DISPERSION EFFECTIVENESS OF CARBON NANOTUBE ADDITIVES IN SELF-SENSING CEMENTITIOUS MATERIALS FOR STRUCTURAL HEALTH MONITORING

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Leonard Aun Chia

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Leonard Chia

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SUPERVISORY COMMITTEE:

Dr.Ying Huang
Chair

Dr. Magdy Abdelrahman

Dr. Zhili" Jerry" Gao

Dr. Achintya Bezbaruah

Approved:

November 1st 2016 — Date

Dr. Dinesh Katti — Department Chair

ABSTRACT

The use of self-sensing materials such as piezo-resistive cementitious materials modified by carbon nanotube (CNTs) additives may be able to achieve a potential real time structural health monitoring in structures. However, due to the small fractions of CNTs in the cementitious materials, the piezo-resistive effect for self-sensing is usually too small to be monitored accurately in field. In this study, a theoretic algorithm is developed to analyze the piezo-resistance of CNTs modified matrix with considerations of CNTs dispersing effectiveness. Three different dispersing methods were investigated using the developed algorithm to search for a method to uniformly disperse the CNTs in cementitious materials. Laboratory experiments showed that the theoretical algorithm analyzed well for all the dispersing effectiveness of the three different methods. The surfactant method is approved to be a very promising approach to disperse CNTs. Further investigation to lower the standard deviation of the co-polymer method are needed in future.

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LIST OF SYMBOLS

R_{tube} ....intrinsic resistance

R_{Inter} ....intertube resistance

ΔR_{tube} ....intrinsic resistance changes of the CNTs

L_0 ....initial length of the tube

L ....tube length with strain

ρ ....resistance change of the tube per unit length

ε ....strain

R^T ....tunneling resistance

R_0 ....base resistance

S ....gap in between nanotubes

S_0 ....initial gap in between the nanotubes

λ ....constant related to the average height of potential barrier

K ....equal to the average height of potential barrier

R_{Total} ....total resistances induced by carbon nanotubes

$\Delta \acute{R}_{mortar}$ ....the piezo-resistive change of CNT cementitious materials

C_A ....contributing factor from percentage of CNT

C_B ....influence factor to consider dispersing effect

1. INTRODUCTION

1.1. Background

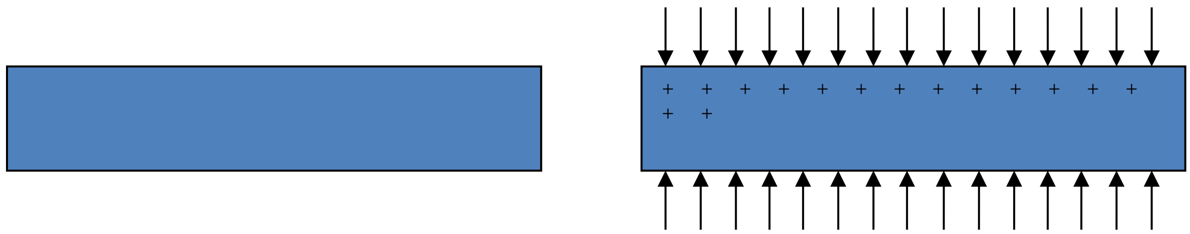
Cementitious materials have been popularly applied as a base material for various civil engineering materials such as concrete and asphalt, which are widely used as structural materials. The onset of local damages in structures with cementitious materials, such as concentrated stresses or strains, cracking, and delamination are often difficult to detect and these damages have a long-term implication on the performance of these composite structures [1]. To detect these local damages and monitor the structural health of the structures with cementitious materials, currently, several non-destructive detection techniques can be considered such as acoustic, ultrasonic, X-ray or eddy current inspection [2,3]. However, the use of non-destructive inspection tools may require intensive labors and time from experienced inspection engineers or sometimes even disassembling of structural components. Quantitative real-time monitoring of structural health for structures with cementitious materials is an ongoing need and yet achieved.

A real-time structural health monitoring of a structure's integrity will minimize the need for scheduled inspections to allow a need-driven maintenance plan rather than a usage-driven maintenance. In the past decade, there are various emerging techniques developed using attachable or embeddable sensors, seeking to achieve a real-time structural health monitoring, including the use of strain gages, electrical accelerometers, piezoelectric or piezo-resistive sensors, and fiber optic sensors [4-7]. These sensors based approaches provide strains or stress information of the structures on the region near where the sensors are installed. Therefore, the sensors need to be placed or installed near or at critical regions of interest to detect damages. Thus, to solve the limitations of these methods and achieve a real-time structural health monitoring in structures, self-sensing materials such as piezo-resistive cementitious materials modified by carbon nanotube additives may be an alternative way to approach.

1.2. Literature Reviews

1.2.1. Piezo-electrical and Piezo-resistive Effect of Materials

Piezoelectricity or piezoresistivity is an electrical effect caused by a change of strains or stresses on certain materials. As shown in Figure 1, a piezoelectric material induces a charge when it is stressed (compressive or tensile) in response to the magnitude and direction of the strain, which is known as piezo-electrical effect. There are two main groups of piezoelectric materials, which are crystals and ceramics [8], including Quartz (SiO_2), Berlinite ($AlPO_4$), Barium Titanate ($BaTiO_3$), and Lead Zirconate Titanate (PZT). There are other materials that have been discovered with piezoelectricity such as Zinc Oxide (ZnO), Aluminium Nitride (AlN), Polyvinylidene Fluoride (PVDF) and so on [9,10]. These piezo-electric materials are unaffected by external electromagnetic fields, pollution free, low maintenance, and easy replacement of equipment, which make them a good candidate to be used as a sensor and ultrasonic transducer. However, the materials with piezoeletrical effect are expensive, so the piezoelectrical sensors are usually in small size. In addition, the piezoelectrical effect requires the materials to remain nonconductive, which may not be true for most of the materials. These materials also may pick up stray voltages in connecting wires which cannot be used for truly static measurements [11,12,13]. Therefore, piezoeletrical materials although popular in sensor development, limited applications noticed in the development of self-sensing materials.



(a) (b)

Figure 1. (a) Piezoelectric material with no externally applied strains and (b) under strains producing charges at surfaces that can be measured

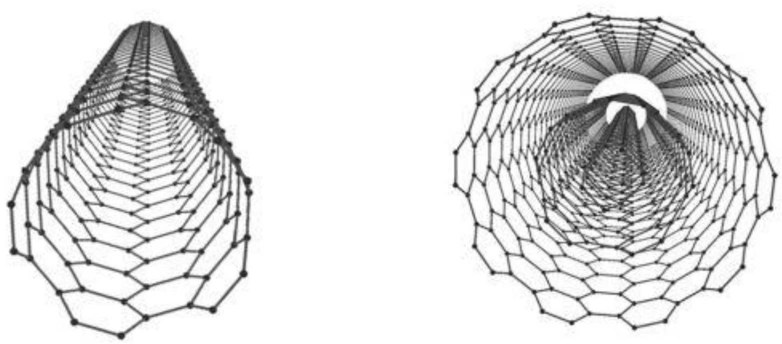
On the other hand, a piezo-resistive material changes its electrical resistance due to mechanical stresses or strains. Materials that are currently known to have piezo-resistive effects include germanium, polycrystalline silicon, amorphous silicon, silicon carbide, carbon nanotubes, graphite, and steel fibers [14]. The piezo-resistive effects have been popularly applied in civil engineering fields as the principles to make strain gauges that can measure strains on structures [15]. Compared with piezoelectric materials, the piezo-resistive effect requires the measured materials to be conductive, and the cost of piezo-resistive materials are relatively affordable, which attracted numerous attentions for developing self-sensing materials using piezo-resistive effects of materials.

Among the piezo-resistive materials, carbon nanotubes, graphite, and steel fibers are extensively investigated for self-sensing cementitious materials such as smart concrete. Carbon nanotubes, due to the fact that a small volume of additives can enable a strong piezo-resistive effect, have been considered a promising candidate to enable the self-sensing capability of cementitious materials. Thus, in this study, we will focus on the application of the piezo-resistive effect of carbon nanotubes for self-sensing cementitious materials.

1.2.2. Carbon Nanotubes

A nanotube is a strong, long, tiny and hollow tube with an outer diameter of a nanometer that is formed from atoms such as carbon. Materials made from nanotubes are very strong with strengths fifty-times stronger than steel, which make them attractive to be used to form/create super-tough lightweight materials [16]. A carbon nanotube (CNT) is an allotrope of carbon sharing a cylindrical nanostructure. The carbon nanotubes have long, hollow structure with walls formed by one-atom-thick sheets of carbon, called Graphene. These graphene sheets are rolled at specific and discrete angles and due to the combination of the different rolling angle and radius. Usually, the length to diameter of the graphene sheets made carbon nanotubes lies in between 132,000,000:1, which enables extraordinary strength and unique electrical properties [17]. These unique properties make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of materials science. For example, the carbon nanotubes are commonly used as additives for various structural materials such as golf clubs or baseball bats [17,18].

Based on the numbers of graphene sheets in CNTs, the CNTs can be either single-walled nanotubes (SWNT) or multi-walled nanotubes (MWNT) as shown in Figure 2 [19]. SWNTs are hollow single cylinders of a graphene sheet, which are defined by their diameter and their chirality. The diameter of SWNTs varies from 0.5nm to 5nm. Depending on the chirality, SWNTs may either be metallic or semiconducting [20]. While, on the other hand, MWNTs are a group of concentric SWNTs capped at both ends, with diameters in the range from several nanometers up to 200 nm. These concentric nanotubes are held together by van der Waals bonding. MWNTs form complex systems with different wall numbers, structures, and properties [21].



(a) (b)

Figure 2. (a) SWNT and (b) MWNT [21]

The strong bonding between the carbons of CNTs provides them a very high Young's modulus and tensile strength for excellent mechanical property. Analytical analysis estimated the Young's modulus of SWNTs to be at least 1 TPa [22,23]. For MWNTs, the experiments from Wong et al. showed a mean value of 1.28 ± 0.5 TPa [24]. CNTs have also shown high tensile strength of 100 GPa without any form of plastic deformation, brittle-like behavior, or rupture, which is approximately a thousand times harder than steel [25]. This is due to the extra energy absorption required for the hollow structures of carbon nanotubes compared to most materials. These superior mechanical properties make CNTs suitable as reinforcing materials in composites. For instance, Andrews et al. [26] showed that by adding 5% of SWNTs, the tensile strength and Young's modulus of the composite increases by 90% and 150%, respectively.

In addition, there has been considerable practical interest in the electrical and conductivity properties of CNTs. The conductivity and the metallic properties of the CNT are due to their structural parameters indicating how much the CNT is twisted. Their conductivity has been shown to be a function of their chirality, the degree of twist as well as their diameter. CNTs can be either metallic or semi-conducting in their electrical behavior [27]. The electronic structure of MWNTs is more complicated due to the various coaxially arranged SWNTs. Electron transport in MWNTs is said to be similar to that of the larger diameter single-walled carbon nanotubes because most of the electric current passing through MWNTs from the outside is mostly confined to the outermost cylindrical layer [28, 29]. The outstanding electronic properties of CNTs make them useful in electronic devices and sensor applications.

When CNTs are subjected to strain, changes in the conductive network of carbon nanotubes would arise which results in an increase in their resistivity. With the change of resistivity, the electrical resistance in CNTs also changes. The resistance in carbon nanotubes can be divided into 2 types; intrinsic resistance and intertube resistance. The piezoresistivity of CNT will be further elaborated in Chapter 2.

1.2.3. Mechanical and Piezo-resistive Effects of CNTs in Cementitious Materials

As a result of the excellent mechanical and piezo-resistive properties of CNTs, many studies have been carried out to study the CNTs modified cement mortars. Previous studies showed that the addition of CNTs with 0.5% and 1% by weight in the cement mortars increased the compressive strength of the cement mortar [30]. SEM micrographs found that CNTs interacted well with the fly ash cement matrix as the carbon nanotubes acts as a filler which then results in a denser microstructure and a higher strength compared with samples with no addition of carbon nanotubes. By acting as a filler, the porosity of the CNTs modified cement mortar was also found to be decreased with samples tested using the Automated Mercury Intrusion Porosimeter with a maximum pressure of 33,000 psi for the measurements of the pore sizes [31]. Researchers also found that the addition of CNTs to the cement mortar would greatly improve the flexural and compressive strength, as well as the failure strain. The compressive strength increases up to 19%

and the flexural strength increases up to 25% [32]. Studies also indicated that the Young's modulus of CNTs modified cement composites exhibited a higher Young's modulus compared to the plain cement paste samples [33].

More importantly, cementitious materials modified with CNTs have been found to significantly increase the electrical conductivity of the cements with piezo-resistive effect which responded well to an applied compressive strain by depicting a reduction in its resistivity. The presence of microcracks can be signified with a steady increase in the resistivity which will then would change to a sudden peak or upsurge when microcracks coalesce and failure occurs [34]. The effects of CNTs concentration level and water/cement ratio were also investigated. The piezo-resistive sensitivity of CNTs modified cementitious composites would first increase then later decrease with the increase of CNTs concentration levels. And a higher water/cement ratio is beneficial for the improvement of piezoresistivity. The optimum for both the carbon nanotubes concentration level and water/cement ratio is at 0.1% carbon nanotubes/cement by weight, and 0.6 water/cement ratio **[**35**].** More studies were performed for the CNTs modified cements on the effects of water/cement ratio, water content, dosage of surfactant and temperature in 2014. Experimental results showed that higher water content and temperature had lower resistivity. The change of resistivity was due to the change in resistance in the cement paste and the field emission-induced tunneling **[**36**].** When adding CNTs in cementitious materials for sensing or other purposes, it is commonly assumed that mixing the CNTs into water and then into cement will result in a uniform mixture for ultimate sensing property.

1.2.4. CNTs Dispersion Methods in Cementitious Materials

1.2.4.1. Direct mixing method

Till recently, studies showed that the assumption that direct mixing the CNTs in water without any dispersing methods will effectively disperse the nano particles into the cement may not be true by itself. Directly mixing the CNTs to water without any dispersion methods would result in small piezo-resistive changes to dynamic loadings [37]**.** In the case of no dispersion methods used, the CNTs are more dispersed in a lower water/cement ratio. Also the variation of piezo-resistive sensitivity and stability induced by water content decreased with lower water/cement ratio **[**38**].** These results showed that various dispersing methods matters in terms of piezo-resistive effects [37] and more investigations are needed. In all these investigations, MWNTs were adopted as they are more sensitive to stress changes compared with SWNTs.

1.2.4.2. Dispersion using surfactant method

More recently, the piezo-resistive response of two different dispersion methods of MWNTs in cement were studied, including the use of acid surface treatment and surfactant Sodium Dodecylbenzene Sulfonate (NaDDBS) surface modification. The experimental results showed that the acid treatment method had a much stronger and accurate response compared to the surfactant wrapping method **[**36, 39**].** The acid treated method although stronger piezo-resistive response, the implication of acid treatment was difficult to scale up for larger samples. The use of strong acid also made it difficult to be implemented as it would pose a danger in the field. Though not as good as acid treated method, the piezo-resistive response from the surfactant dispersion method was also tested to be promising **[**40**].** Further studies performed on two different surfactants for surface modifications including Sodium Dodecyl Sulfate (SDS), and NaDDBS also showed that NaDDBS is more stable and sensitive to the external force compared with SDS in dispersing the CNTs [41].

In addition, superplasticizer and silica fumes have also been used as the surfactant to mix the CNTs into cement, however, the researchers claimed these methods were not effective. **[**34**]** In all these investigations, MWNTs were also adopted.

1.2.4.3. Co-polymer method

In 2012, studies showed that the use of co-polymer could effectively suspend nanoparticles of all sizes (10-90nm) into liquids such as water [42]. The nanoparticles used in that investigation was nano-zerovalent iron (NZVI). The co-polymer coated NZVI achieved better response compared with the noncoated NZVI [42]. However, there is no study yet investigating the possibility or effectiveness of applying this technique to disperse CNTs in cementitious materials.

1.3. Problem Statements

From the above literature reviews, the following challenges can be identified to achieve the development of self-sensing cementitious materials using CNTs:

1) Carbon nanotubes have been found to be a potential candidate for an active self-sensing material that would enable an around the clock monitoring the health of a structure.

2) However, the piezo-resistive responses from the carbon nanotubes cement mortar needs to be improved as the field data may be affected from environment or other factors. Thus, methods are needed to be developed and investigated for better dispersing the CNTs into cementitious materials for a self-sensing material.

3) To date, there is no theoretic models which can easily identify and evaluate the effectiveness of dispersing methods, which is an urgent need for the application of CNTs enabled self-sensing materials.

1.4. Objectives and Arrangement of This Thesis

Thus, in this study, the main objective is to develop and validate a theoretic model to evaluate the effectiveness of various dispersion methods incorporated with CNTs into cementitious materials to advance self-sensing materials using piezo-resistive effect. To achieve this objective, this study identifies three specific tasks which can be summarized as follow:

1) Develop a theoretic model to identify the effectiveness of dispersion method towards the piezo-resistive effect in CNTs modified cementitious materials;
2) Investigate the piezo-resistive responses from CNTs modified cementitious materials using various dispersion methods including direct mixing method, the surfactant method, and co-polymer wrapping method, among which the co-polymer method is the first time to be applied for dispersing CNTs into cementitious materials as far to the author's knowledge;
3) Validate the developed theoretic model through analyzing laboratory experimental results of the three different dispersion methods.

This thesis is thus organized as follows: in Chapter 2, the development of the theoretic model to analyze the piezo-resistive effect of CNTs modified cementitious materials with consideration of dispersing effectiveness introduced; in Chapter 3, the methodologies to disperse CNTs into cementitious materials using three different methods are discussed and samples to investigate the effects of various dispersion methods were prepared in the laboratory; in Chapter 4, the piezo-resistive responses from the prepared samples were tested in the laboratory, the experimental results are analyzed and used to validate the theoretical model developed in Chapter 2; in Chapter 5, conclusions and future work have been presented based on the findings from this study.

2. THEORETIC MODEL

To achieve a self-sensing cementitious material, the piezo-resistive effect of CNTs additives has been used as sensing principles. This chapter develops a theoretic approach to derive the relations between the piezo-resistance changes from the CNTs modified cementitious materials and the corresponding strains on the materials with considerations of CNTs dispersing effectiveness.

2.1. Piezo-resistive Effect of CNTs

The strain sensing phenomenon in a CNT network is attributed to two types of resistances: the intrinsic resistance, R_{tube}, and the intertube resistances, R_{Inter}. In the following sections, detailed relations between the strains to the two types of resistances of CNTs are derived.

2.1.1. Intrinsic Resistance of CNTs

CNTs can act as good conductors because of their one-dimensional structures, which allow electronic transport to occur ballistically [28, 43]. MWNTs have been found to have an intrinsic resistance of 0.2-0.4 kΩs/μm [44, 45]. The intrinsic resistance is subjected to modification under strain. Studies showed that the intrinsic resistance of SWNTs increased considerably at a relatively small strain [46, 47]. The intrinsic resistance of CNTs increases proportionally with the applied strain with a dependence on the chiral angle of the CNTs [48], which can be expressed as below:

$$\Delta R_{tube} = (L_0 - L)\rho = {G_{tube}}^{-1} \tag{1}$$

where, ΔR_{tube} is the intrinsic resistance changes of the CNTs, L_0 is the initial length of the tube, L is the tube length with strain, and ρ is constant which equals to the resistance change of the tube per unit length.

Thus, the intrinsic resistance change of CNTs with the strain, ε, can be derived as:

$$\Delta R_{tube} = \frac{(L_0 - L)}{L}\rho L = \rho L\varepsilon = k_1\varepsilon \tag{2}$$

in which, k_1 is the strain sensitivity of the intrinsic resistance of CNTs to the resistance changes, which equals to ρL.

2.1.2. Intertube Resistance of CNTs

Despite the intrinsically high conductivity of carbon nanotubes, conduction in a CNT network is not correspondingly efficient. This is because intertube resistance is quite high compared to the intrinsic resistance. The intertube resistances include the contact resistance, R^C, which is the resistance between tubes that are physically in contact, and the tunneling resistance, R^T, which is the resistance between tubes that are separated by a small gap.

The contact resistance between nanotubes in CNTs is introduced by physical contact between tubes, such that the conduction takes place between these carbon nanotubes through electron diffusion. The contact resistance has been shown to depend greatly on the contact region and has large values varying from a few hundreds to a thousand kΩs. These values depend on factors like arrangement of molecules across the interface and extent of the interfacial surface [49]. When the arrangement of molecules and extent of interfacial surface are settled, the contact resistance of CNTs remains stable in most cases, resulting insensitive to the external strains on them. Therefore, when measuring intertube resistance changes of CNTs with various strains, the major contribution is assumed to come from the changes of the tunneling resistance, R^T, and the changes of contact resistance is neglected.

The tunneling resistance of the CNTs, R^T, is introduced by conduction between the gaps of the carbon nanotubes. Tunneling resistance can be calculated as below [50]:

$$R^T = R_0 e^{\lambda S} \tag{3}$$

where, S is the gap in between nanotubes, R_0 is the base resistance and λ is a constant related to the average height of the potential barrier, the R_0 and λ can be obtained as below:

$$R_0 = \frac{1}{C_1}\frac{S_0}{\sqrt{K}} \text{ and } \lambda = C_2\sqrt{K} \tag{4}$$

in which, S_0 is the initial gap in between the nanotubes, C_1 and C_2 are constants with a value of 3.16×10^{10} and 1.0125, respectively, K is equal to the average height of the potential barrier which is assumed to be a constant of 6.

If strain, ε, occurs on the CNTs, it will introduce gap distance changes in between the nanotubes, from S_0, the initial gap between the nanotubes, to S, the current gap distance. Thus, based on Equation 3, the tunneling resistance changes, ΔR^T, can be calculated as:

$$\Delta R^T = R_0 e^{\lambda S_0} - R_0 e^{\lambda S} = R_0 e^{\lambda S_0}\left[1 - e^{\lambda(S_0 - S)}\right]$$

$$= R_0 e^{\lambda S_0}\left[1 - e^{\lambda S_0 \frac{(S_0 - S)}{S_0}}\right] = R_0 e^{\lambda S_0}\left[1 - e^{\lambda S_0 \varepsilon}\right] \tag{5}$$

Thus, if we assign $k_2 = R_0 e^{\lambda S_0}$ and $k_3 = \lambda S_0$, Equation 5 can be rewritten as:

$$\Delta R^T = k_2(1 - e^{k_3 \varepsilon}) \tag{6}$$

2.1.3. Total Resistance from CNTs

The total resistances, R_{Total}, induced by the CNTs, therefore, can be derived as the summation of the intrinsic resistance of carbon nanotubes and the intertube resistance of carbon nanotubes:

$$\Delta R_{Total} = \Delta R_{Tube} + \Delta R^T = k_1 \varepsilon + k_2(1 - e^{k_3 \varepsilon}) = k_2 + k_1 \varepsilon - k_2 e^{k_3 \varepsilon} \tag{7}$$

It is obviously from Equation 7 that the piezo-resistance response of the CNTs to the strains on them is a nonlinear behavior. However, with laboratory calibration, k_1, k_2, and k_3 can be obtained and the resistance changes of the CNTs with strains can be derived theoretically.

2.2. Piezo-resistance of CNTs Modified Cementitious Materials with Dispersing Effectiveness Considered

If 100% of CNTs are used as a sensing material, Equation 7 can be used to calculate the resistance change of the CNTs for corresponding strains on them, which is the sensing principle for piezo-resistive sensors made by pure CNTs. However, for practical application, the pure CNTs material sensors are very expensive which limited the size of the sensors. For a self-sensing structural material, such as cementitious materials, it is only affordable to add a small portion of CNTs into the base cementitious materials for modification of material properties and enabling sensing capability.

Thus, the theoretic piezo-resistance response of the CNTs that are incorporated with the cementitious materials may vary from Equation 7. However, Equation 7 can still be used as a base equation to calculate the piezo-resistance of individual CNTs in the cementitious materials. In this study, the hypothesis is that the piezo-resistance of the CNTs modified cementitious materials toward strains, ε, still remains a function of the total resistance of individual CNTs, ΔR_{Total}, with dependence on the percentage of CNTs used for the cement mortar (%CNT), the water/cement ratio (W/C), and the dispersion factor of the CNTs in the cementitious materials. The %CNT will influence both the intrinsic and intertube resistances of CNTs in cement mortar. While with the same % of CNTs, the intrinsic resistance of CNTs will not change much with dispersing effectiveness which contributed by the W/C and dispersing methods. The dispersing effectiveness will influence majorly on the intertube resistance since it changes the distance in between nanotubes which is the tunneling resistance. Thus, based on this hypothesis, the piezo-resistance change of the CNTs modified cementitious materials $\Delta \mathrm{R}_{mortar}$ can then be expressed as follows:

$$\Delta \mathrm{R}_{mortar} = C_A \mathrm{C_B} k_2 + k_1 \varepsilon - \mathrm{C_B} k_2 e^{k_3 \varepsilon} \qquad (8)$$

where, C_A is a contributing factor from percentage of the CNTs by weight used in the cementitious materials, %CNT, C_B is the influence factor to consider the dispersing effectiveness which is contributed from two major factors: the water/cement ratio (W/C) of the cementitious material and the dispersion methods of CNTs. Thus, if 100% of CNTs is used, C_A will equal to 1, and if the CNTs dispersed uniformly and effectively in cementitious materials, C_B=1. In this ultimate circumstance, the resistance will be the total resistance of the CNTs.

Since previous studies [35] have been intensively performed on the influences of percentage of CNTs and water/cement ratios on the piezo-resistance of CNTs modified cementitious materials, in this thesis, we will focus to investigate the contributing factor from the effectiveness of various dispersing methods. To investigate the contributing factor of dispersing effectiveness from various dispersing methods, this study keeps all the samples with the same percentage of CNTs and the same water/cement ratio. Thus, Equation 8 can be the resistance changes of the CNTs modified cement mortar from strains can be further simplified as:

$$\Delta \mathrm{R}_{mortar} = C_A K_B + k_1 \varepsilon - K_B e^{k_3 \varepsilon} \tag{9}$$

where $K_B = C_B k_2$, is the influence factor from the dispersing effectiveness.

In this study, we will perform a systematic study to calibrate the influence factor from dispersing effectiveness induced by various dispersing methods, K_B, based on statistic studies on the laboratory experiments.

2.3. Summary

In this chapter, the operational principle of the piezo-resistive effect of CNTs is described. The strain sensing phenomenon in a CNT network is attributed to two types of resistances, intrinsic resistance and intertube resistances. The total resistance that is induced by the CNTs can be derived as the summation of intrinsic resistances and the intertube resistance from the CNTs. The theoretic piezo-resistive responses of the CNTs that are incorporated with the cementitious materials are derived and would be used to check on the laboratory obtained results.

3. DISPERSING METHODOLOGY AND SAMPLE PREPARATION

In this study, three dispersion methods are tested in laboratory to investigate the influences of dispersing effectiveness of CNTs for self-sensing cementitious materials. These dispersion methods include the direct mixing method without any specific dispersing approaches considered, the surfactant method, and co-polymer wrapping method. In this chapter, the dispersing methodologies and sample preparations using these three methods to disperse CNTs are discussed in details.

The CNTs that are used and added in the cementitious materials in this study are MWNTs supplied by SkySpring Nanomaterials, Inc. and the cement used is Type I Portland cement supplied by Holcim Inc, USA. Figure 3 shows a scanning electron microscope (SEM) image of the used MWNTs and Table 1 presents the detailed material properties of the CNTs used.

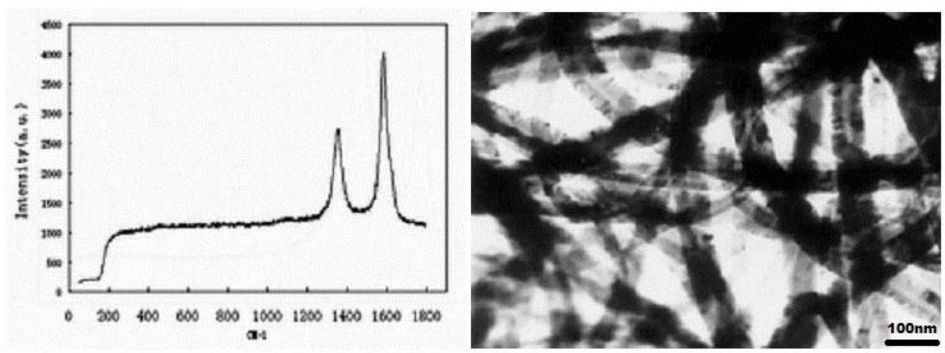


Figure 3. SEM image of the used MWNTs in this study

For all the CNTs modified cement mortar samples to be prepared for investigations on the effectiveness of various dispersing methods, a water/cement ratio of 0.6 and a percentage of CNTs of 0.1% by weight were used. The size of the samples was prepared as 2 in. by 2 in. cubic. Thus, for each sample, there were 400 g of cement, 240 ml of water, and 0.4g of CNTs.

Table 1. Properties of Multi-wall carbon nanotubes

Parameters	Values
Outside diameter	50 – 100nm
Inside diameter	5 – 10nm
Length	5 – 20um
Purity	> 95 weight %
Ash	< 1.5 weight %
Special surface area	> 60 m^2/g
Amorphous carbon	< 3.0%
Bulk density	0.28 g/cm^3
True density	~2.1 g/cm^3

3.1. Methodology

In this section, the methodology on the preparation of the CNTs-Water Solutions is introduced using three different dispersing methods, including the direct mixing method, the surfactant method, and co-polymer wrapping method. All the samples were prepared in room temperature (22°C ± 2°C).

3.1.1. Direct Mixing Method

Direct mixing method is a common practice for mixing CNTs into cement mortar. This method directly mixes the CNTs with cement and water without any treatment of the CNTs. There are three steps to prepare a sample cubic using direct mixing method, including:

1) The 0.4 g CNTs was directly mixed with 240 ml water to have a solution;

2) The solution was fully mixed using a magnetism stirrer for 3 minutes, with the fully mixed solution shown in Figure 4 (a);

3) The solution was further used to mix with 400 g cement to make a cubic sample.

Figure 4. CNTs in water using direct mixing method

3.1.2. Surfactant Method Using NaDDBS (Methodology)

The surfactant dispersion method is also investigated in this study by applying sodium dodecylbenzene sulfonate (NaDDBS) for surface modifications on CNTs. The NaDDBS used was supplied 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. There are four steps to prepare the solution of surfactant treated CNTs solution:

1) 1.17g of NaDDBS was mixed with 240ml of water using a magnetism stirrer for approximately 3 minutes as shown in Figure 5 (a);

2) The 0.4 g of CNTs were added into this aqueous solution and sonicated using a sonicator for 2 hours to make a uniform dispersed suspension as shown in Figure 5 (b);

3) The NaDDBS treated CNTs solution was then mixed with 400 g of cement for about 3 minutes;

4) In order to decrease the air bubble in the CNTs filled with cementitious materials caused by the NaDDBS, 0.25% of defoamer by volume will be added and mix with the modified cement

for another 3 minutes. The defoamer used in this study is the Tributyl phosphate supplied by Sigma-Aldrich Co., USA.

The mixed NaDDBS treated CNTs-water solution is shown on the left in Figure 6. Figure 6 also compares the mixed NaDDBS treated CNTs water solution with that from direct mixing method. The surfactant method produces a much more uniformly disperse CNTs compared to the direct method.

(a) (b)

Figure 5. (a) Mixing NaDDBS in water and (b) mixing CNTs with NaDDBS solution

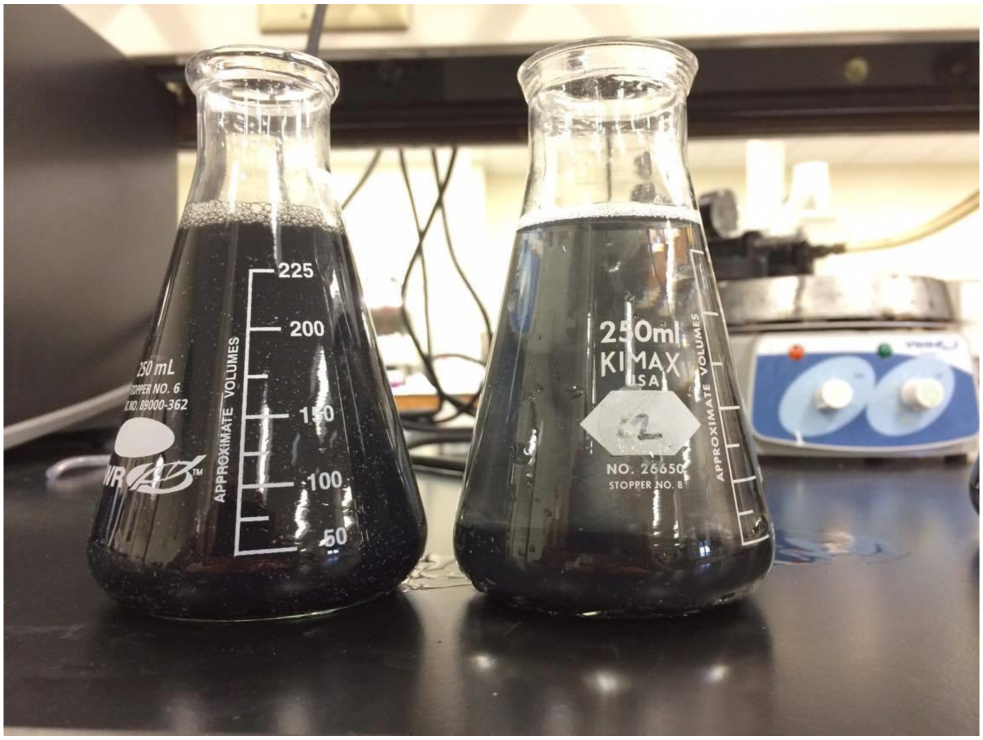


Figure 6. NaDDBS treated CNTs solution on the left compared with the CNTs solution from direct mixing method on the right

3.1.3. Co-polymer Method

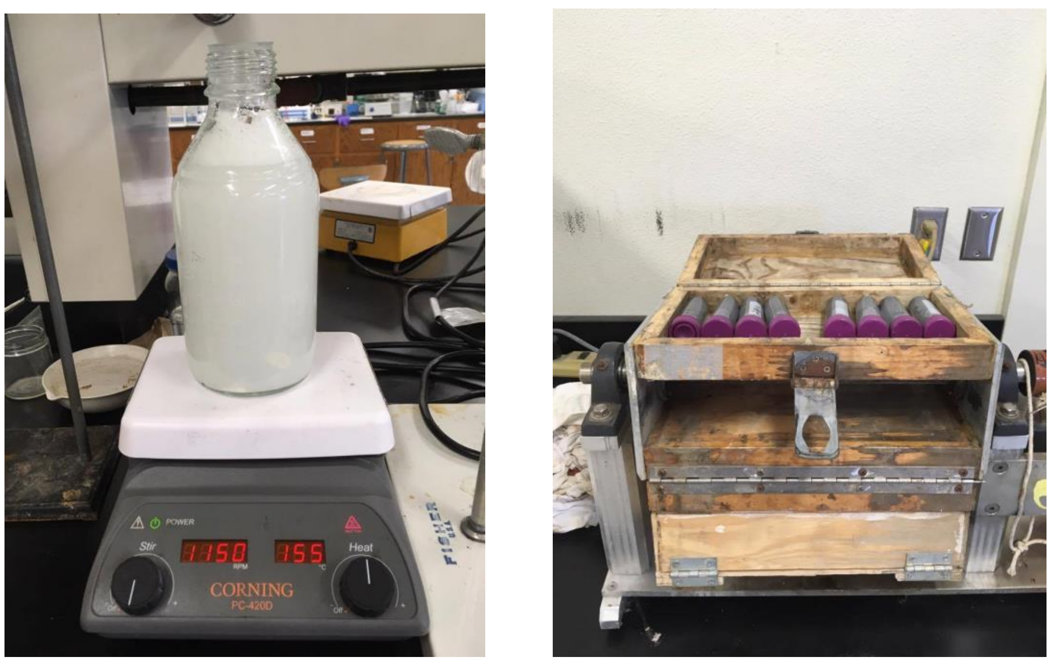
The first time to the author's knowledge, this study uses the co-polymer method to treat the surfaces of CNTs to improve dispersing of CNTs in the cementitious materials. The co-polymer used in this study was the modified corn starch polymer. Five steps are used to prepare a co-polymer dispersed CNTs-cementitious cubic sample, including:

1) A 10 g of modified corn starch was first mixed with 1 liter of water to form a co-polymer-water solution;
2) The co-polymer solution was then heated till boiling point and mixed using a magnetic stirrer for 10 to 15 minutes, followed by continuous mixing at a temperature of 50 °C for the next 24 hours using the magnetic stirrer as shown in Figure 7 (a);

3) After 24 hours of mixing, 0.2 g of CNTs were mixed with 50 ml of co-polymer solution of 50ml in a test tube and placed into a custom-made end-over-end shaker for 72 hours to ensure a proper coating of the co-polymer on the CNTs as seen in Figure 7 (b);

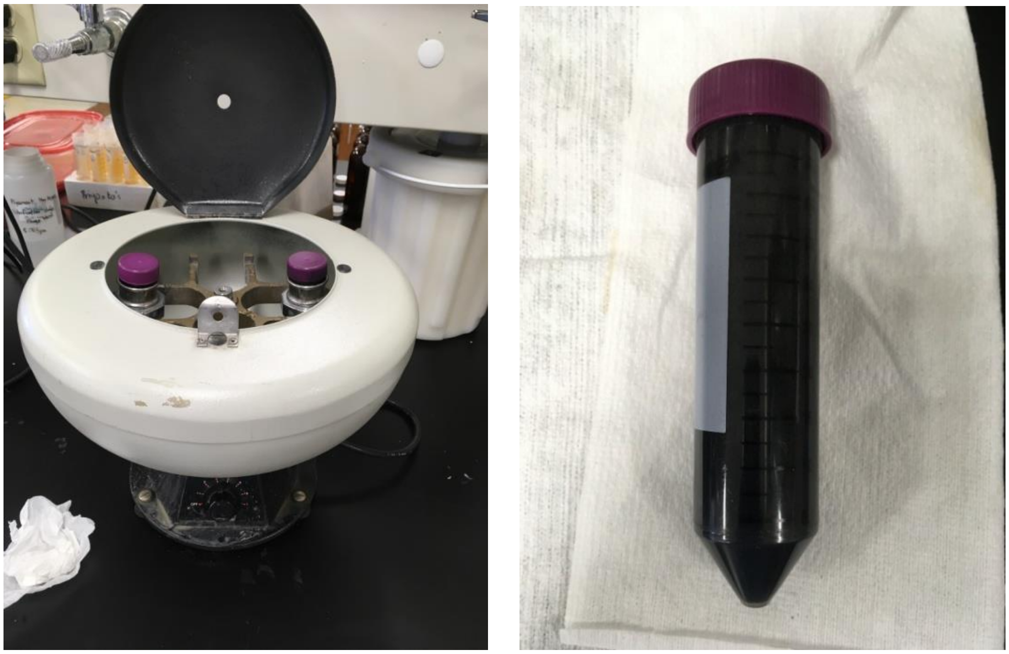
4) After 72 hours, the test tubes with co-polymer modified CNTs solutions were then placed into a centrifuge as in Figure 8 (a) to separate the CNTs wrapped with co-polymer and the excess co-polymer, which makes it to be ready-to-use solution as seen in Figure 8 (b);

5) The co-polymer treated CNTs solution was further mix with 400g of cement to fabricate the cubic samples.



(a) (b)

Figure 7. (a) Preparation of the co-polymer solution under mixing and heating, (b) the test tubes with carbon nanotubes wrapped with co-polymer being placed in the centrifuge



(a) (b)

Figure 8. (a) the custom-made end-over-end shaker, and (b) fully dispersed CNTs using the co-polymer method after 72 hours in the custom made end-over-end shaker

Figure 9 shows the co-polymer treated CNTs solution (left) compared with the CNTs solution prepared by direct method (right) after 5 minutes of mixing. The co-polymer treated CNTs solution stays uniform after 5 minutes of mixing, however, the CNTs solution prepared by the direct method started to settle after 5 minutes of mixing. It is very obvious that the co-polymer method provides a more uniform and more effective dispersing of CNTs in water.

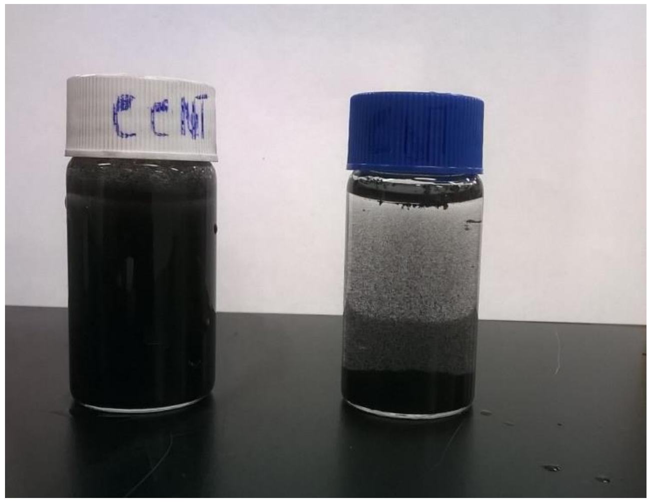
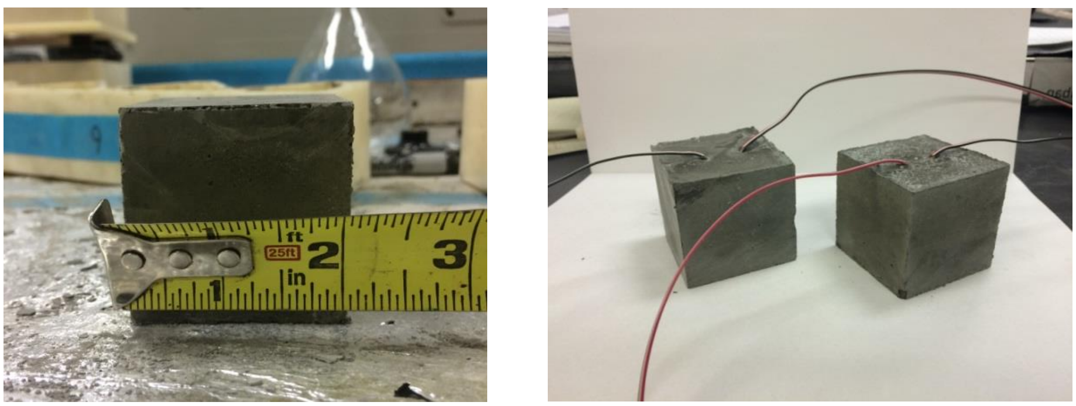


Figure 9. Comparisons of using co-polymer method and the direct method of dispersing carbon nanotubes

3.2. Fabrication of CNTs Modified Cementitious Composites

After dispersing the CNTs into water using the three methods discussed above, including the direct method, the surfactant method and the co-polymer method, the solutions were further mixed with cement and placed into 2 inch cubic molds for preparing the cubic sample as shown in Figure 10. To perform measurements of piezo-resistive effects, two electrical wires were placed 0.5 inch deep into the samples and 0.5 inch apart from each other. The samples were demolded in 24 hours and left to cure in water for 7 days as shown in Figures 11 (a, b) for demolded samples. The samples were then left to air dry at room temperature of 22°C ± 2°C for 10 days.

Figure 10. The 2 inch cubic mold for sample fabrication



(a) (b)

Figure 11. (a) The 2 inch cubic sample and (b) sample with electric wires

To investigate various influence factors, a complex sample matrix was prepared as shown in Table 1. For each dispersion method, three different samples were made including a control sample, CNTs only, CNTs with 0.1% of graphite, 0.2% of graphite, and 0.5% of graphite, respectively. The additives of graphite are included to investigate the influence of graphite on the effectiveness of dispersing methods of CNTs in cementitious materials. In each group from A to M, three samples were made to have a statistic analysis on the methods. Figure 12 shows the final samples made for testing based on the sample matrix of Table 1.

Table 2. Testing Sample Matrix

Dispersion Method	Group	Description
Method 2 Surfactant Method	A	No carbon nanotubes, NaDDBS only
	B	Carbon nanotubes only
	C	Carbon nanotubes + Graphite 0.1%
	D	Carbon nanotubes + Graphite 0.2%
	E	Carbon nanotubes + Graphite 0.5%
Method 1 Direct Method	F	Control
	G	Carbon nanotubes only
	H	Carbon nanotubes + Graphite 0.1%
Method 3 Co-polymer Method	J	Carbon nanotubes only
	K	Carbon nanotubes + Graphite 0.1%
	L	Carbon nanotubes + Graphite 0.2%
	M	Carbon nanotubes + Graphite 0.5%

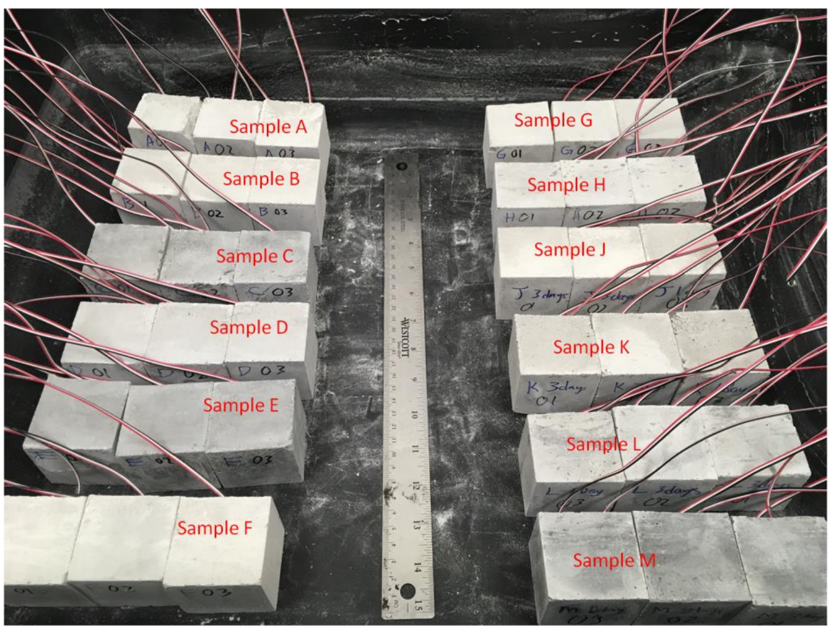


Figure 12. Final testing samples

3.3. Summary

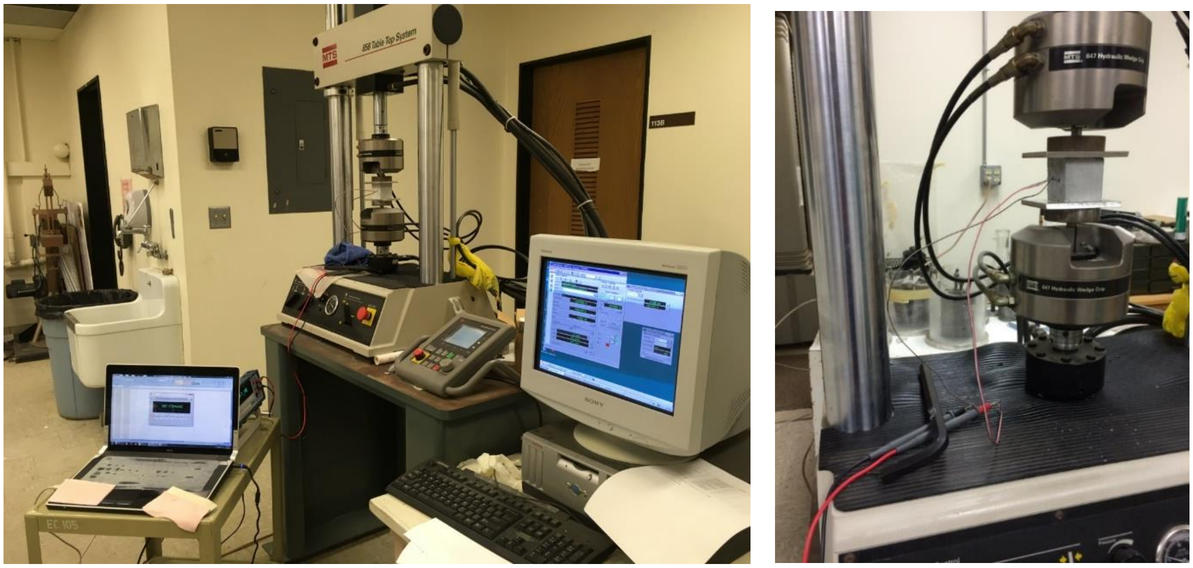
In this chapter, the methodologies of three different methods to disperse the CNTs are described and testing samples were prepared. The three methods are the direct method, surfactant method and the co-polymer method. The direct method which is a direct mixing of water and CNTs, the surfactant method is with the usage of NaDDBS to disperse the CNTs, while the co-polymer method is the usage of modified corn starch to disperse the CNTs. The concentration of CNTs and w/c ratio remains the same throughout the test. The procedures of preparing the CNTs modified cementitious materials are described. The laboratory testing of these prepared samples would be further explained in the next chapter.

4. VALIDATION EXPERIMENTS AND DISCUSSIONS

With the samples prepared in Chapter 3, in this chapter, laboratory experiments on the piezo-resistive responses of the CNTs modified cement mortar with various dispersing methods were performed to test the samples and the test results were analyzed to validate the developed theoretic model derived in Chapter 2. There are two groups of samples tested for each dispersing methods.

4.1. Experimental Setup

Dynamic loading tests were performed on the prepared samples. Figures 13 (a, b) illustrate the laboratory test setup. Compressive loads were applied using a material testing machine (MTS 858, Materials Testing Systems, Inc., USA). The electrical resistance changes of the CNTs modified cement mortar samples were measured in the direction of the compressive stress which was perpendicular to the electrodes under repeated compressive loading. The electrical resistance responses were measured using a two-electrode method using a digital bench multimeter (BK 5492B, B&K Precision Inc., USA). All of the measurements were interfaced with a PC which recorded the data automatically. The samples were subjected to a dynamic loading with an average load of 1,000N with amplitude of 1,000N for 12 cycles as shown in Figure 14. The frequency of the loading was set to be 0.1 Hz. All the samples were tested in room temperature (22°C ± 2°C).



(a) (b)

Figure 13. Laboratory test setup (a) Full experiment set up (b) close up of samples under loading

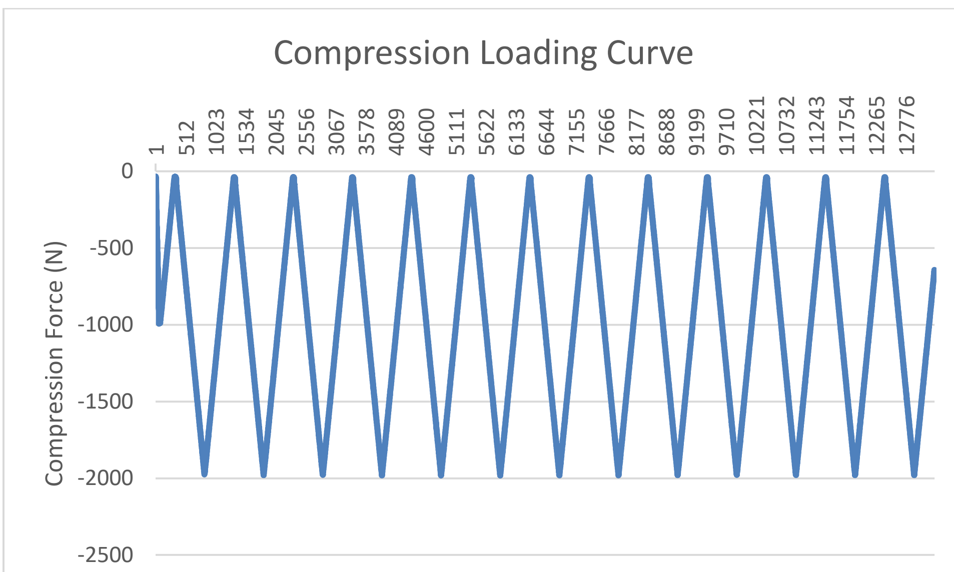


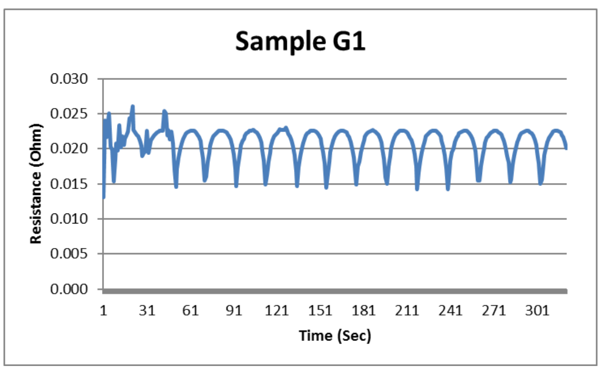
Figure 14. The loading curve that is used throughout the experiments

4.2. Experimental Results

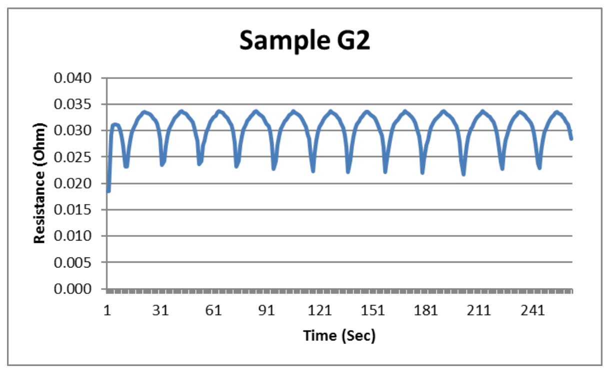
The experimental results on the samples prepared using the three dispersing methods are introduced and presented below.

4.2.1. Direct Mixing Method

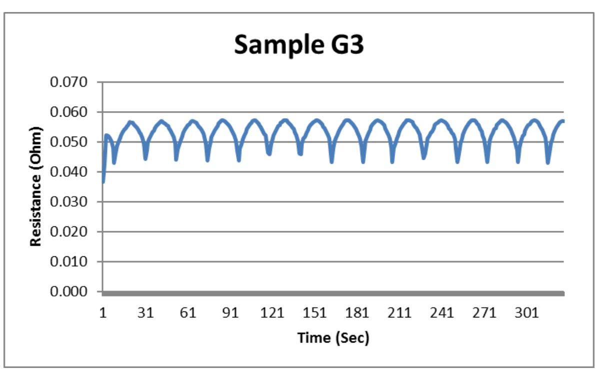
Figures 15 (a, b, c) show the piezo-resistive responses of the three cement mortar mixed with CNTs only using the direct mixing method, sample group G under the dynamic loading from Figure 14. As can be seen, the electrical resistance changes almost linearly with the compressive stress and the changes are proportional to the stress levels. Figure 15 (d) is the summary of samples G. The average piezo-resistance, maximum and minimum resistance under the dynamic loading are demonstrated in Figure 15 (d). It can be seen that with direct mixing method, the average piezoresitivity of the CNTs modified cement mortars using direct mixing method is within the range of 0.01 to 0.06 Ohm for 1,000 N of loading on it.



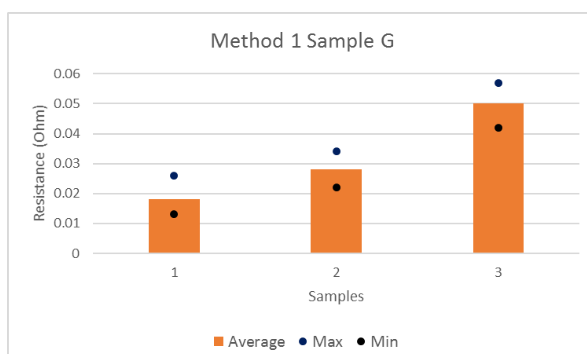
(a)



(b)



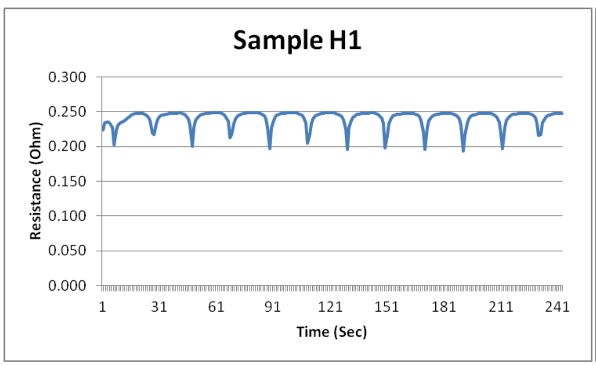
(c)



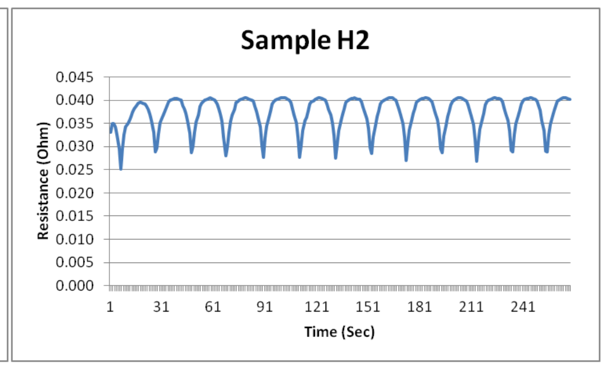
(d)

Figure 15. (a) Piezo-resistance responses for sample G1 (b) sample G2 (c) sample G3 and (d) summary of samples G

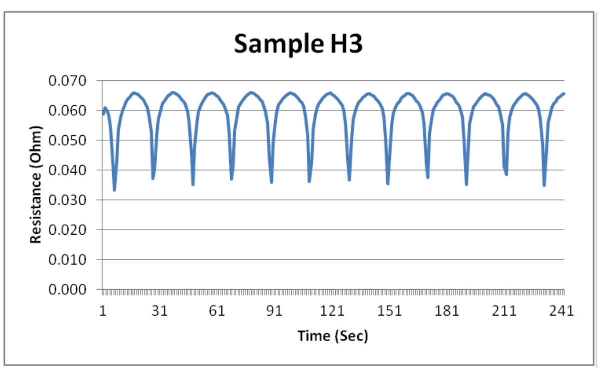
Another group of samples, Sample H, with 0.1% of CNTs and 0.1% of graphite by weight of cement were made using the direct mixing method. Figures 16 (a~c) show the electrical resistance response from the samples H and the summary of the results is presented in Figure 16 (d) with the average piezo-resistance, maximum and minimum resistance under the dynamic loading demonstrated. The average piezo-resitivity of the CNTs using direct mixing method and graphite modified cement mortars is within the range of 0.01 to 0.06 Ohm for 1,000 N of loading on it. However, there is one sample in Group H with high piezoresistivity falls into the range 0.2 to 0.3 Ohm for 1,000 N.



(a)



(b)



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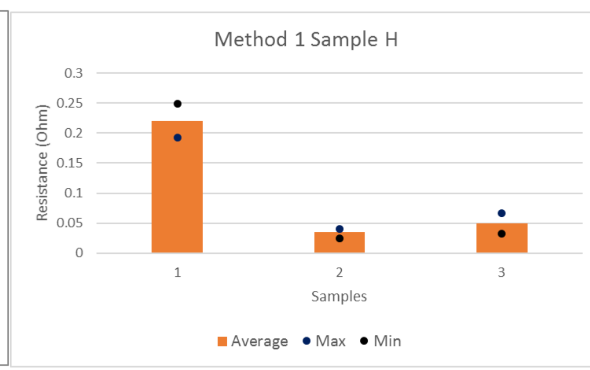
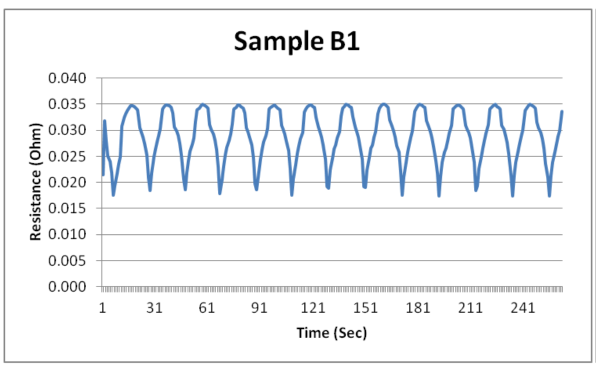


(d)

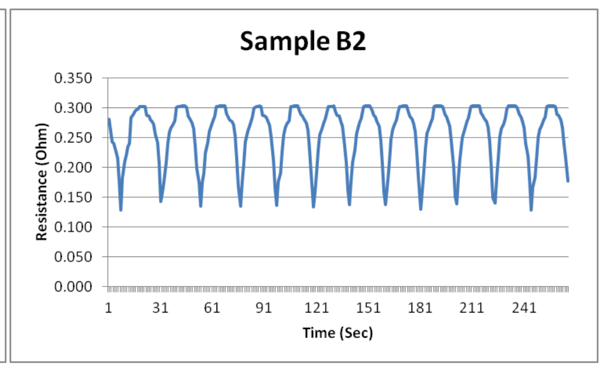
Figure 16. (a) Piezo-resistance responses for sample H1, (b) sample H2, (c) sample H3, and (d) summary of samples H

4.2.2. Surfactant Method

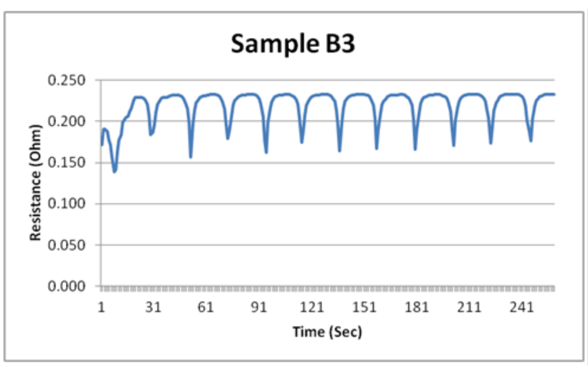
Figures 17 (a~c) depict the electrical resistance responses of the cement mortar mix samples B with only CNTs that were dispersed using the surfactant method under the dynamic loading. The piezo-resistance changes linearly with the compressive stress and the changes are proportional to the stress levels. Figure 17 (d) shows the summary of the results with the average piezo-resistance, maximum and minimum resistance under the dynamic loading demonstrated. The average piezoresitivity of two CNTs modified cement mortar samples using surfactant method are within the range of 0.2 to 0.3 Ohm for 1,000 N of loading on it. One of the samples has a little lower piezo-resistance within the range of 0.02 to 0.035 Ohm of average piezoresitivity.



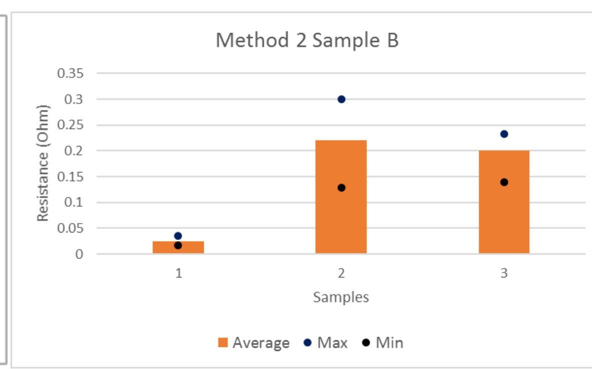
(a)



(b)



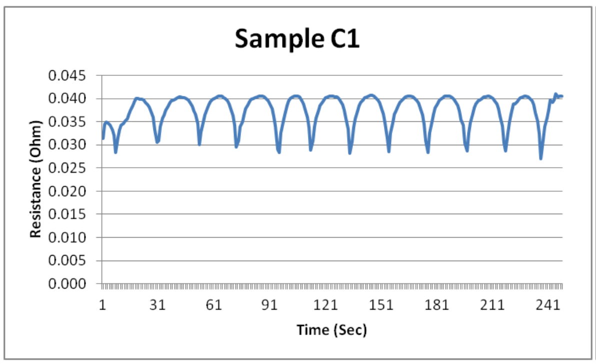
(c)

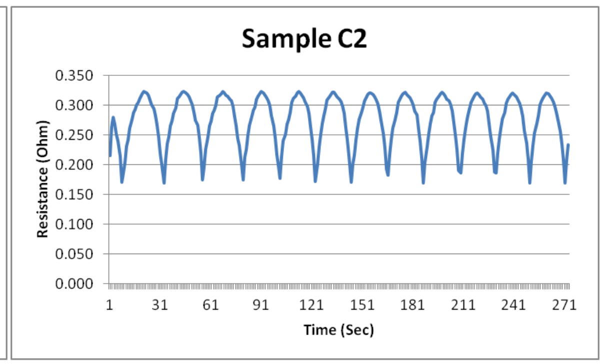


(d)

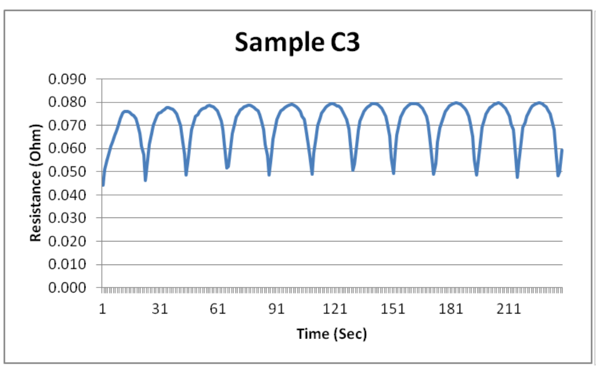
Figure 17. (a) Piezo-resistance responses for sample B1, (b) sample B2, (c) sample B3, and (d) summary of samples B

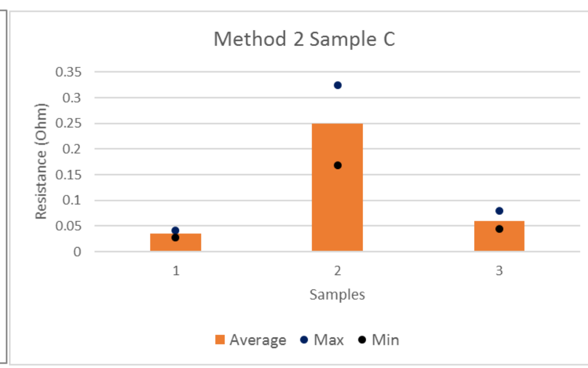
Sample Group C represents the samples with 0.1% CNTs dispersed using surfactant method and mixed with 0.1% of graphite into the cement mortars. The piezo-resistance responses from the sample Group C can be found in Figures 18 (a~c) and summarized in Figure 18 (d) with the average piezo-resistance, maximum and minimum resistance under the dynamic loading demonstrated. The average piezoresitivity of one sample in this group is within the range of 0.2 to 0.3 Ohm for 1,000 N of loading on it and the other two samples have lower piezo-resistance within the range of 0.03 to 0.08 Ohm average piezoresitivity.





(a) (b)





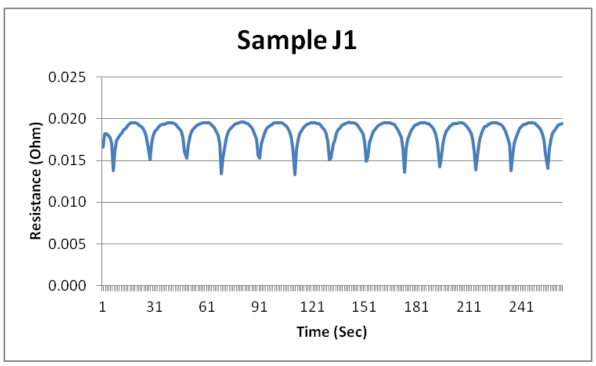
(c) (d)

Figure 18. (a) Electrical resistance responses for sample C1, (b) sample C2, (c) sample C3, and (d) summary of samples C

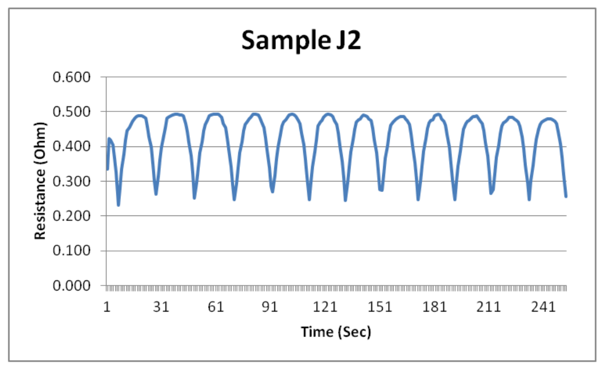
4.2.3. Co-polymer Method

Figures 19 (a~c) show the piezo-resistance responses from the sample Group J cement mortar that are mixed with only CNTs dispersed using the co-polymer method. The samples 1 and

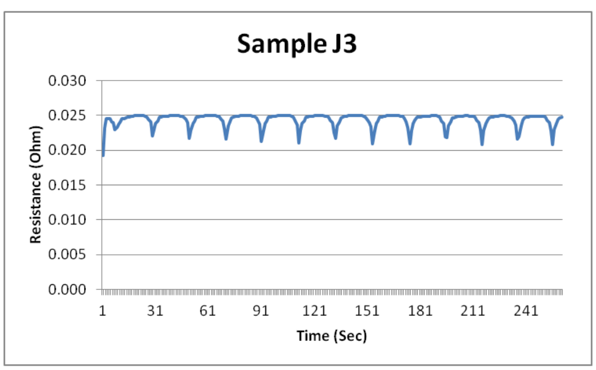
2 of sample J were dispersed in a 3 day mix with the co-polymer, while sample 3 of sample J is only dispersed 1 day with the co-polymer. The difference in days of co-polymer mixing is to test the effectiveness of co-polymer on wrapping the CNTs with the changes of mixing duration. Figure 19 (d) summarizes the results in this group with the average piezo-resistance, maximum and minimum resistance under the dynamic loading demonstrated. The average piezoresitivity of one sample in this group with 3 days of mixing is within the range of 0.3 to 0.5 Ohm for 1,000 N of loading on it and the other two samples have lower piezo-resistance within the range of 0.015 to 0.025 Ohm average piezoresitivity.



(a)



(b)



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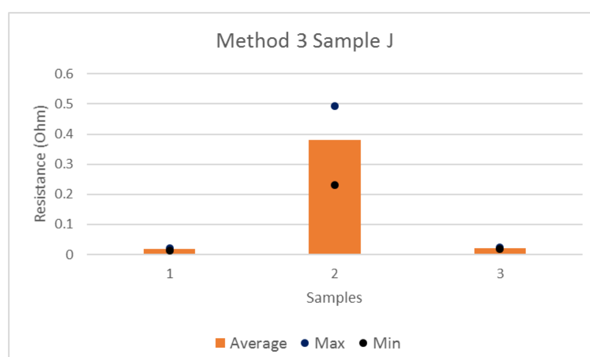
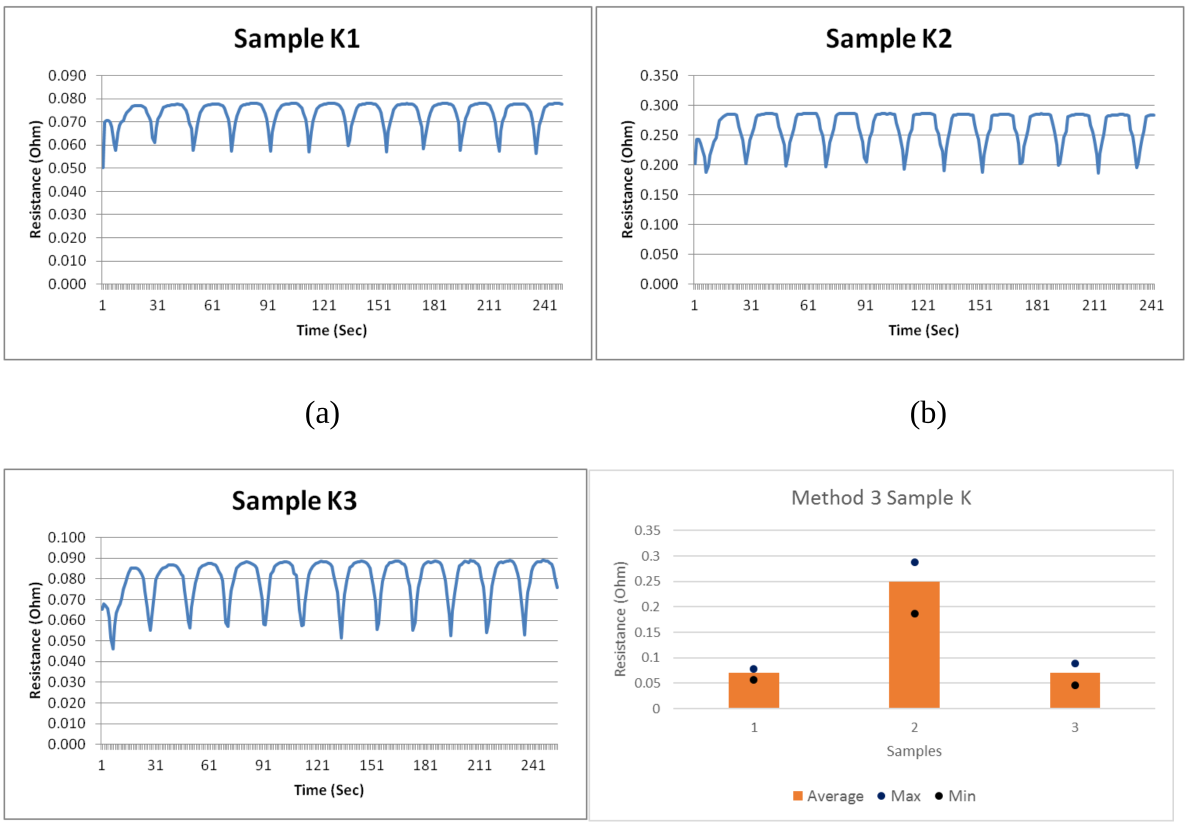


(d)

Figure 19. (a) Piezo-resistance responses for sample J1, (b) sample J2, (c) sample J3, and (d) summary of samples J

Sample Group K tested 0.1% CNTs mixed using the co-polymer method with 0.1% of graphite into the cement mortar. The piezo-resistance responses from the samples K can be found in Figures 20 (a~c). Figure 20 (d) summarizes the results in this group with the average piezo-resistance, maximum and minimum resistance under the dynamic loading demonstrated. The average piezoresitivity of one sample in this group with 3 days of mixing is within the range of 0.2 to 0.3 Ohm for 1,000 N of loading on it and the other two samples have lower piezo-resistance within the range of 0.05 to 0.08 Ohm average piezoresitivity.



(a) (b)

(c) (d)

Figure 20. (a) Piezo-resistance responses for sample K1, (b) sample K2, (c) sample K3, and (d) summary of samples K

4.3. Comparisons Between Various Dispersing Methods

Figure 21 compares the experimental results from the sample Groups G, B and J using the three different methods with CNTs only and Figure 22 summarizes the comparison results of average piezo-resistance of the three groups from all the three samples in these groups. As you can see from Figure 22, the average piezo-resistance response of the samples using co-polymer method is 0.2 Ohm, that of the surfactant method is around 0.15 Ohm, and for direct mixing method, it is 0.025 Ohm. Direct mixing method indicates a poor piezo-resistance response and it is obvious that with proper dispersing methods such as surfactant and co-polymer method, the average piezo-resistance response can increase up to 10 times. The CNTs dispersed using surfactant method has a relatively stable piezo-resistance response with small standard deviation. However, it is also worth noticing that although the co-polymer method has a potential of significantly increase the piezo-resistance response of the CNTs modified cement mortars, the use of co-polymer method shows a relatively large standard deviation. This large deviation may be contributed by the ineffective wrapping of co-polymers on the CNTs. As seen in Figure 21, mixing the co-polymer with CNTs for one day is not sufficient to promise the wrapping of co-polymers on CNTs. Mixing the co-polymers with CNTs for three days, the effectiveness of wrapping the co-polymer on CNTs increased 50%. Thus, further efforts are needed to improve and ensure an effective wrapping of co-polymers on CNTs to increase the effectiveness of co-polymer method to disperse CNTs in cementitious materials.

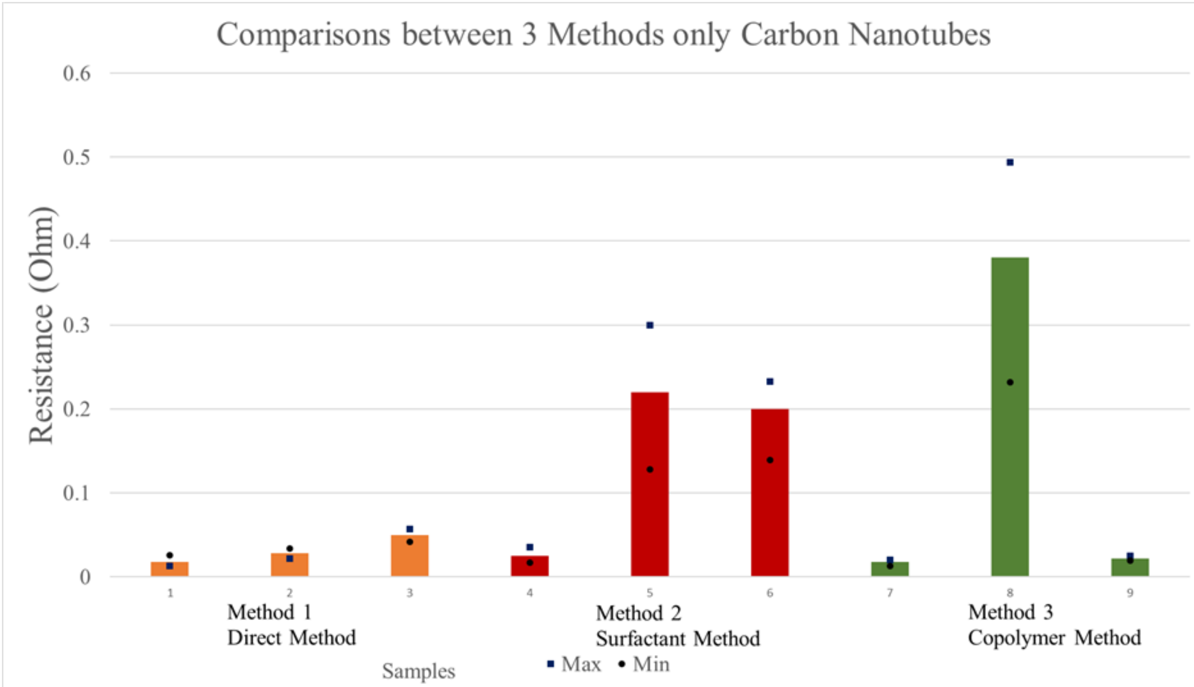


Figure 21. Comparison of the three methods with all the samples in Groups G, B and J

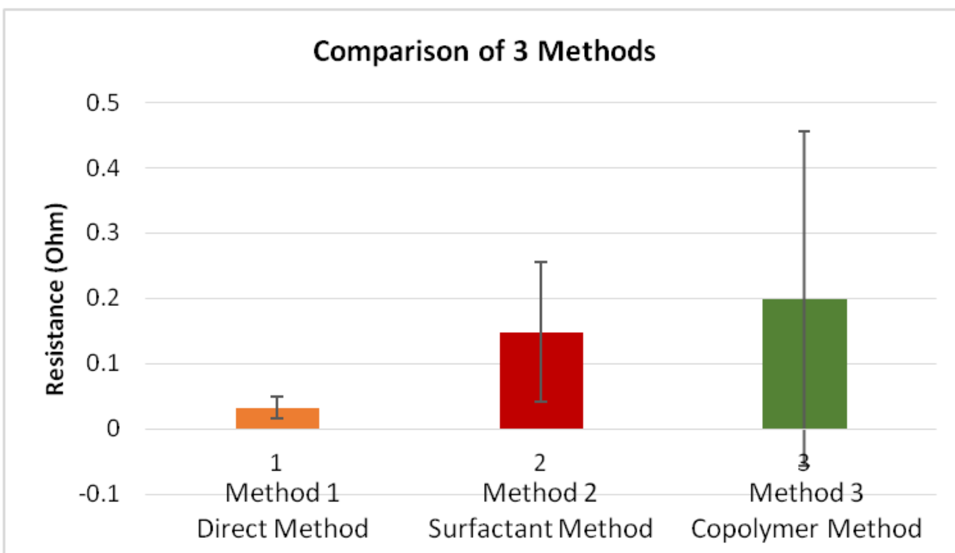


Figure 22. Comparison of the three methods with average piezo-resistance of the samples in Groups B, G and J

Figure 23 compares the experimental results from the sample Groups H, C and K with CNTs dispersed using the three different methods and mixed with 0.1% graphite in the cement mortar. Figure 24 summarizes the comparison results of average piezo-resistance of the three groups from all the three samples in these groups. Comparing Figure 24 with Figure 22, it can be seen that the adding of 0.1% graphite may be able to raise the piezo-resistance response of the CNTs modified cementitious materials using direct mixing method, however, the addition of graphite significantly reduces the dispersing effectiveness of the two dispersing method of CNTs in cement by reducing the piezo-resistance response for surfactant and co-polymer methods from average of 0.15 Ohm and 0.2 Ohm to 0.12 Ohm and 0.16 Ohm. In addition, the inclusion of graphite into the CNTs modified cement mortar samples significantly increases the standard deviations of all the mixing methods. Thus, for field application, it is not recommended to add graphite with small percentages when CNTs is presented for piezo-resistance sensing.

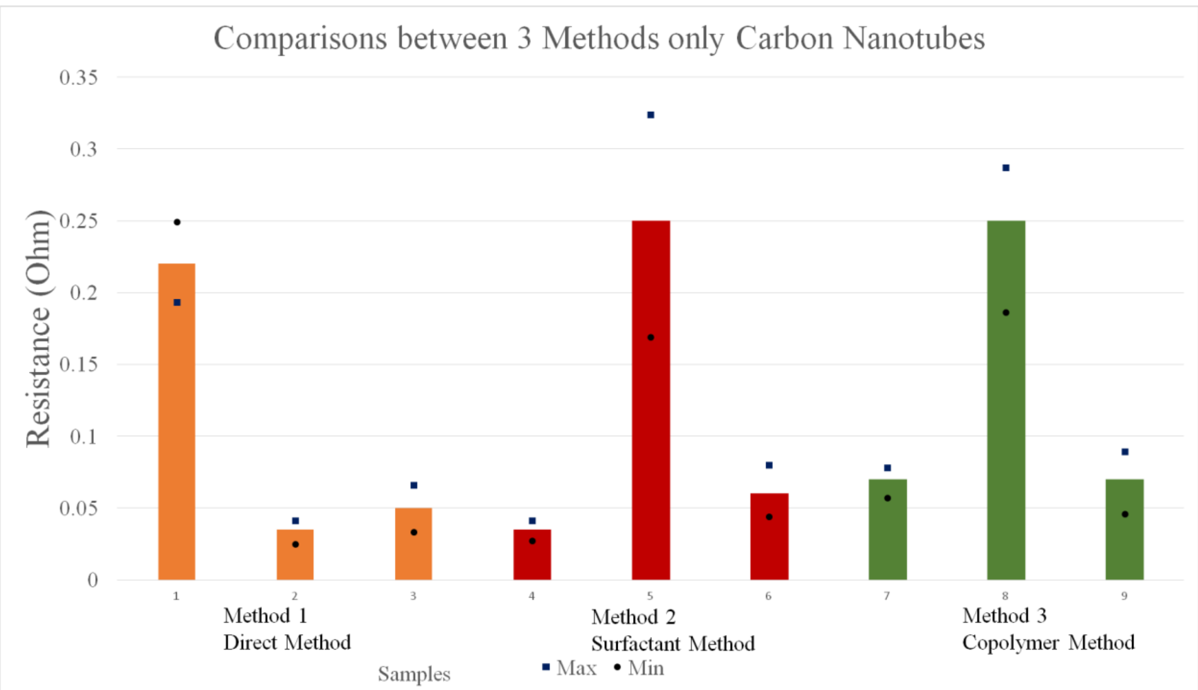


Figure 23. Comparison of the three methods with all the samples in Groups H, C and K

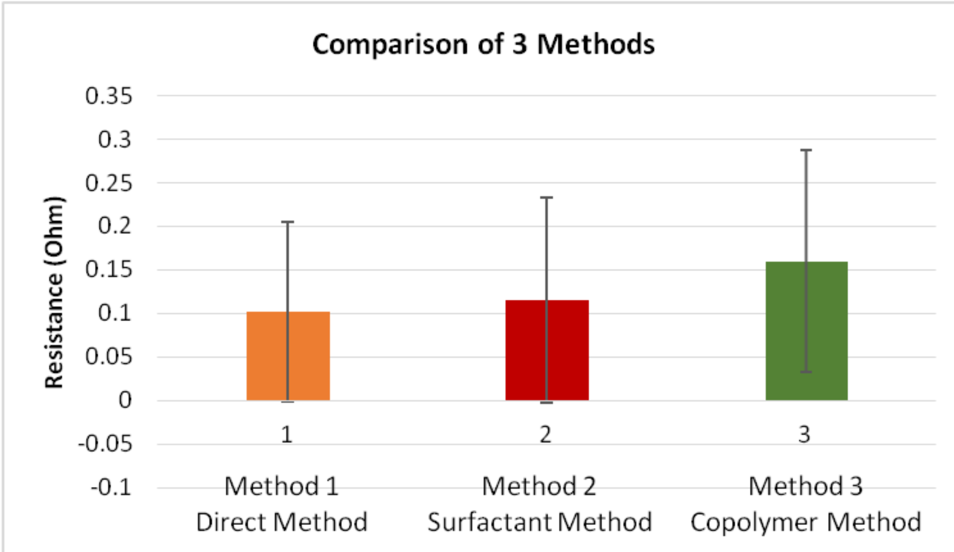


Figure 24. Comparison of the three methods with average piezo-resistance of the samples in Groups H, C and K

4.4. Validation of Theoretic Model

To analyze the theoretical model developed in Chapter 2 for the analysis of the effects of dispersing methods on piezo-resistance in CNTs modified cementitious materials, the responses from the samples were analyzed statistically to find the coefficients in Equation 9 for the three different dispersing methods, which is repeated below:

$$\Delta \mathrm{R}_{mortar} = C_A K_B + k_1 \varepsilon - K_B e^{k_3 \varepsilon} .$$

The piezo-resistive responses of CNTs modified cement mortar samples were analyzed for static loading from 0 to 1,000N as shown in Figure 25 including sample Groups G and H from direct mixing method, sample Groups B and C from surfactant method, and sample Groups J and K from co-polymer method. Based on the loading curve as shown in Figure 25, the strains in Equation 9 were calculated using the relations between loads and the surface area of the sample as below:

$$\varepsilon = \frac{P}{EA} \tag{10}$$

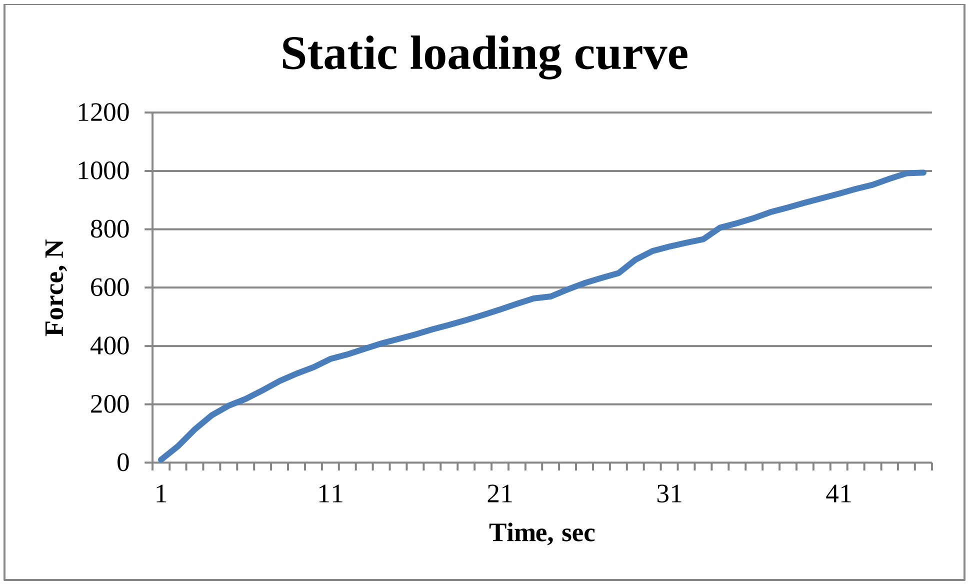
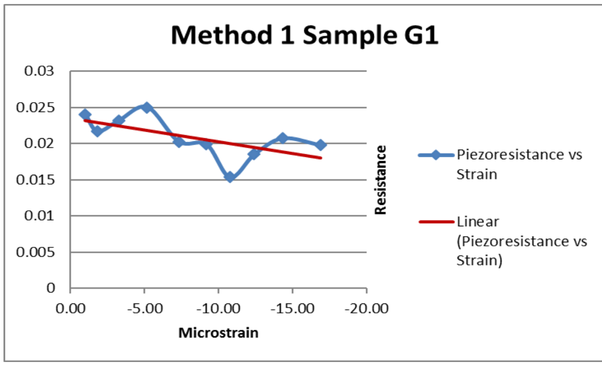
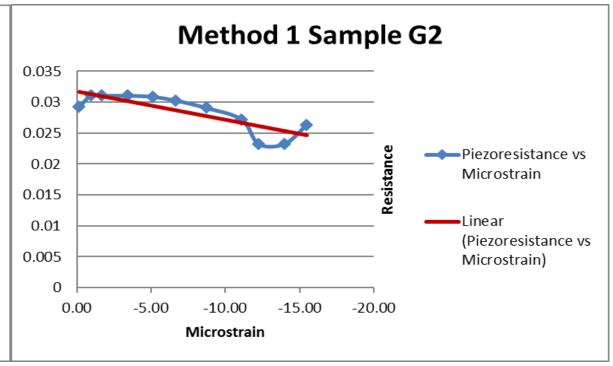


Figure 25. Static Loading Curve

Figures 26 (a~f) plot the piezo-resistance responses with strain changes under static loading process for direct mixing method for sample Group G with CNTs only and sample Group H with 0.1% graphite together with CNTs in cement mortar. Figures 26 (a~f) also show the fitted responses of all the samples in Group G and Group H using Equation 9 with direct mixing methods. Since the piezo-resistances of the samples using direct mixing response is very small and the distribution of the nanotubes in cement matrix is uncertain, the responses do not follow the pattern of Exponential function as in Equation 9 but showing a rather linear behavior, indicating that the piezo-resistance effects of CNTs modified cementitious materials are majorly contributed by the intrinsic resistance instead of the intertube resistance. For the direct mixing methods, Equation 9 does not fit well for the responses since the dispersing is not effective.



(a)



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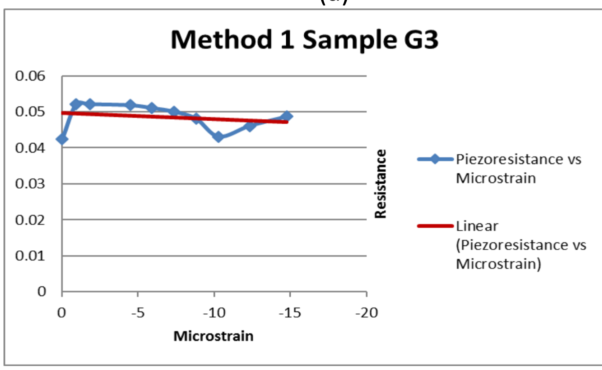

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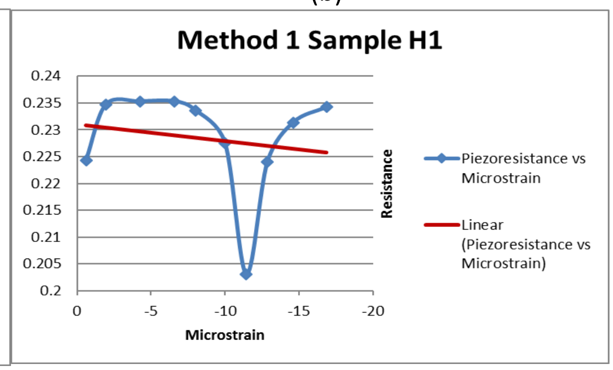
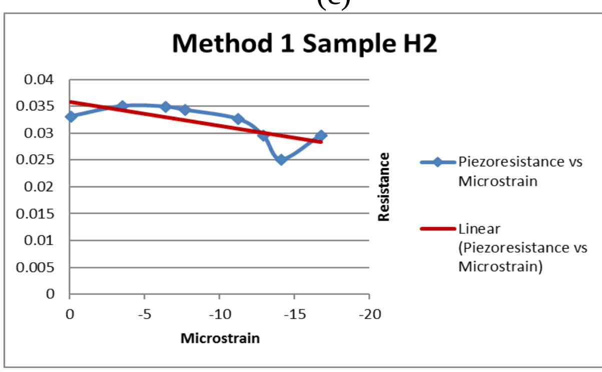
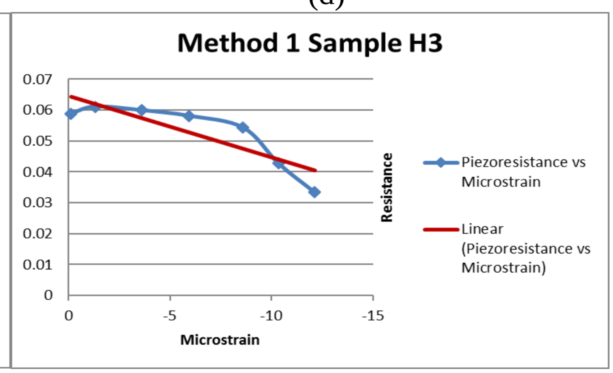


(d)



(e)



(f)

Figure 26. (a~f) Piezo-resistances vs strains of Sample Group G (G1 to G3) and H (H1 to H3) with direct mixing methods and their fitted lines using the Equation 9

Figures 27 (a~f) plot the piezo-resistance responses with strain changes under static loading process for surfactant method for sample Group B with CNTs only and sample Group C with 0.1% graphite together with CNTs in cement mortar. The fitted responses of all the samples in Group B and Group C using Equation 9 with surfactant method are also seen in Figures 27 (a~f). Figure 27 clearly demonstrate that the piezo-resistances of the samples using surfactant method follow well with the predictions of response using Equation 9. It indicates that the surfactant dispersing method dispersed the CNTs effectively so that the intertube resistance of CNTs also contributes to the piezo-resistance effects and dominates the performance of the piezo-resistive effects instead of intrinsic resistance. It also approves that Equation 9 can predict the piezo-resistance responses well if the dispersing method effectively disperses the CNTs in the cementitious matrix.

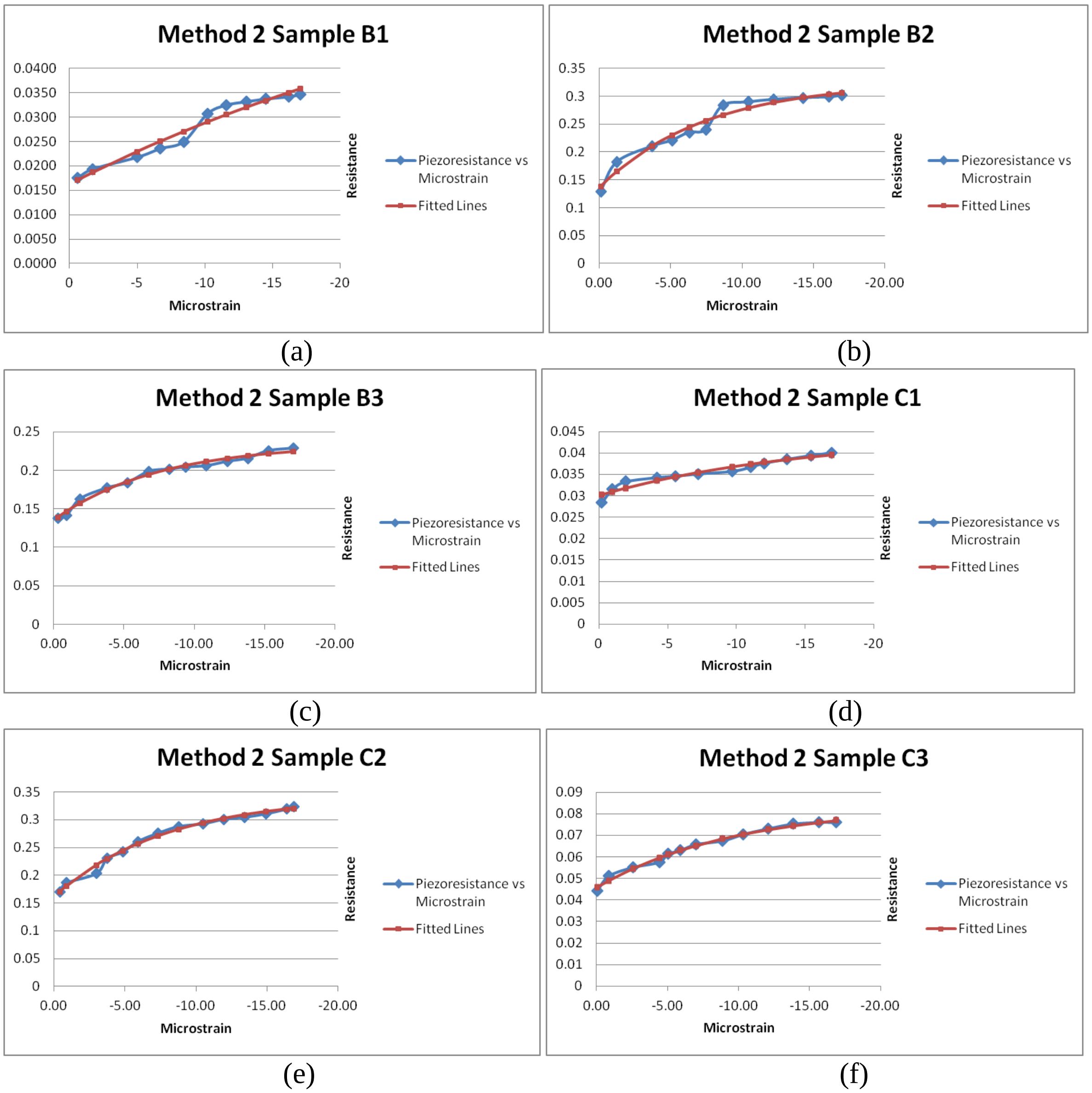


Figure 27. (a~f) Piezo-resistances vs strains of Sample Group B (B1 to B3) and C (C1 to C3) with surfactant methods and their fitted lines using the Equation 9

Figures 28 (a~f) plot the piezo-resistance responses with strain changes under static loading process for co-polymer method for sample Group J with CNTs only and sample Group K with

0.1% graphite together with CNTs in cement mortar. The fitted responses of all the samples in Group J and Group K using Equation 9 with surfactant method are also seen in Figures 28 (a~f).

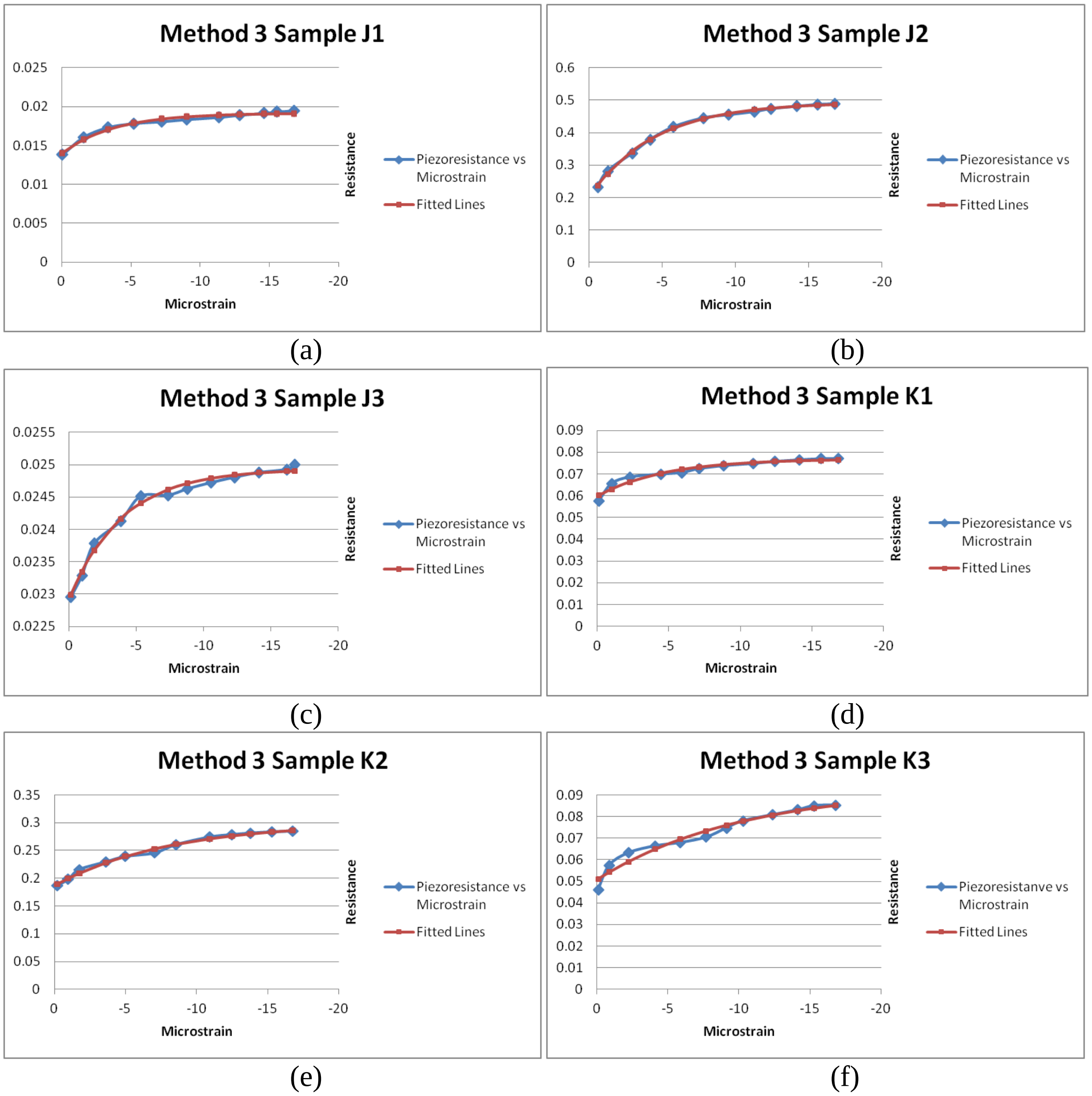


Figure 28. (a~f) Piezo-resistances vs strains of Sample Group J (J1 to J3) and K (K1 to K3) with co-polymer methods and their fitted lines using the Equation 9

The piezo-resistances of the samples using co-polymer method also follow well with the predictions of response using Equation 9. It indicates that the co-polymer dispersing method also dispersed the CNTs effectively so that the intertube resistance of CNTs dominates the performance of the piezo-resistive effects instead of intrinsic resistance. It reinforces the statement that Equation

9 can predict the piezo-resistance responses well if the dispersing method effectively disperses the CNTs in the cementitious matrix.

Table 2 summarizes all the coefficients of dispersing in Equation 9 of the three methods used for dispersing the CNTs. The average K_B and the standard deviation of the group G, group B and group J with samples containing CNTs only dispersed using different methods are plotted in Figure 29. The average K_B and standard deviation of the group H, group C and group K with samples containing CNTs with 0.1% graphite dispersed using different methods are plotted in Figure 30. It can be seen from Table 2 and Figures 28~29 that the dispersing coefficient, K_B, in equation 9 for direct mixing method yields zero, indicating not effective dispersing and no effective intertube resistance is activated using direct mixing method. The surfactant method showed very promising dispersing effectiveness for CNTs only modified cementitious materials with the largest average dispersing coefficient, K_B, of 0.1271 and a small standard deviation of 0.0992. The co-polymer method showed a fair dispersing efficiency with the dispersing coefficient of an average K_B of 0.0996, however, it showed a large standard deviation of 0.1663. In addition, Table 2 also shows that the intrinsic piezo-resistances for both surfactant and co-polymer methods yield a linear response coefficient from intrinsic resistance, k_1, in a range between 0.002 and 0.006 with small standard deviation, indicating that the intertube resistances in an effectively dispersed matrix will dominate the piezo-resistance effect. It is clearly seen from the figures and table that the developed theoretic model can clearly identify the influence of the dispersing effectiveness from different mixing methods.

When comparing the results between Group B and C, Group J and K in Table 2 and Figures 29~30, it clearly indicated that the additives of small faction of graphite will reduce the dispersing effectiveness of CNTs in cementitious materials. Thus, in practice, special analysis is recommended for adding graphite in CNTs modified cementitious materials, since it may not increase the piezo-resistance.

Table 3. Summary of coefficients in Equation 9 for all Groups with three different dispersing methods

	Group	Parameters	Sample 1	Sample 2	Sample 3	Average	Standard Deviation
Method 1 (Direct method)	G	K_B	0	0	0	0	0
		K_1	0.00009	0.00020	-0.00020	0.00003	0.000207
		K_3	15.5649	17.541	1.31896	11.475	8.85067
		C_A	0.90261	0.74185	2.66418	1.43621	1.06648
	H	K_B	0	0	0	0	0
		K_1	0.00030	0.00044	0.00150	0.00165	0.000656
		K_3	1.04893	0.33941	0.33093	0.57309	0.41211
		C_A	1.58E+09	2783.65	117.581	5.3E+08	9.1E+08
Method 2 (Surfactant)	B	K_B	0.05256	0.22927	0.09947	0.1271	0.09154
		K_1	0.00113	0.01143	0.00509	0.00588	0.0052
		K_3	0.02717	0.13573	0.13484	0.09925	0.06242
		C_A	0.30917	0.69794	1.3579	0.78834	0.53018
	C	K_B	0.01377	0.18007	0.00379	0.06588	0.09902
		K_1	0.00056	0.0086	0.00179	0.00365	0.00433
		K_3	0.06819	0.12762	0.10457	0.10013	0.02996
		C_A	2.4931	0.89599	1.20021	1.52977	0.84802
Method 3 (Co-polymer)	J	K_B	0.00521	0.29156	0.00201	0.09959	0.16626
		K_1	0.00026	0.01408	0.0001	0.00481	0.00803
		K_3	0.26794	0.2246	0.25143	0.24799	0.02187
		C_A	2.67562	0.69159	11.403	4.9234	5.6985
	K	K_B	0.01725	0.11375	0.0424	0.0578	0.05006
		K_1	0.0009	0.00574	0.00202	0.00289	0.00253
		K_3	0.2145	0.12358	0.0991	0.14573	0.0608
		C_A	3.46725	1.64563	1.19811	2.10366	1.20191

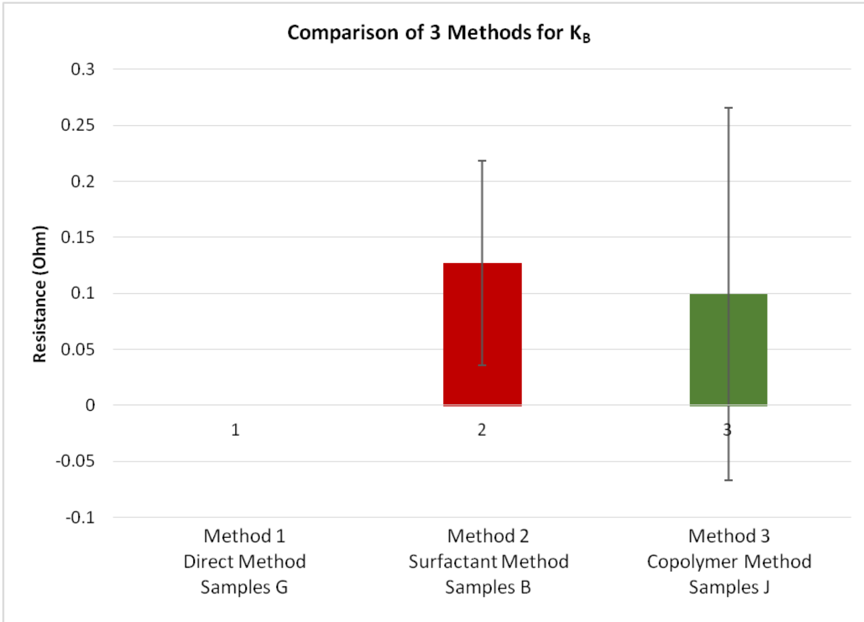


Figure 29. Average and standard deviation for value K_B for samples containing CNTs only

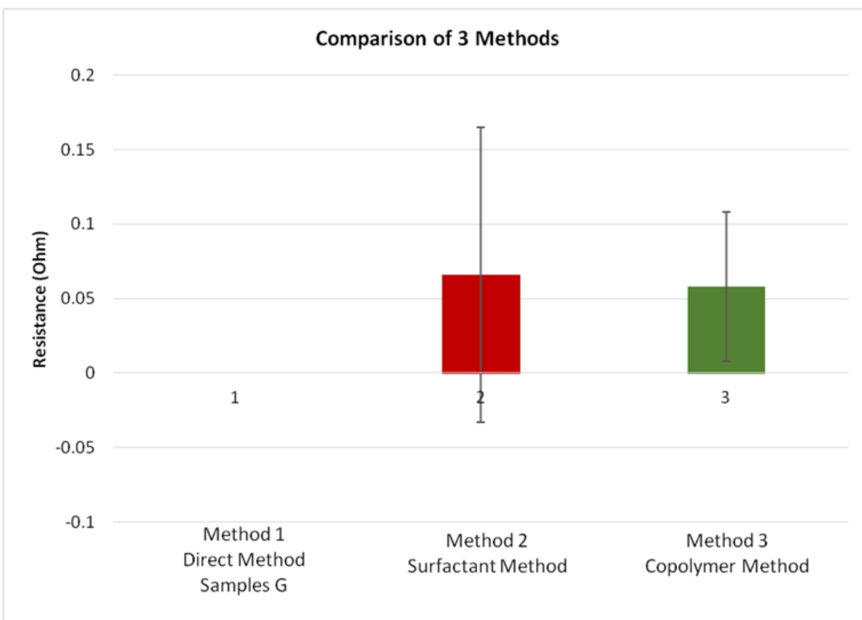


Figure 30. Average and standard deviation for value K_B for samples containing CNTs with 0.1% graphite

4.5. Summary

In this chapter, the piezo-resistance responses from the three different methods including direct mixing, surfactant, and co-polymer methods, are obtained, analyzed and compared with each other. The collected results are then used to validate the theoretic model developed in Chapter 2 to analyze the effect of dispersing methods on CNTs modified cementitious materials. The direct method of dispersing the CNTs showed lower piezo-resistance compared to the surfactant method and co-polymer method of dispersing the CNTs. The surfactant method turned out to be a very promising dispersing method and the co-polymer method works fairly well. However, more studies are needed to lower the standard deviations of the co-polymer method.

5. CONCLUSION AND FUTURE WORK

This thesis developed a theoretic model to analyze the dispersing effectiveness of various mixing methods of CNTs modified cementitious materials for self-sensing purpose using the piezo-resistance effect. The theoretic model was tested and validated using three different method of dispersing CNTs in cementitious material including direct mixing method, the surfactant method, and the co-polymer method. The conclusions of this study can be drawn as follows:

1. A theoretic algorithm to analyze the piezo-resistances in CNTs modified cementitious materials is derived with consideration of dispersing effectiveness;
2. The laboratory tests showed that the developed theoretic model can identify the dispersing effectiveness of mixing methods of CNTs in modified cementitious materials;
3. From the experimental results, it also showed that the direct method cannot uniformly disperse CNTs in cementitious materials, resulting in small piezo-resistance effects and no activation of intertube resistances of CNTs;
4. The surfactant method is an effective approach to disperse CNTs to be used in cementitious materials with high dispersing coefficient and small standard deviation;
5. The co-polymer method of dispersing CNTs to be used in cementitious materials can be effective, however, yields a large standard deviation;
6. The additives of small faction of graphite will reduce the dispersing effectiveness of CNTs in cementitious materials.

This study can serve as a reference to develop new dispersing methods of CNTs in cementitious materials. Future efforts will apply to lower the standard deviation of co-polymer methods and increase the sensitivity and resolution of the piezo-resistance response of the CNT modified self-sensing cementitious materials.

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