CARBOXYMETHYL CELLULOSE SURFACE TREATMENT METHOD TO DISPERSE CARBON NANOTUBES IN SMART CEMENTITIOUS MATERIALS

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Carboxymethyl Cellulose Surface Treatment Method to Disperse Carbon Nanotubes in Smart Cementitious Materials

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

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ABSTRACT

An innovative surface treatment method was proposed using carboxymethyl cellulose (CMC) to surface-treat carbon nanotubes (CNTs) for a consistent dispersion in cementitious materials to achieve high force detection sensitivity. This CMC surface treatment method was compared with two traditional methods, direct mixing and surfactant surface treatment, to validate dispersion effectiveness. Experimental results demonstrated that CMC and CNTs combined can increase force sensitivity of the smart cementitious material more than six times compared with direct mixing and more than three times compared with the surfactant surface treatment. CMC surface treatment significantly improved CNTs dispersion consistency. For CMC surface treatment, the comparison of 0.1%, 0.3% and 0.5% of CNTs by weight to cement demonstrated all percentages showed consistent laboratory dynamic force sensing results. Furthermore, CNTs percentage did not differ for force sensitivity. All experiments indicated the proposed CMC surface treatment method is an effective dispersion method for CNTs in smart cementitious materials.

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LIST OF ABBREVIATIONS

CB .....Carbon Black

CFs .....Carbon Fibers

CMC.....Carboxymethyl Cellouse

CNTs .....Carbon Nanotubes

CoefVar.....Coefficient of Variation

MWNTs .....Multi Walled Carbon Nanotubes

NaDDBS .....Sodium Dodecylbenzenesulfonate

NDE .....Non-destructive Evaluation

PAA.....Polyacrylamide

PEG .....Polyethylene Glycol

SDS .....Sodium Dodecylsulfate

SFs.....Steel Fibers

SWNTs.....Single Walled Carbon Nanotubes

V.....Volts

R.....Resistance

I .....Current

CHAPTER 1. INTRODUCTION

Monitoring structural performance attracted a lot of attention in recent years. Detecting forces and damages on structures is crucial to maintain a good health status of a structure. To detect structural damages on cement-based structures, visual inspections, non-destructive evaluation (NDE), and sensor-based monitoring systems have been introduced. Alternatively, smart cementitious materials can also be a potential candidate which collect data for monitoring loading and damages in the structure. In this chapter, approaches to achieve self-sensing capabilities in smart cementitious materials, their challenges, and possible solutions will be discussed.

1.1. Background

Modified mortar and concrete have become popular materials in highway, bridge, and building constructions (Ohama, 1997). Concentrated loads cause concrete cracking and delamination as shown in Figure 1 (Gunderson, 2015), which has long-term impacts on the structure's performance but can be hard to detect in field (Thostenson & Chou, 2008). Current methods for detecting structural conditions mainly depend on occasional visual inspections, non-destructive detection techniques, or real-time structural monitoring (Chia, 2016).

Figure 1. A bridge in Minneapolis with serious damages (Thompson, 2015)

Visual inspections use human eyes to inspect the damages on the surface of the concrete structures. Although the visual inspections might be performed well, they are time-consuming and not very accurate, especially, the low frequency of inspection requires trust in long-term predictions for ensuring infrastructure integrity. While a novice inspector might assert that the structure is entirely functional, an experienced inspector might find problems in the structure and call for repairs (Siriwardane, 2015). Therefore, the visual inspections are not effective and efficient because they do not sufficiently diagnose the problems.

Non-destructive evaluation (NDE) uses a wide variety of analysis methods to assess the properties and functionality of structural components in a system such as acoustic, ultrasonic, X-ray, and eddy current. For NDE, extensive technical knowledge and special tools like probes and X-ray fluorescence analyzers are needed for inspections. In addition, NDE is often affected by surface conditions (Balayssac & Garnier, 2018). Checking small components in a complex structure can be challenging. Also, the instruments could be costly, and they are difficult to assemble and disassemble in the field, which can be time-consuming.

Sensor based monitoring systems can collect field data through embedded or attached sensors on the monitored structures. A wide variety of real-time structural sensors have been applied to lab testing and practices, such as strain gauges, electrical accelerometers, and piezo-electric strain sensors (Sebastian, et al., 2014). To achieve effective monitoring of structures, a wide range of sensors need to be installed on significant locations of the structure, like in the middle span of a bridge and both ends of a bridge, to detect any damages over a long period of time. Quantitative real-time structural health monitoring for concrete structures have been studied but not fully accomplished yet (Sagar, 2015).

Self-sensing materials have become a cutting-edge technology for detecting damages in civil infrastructure. They utilize their electrical or other property changes when subject to stress to detect loading and structural damages (Yu, 2012). With the use of self-sensing materials, the presence of micro-cracks can be detected (Faezeh, 2008). Thus, self-sensing materials could achieve real-time structural health monitoring with easy installations, wide detection areas, long service life, and low maintenance cost (Han, Yu, & Kwon, 2009), which would improve structural safety and performance. These features indicate that the self-sensing composite has a great potential for detecting structural integrity.

1.2. Literature Reviews

Self-sensing cementitious materials have been found as a new development in construction materials research area in recent years (Ackermann, 2018). When self-sensing cementitious materials are deformed by applying mechanical stress, their conductivity or other properties change simultaneously with the stress applied (Ackermann, 2018). Therefore, stress, cracking, and damage inflicted under dynamic loads could be detected by measurement of these changes (Konsta-Gdoutos & Aza, 2014), (Han, Yu, & Ou, Self-Sensing Concrete in Smart Structures, 2014). Self-sensing cementitious materials can be achieved by adding functional fillers, such as Carbon Nanotubes (CNTs), carbon fibers, and carbon black and others, to cement to enable potential electrical conductivity changes to detect stress, cracking, or damage to the structure while enhancing the mechanical properties of conventional cementitious materials (Materazzi, Ubertini, & D'Alessandro , 2013).

1.2.1. Material Selection

Piezo-electrical or piezo-resistant effects can be used to enable potential electrical conductivity changes as self-sensing cementitious materials. Piezo-electricity is an electrical

charge caused by application of mechanical stress or strain (Yang, 2016), as shown in Figure 2. Essentially, the piezo-electric effect is merely the result of stressing a piezo element, such as CNTs, quartz crystals, ceramic, or biological matter to generate a charge or voltage (Gautschi, 2002). After the initial voltage, the amount of additional charge generation is proportional to the amount of stress placed upon the piezo material (Wang, Ghani, Cheng, & Rakowski, 2012). The piezo-electric materials have a wide range of applications for sensors and ultrasonic transducers since they are small (Polytechnic Hub, 2017), (Kon, Oldham, & Horowitz, 2007). Piezo-resistivity is used to describe the changes in electrical resistance of a material when subjected to mechanical stress, which is a passive effect. carbon fibers, carbon black, steel fibers, and carbon nanotubes (CNTs) have been known for piezo-resistive effect (Yu & Kwon, 2009).

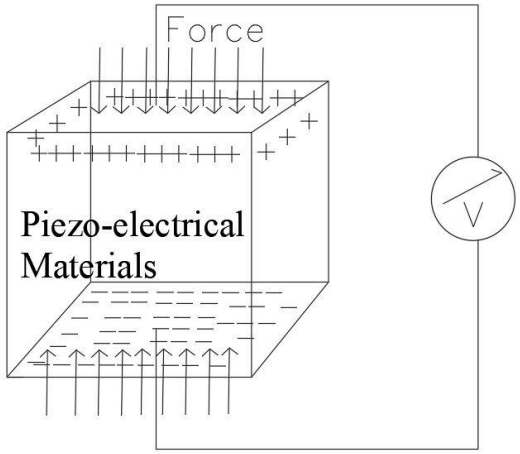


Figure 2. Piezo material under piezo-electric effect

Among piezo-resistant materials, carbon fibers with diameters of about 5-10 micrometers, could improve cementitious materials' mechanical performance for higher stiffness, tensile strength, chemical resistance, temperature tolerance as well as reducing thermal expansion. However, carbon fibers are difficult to mix in cementitious materials for large applications, which yields low electrical resistance changes (Veedu, 2010). Carbon black, on the other hand, is in a form of paracrystalline carbon that has great mechanical properties. While, it

has been noticed for a fairly low resistance changes too (G.Karmankar , 2016). Steel fibers which are made from stainless steel when used as additives to cementitious materials can increase significantly on flexural strength, fatigue resistance, and permeability compared with conventional cement-based materials. However, corrosion of steel fibers is a concerns for long-term applications (Veedu, 2010).

CNTs are tube-shaped made of carbon atoms on nanometer scale and have a much finer scale than common fibers, which are formed by rolling a graphene sheet and closing it on both sides by fullerene hemispheres (Foldyna, Foldyna, & Zeleňák, 2016). Two types of CNTs exist including the single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotubes (MWCNTs) as shown in Figure. 3 (Yellampalli, 2011). The MWCNTs are made of coaxial cylinders, which have interlayer spacing close to that of the interlayer distance in graphite. These cylindrical structures are only few nanometer in diameter, but the cylinder can be tens of microns long, with most end capped with half of a fullerene molecule. CNTs, either SWCNTs or MWCNTs, exhibit a great potential for an efficient enhancement of the electrical conductivity, due to the relatively low surface area and high aspect ratio (length-to-diameter ratio) (Reales & Filho, 2017). Since MWCNTs have more defects, they can be manipulated to increase higher conductivity. In addition, MWCNTs is cheaper when compared with SWCNTs.

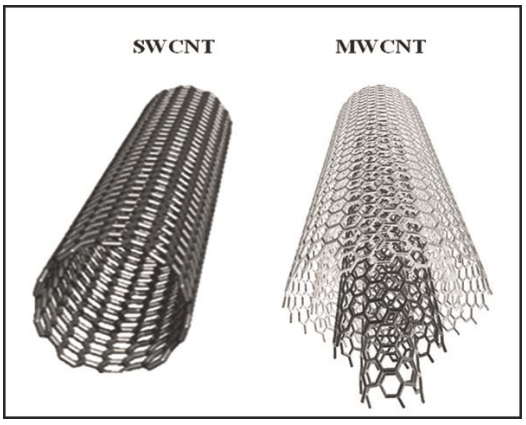


Figure 3. Diagrams of the SWCNT and the MWCNT(Yellampalli, 2011)

The additive of CNTs, in most cases, MWCNTs, in cement mortars would dramatically enhance the electrical conductivity, flexural and compressive strength as well as the failure strain. In particular, compressive strength increased up to 19% and flexural strength increased up to 25% as well as possessing the highest Young's modulus (1.4 TPa), tensile strength (above 100GPa), current density (109 A/cm^2), thermal conductivity (above 3000 W/mK), and high aspect ratio, 0.5 nm to 5 nm diameters (Ganesh, 2013). Bases on comparison between all the piezo-materials, MWCNTs, by adding a small fraction in cementitious materials, can introduce high conductivity changes and improves all mechanical properties, thus, it can be a promising candidate for enabling self-sensing cementitious materials in detecting damages (Konsta-Gdoutos & Aza, 2014). Meanwhile, it has been revealed that the self-sensing capability of nanotube-cement composites could be utilized in various applications, such as under dynamic load and impact, in the elastic and plastic ranges of deformation and for crack development sensing (Reales & Filho, 2017).

When applying CNTs in cementitious materials, its percentage is critical for improvement in electrical and mechanical property (Leonavičius, et al., 2017). Previous studies demonstrated that the optimum percentage of CNTs in cementitious materials is approximately 0.1% of CNT's by mass of cement, which will increase electrical conductivity and almost double the compressive strength (Reales & Filho, 2017), (Spires & Brown, 1996), (Rausch & Mäder, 2010). However, the dispersion of CNTs, especially MWCNTs, is very complicated because of their higher aspect ratio (Min, Shen, Shi, Chen, & Xu, 2010). Thus, the most challenging issue for MWCNTs when applying in cementitious materials is its dispersion effectiveness.

1.2.2. CNTs Dispersion Methods

Although CNTs can be a potential candidate for self-sensing in cementitious materials, its effectiveness is determined based on the proper dispersion. Effective dispersion methods for functional fillers in cementitious materials are necessary to form consistent and optimized conductivity (Han, et al., 2015). Currently, there are three dispersion methods available, as listed in Table 1, including direct mixing, surfactant, and acid treatment methods (Parveen, Rana, & Fangueiro, 2013).

Table 1

Comparison of Current Dispersion Methods

Methods	Procedures	Time
Direct Mixing	Easy (Direct Mixing with Water)	15 Minutes Plus
Surfactant	Medium (Add 0.5% NaDDBS & 0.25% Defoamer)	2 Hours Plus
Acid Treatment	Medium (A Mixture of Sulfuric & Nitric Acid)	1 Hour Plus

NaDDBS: Sodium Dodecylbenzen Sulfonate

Direct mixing method is easy to conduct and very time-efficient. But studies have shown that direct mixing CNTs in water without any dispersing agent would not effectively disperse CNTs into the cement mortar (Kim, Park, & Lee, 2014). More recently, two other different dispersion methods of CNTs in cement were studied, including the use of acid treatment method (Ashour, 2012) and surfactant Sodium Dodecylbenzen Sulfonate (NaDDBS) surface modification. The acid treatment method is to modify the CNTs surface by oxidizing with hydroxyl groups. The presence of hydroxyl groups creates bonding with CNTs to make them more compatible with water to enhance dispersion (Elkashef, Wang, & Abou-Zeid, 2016). CNTs are treated in a mixture of sulfuric acid and nitric acid solution for 1 hour and extracted. After

this, acid-treated CNTs are sonicated with deionized water (Yu & Kwon, 2009). The experimental results showed that the acid treatment method had a much stronger and accurate response compared to the surfactant method (Kim, Park, & Lee, 2014). The acid treatment method induced stronger piezo-resistive response than direct mixing method, however, it was difficult to scale up for larger samples. The use of strong acid also made it difficult to be implemented in field since it would pose a health concern.

To reduce health concerns on acid treatment method, the surfactant dispersion methods were studied using two different surfactants for surface modifications including Sodium Dodecyl Sulfate (SDS) and NaDDBS. The NaDDBS dispersed CNTs were shown to be more stable and sensitive to the external force compared with SDS in dispersing the CNTs (Yu & Kwon, 2009). In addition, superplasticizer and silica fumes had also been used as the surfactant to mix with CNTs into cement. However, the researchers claimed that these methods were not effective due to the lack of consistency of dispersion (Yu, 2012). In all these investigations, MWNTs were adopted as they are more sensitive to stress changes compared with SWNTs.

Recently, studies showed that the use of co-polymer could effectively suspend nanoparticles of all sizes (10-90 nm) into liquids such as water (Krajangpan, Kalita, Chisholm, & Bezbaruah, 2012). The nanoparticle used in that investigation was nanoscale zerovalent iron (NZVI). The co-polymer coated NZVI achieved better response compared with the non-coated NZVI (Krajangpan, Kalita, Chisholm, & Bezbaruah, 2012). The co-polymer method was first brought to our research group's attention in 2017 (Chia, 2016). However, there is limited development in effective co-polymer method to disperse CNTs in cementitious materials yet.

1.3. Problem Statements and Objectives

From the above literature reviews, it can be found that, to achieve effective self-sensing cementitious materials, CNTs can be a promising candidate, however, a proper dispersion is challenging. There are currently several dispersion methods available such as direct mixing, the surfactant method, and acid treatment method, but a uniform, consistent, and optimized dispersion is yet to achieve.

To meet the challenges mentioned above, the objective of this study is to develop an effective dispersion method which could achieve a uniform and consistent dispersion for CNTs in smart cementitious materials. The specific tasks of this study to address these challenges are listed as below:

1) Investigating a proper polymer, specifically, carboxymethyl cellulose (CMC), that potentially having chemical bonds with CNTs has been studied for accomplishing proposed polymer surface treatment method to achieve a better dispersion of CNTs;

2) Developing dispersion methodology using current dispersion methods including the direct mixing method, the surfactant method, and the new polymer surface treatment method for comparison;

3) Validating the proposed new surface treatment method when compared with the two currently available dispersion methods using laboratory experiments to verify a uniform, consistent, and optimized CNTs dispersion procedure.

This thesis is organized as follows: Chapter 1, introduction is discussed by introducing research background, literature reviews, problem statements, and objectives of this research; Chapter 2, polymer surface treatment dispersion method is proposed; Chapter 3, dispersion methodology is introduced by the new surface treatment method, direct mixing method, and

surfactant method as well as making comparisons with those three methods; Chapter 4, experimental results are analyzed and utilized to statistically evaluate each method; Chapter 5, future work and conclusions based upon the findings from this study are discussed.

CHAPTER 2. POLYMER SURFACE TREATMENT DISPERSION METHOD

This chapter introduces polymer selections for the surface treatment dispersion method and the function of CNTs using the selected polymer in addition to the potential chemical bonds between CNTs with the selected polymer and cement particles by analyzing molecular attractions.

2.1. Polymer Selection

Various polymers can be considered to surface treat the CNTs to improve the CNTs dispersion in cementitious materials. The proper polymer needs to be water soluble and must not react with metal for potential reinforcement composite. Tables 2a and 2b compare all the possible polymers which can be used to surface treat the CNTs, including Polyethylene Glycol, Modified Tapioca Starch, Polyacrylamide, Sodium Polyacrylate, and Carboxymethyl Cellulose (CMC). Cost, procedures, and commonly used areas for the five different polymers mentioned above are described in Table 2a. PEG, Modified Tapioca Starch, PAA, and CMC were previously applied in cementitious materials. Among those four polymers, in terms of polymer preparation, PEG and CMC are fairly simple to prepare.

Table 2

Properties of Polymers-I

	Cost	Procedures for Polymer & Solution Preparation	Commonly Used Areas
Polyethylene glycol (PEG) (EI-Dieb, 2007), (Büyükyağcı, Tuzcu, & Aras, 2009), (Mousa, Mahdy, Abdel-Reheem, & Yehia, 2015)	$33/kg	Easy	Concrete self-curing agent
Modified Tapioca Starch (Chia, 2016), (Kibar & Us, 2013), (Rosliza & Nik, 2010), (Rao & Tattiyakul, 1999), (Sweedman, Tizzotti, Schäfer, & Gilbert, 2013), (Naz, Sulaiman, Ariwahjoedi, & Shaari, 2014)	$40/kg	Complex	Cement, concrete admixture
Polyacrylamide (PAA) (Girma, Lorenz, Blaurock, & Edelmann, 2005), (Zhang, Zhai, & He, 2014), (Rai & Singh, 2005)	$61/kg	Complex	Paper making, cement
Sodium Polyacrylate (Wilson, 2018), (Sato, Iwasaki, Terada, Ninomiya, & Nakada, 1980), (Al-Nasra, 2013), (Manzur, Iffat, & Noor, 2015), (Xu, Cao, & Liu, 2015)	$92/kg	Complex	Mainly in Diapers and hair gels, curing agent
Carboxymethyl Cellulose (CMC) (Mishra, Singh, Narang, & Singh, 2003), (Farooque, Yeasmin, Halim, Mahmood, & Mollah, 2010)	$106/kg	Easy	Plastering, cement, underwater concrete works

Table 2

Properties of Polymers-II

	Setting Time	Heat of Hydration	Compressive Strength	Fracture Strength	Water Absorbance	Bio-polymer	Reaction with Metal
Polyethylene Glycol (PEG) (EI-Dieb, 2007), (Büyükyağcı, Tuzcu, & Aras, 2009), (Mousa, Mahdy, Abdel-Reheem, & Yehia, 2015)	N/A	N/A	Increase	Increase	High	Yes	No
Modified Tapioca Starch (Chia, 2016) (Kibar & Us, 2013), (Rosliza & Nik, 2010), (Rao & Tattiyakul, 1999), (Sweedman, Tizzotti, Schäfer, & Gilbert, 2013), (Naz, Sulaiman, Ariwahjoedi, & Shaari, 2014)	60-240 mins	Low	Increase	Increase	Medium	Yes	No
Polyacrylamide (PAA) (Girma, Lorenz, Blaurock, & Edelmann, 2005), (Zhang, Zhai, & He, 2014), (Rai & Singh, 2005)	505-842 mins	Low	Increase	Increase	Very High	No	Yes
Sodium Polyacrylate (Wilson, 2018), (Sato, Iwasaki, Terada, Ninomiya, & Nakada, 1980), (Al-Nasra, 2013), (Manzur, Iffat, & Noor, 2015), (Xu, Cao, & Liu, 2015)	N/A	N/A	Increase	Increase	Extremely High	No	No
Carboxymethyl Cellulose (CMC) (Mishra, Singh, Narang, & Singh, 2003), (Farooque, Yeasmin, Halim, Mahmood, & Mollah, 2010)	160-320 mins	Low	Increase	Increase	Medium	Yes	No

Therefore, after sorting through all the polymers as shown in Tables 2a and 2b, the CMC is a good candidate as the polymer to be a surface treatment of CNTs. CMC as an organic polymer is an anionic hydrophilic polysaccharide and makes up a member of carbohydrate group long chain polymer (Singh, Mishra, Singh, & Narang, 2002). When CMC is used as an additive to the cement, its function is to optimize the conditions to gain material with improved compressive strength and fracture toughness when compared with Ordinary Portland Cement (Mishra, Singh, Narang, & Singh, 2003). Furthermore, after the mass of CMC in the mixture passes 0.3%, there is a noticeable decrease in porosity and water absorbance (Farooque, Yeasmin, Halim, Mahmood, & Mollah, 2010). The HC-OH group from CMC-absorbing H_3O^+ ions on the cement surface interact to slow down the setting time (Mishra, Singh, Narang, & Singh, 2003). The chemical reactions between cement and CMC is important to generate carboxyl group for efficient dispersion of CNTs. Cellulose components with modifiers could be utilized to enhance bending strength on cementitious materials, having a wide range of applications, such as plastering, underwater concrete works, cement, textiles, packaging, glass, and so on (Singh, Mishra, Singh, & Narang, 2002). Thus, CMC is selected as the polymer in this study to surface treat the CNTs in dispersing CNTs in cementitious materials.

After CMC was being selected, the CMC content was an important factor to achieve a uniform coating on CNTs while still increasing the strength properties of the cementitious materials composite. Previous studies indicated that a cement-CMC (0.3% in mass) mix had a significant improvement on mechanical properties and potentials for other applications. 0.3% CMC content stayed at a suitable level for the setting time. When the percentage of CMC increases, the setting time increases dramatically and the water absorption rate begins decreasing from an appropriate level 9% mass gain to about 6% mass gain. In addition, 0.3% CMC has

shown the potential to reach the maximum fracture toughness at 28 and 91 days (Mishra, Singh, Narang, & Singh, 2003). Thus, in this study, a 0.3% cement-CMC mix was utilized as basis for the modified cementitious materials.

2.2. Functionalization of CNTs using CMC

CNT is one of the carbon allotropes, like graphite and shapeless carbon. It is the one-dimensional carbon form, which could have an aspect ratio larger than 1000. The structural bonding of CNTs provides unique strength in CNTs molecules and the properties of CNTs rely on the way that graphite sheets roll together (Yellampalli, 2011).

2.2.1. Covalent Functionalization of CNTs

The end caps of nanotubes have defective side walls on the top, bottom and the sides of each CNT. More specifically, there are defects at four potential locations A, B, C, and D that may occur in SWNT as shown in Figure 4 (Yellampalli, 2011). Location A indicates five or seven membered carbon rings in the nanotube structure rather than the normal six-membered carbon rings at the bending areas. These bending areas could be effectively functionalized for a range of nanotubes with sidewall substituents, wrapped with polymers, or with guest molecules included (Hirsch, 2002). Location B shows sp^3 defects for R=H and OH groups attached on the sidewalls of SWNT. Location C illustrates that the SWNT frame is damaged as the result of being oxidized conditions, which allows it to remain linked with carboxyl groups (-COOH groups) to attach on the CNT frame. Location D indicates that the opening end of SWNT, which provides opportunities to link with other terminal groups, such as $-NO_2$, -OH, -H, and =O molecules. The covalent functionalization of CNTs to get polymers bonded at these defects brings excellent benefit to various solvent polymers and organic solvents because CNTs have a considerable number of functional groups, such as polar or non-polar groups.

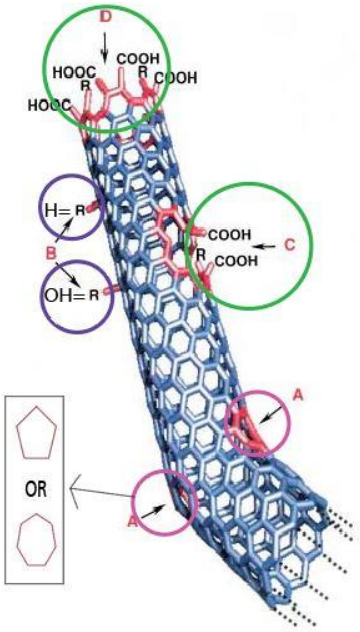


Figure 4. Typical defects in a SWNT (Modified after Yellampalli, 2011)

2.2.2. Non-covalent Wrapping Functionalization of CNTs

A non-covalent wrapping functionalization retains denoting double or triple bonds in a molecule system of the CNTs side walls. It keeps the final structural properties of the material to preserve their own properties while greatly enhancing their solubility. More importantly, surfactants polymers and other types of polymers can be employed to functionalize or surface treat CNTs by using non-covalent wrapping as seen in Figure 5. The physical adsorption of surfactant or other polymers onto CNTs surfaces increase the surface attractive force of CNTs. This increases surface attractive force could effectively prevent the aggregation of CNTs. Moreover, electrostatic/steric repulsive forces of the surfactant or polymer surface treated CNTs successfully overcome significant amount of van der Waals force in CNTs. The efficiency of non-covalent wrapping functionalization relies intensely on the properties of surfactants and polymer matrix. The surfactants applied include non-ionic surfactants, such as polyoxyethylene 8

lauryl or $C_{12}EO_8$, polyoxyethylene octylphenylether, and anionic surfactants, such as sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (NaDDBS).

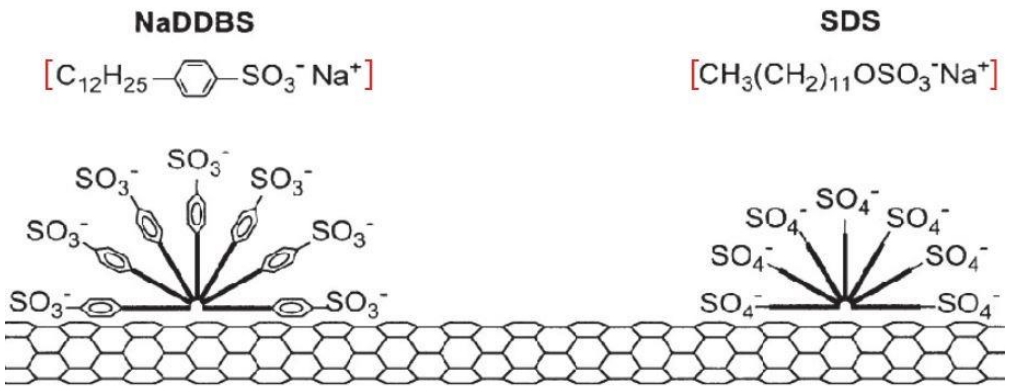


Figure 5. Graphic representation of surfactants adsorbing onto CNTs surface (Modified based on Yellampalli, 2011)

2.3. Surface Treatment of CNTs Using CMC

As it is shown in Figure 6, CMC has HC-OH group in their molecules. When mixed with cement and water, CMC is expected to absorb H_3O^+ ions from cement surface. CMC organic agents are absorbed by hydrogen bonding through their carboxyl group (Yellampalli, 2011). The chemical reaction between cement and CMC causes carboxyl groups to be generated. Therefore, the chemical reaction generated carboxyl groups would potentially interact with CNTs, resulting in both non-covalent polymer wrapping and covalent modification on the surface of CNTs, especially at end of the CNTs, as indicated in Section 2.2 as shown in Figure 6.

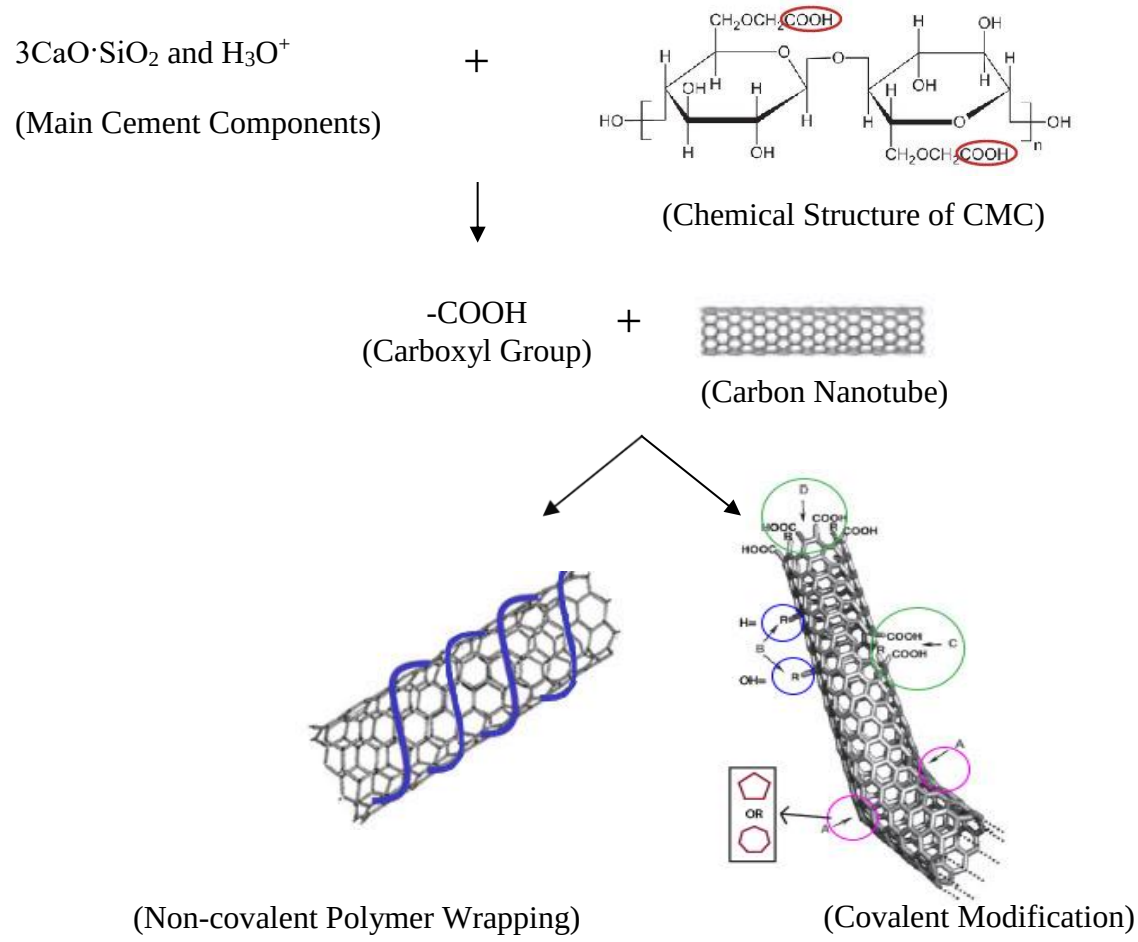


Figure 6. Molecular structures of cement with CMC and CNTs (Modified after Yellampalli, 2011)

In addition, the physical properties between CMC and one of the popular surfactants, NaDDBS, are compared in Table 3. By analyzing the four critical properties of each, CMC showed potential for a stronger attractive force with CNTs when compared with NaDDBS in terms of the number of hydrogen bond acceptors, larger topological polar surface area, less complexity, and smaller exact mass. Overall, the physical adsorption of CMC will possibly reduce the surface tension of CNTs significantly, which effectively prevents the aggregation of CNTs to result in a possible better dispersion in cementitious materials for CMC surface treated CNTs. More studies are needed to further investigate the actual functionalization and chemical reactions between CNTs and CMC, which will be the future study.

Table 3

Physical Properties Comparison between CMC and NaDDBS

	Properties			
Names	Hydrogen Bond Acceptor Count	Topological Polar Surface Area*	Complexity	Exact Mass
CMC	8	156 A^2	169	240.085 g/mol
NaDDBS	3	65.6 A^2	365	348.174 g/mol

*A represents length of a side.

2.4. Summary

To sum up, this chapter compared five different polymers including Polyethylene Glycol, Modified Tapioca Starch, Polyacrylamide, Sodium Polyacrylate, and CMC. The CMC has been selected as the final candidate to surface treat CNTs for a better dispersion in cementitious materials. Literature reviews showed a mixture of cement-CMC (0.3%) and cement-CNTs (0.1%) to be an optimized mix ratio for mechanical properties and potentials for other applications, which was selected to be the cement-CMC-CNTs ratio for the modified cementitious materials as a basis for any further laboratory tests. In addition, this chapter also showed that by using CMC as a polymer to surface treat CNTs for better dispersion of CNTs in cementitious materials. CMC surface treatment method has the potential to functionalize the CNTs through both covalent modification and non-covalent polymer wrapping of CNTs to prevent the aggregation of CNTs and may improve the sensitivity of the resulted smart cementitious materials with more uniform dispersion of CNTs in the cementitious materials mixture. More future studies are needed to further investigate the actual functionalization and chemical reactions between CNTs and CMC.

CHAPTER 3. METHODOLOGY AND SAMPLES PREPARATION

To validate the effectiveness of the CMC surface treatment dispersion method, this chapter introduces the dispersion methods of the CNTs in water by utilizing three different dispersing methods, including direct mixing, surfactant method, and the CMC surface treatment method. MWCNTs were used throughout the study (supplied by SkySpring Nanomaterials, Inc.). After dispersing CNTs in water solution using the three different methods, cement mortar cubic samples with dimensions of 2 in. × 2 in. × 2 in. were made for further testing. All the samples were prepared in room temperature (22°C ± 2°C).

3.1. Dispersion Methodology

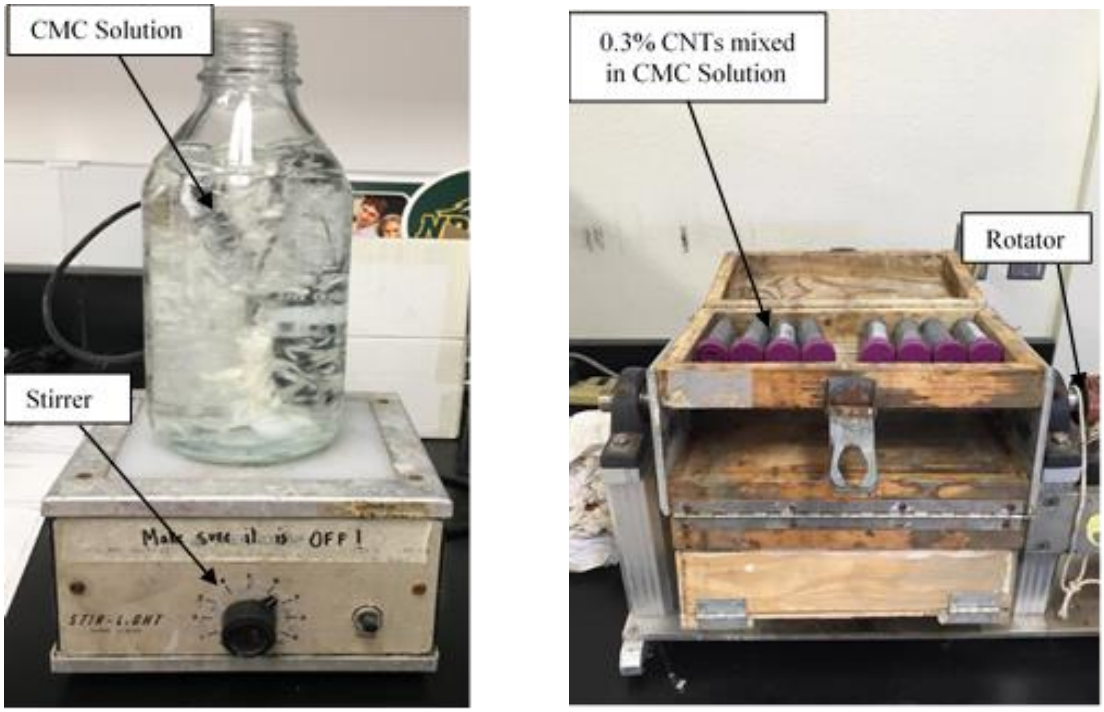
3.1.1. CMC Surface Treatment Method

The methodology to disperse CNTs using CMC surface treatment and fabricate cement mortar samples is described as below:

1) CMC water solution was prepared by mixing 5 g of dry CMC with 1000 mL of deionized water. Since CMC is water –absorbent and has high water retention, it clumps easily. To prevent this, CMC should be slowly added to the center of the vortex. The solution was stirred at 600 rpm for three hours until CMC completely dissolved into deionized water as shown in Figure. 7 (a).
2) The CMC water solution was further mixed with 0.1%, 0.3%, and 0.5% of CNTs in 50 ml test tubes and placed into a custom-made rotator for at least 72 hours rotating to make sure a proper coating of CMC on the CNTs as seen in Figure. 7 (b).
3) The test tubes with CMC modified CNTs solutions as shown in Figure. 7 (c) were placed into a centrifuge as shown in Figure. 7 (d) for approximately 5 minutes

spinning to keep the sediment of CNTs wrapped with CMC and dumped the excess amount of CMC solution.

4) Last, the CMC treated CNTs sediment were mixed with 400 g of cement and 240 ml of water to make cement mortar samples for sensing testing.



(a) (b)

Figure 7. Process of modifying CNTs
(a) Preparation of the CMC solution under mixing, (b) The test tubes with carbon nanotubes wrapped with CMC being placed in the rotator, (c) Fully dispersed CNTs-CMC solution treated by CMC surface treatment method after 72 hours rotating, and (d) Centrifuge process.

(c)

(d)

Figure 7. Process of modifying CNTs (continued)
Figure 7 (a) Preparation of the CMC solution under mixing, (b) The test tubes with carbon nanotubes wrapped with CMC being placed in the rotator, (c) Fully dispersed CNTs-CMC solution treated by CMC surface treatment method after 72 hours rotating, and (d) Centrifuge process.

3.1.2. Direct Mixing Method

Direct mixing method was the most common method for mixing CNTs into cement mortar. This method directly mixes the 0.1% CNTs in cement and water, without any treatment of CNTs. Three steps are followed by using direct mixing method as below:

1) First, 0.4 g CNTs is added in 160 ml of water to have 0.1% CNTs solution.
2) Second, 0.1% CNTs solution is fully mixed with a stirring bar on the magnetism stirrer for 5 minutes.
3) Last, 0.1% CNTs solution is mixed with 400 g cement to make a 2 inch by 2 inch cement block.

3.1.3. Surfactant Dispersion Method

The surfactant dispersion method was also studied in this study to compare with the CMC surface treatment method by using NaDDBS for surface modifications on CNTs. The NaDDBS was provided by Sigma-Aldrich Co., USA. A critical micelle concentration of NaDDBS in water, 1.4×10-2 mol/L, was taken as the input surfactant concentration. Four steps were needed to prepare the surfactant solution with CNTs as follows:

1) First of all, 1.17g of NaDDBS was mixed with 240ml of water using a stirring bar for up to 5 minutes.
2) Secondly, the 0.1% CNTs (0.4g) were added into the aqueous solution and utilizing a sonicator for 2 hours to make uniformed dispersion solution.
3) Thirdly, NaDDBS treated CNTs solution was mixed with 400 g of cement till the solution was dispersed into cement very well.
4) Last, due to the properties of NaDDBS, air bubble would appear in the cement mortars. Therefore, 0.25% of defoamer (by volume) was utilized to decrease the air bubble in CNTs filled cement mortars and mixed till NaDDBS treated CNTs solution with defoamer dispersed well. The defoamer was provided by Tributyl phosphate supplied by Sigma-Aldrich Co., USA.

3.2. Comparison of Three Dispersion Methods

Comparison between the three dispersion methods mentioned above are shown in Figure 8. The CMC treated CNTs solution uniformly dispersed followed by surfactants method is shown in Figure 8. The direct mixing method of CNTs solution became precipitate at the bottom after two hours.

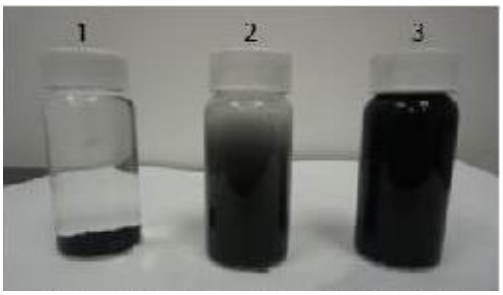


Figure 8. Comparisons of using the direct mixing, surfactant, and CMC surface treatment method (from left to right) of dispersing CNTs after two hours.

3.3. Samples Preparation

All the CNTs solutions from the three different methods prepared in Section 3.2 were mixed with cement and placed into 2in. × 2 in. × 2 in. molds to make mortar samples as shown in Figure 9. The samples were kept in molds for 24 hours at room temperature (22°C ± 2°C). Electrical wires were placed half inch deep and half inch apart from each other in each sample before the samples are cured. The samples were demolded and put into water for 7 days to cure followed by 10 days of air dry at room temperature. Figure 10 demonstrates a ready-mixed sample.

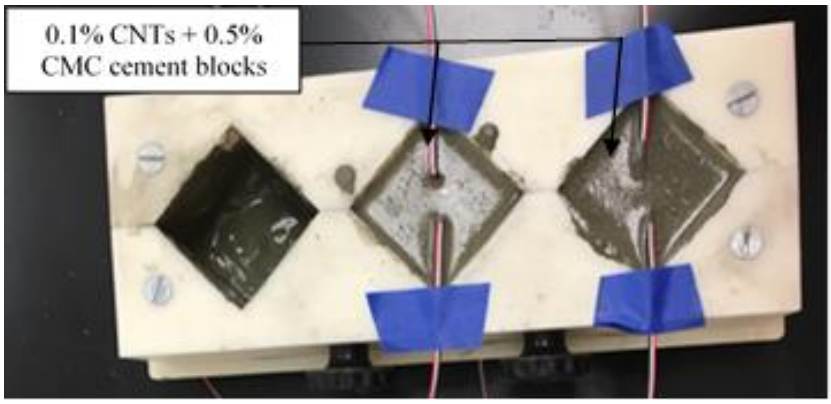


Figure 9. The 2 inches cubic molds for fabricating samples.

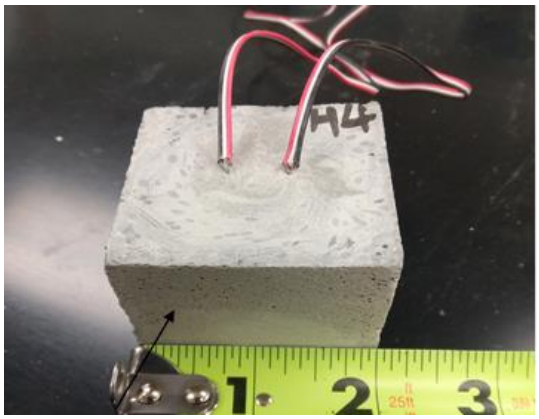


Figure 10. A cementitious block embedded with electrical wires after curing.

The testing sample matrix is shown in Table 4. Group A was control samples, which were made of water and cement. Therefore, no resistance changes are expected. Group B used 0.1% CNTs solution directly mixing with cement to compare between direct mixing and CMC surface treatment method with fixed percent of CNTs content. Group C was designed as control samples to test how CMC affect the property of the cementitious material. Group D were the samples from surfactant method. Group H, I, and J were the samples made by CMC surface treatment method with three different CNT percentages, 0.1%, 0.3%, and 0.5%, to test whether the change of CNT percentage would influence the sensitivity. The sample groups from the three different dispersion methods are shown in Figure 11.

Table 4

Testing Sample Matrix

Dispersion Method	Group	Sample No.#	Description
Method #2 Direct Mixing	A	3	Control (No CNTs and CMC)
	B	3	0.1% CNTs only
	C	3	0.3% CMC only
Method #3 Surfactant Method	D	3	0.1% CNTs + 0.5% NaDDS + 0.25% defoamer
Method #1 CMC Surface Treatment Method	H	3	0.1% CNTs + 0.3% CMC
	I	3	0.3% CNTs + 0.3% CMC
	J	3	0.5% CNTs + 0.3% CMC

Figure 11. The sample groups from three different dispersion methods

3.4. Summary

In this chapter, the dispersion methodology of three different methods, including direct mixing method, surfactant method, and the proposed CMC surface treatment method, were introduced to investigate CNTs dispersion as well as the samples were prepared. The direct mixing method is directly mixing CNTs with distilled water. Surfactant method is mixed with NaDDBS

and defoamer to disperse the CNTs in cementitious materials. Last, the proposed CMC surface treatment method is utilized CMC solution to mix with CNTs. The water/cement ratio remains the same for all three methods. The laboratory testing of these prepared samples will be further explained in Chapter 4.

CHAPTER 4. EXPERIMENTAL RESULTS AND DISCUSSIONS

This chapter presents the experimental setup and the experimental results by using direct mixing method, surfactant method, and CMC surface treatment dispersion method mentioned in Chapter 3. Also, the comparisons between various dispersing methods are conducted.

4.1. Experimental Setup

The prepared samples in Chapter 3 were tested under dynamic loads to compare its sensing capacity. The laboratory test setup is shown in Figure 12. Dynamic loading tests were applied on each cement mortar by utilizing MTS 809 Axial/Torsional Test Systems. The voltage changes were measured by digital bench multi-meter (BK 5492B, B&K Precision Inc., USA). The dynamic loading is shown in Figure 13 with an average load of 1,912 N and a range from approximately 166N to 2,078N for 12 cycles. The frequency of the loading was set to be 0.1 Hz. All the samples were tested at room temperature.

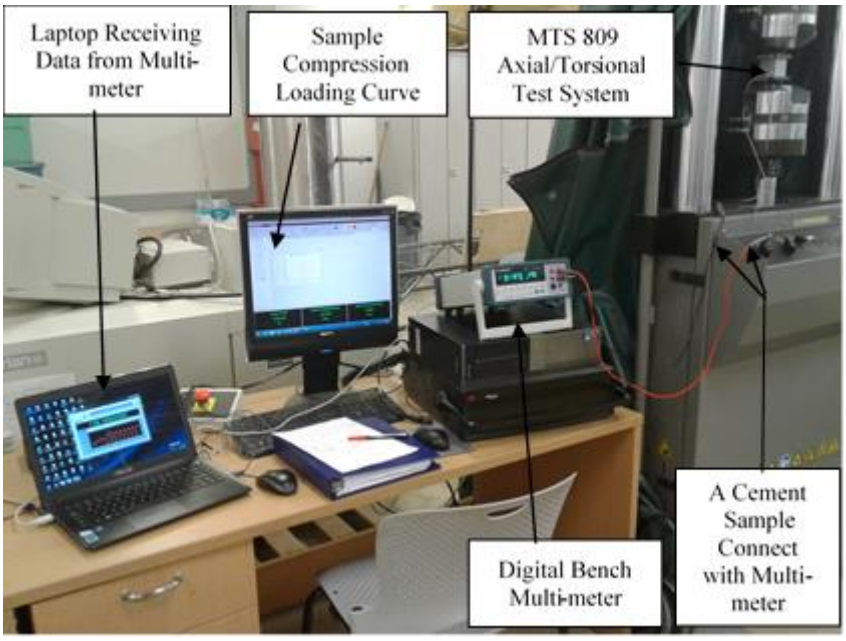


Figure 12. Laboratory setup for testing

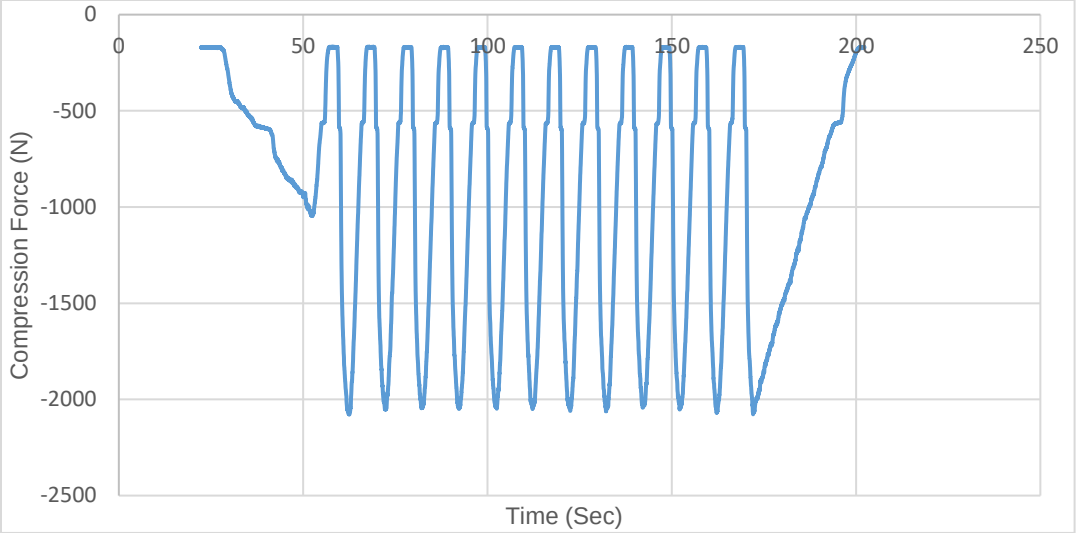


Figure 13. Dynamic loading curve

4.2. Experimental Results and Discussions

This section shows the experimental results of voltage and sensitivity of the smart cementitious materials under dynamic loads in Figure 13 from the samples prepared using the three different dispersion methods, including the direct mixing method, the surfactant method, and the CMC surface treatment method. In addition, it also illustrates the test results from samples from the CMC surface treatment method with three different CNTs percentage from 0.1%, 0.3% and 0.5% under dynamic loading, to validate an effective and reproducible method for CNTs dispersion in cementitious materials.

When the force is applied, voltage will generate in the CNTs modified cementitious materials (Prasad, 2005). Different dispersion methods of CNTs in the cementitious material affects the voltage changes because an effective dispersion of CNTs increases sensitivity. With dynamic loads on the samples, corresponding dynamic voltage changes are expected as in Figure 14. The maximum, minimum, and mean refer to the maximum, minimum and mean voltages in each cycle for the 12 cycles of one dynamic test.

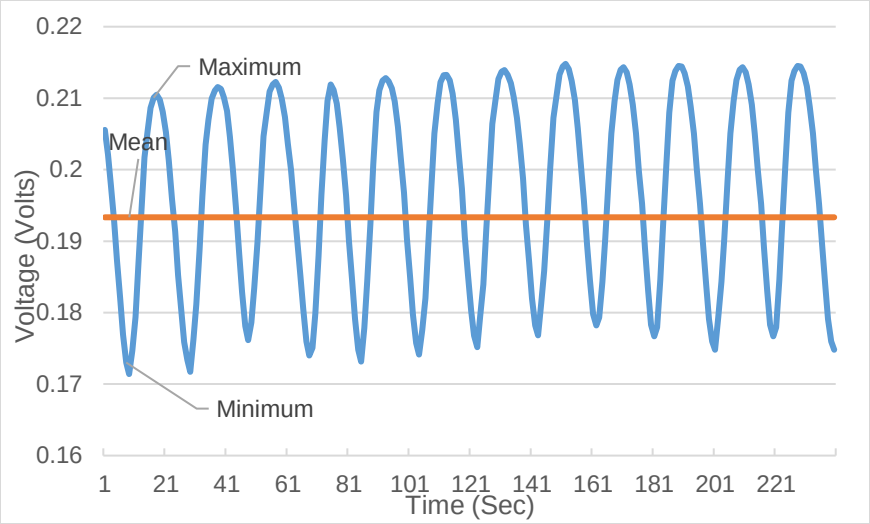


Figure 14. Example graph of maximum, minimum, and mean

4.2.1. The CMC Surface Treatment Method

The voltage responses of the three samples from CMC surface treatment method for dispersing 0.1% CNTs in cement mortars can be seen in Figure 15 (a~c). It illustrates that the voltage changes are proportional to the stress levels. The summary for three samples from H1 to H3 in average, maximum, and minimum voltage under dynamic loading is shown in Figure 15 (d). The mean voltage with CMC surface treatment method (0.1 % CNTs) is 0.177 V with a maximum of 0.22 V and a minimum of 0.099 V in Group H. The average range changes between maximum and minimum is 0.12 V.

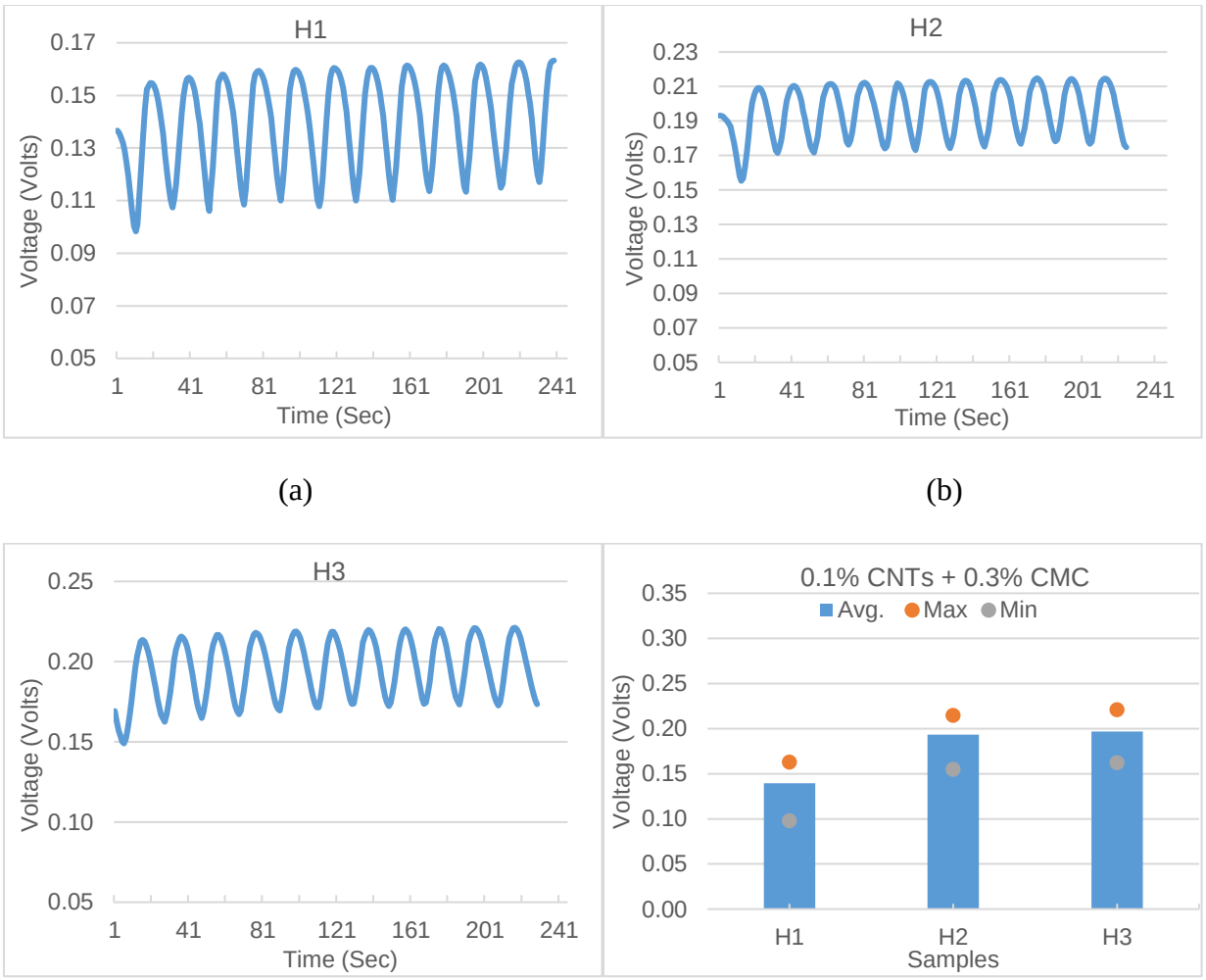


Figure 15. Voltage responses for CMC surface treatment method: sample (a) H1, (b) H2, (c) H3, and (d) samples summary

The voltage responses from the mixture of 0.3% CNTs using CMC surface treatment method into cement mortars are shown in Figure 16 (a~c). Figure 16 (d) depicts a summary of the results of group I1 to I3 in average, maximum, and minimum voltage. The mean voltage with CMC surface treatment method (0.3% CNTs) is 0.152 V with a maximum of 0.19 V and a minimum of 0.080 V in Group I. The average range changes between maximum and minimum is 0.11 V.

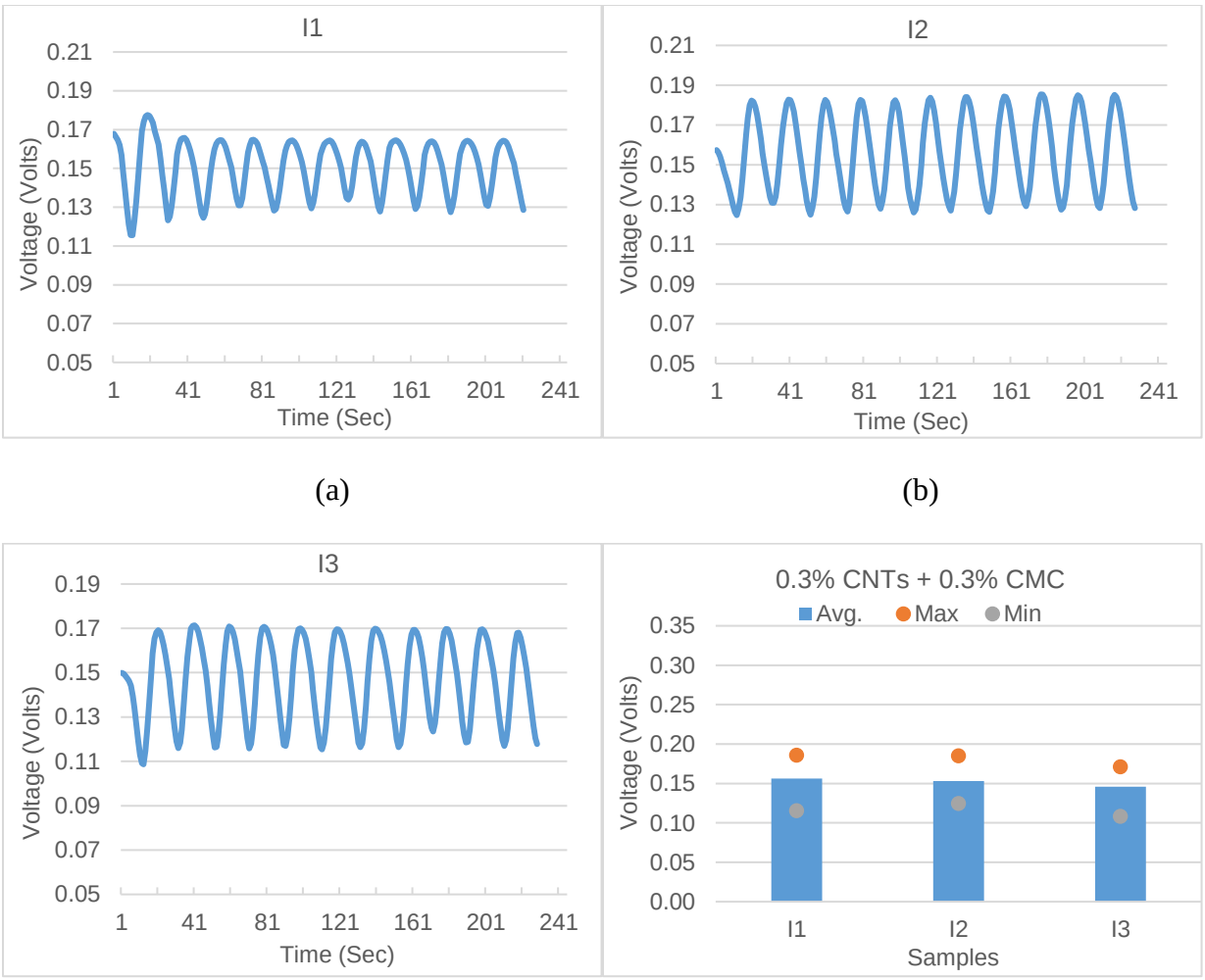
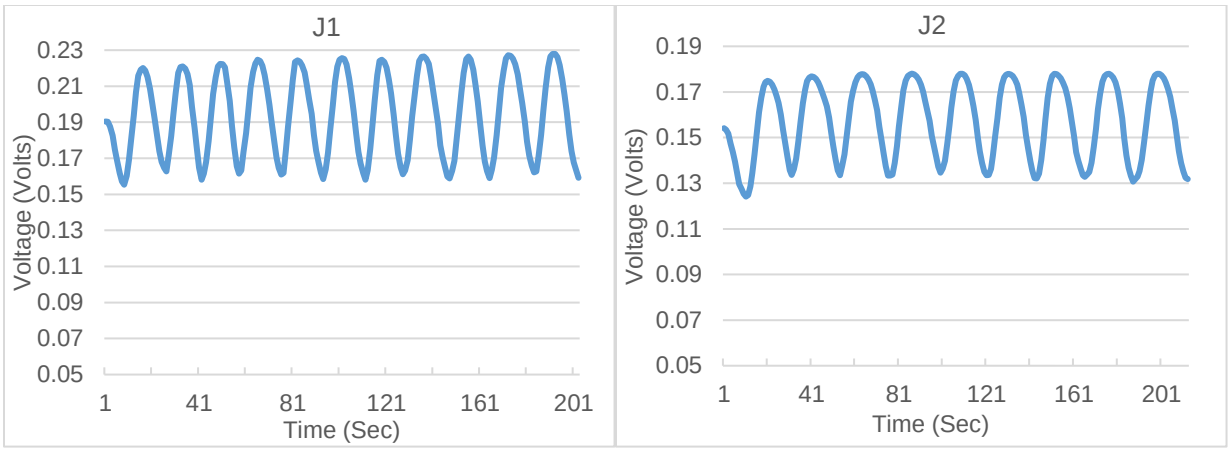


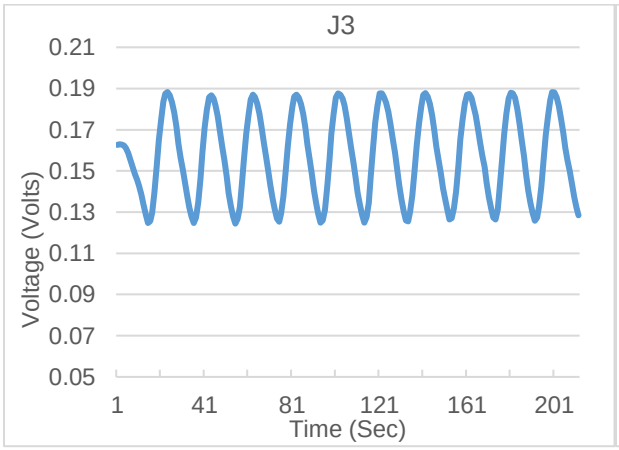
Figure 16. Voltage responses for sample (a) I1, (b) I2, (c) I3, and (d) samples summary

The voltage responses from the mixture of 0.5% CNTs using CMC surface treatment dispersion method into cement mortars are shown in Figure 17 (a~c). Figure 17 (d) depicts a summary of the results of group J1 to J3 in average, maximum, and minimum voltage. The mean voltage response with CMC surface treatment method (0.5% CNTs) is 0.168 V with a maximum of 0.23 V and a minimum of 0.060 V in Group J. The average range changes between maximum and minimum is 0.16 V.

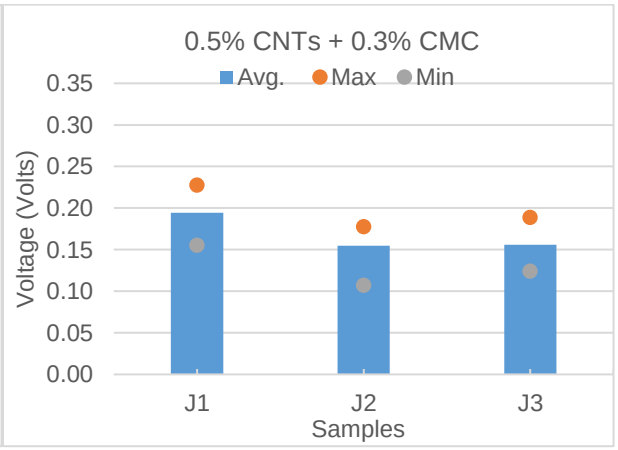


(a)

(b)



(c)



(d)

Figure 17. Voltage responses for sample (a) J1, (b) J2, (c) J3, and (d) sample summary

4.2.2. Direct Mixing Method

The voltage responses of three samples using direct mixing method with 0.1% CNTs in cement mortars are shown in Figure 18 (a~c). A comparison between three samples with average, maximum, and minimum voltage under dynamic loading is shown in Figure 18 (d). The average voltage of using direct mixing method is 0.0348 V with a maximum of 0.057 V and a minimum of 0.014 V in Group B. The average range changes between maximum and minimum is 0.043 V.

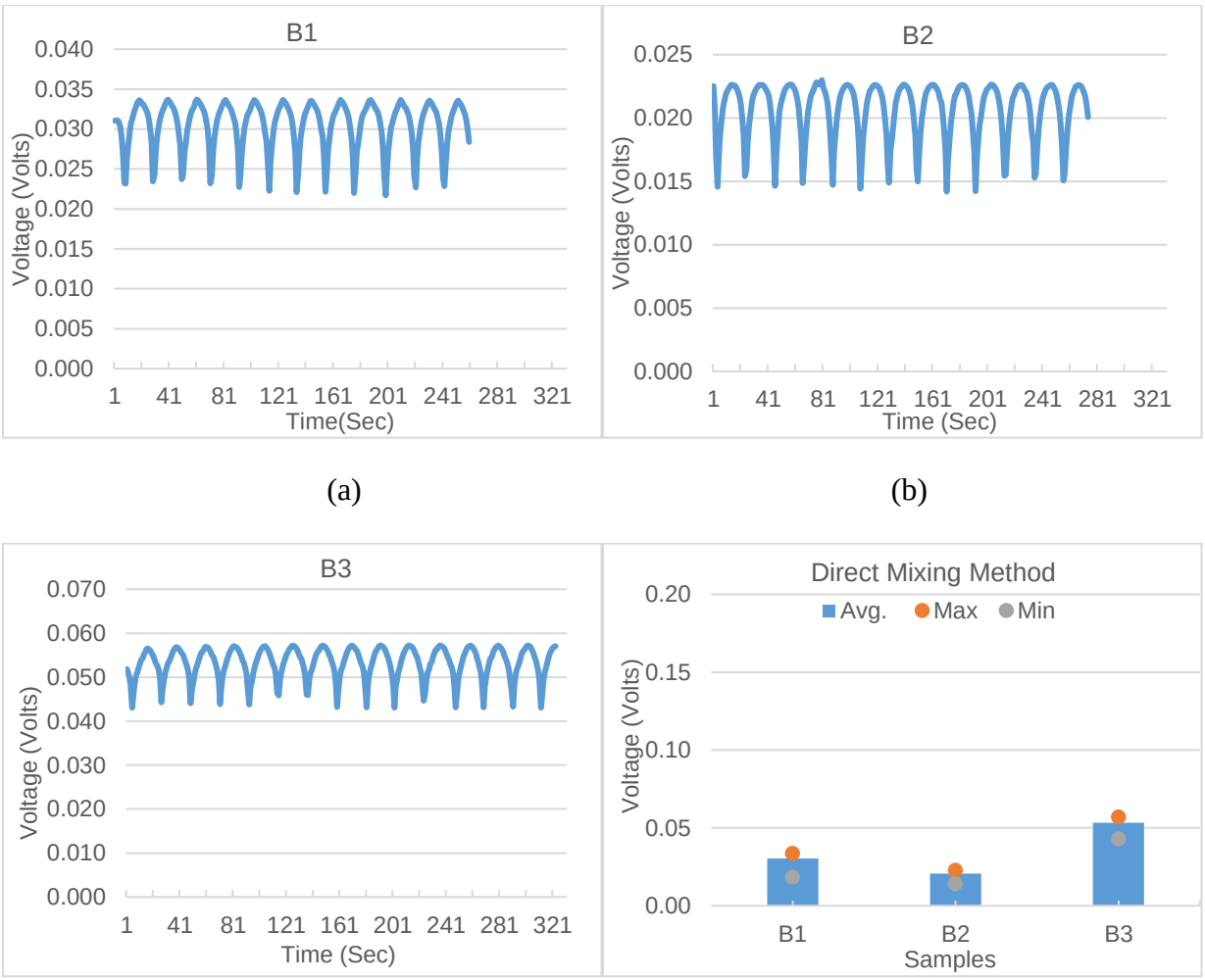
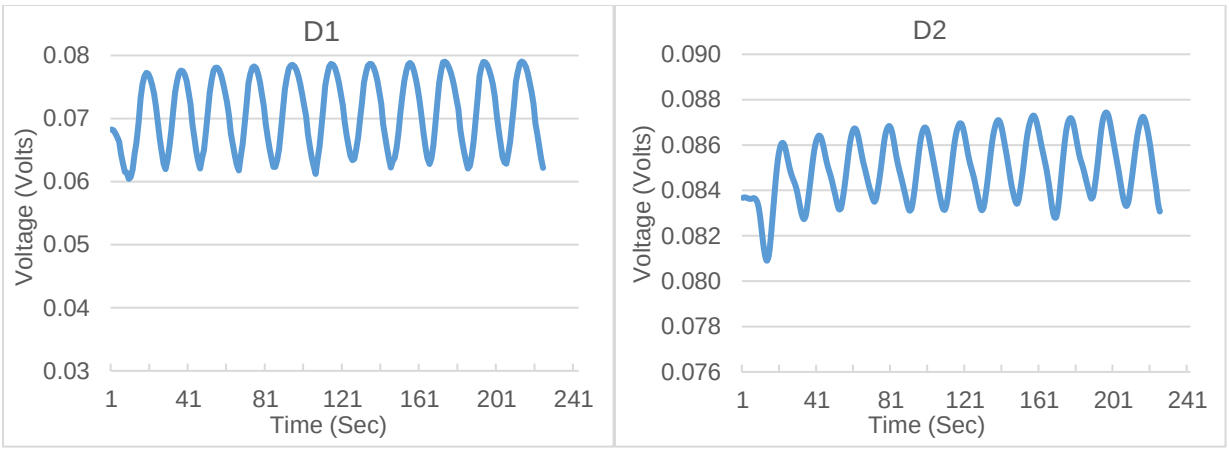


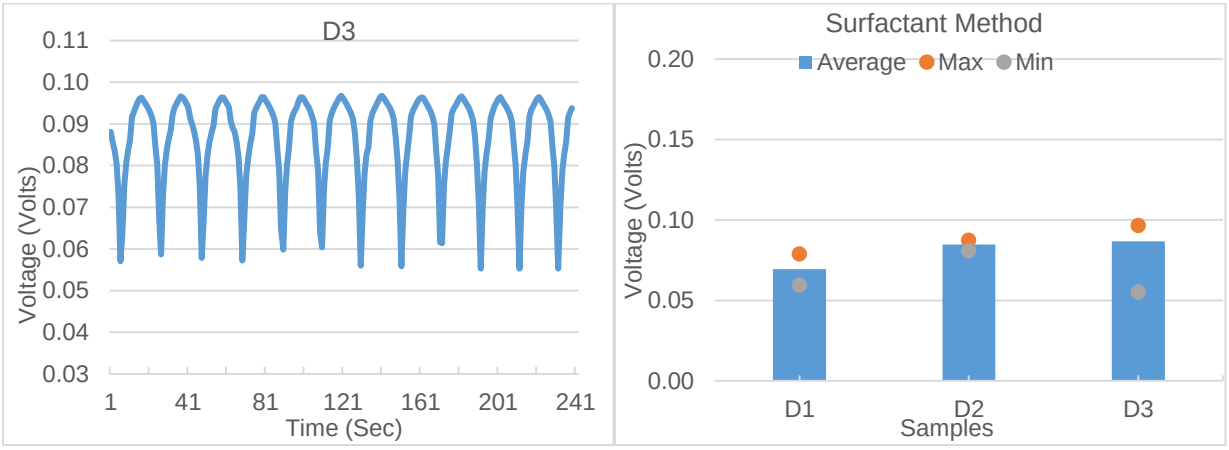
Figure 18. Voltage responses for sample (a) B1, (b) B2, (c) B3, and (d) sample summary

4.2.3. Surfactant Method

The voltage responses of surfactant method with 0.1% CNTs into cement mortar are shown in Figure 19 (a~c). The summary of the results with the average, maximum, and minimum voltage are shown in Figure 19 (d). The average voltage response is 0.0803 V with a maximum of 0.097 V and a minimum of 0.055 V. The sample D2 has extremely small voltage changes between 0.087 and 0.083 V compared with D1 and D3. The average range changes between maximum and minimum is 0.042 V.



(a) (b)



(b) (d)

Figure 19. Voltage responses for sample (a) D1, (b) D2, (c) D3, (d) sample summary

4.2.4. Comparison between Various Dispersing Methods and Discussions

Figure 20 compares the experimental results from three different dispersion methods. Table 5 summarize the mean voltages for group B, D, and H, and their standard deviations. The mean of the CMC surface treatment method (Group H) is approximately twice greater than that of the surfactant method and about five times greater than the direct mixing method.

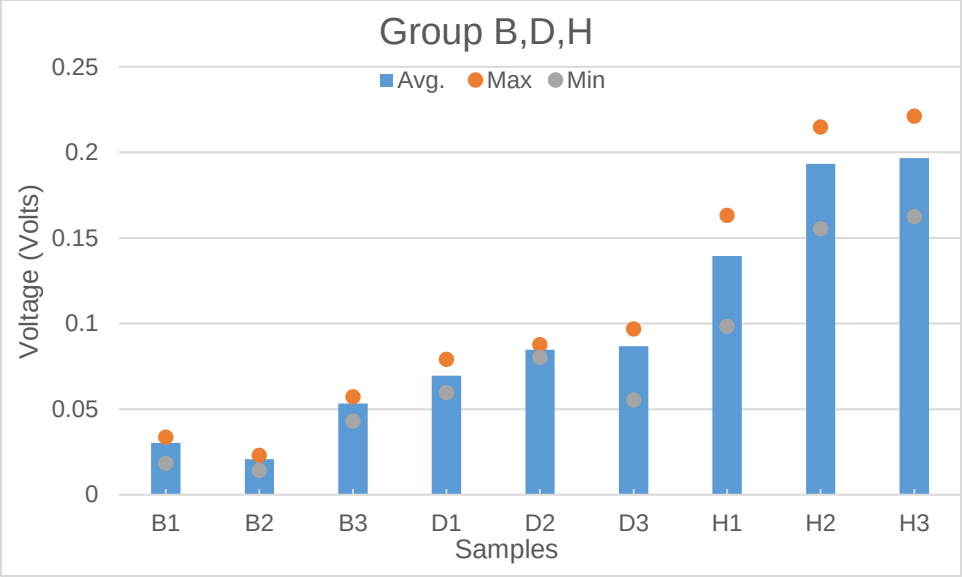


Figure 20. Comparison between direct mixing method (B1, B2, B3), surfactant method (D1, D2, D3), and CMC surface treatment method (H1, H2, H3) of mean, maximum, and minimum voltage.

Table 5

Group B, D, H, I. and J Parameter (Volts)

Group #	Group B	Group D	Group H
Mean	0.027452	0.068771	0.150251
Standard Deviation	0.001378	0.004106	0.00615

Based on the range change (changes in maximum and minimum voltage in Figure 20), force sensitivity can be calcualted by dividing voltage change ranges with applied forces (1912 N). Figure 21 represents the force sensitivity and standard deviation in each group of samples. The force sensitivities of Group H, I, and J were 0.0628 mv/N, 0.0575 mv/N, and 0.0837 mv/N respectively, which leads to an average force sensitivity of CMC surface treatment method 0.068 mv/N. Surfactant method (group D) and direct mixing method (group B) had average force sensitivities of 0.0223 mv/N and 0.022 mv/N respectively. It can be seen that the CMC surface treatment method can significantly increase the force sensitivity of the CNTs modified

cementitious materials for more than three times when compared with surfactant and direct mixing method. Overall, the average voltage response of CMC surface treatment method (group H, I, and J) indicates a consistent and optimized method to disperse CNTs and no significant difference was notified between different percentages of CNTs on force sensitivity when using CMC surface treatment method.

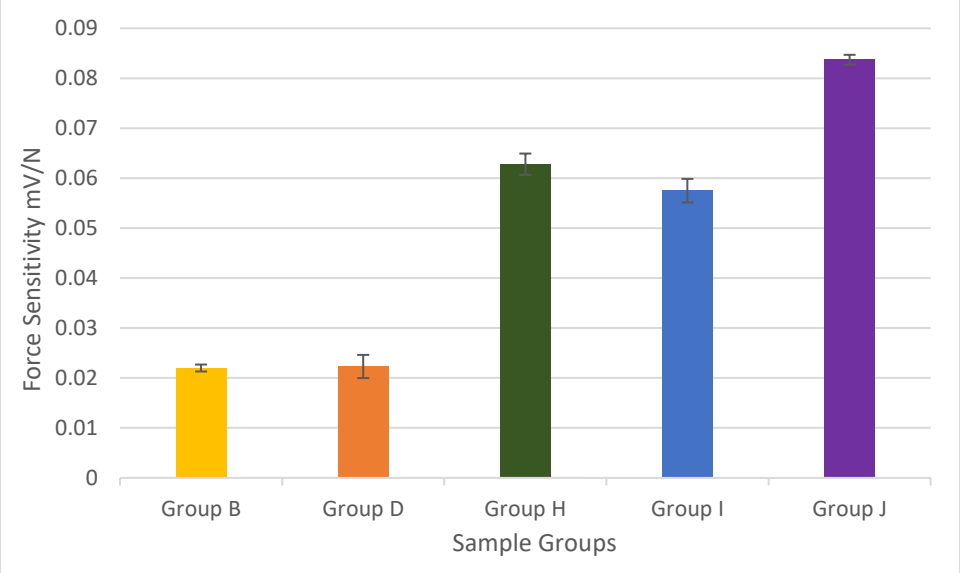


Figure 21. Comparison between Group H, I, and J in range and mean with three different percentage of CNTs content

4.3. Summary

In this chapter, the detailed test procedures on experimental setup were introduced. The experimental results from the dynamic loading tests were presented for all the three dispersion methods including direct mixing method, surfactant method, and the CMC surface treatment method. CMC surface treatment method dramatically increased higher mean voltage responses and force sensitivity.

CHAPTER 5. CONCLUSIONS AND FUTURE WORK

In this study, CMC is proposed to surface-treat the CNTs for an advanced dispersion method of CNTs in smart cementitious materials. Following conclusions can be drawn based the findings from this study:

- The CMC surface treatment may induce both covalent and non-covalent wrapping functionalization of CNTs to improve dispersion of CNTs in cementitious materials.
- Based on the laboratory experiments, after comparing with three different dispersion methods including direct mixing method, surfactant method, and the CMC surface treatment method, it is found that the base voltage responses by using CMC surface treatment method is more than 0.138 V, the surfactant method is around 0.069 V, and the direct mixing method is approximately 0.027 V. The CMC surface treatment method has dramatically increased the base voltage. Each sample has a stable mean in the CMC surface treatment method, showing that the consistency of the dispersion has also improved significantly.
- The CMC surface treatment method's force sensitivity mean is 0.068 mv/N, which is nearly 3 times the force sensitivity of the surfactant method and the direct mixing method.
- For the CMC surface treatment method, the percentage of the CNTs varying from 0.1% to 0.5% showed a small impact on increasing piezo-effect.

More studies are needed for the actual functionalization of CNTs using CMC and the chemical reactions in between, in addition to the different percentage of CMC and micro-structures of CMC surface treatment method.

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