems under laboratory test conditions, (b) To suggest the optimum mix design of CNTs modified polymer concrete suitable for bridge deck overlays and (c) To inform the changes observed in bond strength with the incorporation of three different quantities of CNTs polymer concrete bring for use in bridge deck overlay applications (d) To suggest industry guidelines for effective application of thin polymer overlays to improve safety, and extend service life of bridges.

4. Description of Research Project Tasks

The following is a description of tasks carried out to date.

Task 1 – Development of polymer concrete mix design.

Polymer concrete is typically composed of a binder, a catalyst, and coarse and fine aggregates. The choice of binder for bridge deck overlays is an important factor is achieving several characteristics. Polymeric binders such as epoxy, polyester, vinyl ester and other types of polymers are known for their significantly higher bond strength to many surfaces compared with any cementitious binders. The latest bond tests on several bridges show that epoxy overlays have a higher average value (274 psi) over time compared to Methyl Methacrylate (MMA) overlays (143 psi). However, test results show that the initial friction numbers for epoxy overlays start around 70 and fall to the mid to low 20s in five to seven years [7]. The latest friction numbers show MMA overlays retain friction resistance very well over time, from an initial average value of approximately 40 to a value in the mid-30s after nine years of service. Using a low viscosity silane modified vinyl ester mortar produced a 2.8 mPa bond strength polymer concrete mix [8]. For the polymer concrete mix design, the recommended ratio of binder to aggregate (coarse + filler) is typically 1:3.7 [9]. Studies have shown that the overall performance of polymer concrete could be improved if the ratio of coarse aggregate to filler aggregate was maintained at a rate of 7:3 by weight.

In this study, the selection of the binder material and the design of polymer concrete mix is governed by not only the mechanical properties but importantly the effectiveness of dispersion of nanomaterials in the resin for a homogeneous product. The PI has worked previously with dispersing nanomaterials in MMA binders and achieved homogenized results [10]. Methacrylate adhesives bond the widest range of substrates and are especially good for the structural bonding of metals. They require the least amount of surface preparation, and a faster strength development which means sooner usage favorable for accelerated bridge construction. Therefore, the polymer concrete mix in this study will be developed considering all the above factors. An extensive literature review will be conducted to obtain an optimum mix of polymer concrete suitable for bridge deck overlays.

Up to this period, following is the work performed corresponding to Task 1.

Mixing method: The primary components of the polymer concrete (PolC) used in this design mix were T-17 Polymer Concrete Liquid Component and T-17 Polymer Concrete Powder Component (Transpo Industries). The mix design ratio of T-17 Liquid T-17 Powder component in this study is 1:8, respectively (Murcia et al. 2022). The specimens for this study are relatively small as mentioned above; hence, only fine aggregate with nominal maximum size of 2.36 mm will be used for the concrete mix.

Figure 1: Polymer concrete mixing process

The composite was mixed for 3 minutes using a mechanical drill with mixing paddle and a bucket until a homogenous mixture was obtained. Since polymer concrete is rapid setting material, the concrete specimens were casted within 3-5 minutes to avoid material hardening. The casted beams cured for 24 hours before demolding them and 7-day curing in room conditions prior to testing.

Table 1 : Polymer concrete (PolC) mix design

Material	**Units**	**PC**
Aggregate	$\frac{kg}{m^3}$	2002
Polymer Resin		251

<u>Testing methods</u>:

Determining the compressive strength of concrete shows the quality of the material and its strength to withstand compressive forces. In this study, cylinders of 101.6 mm by 203.2 mm are used to conduct the compressive strength of PolC following ASTM C579 ("C579 Standard Test Methods for Compressive Strength of Chemical-Resistant Mortars, Grouts, Monolithic Surfacings, and Polymer Concretes" 2018). The cylinders are tested using Forney L.P. Standard Frame (F) compression testing machine with a capacity of 1500 kN, Figure 2.

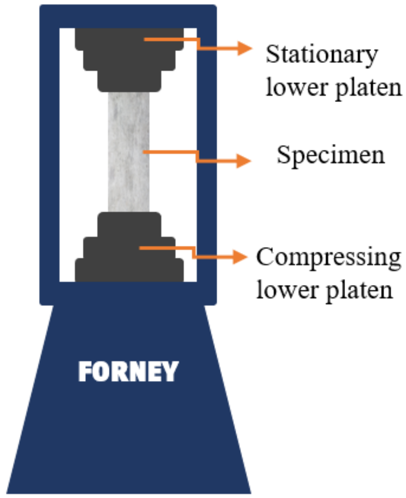


Figure 2: Compression Testing Machine Schematic

Specimens were tested at a loading ramp rate of 100 psi/sec (0.7 MPa/sec) for PolC specimens after 7 days of curing in agreement with ASTM C579 ("C579 Standard Test Methods for Compressive Strength of Chemical-Resistant Mortars, Grouts, Monolithic Surfacings, and Polymer Concretes" 2018). To ensure equal load distribution, silicon caps are used on the cylinders, and the peak load of each cylinder is recorded. The compressive strength equation below from the ASTM C39/C39M-20("C39/C39M Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens" 2018) is utilized to calculate the maximum compressive strength.

$$Compression\ Strength \quad f_c = \frac{4\,P_{max}}{\pi D^2} \qquad \textbf{(1)}$$

Where f_c is the compressive strength, P_{max} is the maximum load, and D is the average diameter of cylinders.

Modulus of rupture test were performed on 3 in. by 3 in. by 12 in. (76.2 mm by 76.2 mm by 304.8 mm) beams using four-point bending test as shown in Figure 3.

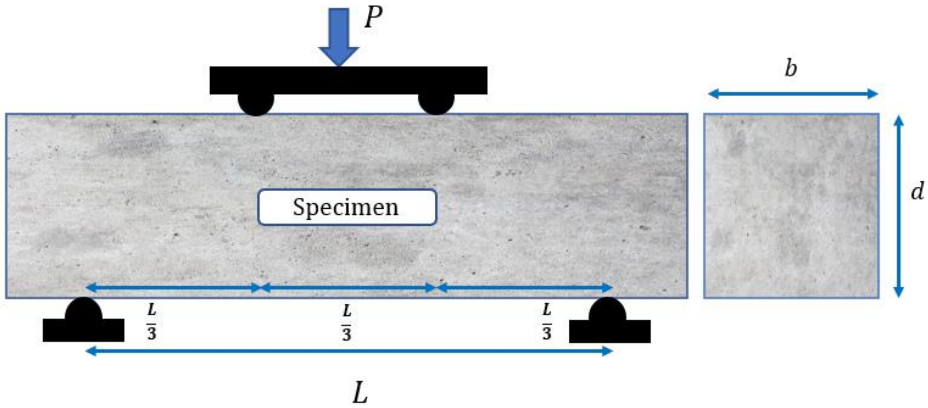


Figure 3: Schematic representation of Four-point bending setup

Similar to compression test, the Forney compression machine was used to test beams after 7 days of curing, respectively, in accordance with the ASTM C580 ("C580 Standard Test Method for Flexural Strength and Modulus of Elasticity of Chemical-Resistant Mortars, Grouts, Monolithic Surfacings, and Polymer Concretes" 2018) for PolC. The specimen is loaded at ramp rate of 3 psi/sec (0.0207 MPa/sec) for PolC. Failures within the middle third of the span length, the modulus of rupture is computed using the below equation ("C78/C78M Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Third-Point Loading)" 2018).

$$\text{Modulus of Rupture,} \quad MOR = \frac{PL}{bh^2} \qquad \textbf{(2)}$$

Where MOR is the modulus of rupture, P is the maximum load, L is the span length, b is width, and h is depth of the beams.

<u>Results:</u>

A total of 6 cylinders were tested to determine the compressive strength of the concrete with respective to ASTM C579 ("C579 Standard Test Methods for Compressive Strength of Chemical-Resistant Mortars, Grouts, Monolithic Surfacings, and Polymer Concretes" 2018). The Figure 4 shows the testing process, and the different modes of failures.

Figure 4 Compression Test Result of PolC Failed Specimen

The average compressive strength of PolC was 59.9 MPa, with a coefficient of variation of two percent which highlights the consistency of the results. A previous study tested five cylinders of 50.8 mm by 101.6 mm for PCC and PolC compressive strength and concluded the mean compressive strength for PCC and PolC was 68.9 ± 5.1 MPa and 53.9 ± 5.8 MPa (Murcia et al. 2022). Therefore, the compressive strength determined in preliminary PolC compressive strength testing falls within the range of the literature values.

Table 2 Compression Test Results

Properties	**Units**	**PolC Specimens**					**Mean**	**STDEV**	**COV**
		1	**2**	**3**	**4**	**5**			
Peak Load	**kN**	495.6	484.8	488.2	484.7	474.4	485.5	7.6	2%
Max. Stress	**MPa**	61.1	59.8	60.2	59.8	58.5	59.9	0.9	2%

The modulus of rupture was determined by testing five beams of using Four-point bending test. Similar to compression test, Forney machine was used for the MOR test, and Figure 5 shows the test setup, and failed specimens.

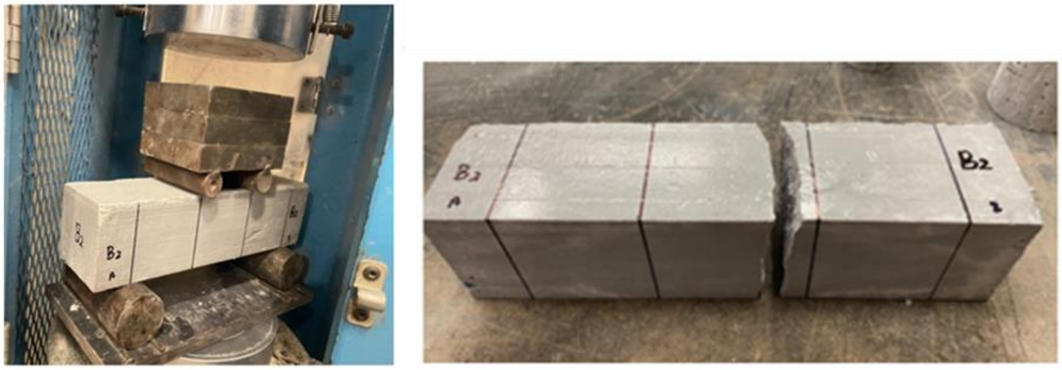


Figure 5 MOR Test Setup with PolC failed specimen on the right

The average MOR stress for PolC was 23.7 MPa. The coefficient of variation was 3% for PolC which demonstrated consistency of the testing.

Table 3 Modulus of Rupture Test Results

Properties	**Units**	**PolC Specimens**			**Mean**	**STDEV**	**COV**
		1	**2**	**3**			
Peak Load	**kN**	33.6	33.6	34.7	33.9	0.62	2%
Max. Stress	**MPa**	24.48	23.11	23.4	23.7	0.72	3%

Based on the compressive strength and Modulus of Rupture results, the tensile strength of polymer concrete measured in using modulus of rupture is about 3 times greater than Portland cement concrete which indicates an appropriate mix design as indicated in literature.

Task 2 – Identification of nanomaterial functionalization for dispersion.

Carbon nanotubes (CNTs), one of the strongest materials available today [11], seem to have significant effects on polymer resins. With appreciable strength and industrial availability, small quantities of carbon nanotubes were used to improve the strength and stiffness of the polymer composite materials [12]. Surface functionalization of CNTs using active chemical groups can be performed to form covalent bonds with the polymer matrix [13]. A detailed discussion about using different dispersion methods and the effect of functionalization of MWCNTs in the polymer matrix is presented elsewhere [14]. Functionalized CNTs were shown to have a chemical reaction with the polymer resins [15]. The nanoscale diameter of CNTs allows them to interfere in the polymerization process, altering the final polymer matrix [13]. Fracture toughness improvement of 112% was observed in polymer concrete using carboxyl functionalized CNTs, however, there was an associated reduced failure tensile strain of 58% [1].

Up to this period, following is the work performed corresponding to Task 2.

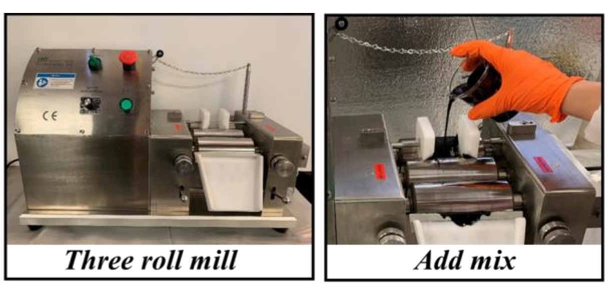
Based on thorough literature review, the most suitable functionalization of COOH and weight content of 0.5 wt.% and 1 wt.% CNTs content with respect to binder amount is identified for effective nano modification and chemical changes in resin.

Task 3- Nano modification process of polymer concrete mix.

The chemical nature of the polymer concrete binder maximizes utilization of nanomaterials by providing an inviting chemical interaction platform within the polymerization process. However, the efficiency of nanomaterials in altering the mechanical performance is greatly dependent on the efficiency of dispersion. Good dispersion of the nanomaterials in the polymer matrix was reported to control the efficiency of the nanomodification process [16]. Dispersion of carbon nanotubes involves techniques such as ultrasonication and mechanical stirring or a combination of both. In addition, three-roll mill known as a “calendaring” technique has been used in the past for the dispersion of high concentrations of CNTs in a variety of resins. A precise control on the gap between the three rolls can be achieved to impact the shear mixing of carbon nanotubes between the rollers resulting in their disentanglement and dispersion in polymer matrix. A standard protocol established in the PI’s prior work will be used in this task for nanomaterial dispersion for the two weight contents of CNTs [10].

Up to this period, following is the work performed corresponding to Task 3.

Ensuring repeatability and consistency with dispersion and resulting CNT mix. The three-roll shown in Figure 6 has been used for this study. The protocol for gaps between rolls has been obtained from past studies as shown.



Pass number	Gap 1	Gap 2
1	50-40 μm	40-30 μm
2	40-30 μm	30-20 μm
3	40-30 μm	30-20 μm
Speed of roller 1-n1	40RPM	
Speed of roller 2-n2	80RPM	
Speed of roller 3-n3	160RPM	

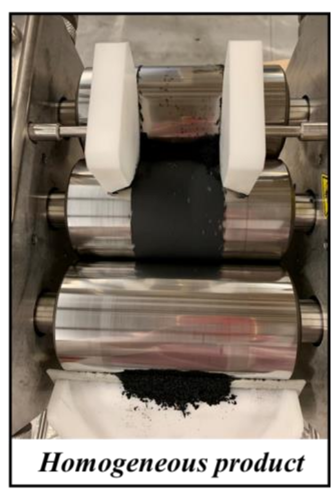


Figure 6 Three roll mixing process and protocol for mixing

Dispersed mixture was obtained using the pristine and COOH functionalized CNTs and Scanning Electron Microscope Images showed efficient dispersion and no segregation after 45 days of dispersion.

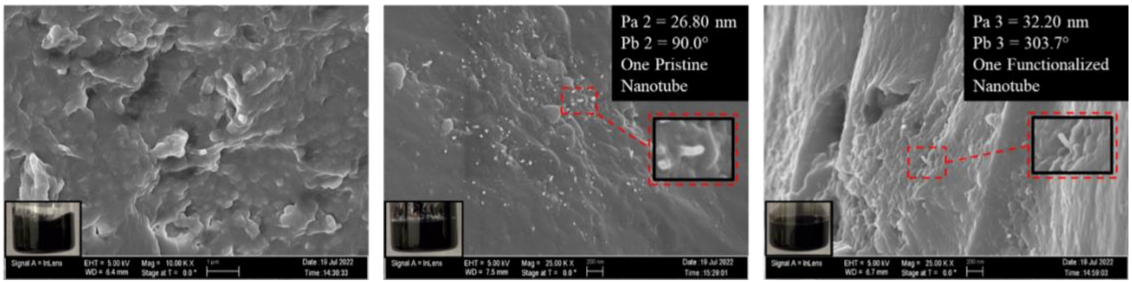


Figure 7 SEM images in sequence: Neat polymer matrix, polymer with pristine CNTs and polymer with functionalized CNTs

Task 4- Evaluation of mechanical properties and bond strength of nano enhanced polymer concrete.

Current state of knowledge on the effects of nanomodification on polymer concrete behavior is limited. Research shows that the flexural strength of polymer concrete can be improved by 50% through nano modification of the polymer binder. Research has previously demonstrated that nanomaterials are capable of increasing the tensile strain at failure of polymer concrete and fracture toughness by 60% and 131% respectively [30]. CNTs have provided 76% and 56% improvement in failure tensile strain and fracture toughness of polymer concrete respectively. In this task, compressive strength tests are performed in accordance with ASTM C579 Test Method B [17]. Flexural strength testing is performed using prismatic beam samples in accordance with ASTM C580 Test Method A [18]. The curing period governed by the standards is 24 hours at 23°C. In this study, the bond strength is measured using the direct pull-off method for laboratory investigation on the tensile bond strength of a polymer concrete specially formulated for overlay applications. The bond strength tests were performed in accordance with ASTM C1583 [19, 20] and the test results were compared with the bond strength value recommended by ACI 548.9-08.

Up to this period, following is the work performed corresponding to Task 4.

Surface preparation of test specimen were governed by the criteria set forth by the International Concrete Repair Institute. Polymer overlays require a concrete surface preparation (CSP) of 5 – 9 achieved by various surface preparation measures. The following figure shows the nature of prepared surfaces vs non prepared surfaces for this study.

Figure 8 Surfaces before and after preparation

ASTM 1583 pull off tests were conducted by first drilling cores into the polymer concrete overlay on the concrete substrate using a universal drilling machine.

Figure 9 Core drilling using universal drilling machine

Steel tensile loading devices were attached to the cores to perform the pull off test using hydrajaws 2000. They were attached using a polymer adhesive.

Figure 10 Pull off tests on cores

The possible three failure modes were identified. However, since the objective for this study is to understand bond behavior, failure in overlay-substrate interface was induced based on geometry of the specimens. For plain polymer concrete with nanomodification, 5 cores were tested and resulting failure was obtained as failure in substrate-overlay interface.

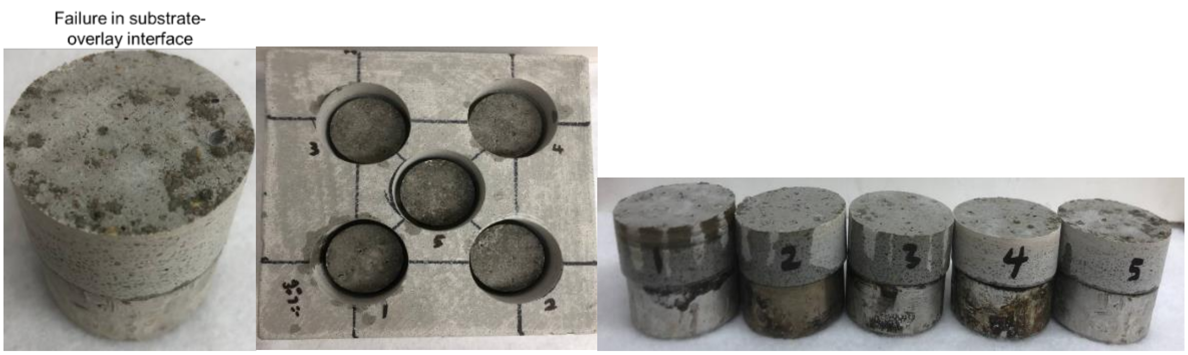


Figure 11 Neat polymer concrete overall pull off test

The results of the pull off tests of neat polymer concrete mix will act as control results when nanomodified polymer concrete mix is developed.

Table 4 Pull off Strength of neat polymer concrete mixes

No.	Result (N)	Area (mm2)	Pull-Off Strength (MPa)
1	5000	2026.8	2.5
2	9100	2026.8	4.5
3	6500	2026.8	3.2
4	10000	2026.8	4.9
5	12500	2026.8	6.2

Task 5- Proposing a dispersion protocol of carbon nanotubes in resin.

Two phases were used to disperse the carbon nanotubes: magnetic stirring and ultrasonication. Before to adding the nanomaterials to the epoxy resin, the precise amount of each material was weighed with a 0.01-gram precision. After that, the resin containing CNTs was heated to 110°C in an oil bath while being stirred magnetically at 800 rpm. To trap heat and keep the resin sealed at the fast-stirring rate, the resin container was sealed with aluminum foil. The resin nanocomposite is placed in an ultrasonication bath after two hours of magnetic stirring. Degassed distilled water heated to 60 °C was present in the bath [18]. Ultrasonic waves are then applied for another two hours. The resin nanocomposite was then taken out of the bath and allowed to cool to room temperature for more than two hours before being used. The chosen temperatures, stirring rate and time, and ultrasonication time are intended to minimize the viscosity of the epoxy resins during dispersion without causing any molecular polymer damage. Figure 12 represents the two stages of nano dispersion.

Figure 12: Carbon nano tubes dispersion stages, a) magnetic stirring, b) ultrasonication

The use of ultrasonication enhances dispersion by creating microscopic bubbles inside the resin that release energy and prevent particle agglomeration, resulting in a more even distribution of the particles. The resin container is kept at a constant temperature by the usage of the oil and water baths. The purpose of using distilled water is to limit the quantity of particles such as minerals and salts that would otherwise reduce the effectiveness of the ultrasonication bath. Degassing removes extra air bubbles from the distilled water solution to guarantee that ultrasonic waves are used to their full potential. Figure 12 depicts the specimens after dispersion. Table 5 represents the different types and percentages of CNTs that have been used in this study.

Table 5: PolC mixes with the varying CNTs content.

Designation	Type of CNT	CNTs wt%
PC-Neat	-	0
PC-FC1	F-COOH	0.25
PC-FC2	F-COOH	0.5
PC-FN1	F-NH_3	0.25
PC-FN2	F-NH_3	0.5

PC-P1	Pristine	0.25
PC-P1	Pristine	0.5

Figure 13 Uniform composite after dispersion (0.5 wt.% COOH in MMA resin)

Task 6- Mechanical properties

To study the effects of carbon nanotubes on compressive strength of polymer concrete, 5*5*5 cm cubic specimens were tested. Two different mix designs, one with 0.5 wt.% CNT and one without any CNT usage were tested. Incorporating COOH-MWCNTs in polymer concrete mix design showed a decrease in compressive strength in comparison with neat polymer concrete. Figure 14, 15 illustrates the neat and CNT incorporated polymer concrete specimens before and after failure, respectively.

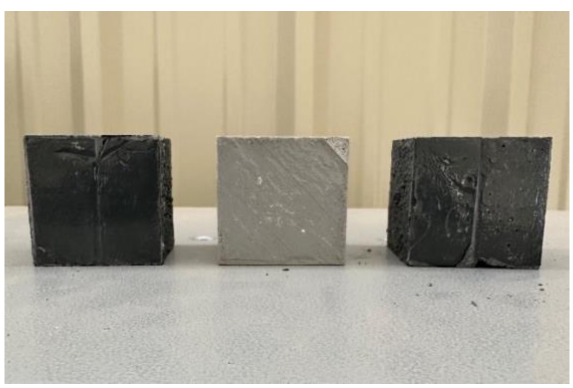


Figure 14 Neat and CNT incorporated polymer concrete specimens before failure.

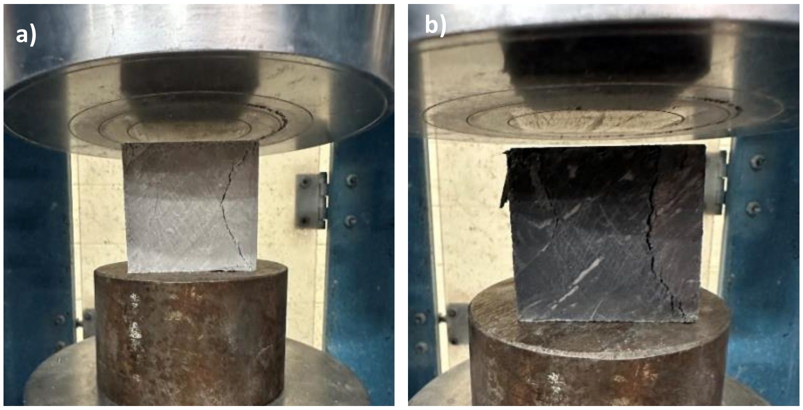


Figure 15 Neat and CNT incorporated polymer concrete specimens before failure, a) neat polymer concrete, b) 0.5 wt.% COOH incorporated polymer concrete.

Task 7- Microscopic analysis

The macro dispersion states of carbon fillers in the unmodified and nanomodified polymer concrete specimens were evaluated using optical microscopy (OM). KEYENCE VHX-7000 Microscope were utilized to study the macro dispersion of carbon nanotubes. The photos clearly show shared morphological characteristics as well as notable variances in the materials under investigation. The MWCNT agglomerates had a characteristic spherical shape with diameters up to 600 μm.

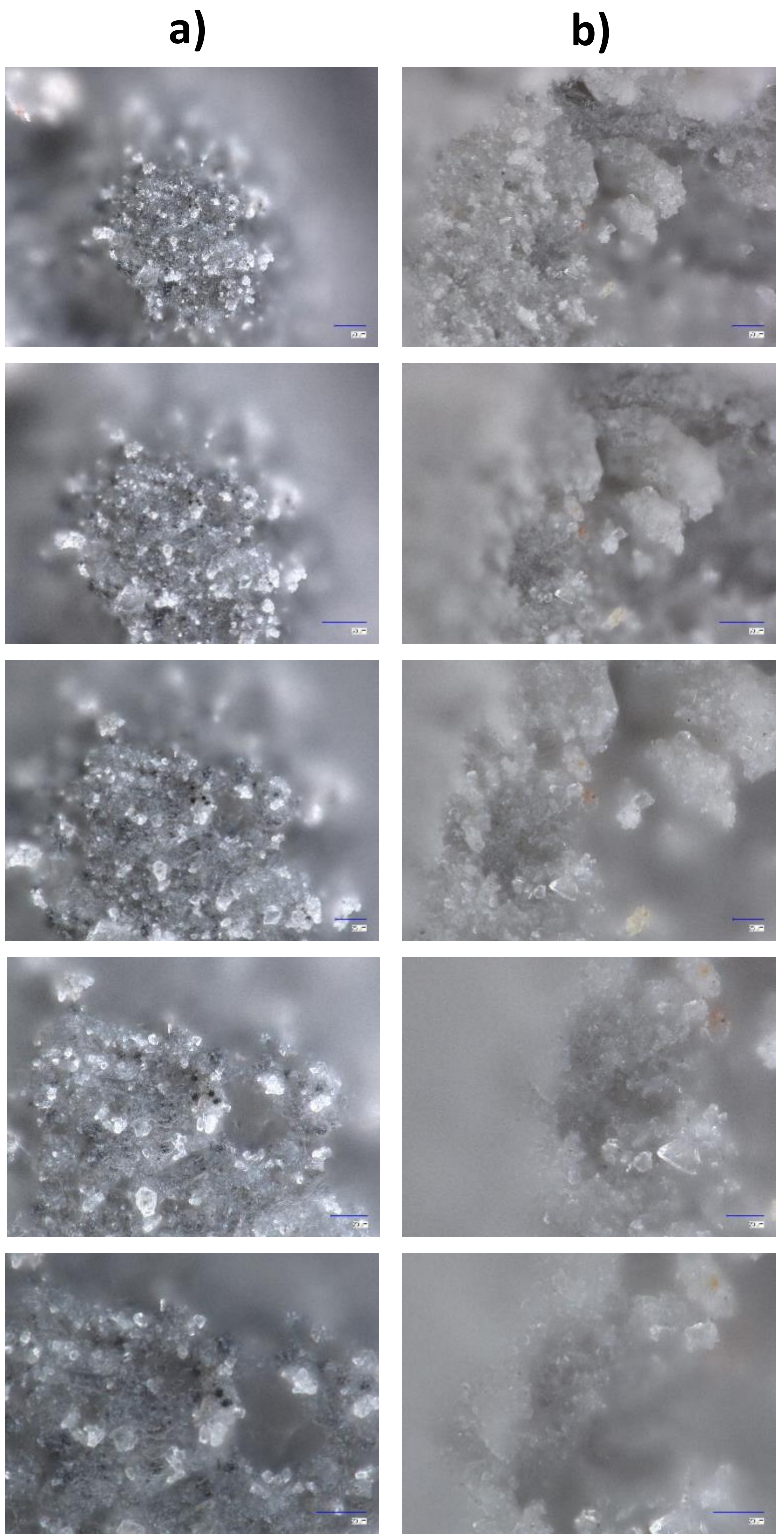


Figure 16 Microscopic image of the neat and nanomodified PolC specimens, column a) PolC incorporating 0.5 wt.% COOH, column b) neat PolC

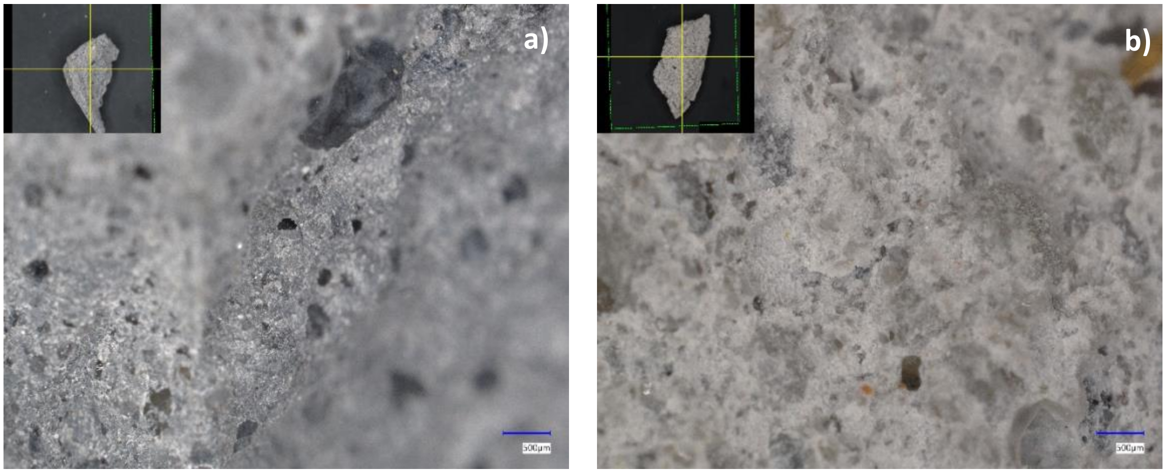


Figure 17 Microscopic image of the neat and nanomodified PolC specimens, a) PolC incorporating 0.5 wt.% COOH, b) neat PolC

5. Expected Results and Specific Deliverables

Based on prior knowledge and effects of CNTs on polymer resins, it is anticipated that 0.5wt.% and 1 wt.% nanomodified polymer concrete will show improved bond strength and performance compared to 0wt.% polymer concrete for enhanced behavior as bridge deck overlays. Bridges are key components of the surface transportation system and bridge overlays can prevent chloride ingress from affecting the structural integrity of the deck and consequently steel corrosion. Traditional overlays are cement-based materials with shrinkage problems and workability challenges. The outcomes of this project will help develop a material that aids in protecting bridge decks, enable longer service life of bridges and ensure durability. The advanced material as a result of this research will help save costs by allowing quick repairs of bridges thereby reducing closures and saving overall maintenance costs over their service lives. The deliverable of this project include a detailed report summarizing efforts and results. A journal publication for construction and building materials will be submitted upon project completion. The American Concrete Institute (ACI) has approved a technical session for Committee 548: Polymers and Adhesives in Concrete. In the Fall, 2023, a technical presentation will be included in this session explaining results of this project.

6. Schedule

Progress of tasks in this project is shown in the table below.

Item	**% Completed**
Percentage of Completion of this project to Date	65

Phase	Research Tasks	2022							2023				
		J	**J**	**A**	**S**	**O**	**N**	**D**	**J**	**F**	**M**	**A**	**M**
I	**TASK 1** Development of polymer concrete mix design												
	TASK 2 Identification of nanomaterial functionalization for dispersion												
	Quarterly Report Submission												
II	**TASK 3** Nano modification process of polymer concrete mix												
	TASK 4 Evaluation of mechanical properties and bond strength of nano enhanced polymer concrete												
	Quarterly Report Submission												
	Project Report Submission												
			Work Performed						Work to be performed				

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