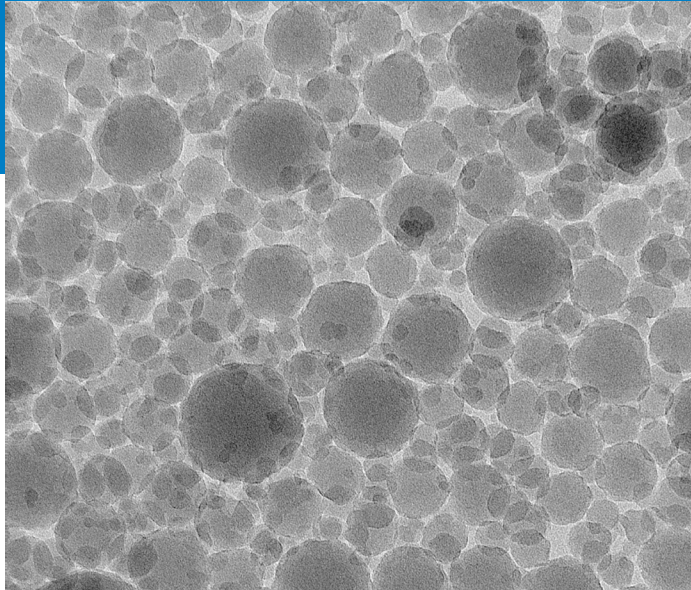


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SYMPOSIUM VOLUME



Nanotechnology for Improved Concrete Performance

SP-335

Editors:
Mahmoud Reda Taha and Mohamed T. Bassuoni



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Nanotechnology for Improved Concrete Performance

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Editors:
Mahmoud Reda Taha and
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PREFACE

Nanotechnology for Improved Concrete Performance

Preface: Many of the papers presented in this volume were included in the two-part session *Nanotechnology for Improved Concrete Performance*, sponsored by ACI Committee 241, Nanotechnology of Concrete at the ACI Convention in Philadelphia, PA, on October 26, 2016. In line with the practice and requirements of the American Concrete Institute, peer review, followed by appropriate response and revision by authors, has been implemented.

In the last decade, there have been considerable research efforts aimed at improving the mechanical and durability performance of concrete using nanotechnology. Exemplar work includes using nanoparticles to improve the hydration process of cement, incorporating nanomaterials to alter the mechanical and durability characteristics of concrete, and providing a new source for the self-sensing functionality of concrete. The scope of these papers encompasses experimental and applied research examining the use of nanomaterials to improve the performance of concrete at large. Readers are urged to critically evaluate the work presented herein, in light of the substantial body of knowledge and scientific literature on this topic.

We dedicate this volume of papers to the memory of Professor Robert (Bob) L. Day (1950-2014), of The University of Calgary, Canada and past Chairman of Canadian Standards Association (CSA) Committee A23.1/A23.2 (Concrete Materials and Construction), for his invaluable contributions to the field of concrete science and his remarkable mentoring of numerous concrete professionals worldwide.

The editors sincerely thank all the presenters in the 2016 session and the authors of the articles included in this special publication, as well as the reviewers for their thorough and objective assessment of the papers. Their technical contributions provide a holistic perspective of *Nanotechnology for Improved Concrete Performance*.

Mahmoud Reda Taha, Editor
Mohamed T. Bassuoni, Co-editor

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MULTI-SCALE FIBER REINFORCEMENT FOR CRACKING RESISTANCE IN CEMENT MORTARS

Joshua Hogancamp, Cesario Tavares, and Zachary Grasley

SYNOPSIS:

The current state of the art in fiber-reinforced cement-based materials indicates that adding multiple fiber types or sizes primarily creates a superpositioned behavior state: the behavior from each fiber type separately is added to the composite behavior of the material. Carbon nanofibers (CNFs) and milled carbon microfibers (MCMFs) can increase cracking resistance in cement-based materials by bridging cracks, although CNFs bridge cracks significantly smaller than cracks bridged by MCMFs. This research suggests that multi-scale fiber reinforcement (CNFs with MCMFs) might add compounded benefits to cracking resistance. Tests evaluating cracking resistance were performed utilizing a restrained-ring drying shrinkage test with Portland cement mortars. The CNFs and/or MCMFs were pre-mixed with cement using a sonication/distillation technique and/or rotary tumbling. Concentrations of CNFs and MCMFs were tested up to 5% and 6% by mass of cement, respectively. Restrained ring tests on mortar with high concentrations of CNFs or MCMFs reveal delayed cracking time by factors up to 6.4 or 2.6, respectively. Combining CNFs with MCMFs delayed cracking by a factor of at least 52. The increase in cracking resistance is attributed to the combined effects of bridging cracks of multiple sizes.

Keywords: Carbon nanofiber; carbon microfiber; mortar; cracking resistance

BIOGRAPHIES

Dr. Joshua Hogancamp graduated from Texas A&M University in 2017 with a focus in using microfine cementitious materials to enhance the efficacy of carbon nanofibers in mortars. He is currently a Post-Doctoral Appointee at Sandia National Laboratories in Albuquerque, NM.

Cesario Tavares graduated in 2014 with a Civil Engineering Master's Degree, with focus on Materials and Construction Processes, at Faculty of Engineering of University of Porto, Portugal. After three years in the construction industry as an Assistant Site Manager, he is currently a PhD candidate and Graduate Research Assistant in Texas A&M University.

Dr. Zachary Grasley received his PhD at University of Illinois at Urbana-Champaign in 2006. He is a professor, Presidential Impact Fellow, and Director of the Center for Infrastructure Renewal at Texas A&M University.

INTRODUCTION

Portland cement-based materials (PCBMs) are known for exhibiting a brittle behavior under load, with a strong resistance to compression contrasting a weak response under tension, and a tendency to crack during all ages of the material. Plastic shrinkage cracking occurs during and immediately after the initial set (period in which the matrix begins to harden); drying shrinkage cracking often occurs in the early life although it can occur at any age; load-induced cracking can occur at any age despite occurring more often during initial loading; fatigue cracking can occur after a significant period of time in the composite life; and degradation such as freeze-thaw, sulfate attack, or alkali-silica reaction can also generate cracks ⁽¹⁾. Fibers reinforcing concrete and mortar have the ability to bridge and restrain cracks after they form, increasing ductility of the composite material and enabling it to retain some tensile capacity after cracking ⁽²⁻⁵⁾. The most common fiber types used in industry are macrofibers such as steel and synthetic or microfibers such as carbon or synthetic ⁽⁶⁻⁸⁾. The advent of mass-produced carbon nanofibers (CNFs) and carbon nanotubes (CNTs) has led to significant advances in nano-reinforced PCBMs including increases in flexural strength, compressive strength, plastic shrinkage cracking resistance, and Young's modulus ⁽⁹⁻¹⁷⁾.

The current state of the art in CNF and CNT fiber-reinforced concretes and mortars (FRCs) suggests that adding multiple fiber types or sizes results in a superpositioned behavior state, that is, the behavior from each fiber type separately is added to the composite behavior of the PCBM ⁽¹⁸⁾. However, research has yet resulted in a significant advance in creating compounded benefits from multiple fiber types or sizes. The objective of this research is to elucidate that using multi-scale fiber reinforcement in PCBMs can add compounded benefits to restrained ring drying cracking resistance that are greater than the sum of the benefits from either fiber alone.

THEORY

Microfibers and macrofibers are typically used in industry to bridge cracks after crack formation, and the fibers add little benefit prior to cracking. The fibers require a certain level of strain in the composite material before they become 'active' in brittle materials such as PCBMs. However, recent studies^(19, 20) prove that high concentrations of CNFs in a microfine cement matrix can delay drying shrinkage cracking in restrained ring tests by bridging nearly undetectable microcracks and preventing the formation of a macrocrack. The plethora of microcracks bridged by CNFs create an 'apparent strain' as demonstrated in Figure 1. The cement paste experiences a mechanical elastic strain from the applied load, and the formation of multiple microcracks bridged by CNFs creates an additional apparent strain.

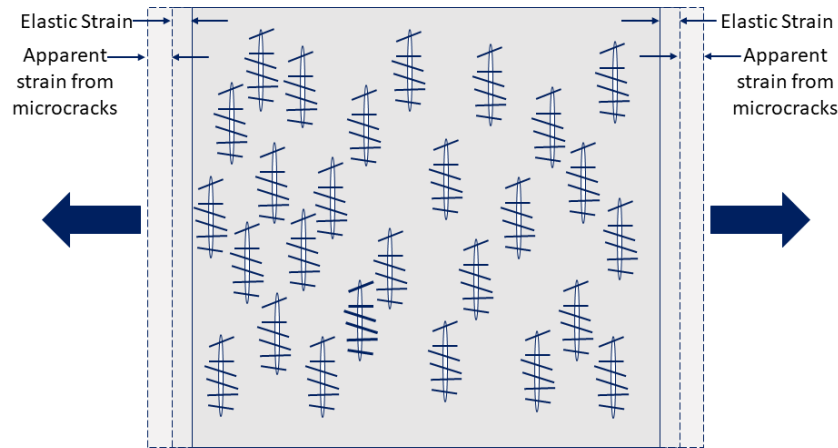


Figure 1—Schematic of mechanical elastic strain and apparent strain from an applied load on cement paste with CNFs bridging across nearly undetectable microcracks.

The combined matrix elastic strain and bridged microcrack apparent strain could together be a significant total strain to ‘activate’ microfibers before the formation of a macrocrack. Another type of fibers chosen for this study are MCMFs, which are some of the smallest microfibers available both in length and diameter, and can be blended with cement in high concentrations with little to no clumping during mixing as shown in Figure 2.

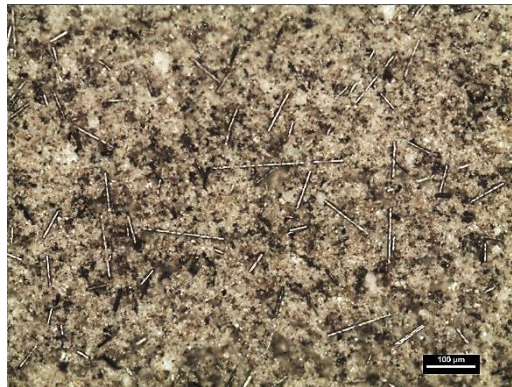


Figure 2—Unhydrated ordinary Portland cement (OPC) with 4wt% MCMFs. The MCMFs are seen as white lines in this image. The size scale in the bottom-right corner is 100 μm (3.9×10^{-3} in).

The primary purpose of this research is to introduce the concept of using high concentrations of CNFs combined with MCMFs to increase cracking resistance, presumably by bridging crack sizes across multiple orders of magnitude. To the authors’ knowledge, cracking resistance improvements on the scale present here using only fiber additions and without the formation of a macrocrack have not been seen before in PCBMs. These cracking resistance improvements require both CNFs and MCMFs. Optimum mixture combinations lie beyond the scope of this document.

MATERIALS, METHODS, AND EXPERIMENTAL DETAILS

Table 1 lists the types and properties of the CNFs and milled carbon microfibers (MCMFs) used in this research.

Table 1—Fiber properties.

Fiber	Diameter	Length	Tensile Strength	Young's Modulus
CNF	~100 nm (3.94×10^{-6} in)	50 – 200 μm ($2.0 - 7.9 \times 10^{-3}$ in)	2920 MPa (423 ksi)	240 GPa (34800 ksi)
MCMF	7.2 μm (0.28×10^{-3} in)	~100 μm^1 ($\sim 3.9 \times 10^{-3}$ in)	4137 MPa (600 ksi)	242 GPa (35100 ksi)

¹Length varies due to ball-milling process.

High concentrations of CNFs (greater than ~0.5wt%) must be pre-mixed with a microfine cement using a sonication/alcohol distillation technique⁽¹⁹⁾, and the MCMFs can be added to the sonication/alcohol distillation process (patent: CARBON Cement⁽²¹⁾). A microfine cement is required in lieu of OPC for high concentrations of CNFs (above ~0.3wt% CNFs) to prevent geometric clustering of fibers⁽²²⁾ and allow higher concentrations. This mixing procedure provides an excellent dispersion of both CNFs and MCMFs in the cement at very high concentrations with no fiber clumping/bundling/balling during mixing. A probe-tipped sonicator at 40% amplitude and 20 kHz sonicated the mixture while using a magnetic stirring plate to keep all solids in suspension. The mixing process for mortar with CNFs is:

1. The CNFs are sonicated in 100% pure ethyl alcohol.
2. Cement and MCMFs are added to the CNF/alcohol mixture in correct proportions to obtain the desired concentration of fibers and cement.
3. The alcohol/cement/fiber slurry is sonicated further with constant mechanical stirring.
4. After sonication, the slurry is distilled in a distillation column to remove and recapture the alcohol, leaving behind a pre-mixed cement/fiber powder.
5. The pre-mixed cement/fiber powder is oven-dried in a well-ventilated oven for 24 hours to ensure removal of all alcohol.

Cement mixtures with ordinary Type I/II Portland cement (OPC) and MCMFs did not require the alcohol sonication/distillation technique. The MCMFs were dry-mixed with the cement in a rotary tumbler in appropriate concentrations, and the pre-mixed cement/MCMF mixture could then be used to make mortar with no fiber clumping issues. Note that, with CNFs and/or MCMFs, the fibers must be mixed with the cement prior to use in mortar or concrete; however, the fiber/cement dry mixture can be directly added with aggregates and water in ready-mix applications.

Restrained ring drying shrinkage tests are often used to assess the cracking tendency of partially restrained concrete⁽²³⁻²⁶⁾. A restrained ring drying shrinkage test developed for use with mortars⁽²⁰⁾ was utilized to determine the efficacy of the CNFs and/or MCMFs at preventing cracking as shown in Figure 3. In the restrained ring drying shrinkage test (or simply the “restrained ring test”), a thick ring of mortar is poured around short thin-walled steel cylinder fitted with strain gages on the internal radial surface. Mortar rings were allowed to cure sealed for 24 ± 0.5 hours at 23°C (73.4°F). The rings were then demolded, the tops of the mortar were sealed with adhesive-backed aluminum foil to prevent moisture loss, and the relative humidity (RH) was reduced to 50% to initiate drying on the outer radial surface of the mortar ring. The rings were kept in an environmental control system to ensure accurate temperature and humidity control during testing. The strain in the steel ring was recorded at 5-minute intervals. The restrained ring test is optimal for this research since any formation of a macrocrack is observed as a sudden drop in strain in the inner steel ring. The initiation of microcracking is observed in this test as a sudden change in slope of strain vs drying time with no reduction in strain⁽²⁰⁾.

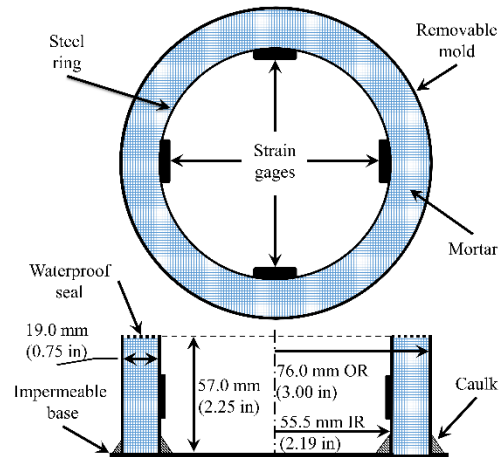


Figure 3—Ring test setup. "IR" and "OR" represent inner radius and outer radius, respectively. A non-stick sheet is placed between the mortar and the impermeable base.⁽²⁰⁾

The mixture nomenclature used in this research is defined as

‘Cement type’ ‘w/c ratio’ – ‘wt% CNFs’ . ‘wt% MCMFs’

For example, F0.5-2.2 is a microfine cement mortar with a w/c ratio of 0.5, 2wt% CNFs, and 2wt% MCMFs. OPC0.4-0.2 is an OPC mortar with a w/c ratio of 0.4, no CNFs, and 2wt% MCMFs.

Conversions between concentrations of fibers by mass of cement (wt%) and by volume of cement (vol%) are shown in Table 2, and mixture details performed in this research are shown in Table 3. All mortar mixtures consisted of cement (either microfine or Type I/II), ASTM 20-30 uniformly graded silica sand with a 1.75 sand-to-cement ratio by mass, and water. The Blaine fineness of the OPC and microfine cements are 350 m²/kg (1710 ft²/lb) and >12,000 m²/kg (58,600 ft²/lb), respectively. The OPC cement particle size ranges from 1 – 100 μm (4*10⁻⁵ – 4*10⁻³ in) while the microfine cement is almost uniformly graded at 0.1 μm (4*10⁻⁶ in). Gradations of each cement type were measured using x-ray fluorescence. Microfine cement mixtures required polycarboxylate high-range water reducing admixture and 3% by mass of cement sucrose-based set retarders; OPC mixtures required neither. Mixture flowability was designed to allow placement of the material into forms without forming voids, segregation, or bleeding. A minimum of two identical tests were performed per mixture. Further testing was not required for proof of concept due to the excellent agreement between the duplicate tests⁽²⁰⁾.

**Table 2—Conversion between concentrations by mass of cement (wt%) and by volume of cement (vol%).
Conversions apply to both carbon fiber types used in this document.**

Wt% Concentration	Vol% Concentration	Concentration of Fibers by Volume of Mortar (%)	
		W/C Ratio 0.4	W/C Ratio 0.5
1	1.97	0.45	0.42
2	3.94	0.89	0.83
3	5.91	1.33	1.24
4	7.88	1.76	1.65
5	9.85	2.19	2.05
6	11.82	2.62	2.45

Table 3—Table of mixtures used in this research.

Mixture Designation	Cement Type	W/C Ratio	Fibers (wt%)	
			CNFs	MCMFs
F0.5-0.0	Microfine	0.5	0	0
F0.5-1.0	Microfine	0.5	1	0
F0.5-2.0	Microfine	0.5	2	0
F0.5-3.0	Microfine	0.5	3	0
F0.5-0.2	Microfine	0.5	0	2
F0.5-2.2	Microfine	0.5	2	2
F0.6-5.0	Microfine	0.6	5	0
OPC0.4-0.0	Type I/II	0.4	0	0
OPC0.4-0.2	Type I/II	0.4	0	2
OPC0.4-0.4	Type I/II	0.4	0	4
OPC0.4-0.6	Type I/II	0.4	0	6
F0.4-0.0	Microfine	0.4	0	0
F0.4-2.0	Microfine	0.4	2	0
F0.4-2.2	Microfine	0.4	2	2

Note: CNF concentrations were modified by 1wt% while MCMF concentrations by 2wt% between mixtures. CNFs have more fibers, a larger specific surface area, and a significantly larger impact on workability per wt% than MCMFs.

RESULTS AND DISCUSSIONS

Restrained ring tests were performed on OPC mortar with only MCMFs as shown in Figure 4. The drying mortar rings gradually developed radial traction against the steel ring, causing the increase in strain; the sudden drop in strain in the steel ring indicates the formation of a macrocrack in the mortar. Up to 6wt% MCMFs were added to the cement prior to mixing the mortar. Both control mixture rings developed a macrocrack at ~2 days of drying. Increasing the concentration of MCMFs to 2wt%, 4wt%, and 6wt% potentially delayed the formation of a macrocrack until ~4.7 days, ~6.5 days, and ~12.2 days, respectively. Figure 4 shows another feature of OPC with MCMFs that requires further addressing. While one sample ring in each mixture with MCMFs had a delayed macrocrack formation, the other sample ring in each mixture with MCMFs developed a macrocrack at ~4.7 days. These data suggest that adding more than 2wt% MCMFs to OPC can - but is not guaranteed to - further delay the formation of macrocracks beyond what is achieved with 2wt% MCMFs. The information with OPC and MCMFs is included not to justify the use of MCMFs in OPC; rather, it is included to highlight that using only MCMFs did not produce repeatable results. Combining CNFs with MCMFs, however, did produce repeatable results as shown later in this document.

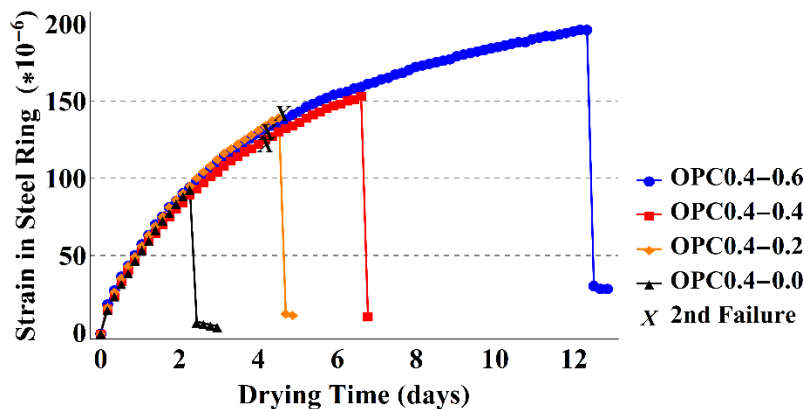


Figure 4—Ring tests with OPC and pre-mixed MCMFs.

Results from the restrained ring test with microfine cement mortars and either CNFs or MCMFs (but not both) are shown in Figure 5. Microfine cement mortar rings without fibers cracked at ~0.5 days. These rings cracked much sooner than the control OPC mortar rings in large part because the microfine cement developed a significantly higher stiffness than the OPC after 24 hours.

The key behavior observed in these microfine cement mortar tests is the knee in the graph at ~0.5 days. This knee is hypothesized to be the initial formation of microcracks in the cement matrix. The mixture with no fibers, F0.5-0.0, forms a macrocrack soon into the knee. The macrocrack timing is evident by a drastic and immediate drop in strain, similar to Figure 4. However, no drop in strain is shown in Figure 5; the data is clipped after the formation of a macrocrack since neither the CNFs nor the MCMFs were able to sustain tensile capacity in the composite after the formation of a macrocrack. Therefore, in Figure 5 through Figure 8, the last data point shown was collected just prior to the macrocrack. In mixtures with CNFs or MCMFs, the material did not break during the knee but continued to gain strain beyond the knee. The post-knee portion of the data represents a change in composite behavior due to the CNFs or MCMFs bridging microcracks and preventing the formation of a macrocrack. All mixtures with fibers out-performed the control mixture by sustaining a higher strain and requiring more drying time to crack. One mixture, F0.6-5.0, used a w/c ratio of 0.6 since the incorporation of 5wt% CNFs reduce the workability to the point that the mixture could not become liquid-like even with high-range water reducer at a w/c ratio of 0.5. This indicates that there is an upper limit to practical fiber concentrations. Excessive fiber concentrations will lead to further fiber re-clumping and consequently reduction in the reinforcement efficiency due to poor fiber distribution in the matrix. Excessive fiber concentrations will also make the mixture less workable due to the high surface area of CNFs that will absorb water.

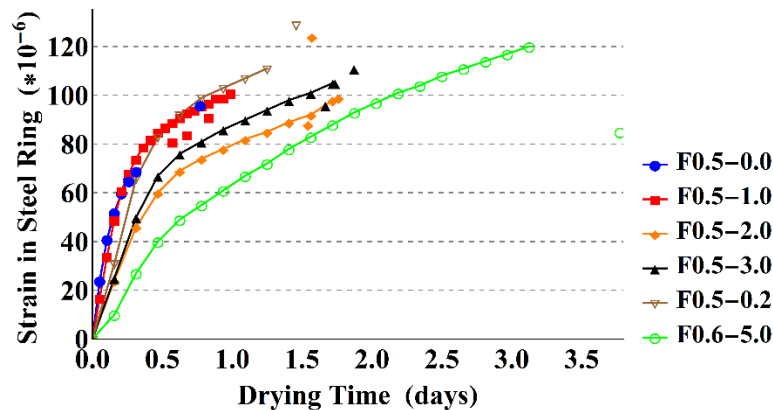


Figure 5—Ring tests with microfine cement and either CNFs or MCMFs. Data points that are not attached to any curve represent the failure point of the second ring test specimen for each mixture.

The most interesting data in this research pertains to combining CNFs with MCMFs in microfine cement as shown in Figure 6. Mixtures F0.5-0.0, F0.5-2.0, and F0.6-5.0 were also shown in Figure 5 and are included again in Figure 6 for reference. Mixture F0.5-2.2 incorporated 2wt% CNFs with 2wt% MCMFs. While the control mixture formed a macrocrack at ~0.5 days, F0.2-0.2 at ~1.3 days, F0.6-5.0 at ~3.1 days, F0.5-2.2 delayed the formation of a macrocrack until ~6.3 days. F0.6-5.5 delayed the formation of a macrocrack until ~10 days. The data in Figure 6 suggest that adding both CNFs and MCMFs allowed the mortars to withstand damage and delay the formation of a macrocrack more than the sum of delays from either CNFs or MCMFs alone.

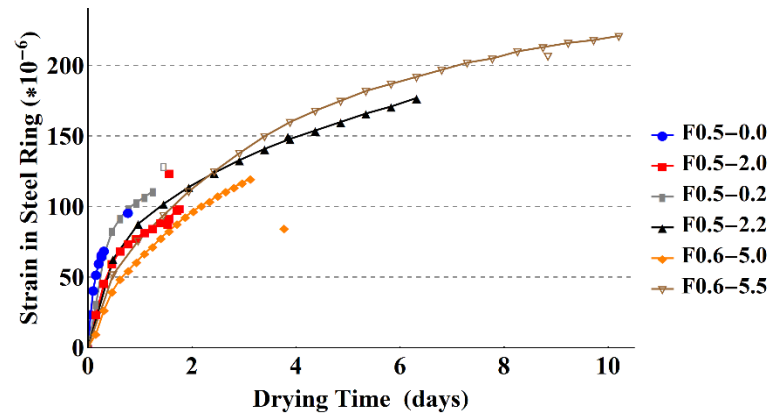


Figure 6—Ring tests with CNFs, MCMFs, or both. Data points that are not attached to any curve represent the failure point of the second ring test specimen for each mixture.

The next step in the experiment was to lower the w/c ratio of the mortar to 0.4. Due to the high water demand of CNF mixtures, the highest concentration of CNFs that could be incorporated into a w/c ratio of 0.4 mortar was 2wt% CNFs. Figure 7 shows the data from restrained ring tests of F0.4-0.0, F0.5-0.0, F0.4-2.0, and F0.5-2.0. Comparing the curves for F0.5-2.0 and F0.4-2.0 suggests that lowering the w/c ratio from 0.5 to 0.4 can increase the efficacy of the CNF composite mixture. The lower w/c ratio mixture out-performed the higher w/c ratio mixture with the same amount of fibers.

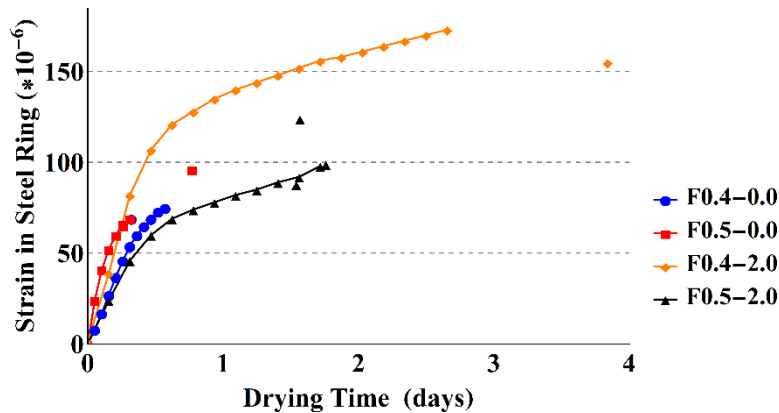


Figure 7—Ring tests with CNFs at w/c ratios of 0.5 and 0.4. Data points that are not attached to any curve represent the failure point of the second ring test specimen for each mixture.

The final step in this experiment was to test various concentrations of fibers in mortars with a w/c ratio of 0.4 as shown in Figure 8. The control test is F0.4-0.0 and cracks at ~0.6 days. F0.4-2.0 cracks at ~2.8 days. The mixture with both CNFs and MCMFs, F0.4-2.2, did not crack after 28 days of drying in 50% RH. The RH was dropped to 35% at 28 days to accelerate drying, and the specimens cracked at ~30 days total (~28 days exposed to 50% RH and ~2 days exposed to 35% RH). Combining CNFs with MCMFs drastically out-performed the control mixture or the mixture with only CNFs.

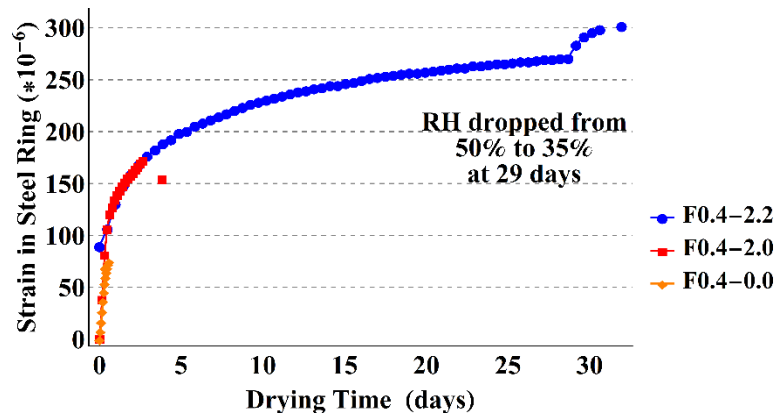


Figure 8—Ring tests with CNFs or CNFs with MCMFs at w/c ratio of 0.4. Data points that are not attached to any curve represent the failure point of the second ring test specimen for each mixture.

Figure 8 shows that adding CNFs with MCMFs at a w/c ratio of 0.4 drastically increases drying shrinkage cracking resistance compared to 1) the same combination of fibers with a w/c ratio of 0.5 or 2) the same w/c ratio mortar with only CNFs. After the specimens F0.4-2.2 were subjected to 50% RH for 29 days with no formation of a macrocrack, the RH was lowered to 35% to break the specimen. Thus, the true time to cracking of this mixture at 50% RH is not known – it is only known that it must be greater than 31 days. The drop in RH is evident by the sudden rise in strain at 29 days. F0.4-2.2 formed a macrocrack at 31.2 days with a final strain of 301 $\mu\epsilon$ in the steel ring. All ring tests performed in this document are summarized in Table 4; cracking time and microstrain are calculated as the average of the two identical specimens with the exception of mixtures OPC0.5-4.0 and OPC0.5-6.0.

Table 4—Mixture cracking time, cracking microstrain, and cracking delay factors.

Mixture	Cracking Time (days)	Cracking Microstrain ($\mu\epsilon$)	Cracking Delay Factor ¹
F0.5-0.0	0.5	89	--
F0.5-1.0	0.8	89	1.6
F0.5-2.0	1.6	106	3.2
F0.5-3.0	1.8	107	3.6
F0.5-0.2	1.3	112	2.6
F0.5-2.2	6.5	179	13
F0.6-5.0	3.2	121	6.4
OPC0.4-0.0	2.3	97	--
OPC0.4-0.2	4.9	133	2.1
OPC0.4-0.4 ²	6.7	154	2.9
OPC0.4-0.6 ²	12.5	197	5.4
F04.-0.0	0.6	77	--
F0.4-2.0	2.7	174	4.5
F0.4-2.2 ³	31.2	301	>52

¹Calculated as the ratio of (mixture cracking time) / (control mixture cracking time)
²Potential cracking time and microstrain; not guaranteed
³The RH was lowered from 50% to 35% to end the test sooner due to time constraints on the equipment; the test would likely have continued longer if the RH were kept at 50%

No issues are expected using small fiber sizes when upscaling these mixtures from mortar to concrete. The fine ASTM 20-30 uniformly graded silica sand was chosen so that the properties of the mortar would be primarily dependent on the cement matrix instead of the fine aggregate. The sand was non-absorbent, uniformly graded, and used mainly as a mixing aid, e.g. breaking apart clumps of cement. Therefore, all of the results from experiments

above are from the effects of the fibers in the cement matrix. Since the fibers are well blended into the cement matrix prior to mixing with water, the effects should be similar when upscaling from mortar to concrete.

CONCLUSIONS

This research documents the drying shrinkage cracking resistance in cement mortars achieved by incorporating high concentrations of CNFs, MCMFs, or both into the cement. A restrained ring drying shrinkage test was utilized to determine the effect of the fibers on the mortar and time until the formation of a macrocrack. Concentrations of CNFs and MCMFs were tested up to 5% and 6% by mass of cement, respectively.

Restrained ring tests on mortar with high concentrations of CNFs or MCMFs reveal delayed cracking time by factors up to 6.4 or 2.6, respectively. Combining CNFs with MCMFs delayed time until cracking by a factor of at least 52. The increase in cracking resistance is attributed to the combined effects of bridging cracks of multiple sizes prior to the formation of a macrocrack.

Furthermore, lowering the w/c ratio from 0.5 to 0.4 in tests using CNFs or MCMFs in microfine cement significantly improved the efficacy of the fibers; further testing is required to optimize fiber concentrations at various w/c ratios.

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Tailoring the piezoresistive sensing of CNT reinforced mortar sensors

Maria S. Konsta-Gdoutos, Panagiotis A. Danoglidis, Surendra P. Shah

Synopsis: The piezoresistive response and self-sensing ability of carbon nanotube reinforced mortar sensors have been investigated. The study aims on optimizing the development of a self-sensing nanoreinforced cement-based sensor for monitoring and evaluating the condition of concrete elements, in real time applications. It has been shown that the piezoresistive response of the nanomodified mortars was substantially enhanced just by adding a low amount of carbon nanotubes (CNTs), 0.1 wt%. Resistance measurements, using direct current (DC) and alternating current (AC), were conducted under the application of cyclic or monotonic compressive loading. The results show the sensor's great ability to detect crack propagation and damage accumulation at all stages of deformation up to failure.

Keywords: Carbon nanotubes, mortars, Self-sensing ability, piezoresistivity, multifunctionality, Young's modulus, fracture toughness

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INTRODUCTION

In civil engineering, the process of collecting and analyzing data related to the condition or behavior of constructed facilities, have been attracted much attention from the engineering community and construction industry for more than two decades, to promote safe and efficient service at a reasonable cost. Maintenance and repairs costs of today's reinforced concrete infrastructures, such as bridges, buildings of great importance, tunnels, tall buildings, is of major concern, as most of these are at or beyond their design life and the need to remain in service for an extended period is of profound importance. The use of a smart health monitoring system on new and existing structures is even of greater importance, as the collection of reliable and consistent information will not only reduce the life-cycle cost, but also provide information that will lead to an improved and safer design.

Especially for the reinforced concrete structures, the development of low-cost reliable techniques for real time condition and damage assessment still remains a challenge. Today, the "smart sensor" technology consists of a monitoring system comprised of piezoceramic-based devices or piezoelectric sensors for acoustic emission applications. However, these transducers are easily damaged inside the concrete matrix and their functionality can be compromised (Gu et al. 2006). Damage detection and assessment caused by mechanical stresses is a multidisciplinary process due to the heterogeneity that cementitious materials exhibit. In order to overcome this, the idea is to monitor the concrete matrix by taking advantage of recent advances in the field of nanotechnology.

Recent advances in the field on nanotechnology have developed nanoscale fibers with remarkable intrinsic mechanical properties and electromechanical response, making possible the development of multifunctional cementitious nanocomposites with high mechanical performance and strain sensing ability than can be used as sensors. Carbon fibers at the nanoscale, such as carbon nanotubes, CNTs exhibit a unique combination of (a) extremely high stiffness and flexibility (Ruoff et al. 2003) as well (b) superior conductivity and a linear and reversible electromechanical response (Cao et al. 2003). To date, carbon fibers (CFs) have been extensively used for the development of smart cementitious composites. However, it was found that for strains larger than 0.2% the resistivity of the carbon fibers changes irreversibly due to fiber breakage, making the carbon fiber composite inadequate for the detection of a structure's high stress areas (Fu and Chung 1996). On the other hand, it is well established that the carbon nanoscale fibers' piezoresistive characteristics are reversible for strains up to 3.4%. This characteristic, along with their unique mechanical properties and high aspect ratio make them ideal candidates for new potential applications in the field of development of sensors for reinforced concrete structures (Shah et al. 1995).

Limited studies have been carried out on the piezoresistive behavior and sensing ability of cementitious nanocomposites embedded with CNTs. Li et al. (Li et al. 2007) researched CNTs treated with acids and untreated CNTs as reinforcement material and conducted experiments that resulted both types to reduce the electrical resistance. Han et al. (Han et al. 2012) conducted experiments to examine the piezoresistivity response of cement nanocomposites reinforced with carbon nanotubes at amounts of 0.05, 0.1 and 1.0 wt% of cement. They concluded that change in electrical resistivity first increased and then decreased as the amount of the CNTs reinforcement increased, with the specimen reinforced with 0.1 wt% of cement CNTs presenting the best response among all specimens. Konsta-Gdoutos and Aza (Konsta-Gdoutos and Aza 2014) investigated the self-sensing and piezoresistive properties of cement paste reinforced with well dispersed CNTs at different amounts. The nanoengineered cement pastes containing 0.1 wt% CNTs exhibited the greater change in electrical resistance. The authors also concluded that the piezoresistive behavior of cement pastes reinforced with 0.1 wt% CNTs presented the higher fractional change in resistivity among all specimens. Azhari and Banthia (Azhari and Banthia, 2014) investigated the piezoresistive response of cementitious composites reinforced with carbon fibers (CFs) and CNTs. The authors measured the electrical resistance of the composites by using the AC measurement method under cyclic or monotonic compressive loading up to failure. The cement based composites respond well to an applied compressive strain by depicting a reduction in its resistivity, and this applies to both monotonically and cyclically applied strain fields. Kim et al. (Kim et al. 2014) investigated the effect of water to binder ratio on piezoresistivity of mortar nanocomposites with 0.4, 0.5 and 0.6 water/binder ratios, reinforced with different amounts of CNTs. They concluded that when the water/binder ratio of the cement composites is decreased, the specimens achieved better piezoresistive response. Han et al. (Han et al. 2015) conducted piezoresistivity measurements using DC two electrode method to measure the resistance of mortars reinforced with electrostatic self-assembled CNT/nano carbon black (NCB) composite fillers. Experimental results showed that the amount of CNT/NCB composite fillers that achieved the better piezoresistivity response is 2.40 vol%. Danoglidis et al. (Danoglidis et al. 2016) determined the impact of the addition of CNTs on the toughening effect and the smartness of nanoreinforced mortars. Experimental results of piezoresistivity tests under cyclic compressive loading, showed that the nanocomposites reinforced with highly dispersed 0.1 wt% Multi-walled carbon nanotubes (MWCNTs) yielded a high fractional change in resistivity

(10.6%) which is indicative of the amplified sensitivity of the material. Konsta-Gdoutos et al. (Konsta-Gdoutos et al. 2017) studied the self-sensing ability of mortars reinforced with pristine, mechanical and functionalized MWCNTs at amount of 0.1 wt%. It was found that mechanical and chemical functionalization introduces structural defects and disrupts the single and multiple bonds of electrons, (called as p-conjugation system), on the surface of carbon nanotubes; hence functionalized MWCNTs do not always retain the electrical properties of pristine MWCNTs and strain sensing ability.

Given the limited data available in the literature on the electromechanical behavior of CNT reinforced cement based materials, a thorough experimental approach was followed in this study to evaluate the multi-functionality and smartness of nanocomposites in order to develop a novel self-sensing nanoreinforced cement based sensor for monitoring and evaluating the condition of concrete matrix, in a real time application. In order to assess the mechanical properties of the proposed nanoreinforced sensors, the experimental determination of the flexural strength, Young's modulus and fracture toughness were initially took place through fracture mechanics tests following the (a) Linear Elastic Fracture Mechanics theory (LEFM) and (b) Two Parameter Fracture Model (TPFM) on notched 2×8 cm specimens. The investigation of the self-sensing ability of the CNT reinforced mortars took place through DC and AC measurements. The application of the compressive loading was achieved (i) cyclically in the elastic region and (ii) monotonically up to failure. The piezoresistive response of the nanomodified mortars, under cyclic and monotonic compressive loading, was substantially enhanced just by adding a low amount of CNTs, 0.1 wt%. The sensor's ability to detect crack propagation and damage accumulation, in the form of mortar prism embedded into concrete matrix, was determined. The findings show that this innovative sensor is able to perform damage and failure detection on the concrete matrix, through the recorded changes of its resistivity.

EXPERIMENTAL METHODS

In the present study cement-based composites with the matrix reinforced by CNTs were fabricated. Type I ordinary Portland cement (OPC) 42.5 R was used. The fine aggregate used to prepare the mortars was a dry siliceous natural sand calibrated to 0/2 mm (0/0.078 in) conforming to standard EN 196-1. Graded crushed limestone with a minimum and maximum nominal size of 4 and 16 mm (0.15 and 0.63 in), respectively, was used as coarse aggregates for casting concrete specimens. CNTs were added in mortar matrix at amounts of 0.1%, 0.2%, 0.3% and 0.5 wt%. The characteristic properties of the CNTs can be seen in Table 1.

Table 1 - Properties of carbon nanotubes (CNTs)

Fiber Type	Diameter, nm (in)	Length, μm (in)	Purity, %	Surface area, m ² /gr (in ² /lb)	Bulk density, gr/cm ³ (lb/in ³)	Aspect Ratio
CNTs	20-45 (7.9·10 ⁻⁷ -1.8·10 ⁻⁶)	≥10 (3.9·10 ⁻⁴)	>98	>100 (7.0·10 ⁻⁷)	≤0.18 (0.0065)	307

Dispersion of CNTs/Preparation of specimens

A major challenge for processing and manipulation of CNTs in cementitious matrices is the van der Waals forces that cause their agglomeration. In this work, a mechanical dispersion method (Hersam et al. 2014), (Shah et al. 2016) was followed to functionalize the surface of the carbon nanotubes and to achieve a homogeneous dispersion in the mortar mixture. According to this typical, one step dispersion procedure, the CNT/suspensions are prepared by adding CNTs to an aqueous polycarboxylate based surfactant solution, at a surfactant to nanotube weight ratio of 4.0. Ultrasonication is applied to the carbon nanotube/aqueous suspension by a 500 W cup-horn high intensity ultrasonic processor with a standard probe of a diameter of 19 mm and a temperature controller. The sonicator is operated at amplitude of 57% so as to deliver constant energy rate of 1900-2100 J/min, at cycles of 20 seconds in order to prevent overheating of the suspensions. The CNT/suspensions were then added into the OPC and sand at a constant water to cement ratio w/c of 0.485, and sand to cement ratio s/c of 3.0. Mixing of the materials was performed according to the procedure outlined by ASTM 305 using a standard robust mixer capable of operating from 140 ± 5 revolutions per minute (r/min) to 285 ± 10 r/min. After mixing, the mixture was cast in 2×2×8 cm (0.79×0.79×3.15 in) oiled molds for the fracture mechanics tests, resistivity and capacitance measurements and piezoresistivity experiments. Following demolding, the samples were cured in lime-saturated water until testing. For the AC measurements titanium grids with large opening (3×3mm) (1.18×1.18 in) were embedded into the specimens immediately after casting.

Strength, stiffness and fracture toughness of CNT reinforced mortars

Three point bending tests according to LEFM (Gdoutos et al. 2016) were conducted to evaluate the flexural strength, σ_f , and Young's modulus, E , of the notched $2 \times 2 \times 8$ cm ($0.79 \times 0.79 \times 3.15$ in) mortar specimens at the age of 28d. A 6 mm (0.23 in) notch was introduced into the prismatic specimens using a water-cooled band saw machine. The length of the notch was calculated based on the RILEM standard (Shah et al. 1995) which requires a notch to depth ratio of close to 1/3. The test was performed using the 25 kN MTS machine. A Crack Mouth Opening Displacement (CMOD) extensometer was used as the feedback signal to produce stable crack propagation at the rate of 0.008 mm/min ($3.1 \cdot 10^{-4}$ in/min), such that the peak load is reached about 5 min. Fracture mechanics tests according to the Two Parameter Fracture Model (TPFM) was also conducted to obtain the fracture toughness (also known as stress intensity factor), K_{IC} , based on the load versus CMOD curve for a loading-unloading cycle of a three point bend specimen. The critical value of stress intensity factor is the most important parameter in order to characterize a material's resistance to cracking and it is independent of the specimen type and size, thus a true material property.

Table 2 presents the flexural strength, σ_f , Young's modulus, E , and fracture toughness K_{IC} , of 28 d plain mortar and mortars reinforced with CNTs at amounts of 0.05%, 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt%. The estimated fiber count, the number of individual CNTs, which are distributed in a unit volume of the matrix, assuming perfect dispersion, according to ACI 544.1R-96: Report on Fiber Reinforced Concrete (American Concrete Institute 1996) is also included in the Table. As expected, the effect of the nanotubes on the mortar matrix was substantial. The mortars reinforced with CNTs at amounts of 0.05%, 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt% exhibit a 41%, 64%, 87%, 66%, 52% and 46% higher flexural strength than plain mortar, respectively. The 0.1 wt% CNT mortars outperformed all other mixes, exhibiting the largest increase in flexural strength. Nonetheless, samples containing 0.2%, 0.3% and 0.5 wt% CNTs exhibit consistently lower strength than the 0.1 wt% mixes. It is also observed that 0.05%, 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt% CNT mortars exhibit 1.6, 1.8, 1.9, 1.6, 1.5 and 1.4 times higher Young's modulus over the plain one, respectively. The complete dispersion of 0.1 wt% CNTs and their high aspect ratio result in an enormous interfacial bonding strength between the nanotube and the surrounding mortar matrix that fundamentally affects the load bearing capacity, hence the strength and stiffness of the nanocomposite. Considering the fact that both flexural strength and stiffness of all nanoreinforced mortars were greatly improve, their fracture toughness is expected to be higher than this of the plain mortar. The 28 d 0.05%, 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt% CNT reinforced mortars yield approximately 43%, 71%, 86%, 57%, 43% and 29% higher fracture toughness, respectively. The improved toughening in CNT reinforced mortars can be explained by an effective crack arresting mechanism at the nanoscale provided by the CNT network which leads to a more stable coalescing and propagation process of cracks to the micro and macro scale.

Table 2 - Effect of the CNT count on the flexural strength, Young's modulus and fracture toughness of nanoreinforced mortars

	CNT count	Flexural strength, σ_f MPa (ksi)	Young's modulus, E GPa (ksi)	Fracture toughness, K_{IC} MPa $\cdot\sqrt{\text{mm}}$ (ksi $\cdot\sqrt{\text{in}}$)
M	-	5.9 $\pm$ 1.1 (0.86 $\pm$ 1.16)	14.1 $\pm$ 0.7 (2045 $\pm$ 102)	0.7 $\pm$ 0.011 (2.4 $\pm$ 0.04)
M+CNTs 0.05 wt%	1.8 $\cdot 10^{11}$	8.3 $\pm$ 0.7 (1.20 $\pm$ 0.10)	22.3 $\pm$ 0.5 (3234 $\pm$ 70)	1.0 $\pm$ 0.008 (3.5 $\pm$ 0.02)
M+CNTs 0.08 wt%	2.9 $\cdot 10^{11}$	9.7 $\pm$ 0.6 (1.41 $\pm$ 0.10)	25.0 $\pm$ 0.4 (3626 $\pm$ 56)	1.2 $\pm$ 0.006 (4.2 $\pm$ 0.01)
M+CNTs 0.1 wt%	3.6 $\cdot 10^{11}$	11.1$\pm$0.5 (1.61$\pm$0.07)	27.6$\pm$0.1 (4003$\pm$14)	1.3$\pm$0.005 (4.5$\pm$0.01)
M+CNTs 0.2 wt%	7.2 $\cdot 10^{11}$	9.3 $\pm$ 0.6 (1.34 $\pm$ 0.10)	23.0 $\pm$ 0.3 (3336 $\pm$ 44)	1.1 $\pm$ 0.008 (3.8 $\pm$ 0.003)
M+CNTs 0.3 wt%	10.8 $\cdot 10^{11}$	9.1 $\pm$ 0.8 (1.32 $\pm$ 0.12)	21.6 $\pm$ 0.5 (3133 $\pm$ 73)	1.0 $\pm$ 0.009 (3.5 $\pm$ 0.003)
M+CNTs 0.5 wt%	18.0 $\cdot 10^{11}$	8.6 $\pm$ 0.9 (1.25 $\pm$ 0.13)	20.4 $\pm$ 0.6 (2959 $\pm$ 87)	0.9 $\pm$ 0.010 (3.1 $\pm$ 0.03)

RESULTS AND DISCUSSION

Resistivity and piezoresistivity measurements using DC

Previous results of experimental studies on CNT reinforced cementitious materials converge to the point that the addition of carbon nanotubes improve the electrical properties of the nanocomposite material by reducing its resistivity and providing self-sensing properties, under the condition that an effective degree of the nanotubes' dispersion has been achieved. Konsta-Gdoutos et al. (Konsta-Gdoutos and Aza 2014) (Danoglidis et al. 2016) dealt with the study of the electrical resistivity of both cement pastes and mortars reinforced with well dispersed CNTs and CNFs at amounts of 0.08%, 0.1%, 0.3% and 0.5 wt% using direct current (DC). It was found that the resistivity measurements under cyclic compressive loading provided an insight in the piezoresistive properties of selected nanocomposites. It is observed that resistivity decreases during loading in the elastic region, where cracks are closing, and increases during unloading of the specimen where cracks are opening. The most important parameters affecting the electromechanical properties of the CNT reinforced cement based materials is the dispersion of CNTs. Characteristics such as the aspect ratio and the bulk density also play a crucial role on the self-sensing ability of nanocomposites. From the DC piezoresistivity results it was concluded that both cement paste and mortar nanocomposites reinforced with 0.1 wt% of cement yielded the highest fractional change in resistivity, approximately 4.6% for cement pastes and 10.6% for mortars. Interestingly, smaller resistivity changes under the same load were observed for the 0.3% and 0.5 wt% CNT mixes. This in turn results in an inadequate conductive network that allows electrical current passage with difficulty.

In this study, the piezoresistive behavior of 28 d mortar nanocomposites reinforced with 0.2 wt% CNTs was investigated by measuring the resistivity using the DC four pole method, while monotonic uniaxial compressive loading up to failure was simultaneously applied to the specimens from a hydraulic 25 KN testing machine MTS. The compressive load was applied at a rate of $3 \cdot 10^{-3}$ mm/sec ($1.2 \cdot 10^{-4}$ in/sec). To measure the electrical resistance of the mortar nanocomposites two digital multimeters (Fluke 289 AC/DC True RMS) with the ability to measure I_A and V, and a power supply unit (Mastech HY3005D) capable of supplying DC up to 30 V were used. The piezoresistivity results are presented in the Fig. 1. The nanocomposites exhibit a high sensitivity in recognizing the change in the applied stress, the induced mechanical deformation and the formation of the cracks and can be considered to be a piezoresistive sensor. In the elastic region (normalized stress up to 0.2) the resistivity was decreased by 25% (from 10.4 kΩ·cm ($4.2 \text{ k}\Omega\cdot\text{in}$) to 7.9 kΩ·cm ($3.2 \text{ k}\Omega\cdot\text{in}$)) while the change of its strain was 27%. The discontinuity at the point where normalized stress is 0.2%, is attributed to the formation of a crack in the area between the specimen and the metallic electrode. This is also reflected in the resistivity-strain curve as no obvious change in the resistivity values was recorded (from 7.9 kΩ·cm to 7.8 kΩ·cm). Significant higher changes in resistivity values, by 39%, (from 7.9 kΩ·cm ($3.2 \text{ k}\Omega\cdot\text{in}$) to 4.8 kΩ·cm ($1.9 \text{ k}\Omega\cdot\text{in}$)) were recorded up to the application of the 80% of total compressive load. The deformation (strain) of the specimen is also higher (157%). At the final stage of the application of applied load, the specimen was deformed by 35%. Simultaneously, the specimen exhibits a decreased change in resistivity, by 4% (from 6.0 kΩ·cm ($2.4 \text{ k}\Omega\cdot\text{in}$) to 5.8 kΩ·cm ($2.3 \text{ k}\Omega\cdot\text{in}$)). After the total failure the normalized stress was suddenly decreased and the resistivity increased, reaching a plateau.

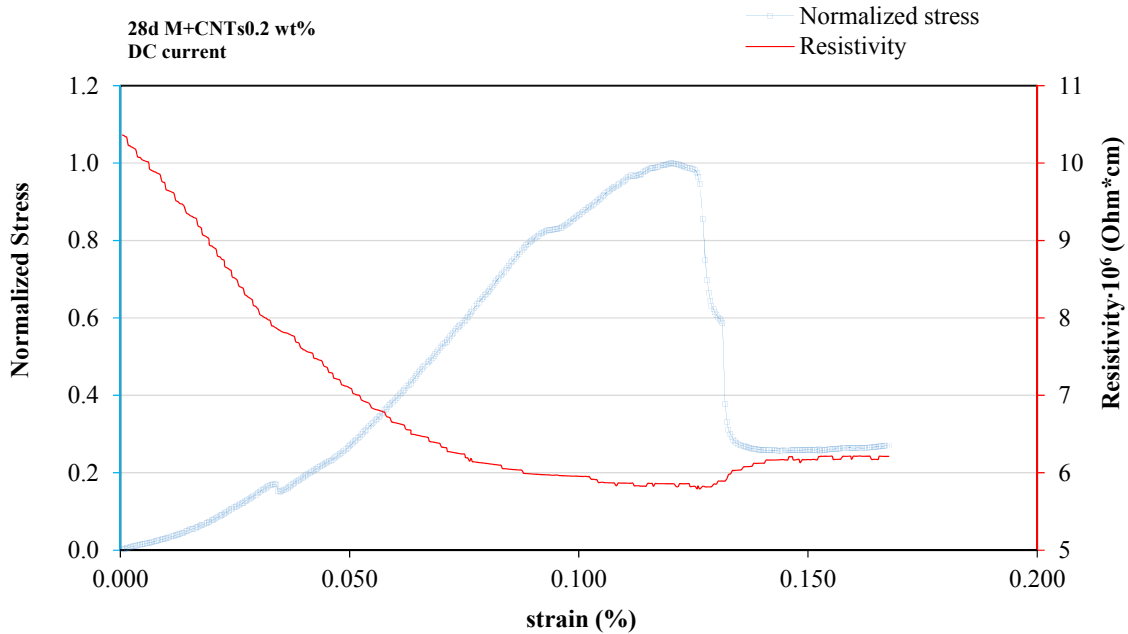


Figure 1—Piezoresistive behavior (DC) under monotonic loading of 28 d mortar reinforced with 0.2 wt% CNTs
(Note: $1 \text{ kOhm} \cdot \text{cm} = 0.4 \text{ kOhm} \cdot \text{in}$)

Piezoresistivity evaluation using (AC)

Resistance measurements using AC offer distinct advantages over DC, because of the effect of the electrode polarization that occurs when using DC, which may cause an exponential rise in the measured resistivity (Millard 1991). In order to eliminate the polarization effect, the piezoresistive properties of 28 d CNT reinforced mortars, in this work were also determined using AC, following the two pole method, according to which only two (and not four) titanium electrical contacts are embedded in the matrix in two parallel planes. The electrical resistance was measured using an Agilent E4980 LCR meter at 100 kHz frequency (Konsta-Gdoutos et al. 2017). Amplitude of the sinusoidal voltage was chosen to be 2 V. The application of the compressive loading was performed either cyclically in the elastic region or monotonically up to the failure at a rate of $3 \cdot 10^{-3} \text{ mm/sec}$ ($1.2 \cdot 10^{-4} \text{ in/sec}$) by using a hydraulic testing machine MTS with a 25 kN capacity. A typical set up of the method is shown in Fig. 2.

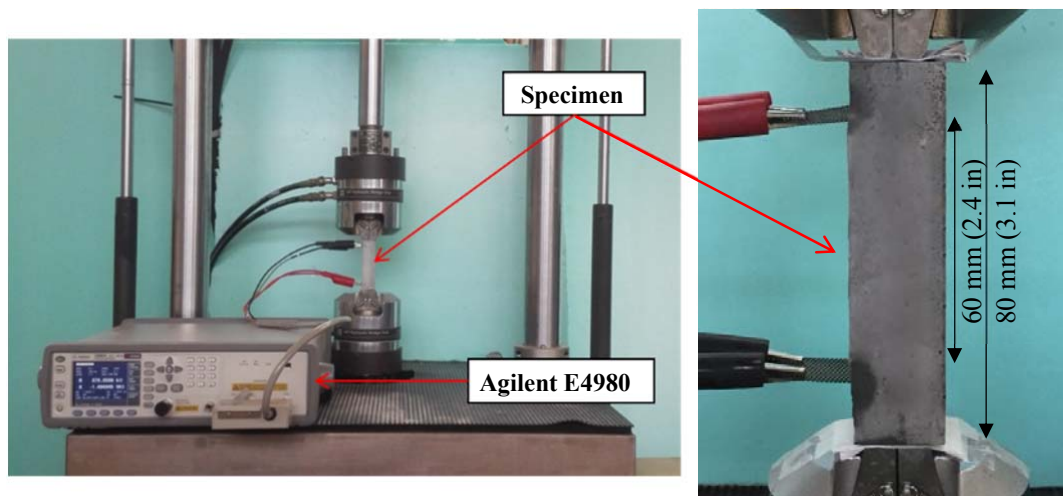
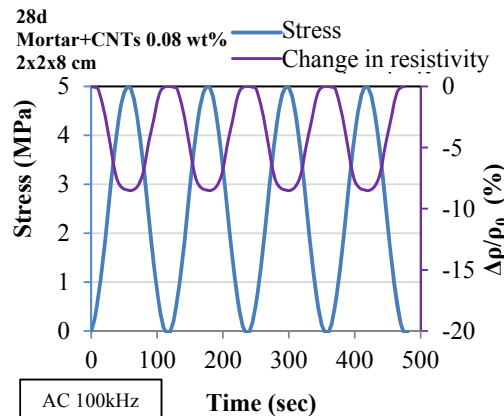


Figure 2—Experimental set up for AC piezoresistivity measurements

The piezoresistivity response of 28 d mortars reinforced with CNTs at amounts of 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt% under cyclic compressive load in the elastic region, is shown in Fig. 3. The values of the compressive

load applied over time are taken on the left vertical axis and the fractional change of resistivity (%) on the right vertical axis. The fractional change is calculated by dividing the difference in values of resistivity each time and initial resistivity, $\Delta\rho$, to the value of the initial resistivity, ρ_0 . Nanomodified mortars exhibit a unique nonlinear response reflecting by the correlation between resistivity and stress values: during each loading-unloading cycle, the resistivity values decreased with an increase in compressive load; then increased to the initial value during unloading. Mortars reinforced with CNTs at amounts of 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt% exhibit an 8.5%, 9.5%, 14.9%, 5.3% and 3.1% fractional change in resistivity, respectively. To further investigate the sensitivity of nanomodified mortars to their deformation under the application of the compressive load, the fractional change in resistivity to strain curves of all mortars reinforced with CNTs at amounts of 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt%, for a single cycle of loading, are presented in Fig. 4. It is observed that all the nanomodified mortars also exhibit an amplified ability to recognize the changes in the mechanical deformations, under the application of compressive load, through the changes of their resistivity. The nanocomposites reinforced with 0.2 wt% CNTs yielded the highest fractional change in resistivity, 14.9%. As mentioned above, a complete conductive network can be established with CNT addition at an amount of 0.2 wt% where the resistivity reaches the lowest value. Therefore, the network formed by 0.2 wt% CNTs is able to effectively deform during the application of cyclic compressive loading at the elastic stage ($\approx 17\%$ of the total strain at the failure), presenting the highest nonlinear piezoresistive response. Mortars reinforced with CNTs at amounts of 0.3% and 0.5 wt% however exhibit lower piezoresistivity. This may be attributed to a less effective dispersion of the CNTs inside the matrix. This in turn results in an inadequate conductive network that allows electrical current passage with difficulty.



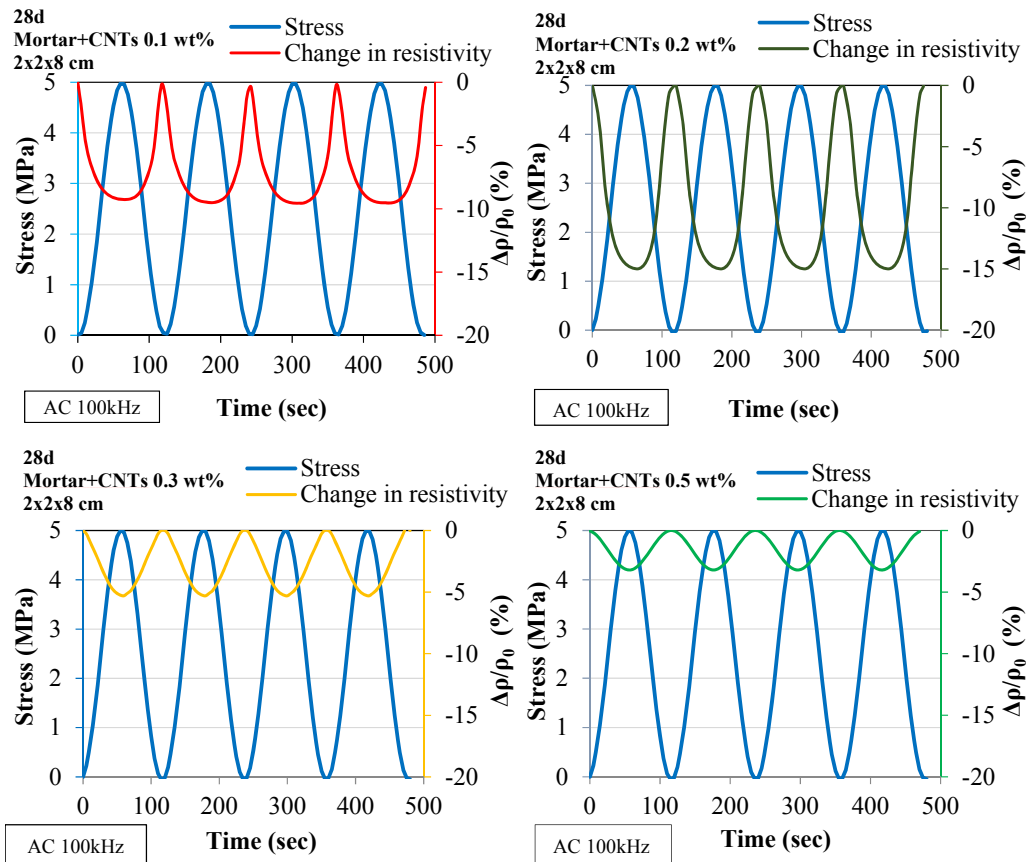


Figure 3—Piezoresistive behavior of 28 d mortars reinforced with CNTs at amounts of 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt% (Note: 1 cm=0.4 in, 1 MPa=0.15 ksi)

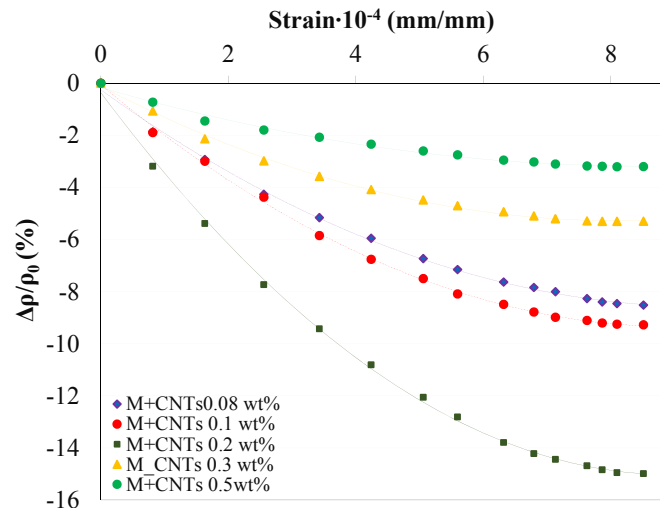


Figure 4—Fractional change in resistivity to strain correlation of 28 d mortars reinforced with CNTs at amounts of 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt%, for a cycle cyclic of loading

To further assess the self-sensing ability of CNT mortars, piezoresistivity experiments were also conducted by applying monotonic compressive load up to failure. Fig. 5 presents the piezoresistive response of 0.1 wt% CNT mortar. As can be seen, at the elastic stage the resistivity values linearly decreased from over 8.5 kOhm·cm (3.3 kOhm·in) to 6.2 kOhm·cm (2.4 kOhm·in) with the increase in load. Under the application of the compressive

load, the CNTs get closer to each other and form a more efficient conductive network, as the specimen's cracks are closing and the thickness of the mortar matrix between neighboring nanotubes tends to decrease, resulting in a decrease of the nanocomposite's resistivity. After this stage, at a strain value of 0.03%, a small jump is observed in the stress-strain curve possibly due to cracking in the specimen (Fig. 6). The same jump is also observed in the resistivity-strain curve. The resistivity of the nanocomposites is then decreased to less than 1.5 kOhm·cm (0.59 kOhm·in) with the increase in load up to the maximum value (normalized stress 1.0). At this point, the piezoresistivity response of the 0.1 wt% CNT mortar is 160%. After the failure, through-specimen cracks are formed in the cement matrix and percolative network of CNTs are interrupted, causing a sudden increase in the electrical resistance of the nanocomposite. For strain measurements higher than 0.17%, both stress to strain and resistivity to strain curves reach a plateau. Thus, it is safely attributed that the nanomodified mortar is able to perfectly recognize its mechanical deformation and the cracking at the nano, micro and macroscale, throughout the application of the compressive load.

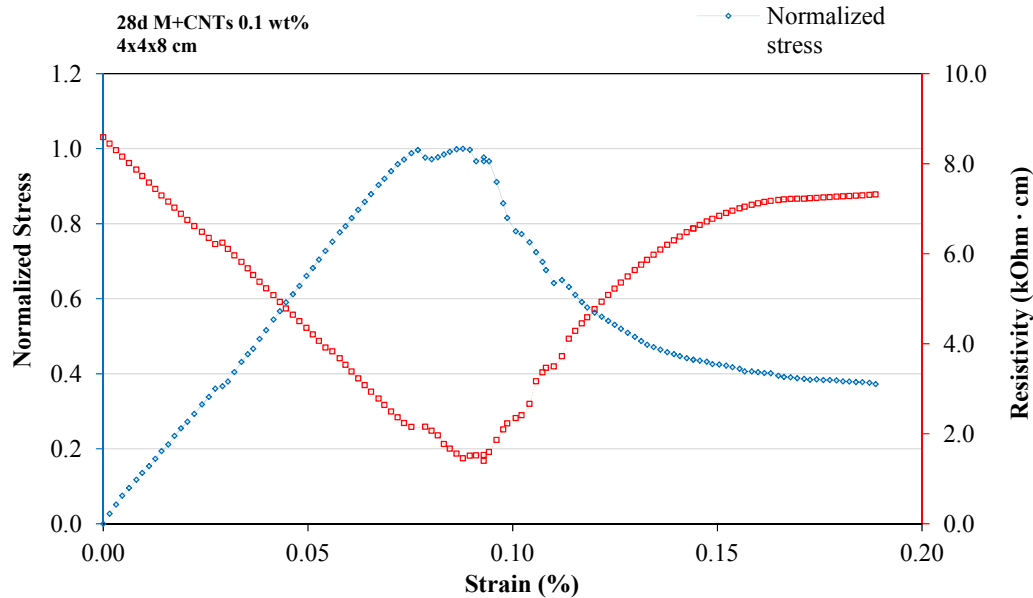


Figure 5—Piezoresistive behavior under monotonic loading of 28 d mortar reinforced with 0.1 wt% CNTs

(Note: 1 kOhm·cm=0.4 kOhm·in)

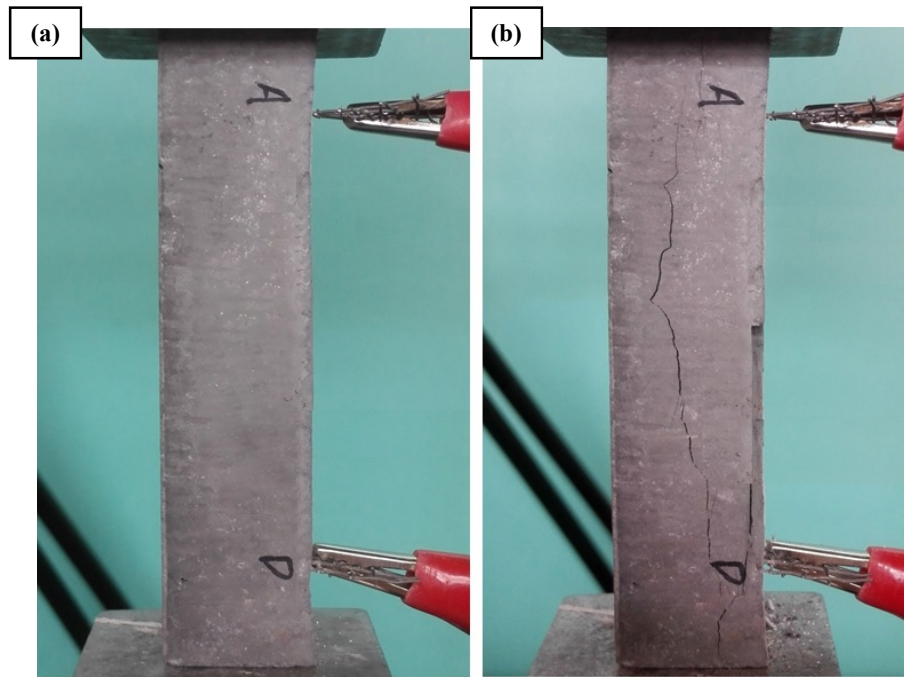


Figure 6—Pictures of (a) undeformed specimen and (b) specimen with macrocracks

The self-sensing ability of the 0.2 wt% CNT mortar under the monotonic compressive load is presented in Fig. 7. Similarly to the 0.1 wt% nanocomposites, the mortars reinforced with nanotubes at amount of 0.2 wt% exhibit an impressive sensitivity to detect the applied load and the mechanical deformation at all stage, elastic, post-crack and total failure. The piezoresistive response of the 0.2 wt% mortar at the normalized stress of 1.0 is 118%. Interestingly, and despite the fact that the estimated CNT count is twice as much ($7.2 \cdot 10^{11}$) as the 0.1 wt% CNT mortar, the piezoresistive response is 35% lower than the response of the corresponding 0.1 wt% mix. This finding is in good agreement with the previous results on the mechanical properties (Table 2) of carbon nanotubes reinforced mortars. Fig. 8. presents the Young's modulus and the change in resistivity up to failure of both 0.1% and 0.2 wt% CNT mortars. As mentioned before, the addition of 0.2 wt% CNTs results in a Young's modulus of 23 GPa while the 0.1 wt% CNT reinforced mortar exhibit an 20% increased flexural stiffness (27.6 GPa) indicating the formation of a more effective carbon nanotube network at the amount of 0.1 wt%. This network has a higher ability to deform and transfer the current during the application of the compressive load and the formation of cracks at the nano, micro and macro scale. It should be noted that the flexural strength and fracture toughness of 0.2 wt% mortars is 19%, 18% lower than the 0.1 wt% one, respectively.

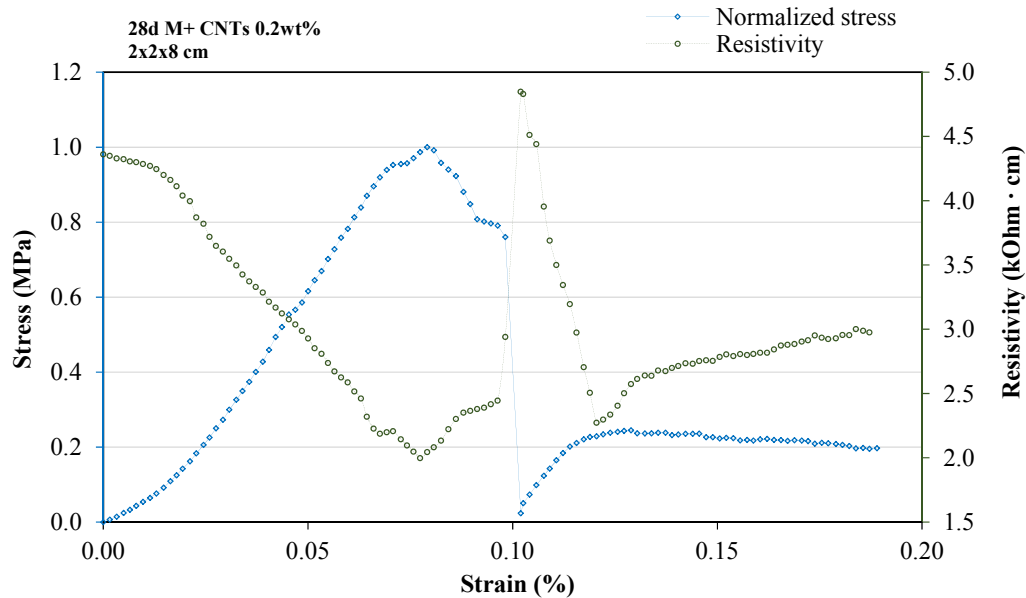


Figure 7—Piezoresistive behavior under monotonic loading of 28 d mortar reinforced with 0.2 wt% CNTs

(Note: 1 MPa=0.15 ksi, 1 kOhm·cm=0.4 kOhm·in)

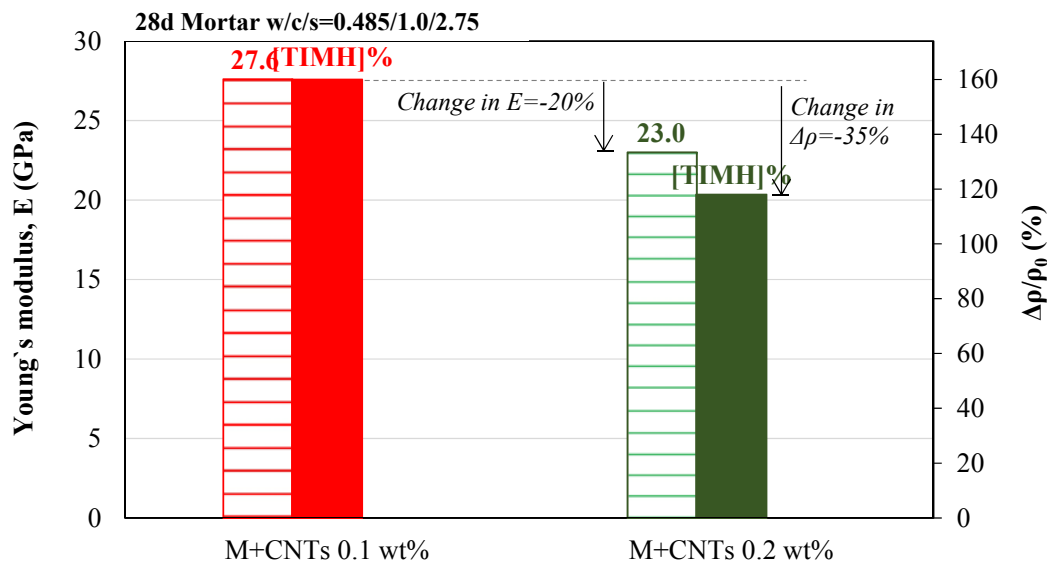


Figure 8—Young's Modulus and average change in resistivity of 28 d mortars reinforced with CNTs at amounts of 0.1% and 0.2 wt% (Note: 1 GPa=150 ksi)

The excellent piezoresistive response of nanomodified mortars clearly indicates their capability to be used as sensors that can detect strain variation and cracking in concrete, through their resistivity measurements, leading into a new era of monitoring and evaluating in real time the condition of any concrete element. To evaluate the sensing performance of the proposed nanomodified mortars in concrete members, subjected to monotonic compressive loading, 4×4×16 cm prismatic concrete specimens with an 2×2×8 cm mortar sensor reinforced with CNTs at amount of 0.1 wt% embedded in an appropriate location as presented in Fig. 9. The system was subjected to monotonic compressive load up to failure with a loading rate of 0.005 mm/min ($2.0 \cdot 10^{-4}$ in/min) and the electrical resistance of the embedded sensor is simultaneously measured. Fig. 10. depicts the piezoresistive response of the embedded mortar sensor. As can be seen, the resistivity of the sensor decreased from 12.5 kOhm·cm to 5.1 kOhm·cm with the increase of the applied load up to strain of approximately 0.1%.

At that particular point, where strain is 0.09%, the applied load decreased and the 0.1 wt% CNT reinforced mortar's resistivity suddenly increased by 41% (from 5.1 kOhm·cm to 8.2 kOhm·cm). This sudden increase is attributed to cracking of the concrete matrix, as indicated in the stress-strain response of the specimen. As the applied load, increases up to failure, microdamage in the concrete expands causing higher stress in the sensor and a stronger and more conductive nanotube network as the ends of the CNTs moved close from each other. After the application of the maximum compressive load, the concrete matrix was totally failure and the applied load was decreased. At the same time, the applied stresses from the concrete to the mortar sensor were decreased, as a result an increase of the mortar's resistivity from 7.2 kOhm·cm to 12.9 kOhm·cm was observed, and finally both stress-strain and resistivity-strain curves reach a plateau. It is worthy to note, that the no damage is observed in the structure of the 2×2×8 cm sensor after the completion of the experiment (Fig. 11), indicating that the exceptional mechanical response and sensing ability of the 0.1 wt% CNT reinforced mortar, are the same at all stages of the concrete's deformation, from the elastic stage to the micro and macro cracking and to the total failure of the matrix.

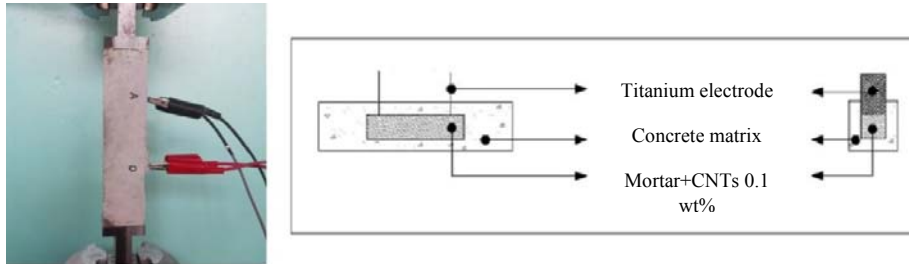


Figure 9—Experimental setup of piezoresistive behavior of CNT reinforced mortar sensor embedded into concrete matrix

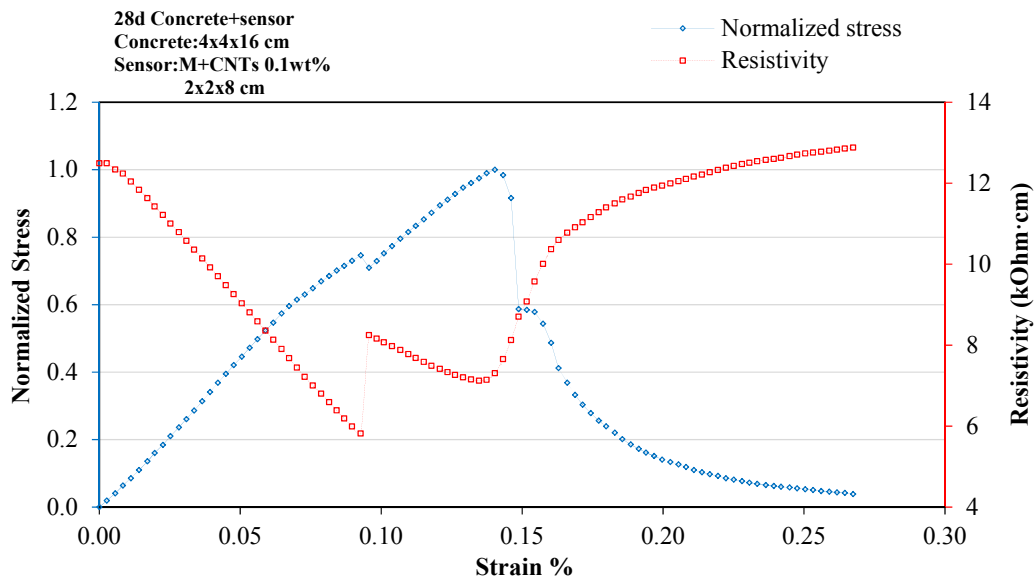


Figure 10—Piezoresistive behavior of 0.1 wt% CNT mortar sensor embedded into concrete beam and subjected to monotonic loading (Note: 1 kOhm·cm=0.4 kOhm·in)

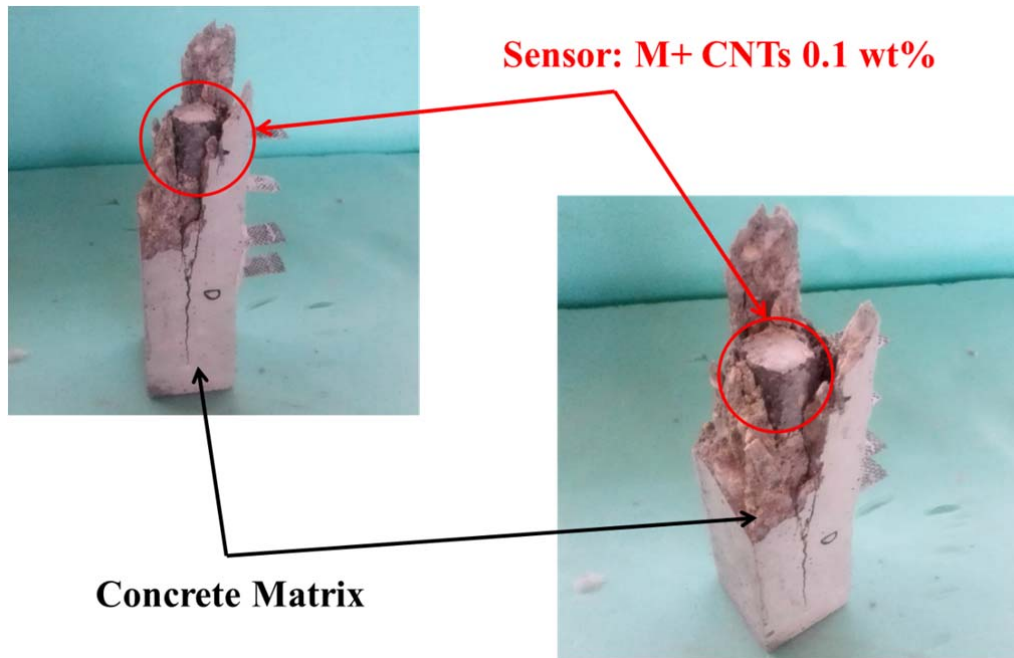


Figure 11—Concrete specimen with the embedded mortar specimen after the completion of the piezoresistivity experiment

CONCLUSIONS

In this study, a thorough experimental approach was followed to evaluate the multi-functionality and smartness of cement mortars, reinforced with CNTs in order to develop a novel self-sensing nanoreinforced cement based sensor for monitoring and evaluating the condition of concrete matrix, in a real time application. The mechanical performance, flexural strength, Young's modulus and fracture toughness of mortars reinforced with CNTs at amounts of 0.05%, 0.08%, 0.1%, 0.2%, 0.3% and 0.5 wt% was firstly evaluated. As expected, the effect of the nanotubes on the mortar matrix was significant. All the nanoreinforced mortars exhibit impressively increase in flexural strength, stiffness and toughness up to approximately 90% than plain mortar. The 0.1 wt% CNT mortars outperformed all other mixes, exhibiting the largest increases in the mechanical properties. The strain sensing ability of the CNT reinforced mortars under cyclic and monotonic compressive loading was determined by DC and AC measurements. Consistently with the mechanical properties, the nanocomposites reinforced with 0.1 wt% CNTs yielded the highest fractional change in resistivity (160%) up to the total failure which is indicative of the amplified sensitivity of the material. To further evaluate the sensing performance of the proposed 0.1 wt% CNT nanomodified mortar and their capability to be used as sensor that can detect strain variation and cracking in structural elements, concrete specimens with a mortar sensor embedded in an appropriate location were subjected under monotonic compressive loading. The exceptional mechanical response and sensing ability of the embedded mortar specimen, at all stages of the concrete's deformation, clearly shows that this innovative sensor will be able to perform damage and failure detection of the concrete matrix and compromise of the structural integrity of the concrete component, mainly through the recorded changes of its resistivity.

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Performance of fiber-reinforced carbon nanotubes-nanofibers composites

Joshua Hoheneder, Ismael Flores-Vivian and Konstantin Sobolev

SYNOPSIS: Fiber additions in portland cement composites is a regular practice for crack prevention and for increasing the flexural strength. In this research, fiber-reinforced composites (FRC) with polyvinyl alcohol (PVA) fibers and carbon nanofibers (CNF) or carbon nanotubes (CNT) were investigated. Specimens were tested to measure their flexural strength, water absorption and electrical conductivity in water or sodium chloride solution. It was found that the developed composites, depending on applied stress and exposure to chloride solutions, exhibit some electrical conductivity. These dependencies can be characterized by piezoresistive and chemo-resistive coefficients demonstrating that the material possesses self-sensing capabilities. The sensitivity to strain, crack formation, and chloride solutions can be enhanced by incorporating small amounts of CNF or CNT into a composite structure. Conducted research has demonstrated a strong dependency of electrical properties of the composite on crack formation in moist environments. The developed procedure is scalable for industrial application in concrete structures that require nondestructive stress monitoring, integrity under high service loads and stability in harsh environments.

KEYWORDS: Composites, carbon nanofibers, carbon nanotubes, electrical conductivity, flexural strength, polyvinyl alcohol fibers.

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INTRODUCTION

Concrete is the most used human-made material extensively applied in all for construction projects. Concrete, however, is prone to drying shrinkage cracking and micro-cracking due to service loading, which can lead to a progressive increase in permeability and deterioration of reinforcement. The monitoring of infrastructure conditions can allow for higher quality infrastructure and ability to save on the rehabilitation costs. Visual inspection of cracks in various elements of structures is expensive, subjective, and some parts of a structure may not be accessible or can be unsafe to reach. Monitoring of structure conditions for crack formation and propagation, as well as detecting the chloride ingress, is an attractive option which can reduce the inspection costs and increase safety. Structural Health Monitoring (SHM) systems can be used as sensor-based detection and monitoring for different stages of damage. Advanced SHM systems can use Fiber-Reinforced Composites (FRC) tuned for self-sensing purposes. Commonly, FRCs have better durability when compared to reference concrete due to reduced drying shrinkage, pore size, increasing the electrical conductivity, increasing flexural strength and toughness (Wang, et al., 2006).

Common components of FRC are glass and steel fibers with some new materials such as polyvinyl alcohol (PVA) fibers, carbon nanofibers (CNF) and carbon nanotubes (CNT) just approaching the field. (Li, et al., 2010) (Metaxa, et al., 2010). The PVA fibers have been used to improve the response under flexural loading. Carbon fibers have been used to improve the mechanical and electrical properties of concrete (Li, et al., 2009), especially, to increase the flexural strength, flexural toughness, and reduce drying shrinkage. Steel and carbon fibers are electrically conductive and so can improve the conductivity of cementitious materials (Chung, 2002) (Hou & Lynch, 2009). The piezoresistivity of conductive FRC materials changes with strain. The CNT and CNF based composites can effectively serve as strain sensors (Fu & Chung, 1995). Carbon nanofibers uniformly dispersed within concrete matrix allow for the bridging of microcracks, which makes otherwise insulated space electrically conductive (Ozyurt, et al., 2006). For this reason, it is important to disperse the fibers within the mix uniformly. The method of dispersion depends highly on the material to be dispersed. The PVA and steel fibers are easier to disperse than CNF and CNT and only require the use of superplasticizer mixed in water to achieve proper dispersion (Fu & Chung, 1995). The CNT and CNF, however, are more of a challenge to realise a proper dispersion within concrete matrix. Higher degree of difficulty associated with dispersing CNT is due to the large van der Waals interactions between the CNT macromolecules (Wang, et al., 2006). The percolation threshold is the critical fraction of lattice points that must be filled to create a continuous path of nearest neighbors from one side to the other (Chacko, et al., 2007). To ensure the workability, compressive strength, and to reduce materials costs, the fiber content is kept below the percolation threshold (Wen & Chung, 2007).

The use of self-sensing concrete based on carbon nanofibers/nanotubes can add some additional capabilities for nondestructive monitoring of moisture conditions, chloride profiles, stresses, and crack propagation in concrete structures. Self-sensing concrete is an essential component of smart buildings - the structures detecting possible failures before reaching the critical deterioration threshold - can save lives and reduce the financial burdens for building owners. In this research, for the development of Structural Health Monitoring

(SHM) systems, smart FRC with PVA fibers and CNF/CNT were investigated to evaluate the flexural strength, water absorption and electrical conductivity in water or in sodium chloride solution.

EXPERIMENTAL METHODS

Materials

The ASTM-C105 Type I portland cement (Lafarge-North America) and ASTM-C778 standard graded silica sand (US Silica, Ottawa, IL) were used. A high-range water-reducing admixture (polycarboxylate PCE from Handy Chemicals Montreal, Canada) was used in the composition at a dosage of 0.125% by weight of cement. Kuralon K-II PVA fibers (Kuraray, Japan), PR-24-XT-PS CNF (Pyrograf Products, USA) and CNT (Eden Nanomaterials, USA) were incorporated to increase the flexural strength and assure the electrical conductivity (Wang, et al., 2006). All tested compositions incorporated PVA fibers, which geometric properties are summarized in Table 1. The geometric properties of CNF and CNT are reported in Table 1.

Table 1. Properties of PVA fibers, carbon nanofibers, and carbon nanotubes

ID	Material	Length	Diameter
PVA	PVA fibers	6 mm (0.24 in)	0.027 mm (0.0011 in)
CNF	PR-24-XT-PS carbon fibers	-	100 nm (3.9E-6 in)
CNT	carbon nanotubes	-	20-30 nm (7.9E-7...1.2E-6 in)

Mixture proportions

The water to cement ratio (w/c) used for the experimental mixtures was 0.3. This was done to keep a dense matrix with little volumes of electrically insulating voids to maximize the flow of electrical current through the composite. Silica sand was used at a sand-to-cement ratio of 0.5. The composition of the samples tested is listed in Table 2. The comparison of the performance of PVA-FRC composites with carbon nanofibers or nanotubes, (CNF vs. CNT), respectively, were performed against a reference (Ref) mixture. The optimization of the CNT/CNF volume at 0.2% of matrix was reported by previous work (Hoheneder, et al., 2015).

Table 2. Mixture proportions of investigated composites

Composition	Ref	CNF	CNT
W/C	0.3	0.3	0.3
S/C	0.5	0.5	0.5
SP, % w cement	0.175	0.175	0.236
PVA, % vol	2	2	2
CNF, %vol	0	0.2	0
CNT, %vol	0	0	0.2

Mixing procedures

Incomplete dispersion of CNF or CNT may have an adverse effect on the flexural strength and result in a matrix with inconsistent conductivity. To realize the proposed concept of smart FRC, very even distribution of carbon fibers/tubes within the cementitious matrix is essential. The dispersion of the CNF or CNT was performed before the use of these components in FRC. Preliminary tests demonstrated that it was impossible to disperse the CNF in water under ultrasonic treatment. Details of the dispersion procedure of the CNF in water using PCE based superplasticizer and ultrasound treatment can be found in previous work (Hoheneder, et al., 2015). Proper dispersion of CNT in water was achieved by the same procedure of the CNF through the use of silica sand added to the mixture of PCE and CNT. The addition of silica sand was crucial for the dispersion of CNT since the nanotubes remained clumped (Figure 1) when following procedure described in previous work (Hoheneder, et al., 2015). Up to 5% of the total sand added during the ultrasonication was used to improve the dispersion of CNT. Finally, the CNT material was dispersed using the ultrasound processor (Hielscher UIP1000hd) at 90% of the maximum power 900 J/s (900 W) at 20s⁻¹ (20kHz) for 20 minutes. A small sample of CNT suspension was collected at 5, 10, 15 and 20 minutes and analyzed under the optical microscope (Olympus BH-2) at 100x magnification (Figure 1).

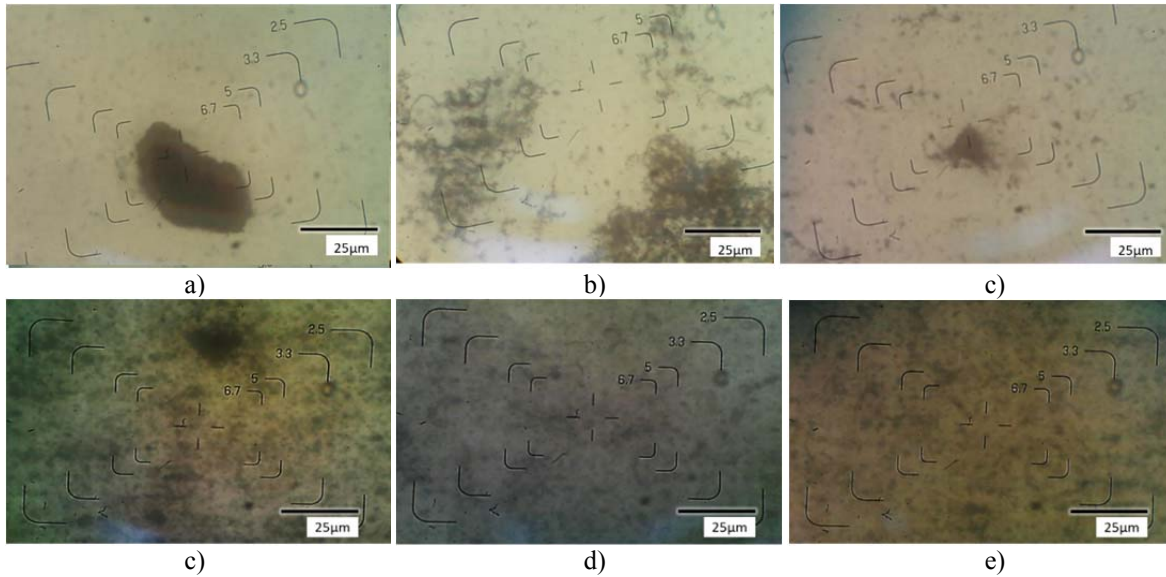


Figure 1. The dispersion of CNT by ultrasonification without silica sand (top): for a) 5 min, b) 10 min c) 20 min; and (bottom) with the addition of silica sand: for c) 5 min, d) 10 min, e) 20 min, all at 100x

For effective mixing, a portion (75%) of water was added to the 19-liter (20 quarts) Hobart HL-200 mixer with silica sand and mixed at low speed (107 rpm) for 30 seconds. After the sand and water were pre-mixed, half of the PVA fibers were added and mixed for another 30 seconds at a low speed. Once that was completed, the rest of the fibers were added and mixed at the same speed for an additional 30 seconds. Half of the portland cement was added to the bowl and mixed for 30 seconds at a low speed, followed by the second half at the same speed. The dispersion of the 25% of water with PCE and CNF (or CNT) was added and mixed at a low speed for 30 seconds then for another 30 seconds at a medium (198 rpm) speed.

Sample preparation

Once the PVA-based FRC was mixed, 12 specimens with a size of 14 x 40 x 160 mm (0.5 x 1.5 x 6.3 in) were cast. Samples were placed into the molds in two layers and each layer was compacted by a rubber tamper. After initial compaction, samples were consolidated by 20 drops on a jolting table and vibrated for 30 seconds on a vibrating table. After compaction, the samples were cured in the molds for 24 hours at 23 °C and 95% relative humidity. Upon this period, the samples were demolded and cured in a lime saturated water at 23 °C (73 °F) for 14 days. The specimens were dried at 90 °C (194 °F) for 24 hours prior to installation of the electrodes.

Upon curing, external electrodes were attached to the specimens. The electrical contacts were glued to the surface of a specimen on both the tension and compression sides using “Wire Glue” (from Anders Products). A coating of latex (Daraweld, from WR Grace) and rubber mastic were placed over the dried glue to make a firm and waterproof connection. The electrodes were attached to the specimen in pairs to investigate the electrical drop over the distance between the electrodes (Figure 2). Monitoring the change in conductivity to determine the crack formation was an essential part of this experiment. When using the four-point bending test, it was necessary to have multiple locations for electrodes along the side loaded in tension. The grips, as stated before, act as an electrical bridge and do not allow for the electrodes to be placed in these areas. Two channels of the external electrodes were placed on either side of the sample located at 20 mm (0.8 in) (channel 1) and 40 mm (1.6 in) (channel 2). Figure 2 shows the external electrode placement for samples loaded for tensile testing.

For the reported experiment, the two-probe DC testing method was chosen because of standard instrumentation and ease of implementation in the field (Ozyurt, et al., 2006) (Wen & Chung, 2007). Therefore, the electrical resistance was directly measured for a particular channel and recorded using a data acquisition unit (HP 34970A from Hewlett-Packard).

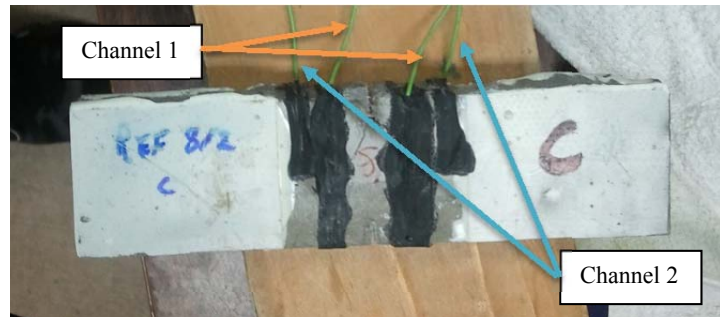


Figure 2. Placement of electrodes and channel coding

Testing of flexural strength and the conductivity

Specimens were tested to evaluate the flexural strength and conductivity. Flexural strength was evaluated using four-point bending on a universal testing machine (Instron 3369). The top-point loading rollers were placed 40 mm (1.5 in) apart, while the bottom loading rollers were spaced at 120 mm (4.7 in) [12]. The specimens were tested until failure at a deformation rate of 1.2 mm (0.05 in) per minute and the change in conductivity was observed. The data acquisition HP 34970A (Hewlett-Packard) recorded the conductivity of the samples in four-second intervals.

Resistivity measurements

Polarization is an important parameter to consider when DC is used to probe the self-sensing materials and is a limiting factor in most techniques for conductivity monitoring. Polarization interferes with resistivity measurements (Wen & Chung, 2007) (Wen & Chung, 2001), and it continues to grow over the time of measurement until it reaches a plateau, at which the readings can be attributed to “saturated” conditions and used as an indication of the stresses experienced by the sensor. This work allowed for the exclusion of the effects of polarization effects by analyzing the change in conductivity instead of monitoring the conductivity.

Exposure to moisture and Na chloride solutions

The procedure used in the initial study for exposing the samples to moisture conditions was adjusted to meet ASTM C1202 testing requirements. The ASTM procedure requires that tested cement-based materials be subjected to a vacuum (at a pressure of 271 kPa, or 39 psi) for 3 hours before coming in contact with de-aerated water. It was important that samples are saturated in de-aerated conditions as described by the ASTM. To de-aerate the specimens, tap water was allowed to boil and cool to ambient temperatures in a sealed container before coming into contact with the samples. Once the water was prepared, it was placed in a container attached to the airtight container containing the prepared samples. To remove all the air trapped in the pores of the samples, the samples were placed under a vacuum to a pressure of 271 kPa, or 39 psi for 3 hours. After 3 hours, water was allowed to enter the chamber under the applied pressure for an additional hour. After the hour had elapsed, the pressure was removed from the chamber, and the samples remained submerged for an additional 18 hours. After the procedure was completed, samples were tested to determine the effect of moisture conditions on the conductivity of concrete samples. Before testing, specimens were immersed in water (or 2% Na chloride solution) for 24 hours to simulate the effect of different exposure conditions. The flexural stress-strain of the reference FRC specimens was compared with CNF- and CNT-based FRC composites. Two exposure conditions allowed the investigation of the sensitivity of composite to detect the presence of chlorides; therefore, the reported experiment was designed to observe the change in relative conductivity of CNF- and CNT-based specimens under flexural conditions.

Crack detection

Concrete does not conduct electrical current; however, it is not entirely insulating. Monitoring the change in electrical conductivity due to air void formation through the development of cracks under loading can lead to crack detection. The piezoresistivity and conductivity of PVA-FRC materials change in proportion to strain and so the proposed relative conductivity method can be used for crack detection of FRC. When comparing the data for the relative conductivity C/C_0 with the stress-strain curve, strong correlation between the cracking of the FRC and the relative change in conductivity can be observed.

The relative conductivity and the differential change conductivity are defined as in Equations 1 and 2, respectively:

$$\Delta C / C_0 = \frac{C_t - C_0}{C_0} \quad [\text{Eq. 1}]$$

$$\Delta C_t / C_t = \frac{C_t - C_{t-\Delta s}}{C_t} \quad [\text{Eq. 2}]$$

where ΔC is the change in conductivity, $(\Omega\text{m})^{-1}$, C_0 is the initial conductivity, $(\Omega\text{m})^{-1}$, $C_{t-\Delta s}$ is the conductivity at a testing time $t - \Delta s$, $(\Omega\text{m})^{-1}$, ΔC_t is the change in conductivity at sampling rate Δs , $(\Omega\text{m})^{-1}$, Δs is the sampling rate and C_t is the conductivity value at a testing time t , $(\Omega\text{m})^{-1}$

RESULTS AND DISCUSSION

Flexural strength and water absorption

The maximum flexural stress achieved are summarized in Table 3. Reference specimens containing only PVA fibers had the highest flexural capacity. Reference composition had the same dosage of superplasticizer as mixtures with CNF/CNT; however, the addition of nanomaterials reduced the workability. The reduction in flexural capacity is probably due to the loss of workability and compaction imperfections as by the addition of the CNF/CNT could have led to more voids as demonstrated by higher water absorption, Table 3.

Table 3. Flexural strength and water absorption of specimens

Mixture ID	Flexural Strength	Average moisture absorption (%)
Ref.	13.3 MPa (1933 psi)	1.1
CNF	10.5 MPa (1529 psi)	2.9
CNT	12.5 MPa (1806 psi)	3.1

Crack detection

Specimens were loaded until failure using a universal testing machine (Instron 3369). Changes in the conductivity were observed during the flexural loading to aid in the detection of crack formation. Crack detection was found to be possible through the use of the equations Eq.1 and Eq.2 with relative conductivity and differential change in conductivity as defined earlier. Figure 3 and Figure 4 represent the measurements made for Ref., CNF, and CNT samples for crack formation under flexural loading for specimens saturated in water and in 2% Na chloride solution, respectively.

Sample exposure to moisture affected the material's ability to conduct the electrical current. Tap water can conduct the current due to the impurities in the water's composition. The Na chloride solution has the ability to conduct electricity due to the presence of ions. This performance was demonstrated in Figures 3 and 4. The differential conductivity was observed to have higher differential changes in conductivity for all samples exposed to Na chloride solution compared to the specimens exposed to water. Reference, CNF, and CNT samples were compared to determine the differences in conductivity when comparing chlorides to water exposure with corresponding values of 1.12, 1.00, and 0.16%. The increase in conductivity can demonstrate that the proposed equations and data analysis were useful for chloride detection by the developed composite.

CONCLUSIONS

Through the experimental work, the feasibility of NDT for crack and chloride detection through the monitoring of conductivity of smart FRC sensor was explored. The use of electrically conductive nano-scale fibers such as carbon nanotubes and carbon nanofibers in concrete matrix was explored to increase the sensitivity of the material to detect the formation and propagation of cracks. The CNF and CNT can be used in smart composite to bridge the submicron cracks that form in the concrete matrix and, in combination with larger PVA fibers, allowing to enhance the performance of composite through strain hardening. Furthermore, the developed smart FRC material can be used in the form of stress-sensing skin with a thickness of 2 – 15 mm (0.08 – 0.6 in) incorporated into existing concrete. The formation of multiple cracking patterns can

improve the response of the stress-sensing skin and also increase the ductility of the material minimizing the possibility of brittle failure of the structural element.

In addition to the savings during construction and installation, the proposed stress-sensing skin method is cost effective when compared to other techniques while in service. The proposed technique does not require the use of expensive equipment for monitoring of structural elements. Conductivity readings can be taken through the use of a simple data acquisition system connected to simple electrodes. The proposed concept does not require a trained professional to make the observations in situ.

Polarization is a limiting factor in most techniques used for conductivity monitoring. Typically, DC measurements of conductivity would include the polarization and would make the detection of cracks much challenging. Here, instead of monitoring the conductivity, this work proposed to exclude the effects of polarization by recording and analyzing the change in conductivity. Comparing current readings to previous readings allowed for polarization effects to be neglected and cracks to be directly measured through the differential and relative conductivity parameters proposed in this work. The fibers used in this work are often hard to disperse within the mix. The dispersion of CNF and CNT was greatly improved through the use of ultrasonic mixing combined with the use of superplasticizer. To break up the Van der Waals forces holding the CNT agglomerates, the inclusion of a small portion of the sand into the mixing process increased the ability of the nanomaterial to be dispersed in a given medium.

The monitoring of chloride penetration into concrete element through conductivity measurements was demonstrated to be feasible. The electromechanical response of reference FRC subjected to water and Na chlorides was similar to CNF- and CNT-based FRC. The PVA based composites exposed to the 2% Na chloride solution demonstrated higher changes in differential conductivity than those exposed only to water. This change in relative conductivity can be observed most definitively at the first crack in the composite matrix and can be used for chloride detection. Generally, samples exposed to Na chlorides had a steeper slope of relative conductivity than the sample exposed only to water. The results of this study demonstrated the ability of self-sensing CNF- and CNT-PVA based composites to provide safe, systematic, and nonbiased monitoring of concrete structures.

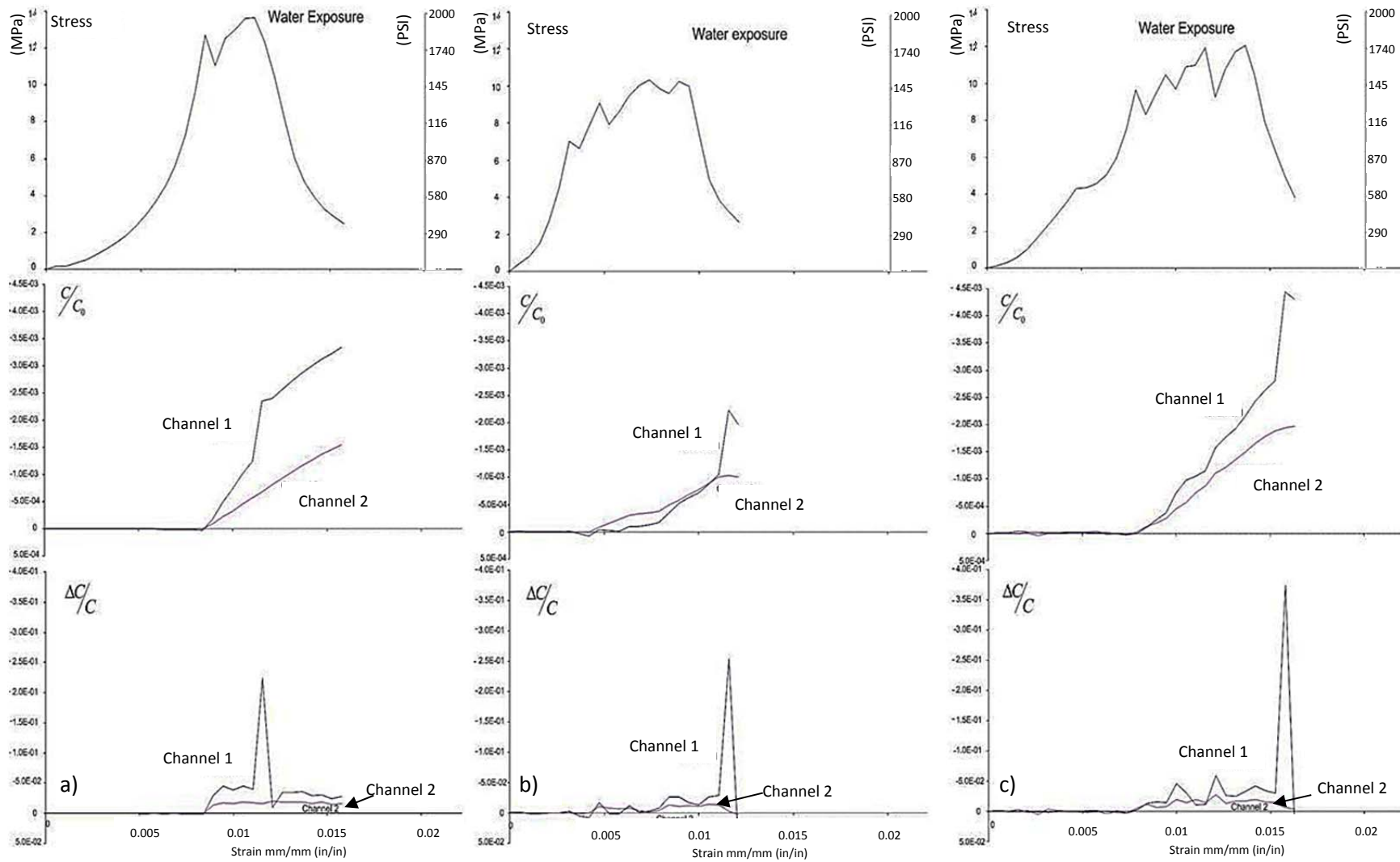


Figure 3. The performance of FRC specimens exposed to water: a) Reference, b) with CNF, and c) with CNT

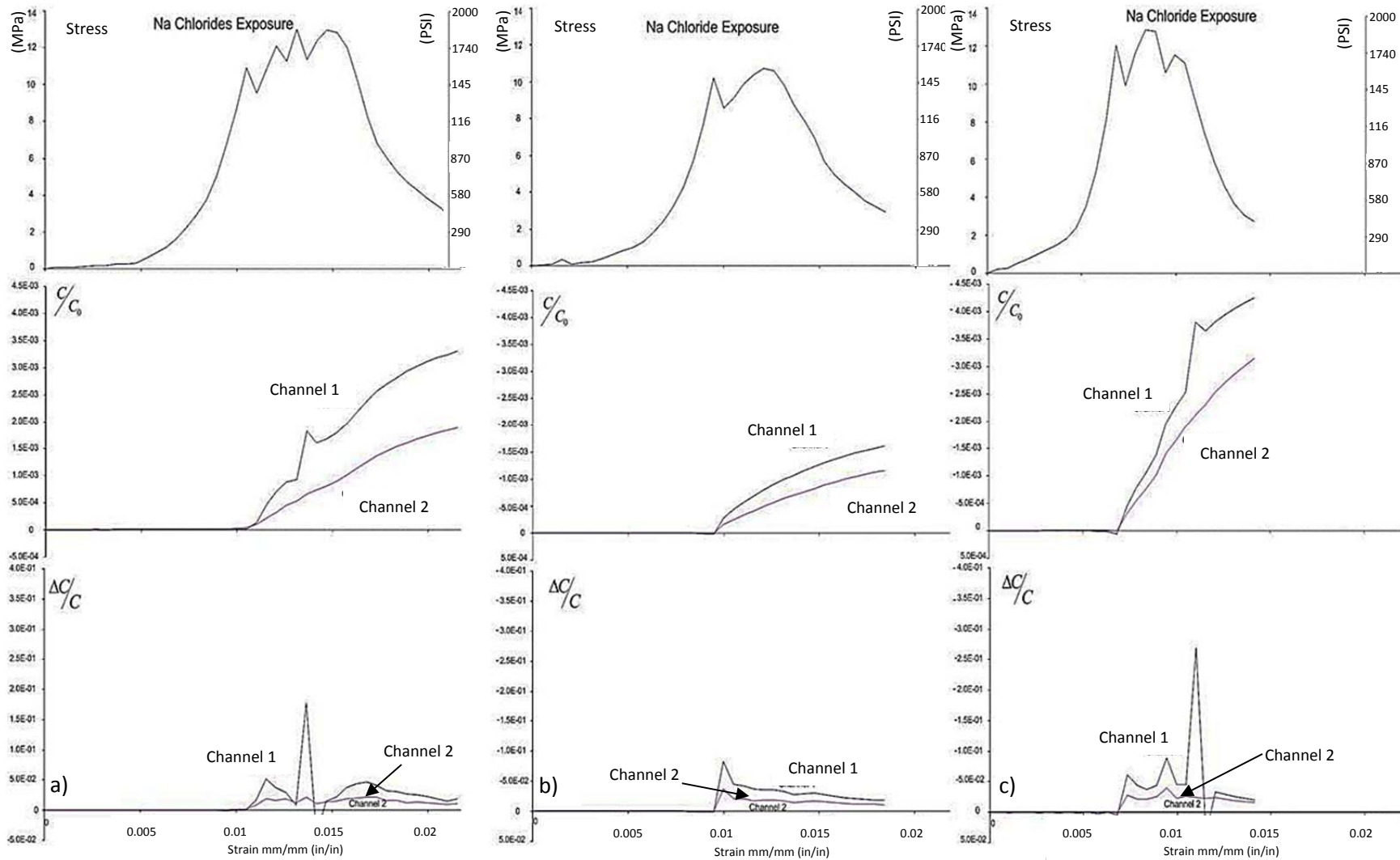


Figure 4. The performance of FRC specimens exposed to NaCl solution: a) Reference, b) with CNE, and c) with CNT

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Investigation Methods for Characterizing Nanoparticles in Concrete

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Synopsis There is significant potential for the use of nanoparticles in cementitious materials, especially in ultra-high performance concrete. These nanoparticles can further increase packing density, accelerate the pozzolanic reaction or can be used to induce new properties to the material, such as air purification or self-cleaning. Little is known about the interaction mechanisms between nanoparticles in cementitious materials, including their dispersion quality. The characterization of these nanoparticles can be challenging, especially when these nanoparticles interact with cementitious materials and their reaction products during hydration. Thorough characterization of the nanoparticle system is essential to understand how to optimize mixing constituents, procedures, and parameters.

This study explores the feasibility and potential use of several characterization methods for investigating colloidal nanosilica in a concrete environment. These techniques include dynamic light scattering, zeta potential, atomic force microscopy, scanning electron microscopy, cryogenic SEM, and focused ion beam microscopy. These methods allow for characterization of nanoparticles, nanoparticles interacting with pore solution that represents a concrete environment, nanoparticles interacting with polymers used as superplasticizers, and nanoparticles interacting with a cementitious material. These tools allow for studies on the nano-length scale at short times to observe and measure parameters such as particle size distribution, polydispersity index, and zeta potential.

Keywords: characterization, nanoparticles, cementitious material, concrete, dispersion, size distribution, dynamic light scattering

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INTRODUCTION

There is an ever-growing desire to improve material properties such as strength, toughness, ductility, and density. These are driven by a variety of factors including cost reduction and environmental concerns. The concrete industry is no exception to this. The strength of concrete has increased dramatically over the past decade, resulting in a type of concrete known as ultra-high performance concrete (UHPC).¹⁻³ UHPC is defined as having a minimum compressive strength of 150 MPa (22,000 psi).⁴ With the use of fibers, UHPC can possess high strength and high ductility simultaneously.⁵⁻⁷ UHPC achieves these properties through increased particle packing and increased pozzolanic reactions.⁸⁻¹²

The desire to further push the limits of UHPC has led to the use of nanoparticles in the cementitious matrix. It is hypothesized that nano-sized particles can further enhance the particle packing and contribute to the pozzolanic reaction.¹³⁻¹⁶ Implementation of nanoparticles in cementitious materials has proved to be challenging due to several factors including their high surface area to volume ratio, resulting in large surface energies.¹⁷⁻¹⁹ These surface energies often result in agglomeration of nanoparticles, as their attractive forces are much greater than their repulsive forces. It is a challenge across many disciplines to achieve a uniform and stable dispersion of nanoparticles.²⁰⁻²³ This is also the case in cementitious materials which have a high pH and many different ions dynamically reacting in the system.²⁴⁻²⁶

The characterization of nanoparticles is critical to understanding how they react in a cementitious material. There are many methods available for the study of nanoparticles, often found in the materials science, chemistry, and electronics disciplines. A further challenge is studying these particles in a cement-based material. Since concrete is one of the most complex materials systems to study, introducing highly reactive nanoparticles into the system only complicates matters.^{27,28}

Researchers have attempted to study nanoparticles, the effects of superplasticizers, and how these affect concrete properties.²⁹⁻³² There are a variety of techniques that have been used to study nanoparticles, such as forms of electron microscopy, laser light scattering, scanning probe microscopy, x-ray microscopy, Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and many more.³³⁻⁴² There has been a desire to bridge the gap between macroscopic properties of concrete in the civil engineering field down to the nano-scale materials properties and interactions in the materials science arena.

This study compares several characterization techniques that are useful in the study of nanoparticles, nanoparticles interacting with superplasticizers, and nanoparticles in cement-based systems. Techniques investigated were dynamic light scattering (DLS), zeta potential (ζ p), scanning electron microscopy (SEM), cryogenic SEM (cryoSEM), focused ion beam (FIB), and atomic force microscopy (AFM).

MATERIALS AND METHODS

Nanoparticles

The nanoparticles used in this study were colloidal silica. Colloidal silica was chosen over powdered silica because colloidal silica is already uniformly dispersed in solution. Four different sols of varying average diameters in different stabilizing ions were used: 5 nm (1.97×10^{-7} in) with ammonium (NS-5), 20 nm (7.87×10^{-7} in) with no stabilizing ion (NS-20a), 20 nm with sodium (NS-20b), and 75 nm (2.95×10^{-6} in) with sodium (NS-75). A full list of materials properties as provided by the manufacturer are in **Error! Reference source not found.**

Table 1— Properties of nanosilica sols. 5 nm $\approx 1.97 \times 10^{-7}$ in. 100 m²/g $\approx 7.03 \times 10^7$ in²/lb. 10 cP $\approx 5.60 \times 10^{-4}$ lb/in s

	NS-5	NS-20a	NS-20b	NS-75
Particle Size (nm)	5	20	20	75
Surface area (m ² /g)	600	150	150	40
% SiO ₂	15	34	50	40
pH	9.0	2.8	9.0	8.4
Specific Gravity	1.09	1.23	1.39	1.29
Viscosity (cP)	< 10	< 10	55	10
Stabilizing Ion	Ammonium	--	Sodium	Sodium
% Na ₂ O	0.02	0.04	0.40	0.30