Carbon nanotube (CNT) reinforced cementitious composites using carboxymethyl cellulose (CMC) treatment for enhanced dispersion, mechanical, and piezoresistive properties

Leonard Chia [a,b], Ying Huang [a], Wenjie Xia [a], Pan Lu [b], and Dawei Zhang [a]*

[a] *Department of Civil, Construction and Environmental Engineering, North Dakota State University, USA 58108*

[b] *Upper Great Plains Transportation Institute, North Dakota State University, USA 58108*

**Corresponding author: North Dakota State University, CIE204, 1340 Administration Ave., Fargo, ND 58108, USA, Email: dawei.zhang.1@ndsu.edu; Phone: 701-799-8358; ORCID number: 0000-0002-0277-6342*

Abstract

Controlling CNT dispersion has been the key challenge for CNT nanocomposites. This study investigated the dispersion, mechanical and piezoresistive properties of CNT reinforced cementitious composites using carboxymethyl cellulose (CMC) treatment by comparing with three other existing mixing methods, including direct mixing, surface treatments using octenyl succinic anhydride (OSA) modified tapioca starch as a polymeric additive, and sodium dodecylbenzene sulfonate (NaDDBS) as a surfactant. The experimental results first indicated that the CMC treatment was categorized as a noncovalent functionalization and showed effectiveness in improving CNT dispersion, compressive strength, modulus of elasticity, Poisson ratio, and piezoresistive sensitivity of CNT reinforced cementitious composites.

Keywords: carbon nanotubes, cementitious composites, carboxymethyl cellulose, noncovalent functionalization, dispersion, mechanical properties, piezoresistive sensitivity

1. Introduction

Cement-based materials such as concrete are widely used in the construction of various civil structures, e.g. high-rise buildings, bridges, piles, etc. [1]–[3]. Conventionally, to improve both mechanical and electrical behaviors of the cement-based materials, carbon filaments and carbon fibers have been added as fillers in the cement to form cementitious composites [4], [5]. Although those carbon microfibers are capable of enhancing energy absorption and ductility of the cementitious composite through bridging the existing microcracks, they do not prevent crack initiation [6]. The attempt to constrain crack initiation has resulted in a new reinforcement through the addition of nanosized fibers within cement-based materials. Nanofibers improve not only strain capacity of cementitious matrix at the early age, but also the fracture properties of cementitious matrix by delaying crack initiation at the nanoscale level [7], [8].

Among all the nanofibers, carbon nanotube (CNT) possesses extremely high strength and stiffness [9]. The excellent mechanical properties of CNT manifest immense potential to be used as reinforcements in cement-based materials. Previous research showed that CNT reinforced cementitious materials exhibit remarkably higher flexural, tensile, and compressive strength than plain cement mortar in general [10]–[13]. However, the improvements of the mechanical properties of CNT reinforced cementitious materials vary significantly from around 10% to 85% as reported in the literature [14]–[16]. Several contributors to such variations of the improvements have been identified, including CNT dosage [17], dispersion, and geometries [18]. Among these factors, CNT dispersion or mixing procedure is of critical importance for the consistency of mechanical properties of any CNT reinforced composites.

Due to the extraordinary high aspect ratio of CNT (typically higher than 1,000 and reaching as high as 2,500,000), CNTs have strong intermolecular attractions to agglomerate or entangle with each other in the form of CNT clusters [19]. CNT clusters deteriorate the mechanical properties of CNT reinforced cementitious composites by inducing stress concentration and other detrimental impacts as defects or imperfections. Severe CNT agglomeration with a large amount of CNT clusters is an indication of non-uniform CNT dispersion [20]. It is widely believed that conventional dispersion methods using manual mixing or a standard mixer cannot guarantee a homogeneous CNT dispersion in the cement mortar [18], [21]. Therefore, dispersing CNTs uniformly in cementitious materials has always been a challenge. Since the advantageous properties of CNTs cannot be fully harnessed without good dispersion, the differences of mechanical properties obtained by the CNT reinforced cementitious composites in the literature may be induced by the different CNT dispersions.

Various dispersion techniques have been developed to achieve more uniform and stable CNT aqueous dispersion, such as sonication and CNT functionalization [21]. CNT dispersion by sonication have been found to be reversible over time due to the CNT re-agglomeration. CNT functionalization using chemical or physical admixtures are expected to maintain a consistent dispersion stability [22]. However, compared to chemical or covalent functionalization, physical or noncovalent functionalization is generally regarded as the more favorable method, given that it was found to provide a decent aqueous dispersion of CNTs as well as preserve the original chemical structure of the carbon system [23]–[25]. Surfactants such as sodium dodecylbenzene sulfonate (NaDDBS) and sodium dodecyl sulfate (SDS) along with polymeric additives such as starch and chlorinated polypropylene (CPP) are the most commonly used dispersion agents for noncovalent functionalization [26]–[27]. Noncovalent functionalization improves CNT dispersion by reducing the surface tension of CNTs as a result of electrostatic and/or steric repulsions

between the surfactant molecules which are absorbed on the CNT surface [24]. Literature indicates that noncovalent functionalization using surfactants or polymers have great potential to offer enhancement in mechanical and electrical properties of CNT reinforced cementitious composites [29]. However, current prevailing surfactants and polymeric additives have their own drawbacks. One major drawback of surfactants is the lack of connectivity of nanomaterials within cementitious matrix due to blocking of surfactant molecules, which often affects the electrical properties of the composite [30]. In addition, the interaction between CNTs and polymeric additives may cause energetically unfavorable conformation of the polymers, resulting in excessive interfacial strain and low dispersion consistency [23], [31].

Carboxymethyl cellulose (CMC) is a semi-synthetic derivative of cellulose produced by partial substitution of the -2, -3, and -6 hydroxyl groups of cellulose by carboxymethyl groups [32], which serves as one of the most popular admixtures in various industries. To date, a few previous studies found it is promising to use CMC as a dispersion agent for the purpose of modifying aqueous dispersion of nanomaterials such as CNTs [32]. However, these studies only focus on CNT dispersion characterizations or electrical properties of CNT reinforced cementitious composites, related investigations on mechanical properties or dispersion mechanism have not been reported yet. In addition, when proposing a new dispersion method or agent, most research studies only distinguish such a specific method or agent over pristine CNTs without any modifications; there are rather limited studies comparing the reinforcing efficiency of the proposed dispersion method with other well-established methods.

For the first time upon the authors' knowledge, this paper investigated the functionalization mechanism of the CMC treatment as a CNT dispersion method. The effects of the CMC treatment on both mechanical and piezoresistive properties of CNT reinforced cementitious composites were systemically by compared with three other well-established dispersion methods, surface treatment using one fashionable polymer, octenyl succinic anhydride (OSA) modified tapioca starch, and one prevailing surfactant, NaDDBS, along with traditional direct mixing. Fourier Transform Infrared (FTIR) analysis was conducted to categorize the functionalization mechanism of the CMC-based dispersion method. The CNT dispersion characterization was directly revealed by visual observation and transmission electron microscopy (TEM) analysis, and then quantitively compared by zeta potential measurement. The mechanical and piezoresistive properties of CNT reinforced cementitious composites including compressive strength, modulus of elasticity, Poisson ratio, and piezoresistive sensitivity were evaluated by compression tests.

2. Experimental Study

2.1 Materials

The CNTs used in this study were multi-walled CNTs (MWCNTs) supplied by SkySpring Nanomaterials, USA. It was reported that CNTs with large diameter and long length had superior reinforcing efficiency [18]. Accordingly, this study selected the MWCNTs with relatively larger diameter and longer length. The supplier's specification shows that the MWCNT particulates had an outer diameter of 50-100nm with an inner diameter of 5-10nm and a length of 5-20μm. The detailed predetermined properties of the MWCNTs are present in Table 1.

The OSA modified tapioca starch copolymer with a substation degree of 0.019 was selected as the polymeric additive since it has been reported that OSA modified tapioca starch was effective in dispersing several nanoparticles including CNTs in cementitious materials [33]–[35]. Commercially available OSA and native tapioca starches were purchased from Ingredion Inc, USA, which were used to synthesize the polymeric additive. The detailed synthesis procedures could be found in the literature [34]. The surfactant used in this study was NaDDBS ($CH_3(CH_2)_{11}C_6H_4SO_3Na$) obtained from Sigma-Aldrich Co., USA, which has found its vital applications of improving the CNT dispersion in polymeric and cementitious composites [36]–[38]. The sodium salt of CMC ($CH_3(CH_2)_{11}C_6H_4SO_3Na$) used in this study was also provided by Sigma-Aldrich Co., USA. The cementitious material as the composite matrix was Portland cement provided by Holcim, Inc., USA. Table 2 displays the major specific properties of the Portland cement, complying with the requirements of ASTM C150. The CNT concentration in all four different dispersion methods was selected to be 0.1% by weight of cement since a small amount of CNTs is sufficient for cementitious composites to attain satisfying mechanical and electrical properties improvements [30], [36], [39]–[41].

Parameter	Value
Type of CNT	Multi-walled
Outside diameter	50 – 100nm
Inside diameter	5 – 10nm
Length	5 – 20μm
Purity	> 95 wt %
Ash content	< 1.5 wt %
Specific surface area	> 60 m^2/g
Amorphous carbon content	< 3.0%
Bulk density	0.28 g/cm^3
True density	~2.1 g/cm^3

Table 1. Properties of the Carbon Nanotubes Used in this Study

Property	Value
Fineness, m/g	

Turbidimeter (min)	160
Air permeability (min)	280
Time of set	
Vicat (minutes)	
Initial (min)	45
Final (max)	375
Gilmore (minutes)	
Initial (min)	60
Final (max)	600
Air content (max)	12%
Autoclave expansion (max)	0.80%
Compressive strength (min)	
3 days, MPa	12
7 days, MPa	19

Table 2. Holcim Cement Physical Properties

2.2 Dispersion methods

In this study, four different dispersion methods were employed to disperse CNTs, including OSA modified tapioca starch, NaDDBS, and CMC treatments, along with direct mixing method. Before mixing with cement mortar paste, CNTs were first dispersed in water to promote dispersion. For the direct mixing, CNTs (0.4g) were gradually added into 240 mL of deionized (DI) water while mixing with a magnetic stirrer for 15 minutes.

As for the OSA modified tapioca starch based dispersion method, a 10 g/L (1%) OSA modified tapioca starch slurry was prepared in DI water based on previous studies [35], [42]. The starch slurry was first boiled and then cooled to 50°C while constantly stirring and heated overnight to produce a gelatinous solution. Then, CNTs (0.4g) were combined with 240 mL of starch slurry in multiple test tubes. To ensure a proper absorption of OSA modified tapioca starch onto the surface of CNTs, the slurry was sonicated for 30 minutes and further mixed in a rotator for 72 hours at a speed of 30 rpm.

For the preparation of NaDDBS functionalized CNTs, a critical micelle concentration of NaDDBS in water, 1.4×10^{-2} mol/L, was taken as the input surfactant concentration [22], [43]. The critical micelle concentration was derived from the strong hydrophobic attraction between the solid surface and the tail group of the surfactant. Once the NaDDBS is adsorbed onto the CNT surface, any additional surfactant molecules above the critical micelle concentration are self-assembled into micelles of 1.4×10^{-2} mol/L [22]. Thus, 1.17g of NaDDBS was added in 200 mL of water yielding a weight percentage of around 0.48%. After NaDDBS aqueous solution was magnetically stirred for 15 minutes, CNTs (0.4g) were added to the mixture followed by another 15-minute magnetic stirring. The same ultrasonication and rotating mixing as mentioned above were performed as the last step. The mixing procedures of

CMC were very similar to those of NaDDBS surfactant except that the CMC concentration was optimized at 0.5% based on the literature [33].

2.3 Dispersion characterizations

FTIR analysis was used to analyze the elemental compositions of CNT reinforced cementitious materials using different dispersion methods [44]. Pristine CNTs along with different dispersion agents were scanned using NicoletTM iS50 FTIR Spectrometer at a spectral range of 4000-400 cm^{-1} and a resolution of 4 cm^{-1}. In addition, a Colloidal Dynamics AcoustoSizer IIs was used to obtain the zeta potential of CNTs with different dispersion methods for quantitative comparisons. The testing conditions were controlled at a temperature of 25℃. Before taking any measurements, all CNT suspensions were ultrasonicated for another 15 minutes. For each dispersion method, three identical samples were prepared and assessed to ensure good reproducibility. TEM analysis was performed at the Electron Microscopy Core of North Dakota State University.

2.4 Preparation of CNT reinforced cementitious composites

To prepare CNT reinforced cementitious composites, 400g of cement were added into the well-mixed CNT suspensions. The water/cement ratio in this study was kept at a constant value of 0.6. Based on ASTM C109, the test sample of the CNT reinforced cementitious composites was designed as cubic blocks with a side length of 50 mm as shown in Figure 1. Two electrical wires with naked ends were placed and embedded approximately 20 mm apart from the edge of each block to capture electrical responses. In addition, strain gauges were adhered onto the surfaces of the samples to collect lateral and longitudinal strains of the cubic blocks for modulus of elasticity and Poisson ratio measurements according to ASTM C469. All samples were made and prepared at room temperature (22°C ± 2°C) and cured in water for 7 days. The curing time of 7 days was selected based on the common practice of cement composites samples used in field [44], [45]. For each dispersion method, six identical samples were made and tested. The test matrix is displayed in Table 3.

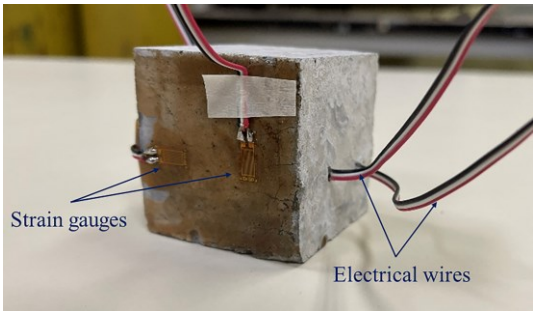


Figure 1. A test sample of CNT reinforced cementitious composites with electrical wires and strain gauges.

2.5 Compression tests

The mechanical and piezoresistive properties of CNT reinforced cementitious composites including compressive strength, modulus of elasticity, Poisson ratio, and piezoresistive sensitivity were determined by compression tests using MTS Flex Test® SE loading frame. The test sample were placed in the center of the lower platen so that the axis of the sample coincided with the center line of upper platen and the sample was under uniaxial compression. The displacement-controlled monotonic loading mode was adopted throughout the tests with a loading rate of 0.02 mm/s. The real-time loading and displacement were automatically recorded by the loading machine, while strain gauges and electrical wires collected strain and piezoresistive response by Model D4 Data Acquisition Conditioner (Micro-Measurements, Vishay Precision Group) and Digital Bench Multimeter (BK 5492B, B&K Precision, Inc., USA). Figure depicts the whole test configuration.

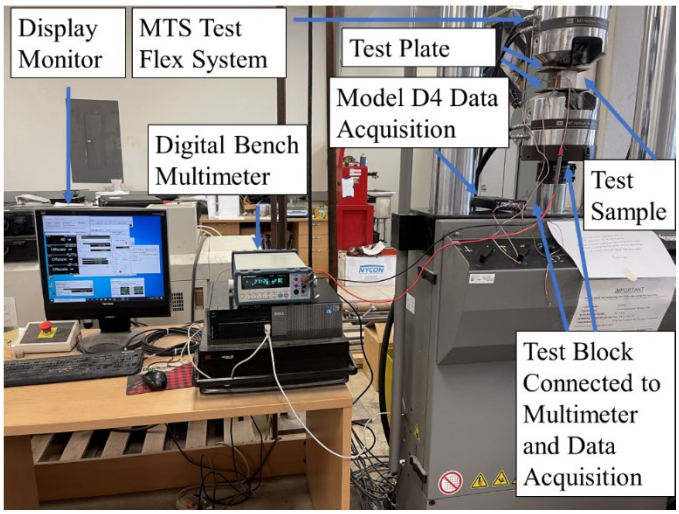


Figure 2. Test Configuration.

3. Results and Discussion

3.1 CNT functionalization

Although a few existing studies have reported the usage of CMCs for CNT functionalization, whether covalent functionalization engages in the CMC method has not been determined or proved yet. FTIR analysis was used in this study to categorize the functionalization mechanism of CMCs as well as differentiate the effectiveness among different dispersion methods. Figure 3 illustrates the comparison of FTIR spectra among pristine CNTs and CNTs with the three different dispersion agents. For pristine CNTs, the bands at 3357.55 cm^{-1} and 1094.48 cm^{-1} were attributed to the presence of hydroxyl groups (-OH) on the surface of CNTs, which are assumed because of the aqueous solution environment. The peaks at 1643.88 cm^{-1} corresponded to -C=C- stretching mode of the CNTs showing the

carbon system. The FTIR spectrum of pristine CNTs was consistent with the previous studies [45], [46]. By comparing the FTIR spectra between pristine CNTs and CNTs with the three different dispersion agents, it was noted that all the FTIR spectra exhibited similar peak locations. There was no new bond or functional group being formed after CNT functionalization, and no obvious difference was found among the three functionalized CNTs. Since OSA modified tapioca starch and NaDDBS are two well-defined noncovalent CNT functionalization methods without any chemical composition changes, it was verified that the CMC treatment method also fell into the category of physical or noncovalent functionalization which was expected to modify the CNT dispersion.

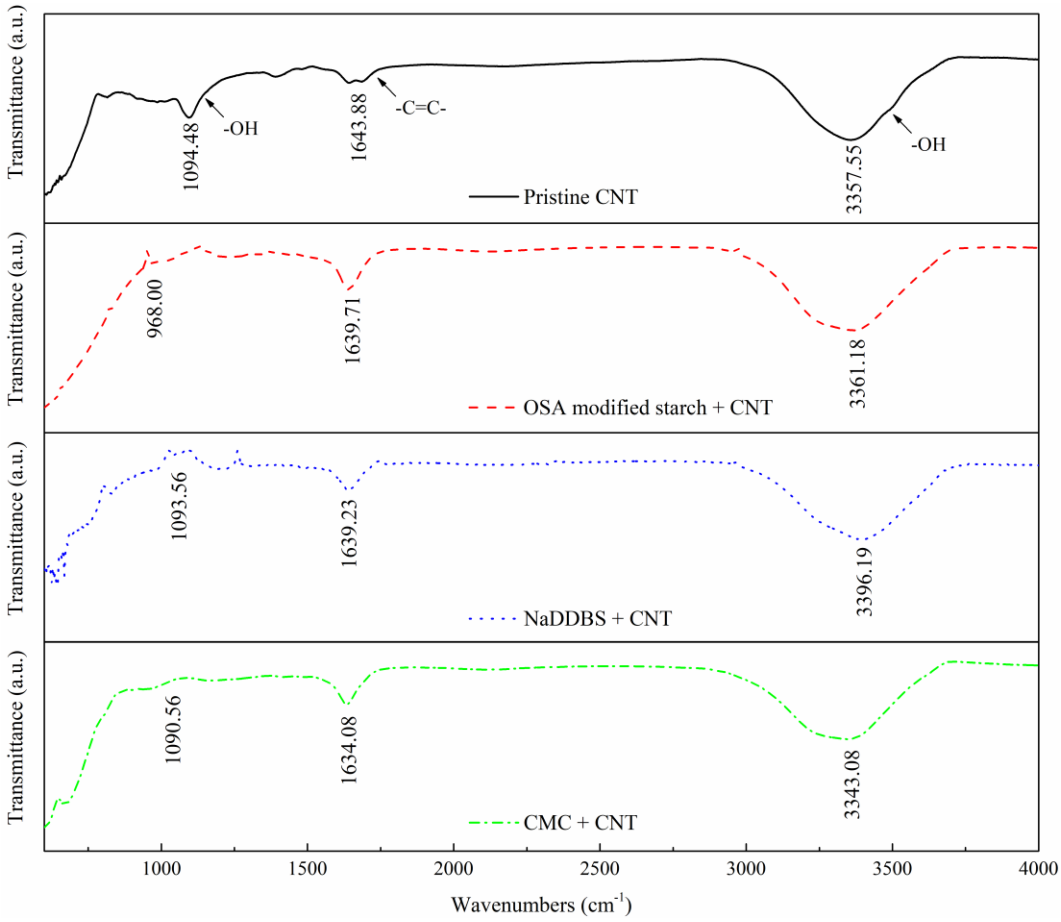
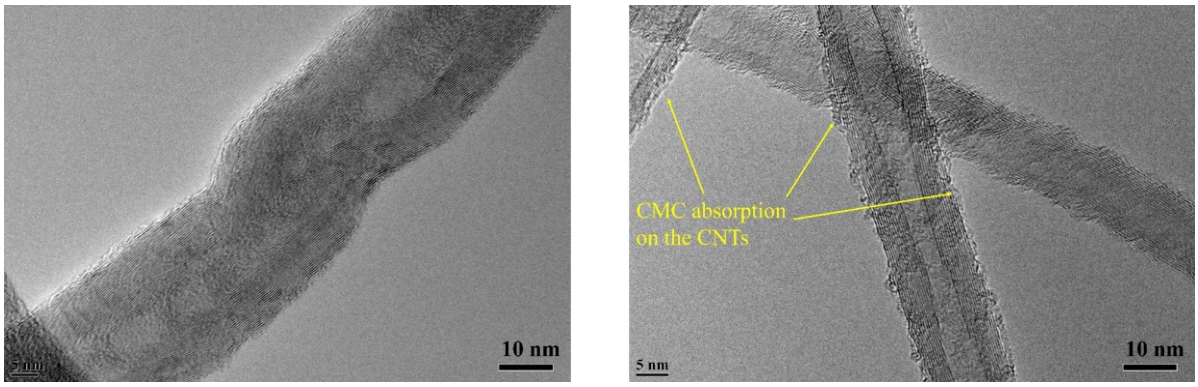


Figure 3. Comparison of FTIR spectra among pristine CNTs and CNTs with the three different dispersion agents.

The functionalization mechanism of CMC surface treatment method was further revealed by TEM analysis. Figure 4(a-b) show the TEM images of individual pristine CNT and CMC functionalized CNT at high magnification. Figure 4(a) shows that the pristine CNT had a smooth and plain sidewall. For the CMC functionalized CNT as shown in Figure 4(b), the boundary of the CMC functionalized CNT was rough and jagged with a thin amorphous layer surrounding the outside wall of the CNT, which was believed to result from CMC absorption on the CNT. Since the

mechanism of noncovalent CNT functionalization is to reduce the intensive intermolecular attractions of CNTs by attaching or absorbing on the surface of CNTs, it was confirmed that CMC surface treatment was another physical or noncovalent method to functionalize CNTs for CNT dispersion modification.

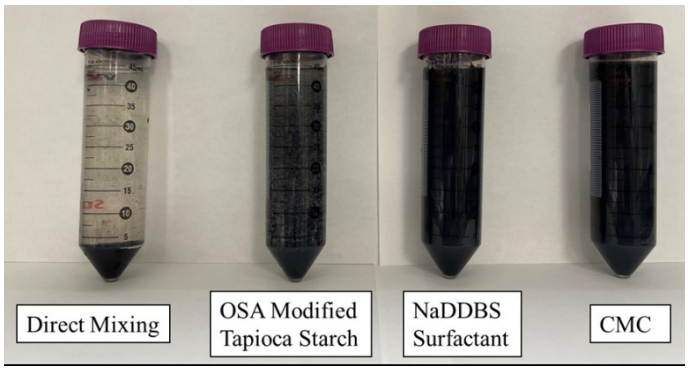


(a) (b)

Figure 4. TEM images of individual pristine CNT and CMC functionalized CNT at high magnification: (a) pristine CNT; (b) CMC functionalized CNT.

3.2 CNT dispersion

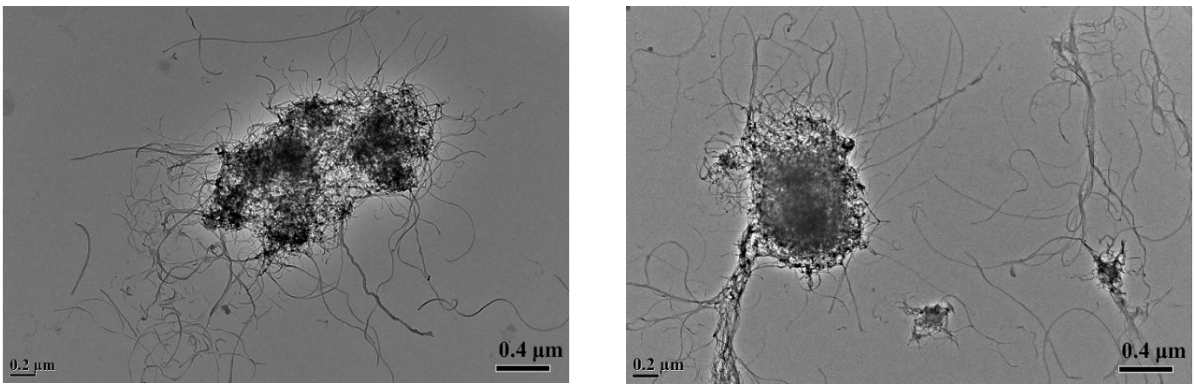
The dispersion characterization of CNT aqueous solutions was directly revealed by visual observation and TEM analysis. Figure (a-d) present the visual observations of CNTs with different dispersion methods after 30 minutes. From Figure 5(a) for pristine CNTs with direct mixing method, almost all the CNTs settled at the bottom of the test tube causing sever sedimentation. Without any functionalization, CNTs remained the instinct nature to agglomerate into large CNT clusters with higher density than water, indicating a typical non-uniform dispersion. According to Figure 5(b) for OSA modified tapioca starch functionalized CNTs, a large number of small CNT 'particles' were observed all over the solution without significant sedimentation. It was believed that CNT cluster sizes and the degree of agglomeration were reduced since the density of quite a lot of CNT 'particles' were similar to that of water, implying improved CNT dispersion. For NaDDBS and CMC functionalized CNTs as shown in Figure 5(c-d), there were no individual CNT 'particles' detected in the solution. The CNT aqueous solution turned completely dark reflecting a relatively uniform CNT dispersion.



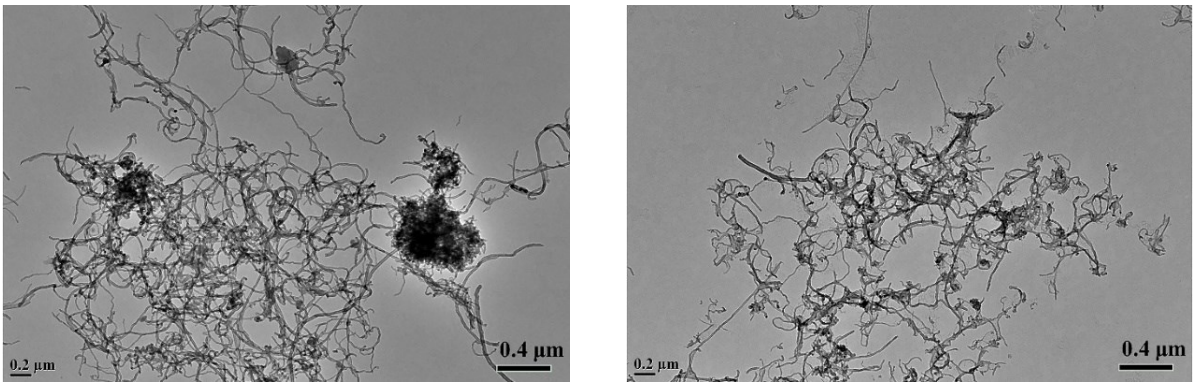
(a) (b) (c) (d)

Figure 5. Visual observation of CNTs with different dispersion methods: (a) direct mixing; (b) OSA modified tapioca starch; (c) NaDDBS; (d) CMC functionalization.

Figure 6(a-d) show the typical TEM images of CNTs with different dispersion methods. It was clear in Figure 6(a) that after direct mixing, CNTs primely stayed in the form of a sizable CNT cluster, and only a small proportion of CNTs was observed outside the cluster. Compared to direct mixing, the CNT agglomeration was not remarkably modified with OSA modified tapioca starch dispersion method as shown in Figure 6(b), even though a few undersized CNT clusters were found beside a giant cluster. The dispersion energy of OSA modified tapioca starch was not sufficient to overcome the strong interaction among the CNTs. From Figure 6(c) for NaDDBS functionalized CNTs, although small-sized CNT clusters still persisted, the majority of the CNTs were well dispersed suggesting a considerably improved dispersion. For CMC functionalized CNTs in Figure 6(d), the visible CNTs were homogeneously dispersed and free of any clusters.



(a) (b)



(c) (d)

Figure 6. Typical TEM images of CNTs with different dispersion methods: (a) direct mixing; (b) OSA modified tapioca starch; (c) NaDDBS; (d) CMC functionalization.

Zeta potential is an important indicator of the stability and dispersion of colloidal suspensions. By knowing the magnitude of the net surface potential (either positive or negative), the aggregation behavior of the colloidal particles could be predicted and reflected. Thus, in this study, zeta potential measurement was used to quantitively compare the CNT dispersion. Figure 7 illustrates the standardized zeta potential distributions as well as the zeta potential values with different dispersion methods. As shown in Figure 7, all the curves shared a pattern of normal distribution, and zeta potential values were obtained from the peaks of the curves. A high magnitude (absolute value) of zeta potential originates from high surface charge on CNTs with considerable electrostatic repulsion which prevents CNTs from agglomeration, otherwise CNTs with a low surface charge tend to agglomerate and entangle due to insufficient repulsion to overcome the strong van del Waals forces. The higher the zeta potential value, the more stable and uniform suspension dispersion. In general, colloidal suspensions with zeta potential above ± 30 mV is considered as stably and uniformly dispersed [47]. According to Figure 7, CMC functionalized CNTs produced a zeta potential value of 33.4 mV suggesting a good CNT dispersion. Although the zeta potential values of the rest dispersion methods were all below the critical threshold, NaDDBS functionalized CNTs attained a moderately smaller zeta potential of 26.1 mV, while the zeta potential values of CNTs with direct mixing and OSA modified tapioca starch were tremendously lower. Based on all the CNT dispersion characterizations above, it was evident that among all the dispersion methods included in the study, the CMC surface treatment method achieved the best effectiveness in CNT dispersion modification, implying great potentiality of pursuing advanced mechanical and electrical properties of CNT reinforced cementitious composites.

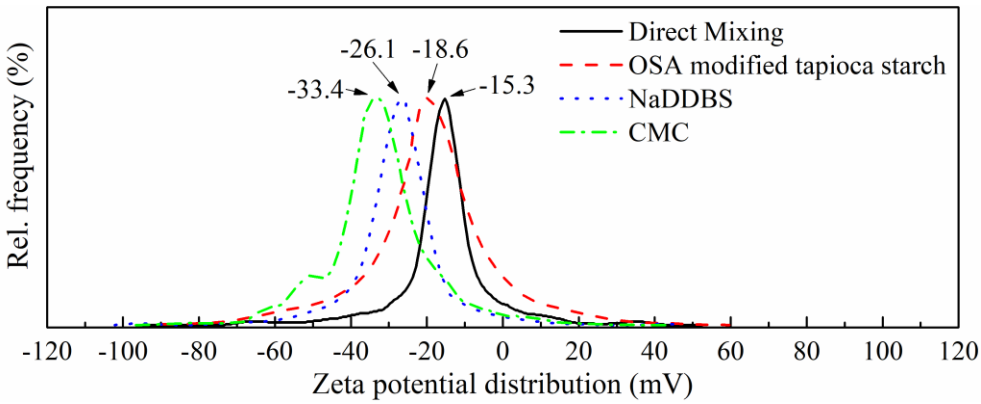


Figure 7. Zeta potential distributions.

3.3 Mechanical properties

Figure 8 shows the typical compressive stress-strain curves of CNT reinforced cementitious composites using various dispersion methods. Initially, all the stress-strain curves exhibited an approximate linear pattern, indicating the elastic range. Within the elastic range (40% of the failure strain based on ASTM C469), the stress was nearly proportional to the strain, and the slope or proportion between the stress and the strain was used to estimate modulus of elasticity of the composites. After the elastic range, the curves entered the non-linear portion, and the composites began to show plastic behavior until reaching the maximum stress which is defined as the compressive strength.

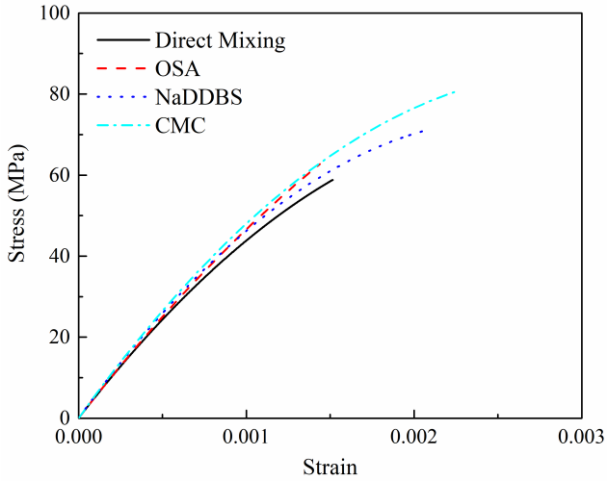


Figure 8. Compressive stress-strain curves.

Figure 9 summarizes the compressive strength and modulus of elasticity of CNT reinforced cementitious composites using various dispersion methods. From Figure 9, the CNT reinforced cementitious composites by direct mixing had a compressive strength of 58.62 MPa and a modulus of elasticity of 34.01 GPa, whereas neither of the two parameters with OSA modified tapioca starch significantly differed from those with direct mixing method producing

a compressive strength of 62.91 MPa and a modulus of elasticity of 37.67 GPa. CNT reinforced cementitious composites mixed by NaDDBS and CMC dispersion method, however, acquired 20.2% and 37.3% improvements in compressive strength reaching 70.45 MPa and 80.51 MPa, as well as 42.2% and 49.0% in modulus of elasticity reaching 48.35 GPa and 50.66 GPa, respectively.

The variation of the compressive strength and modulus of elasticity with different dispersion methods could be interpreted by the variation of CNT dispersion. Among the three dispersion methods, CMC treatment method was shown to be the most effective dispersion method followed by NaDDBS and OSA modified tapioca starch method, while direct mixing as the last. A uniformly dispersed CNTs conceivably provided a massive surface area for the precipitation of the cement hydrates, which contributed to the formation of denser cementitious materials with high stiffness and therefore improved such mechanical properties of CNT reinforced cementitious composites [48]. Moreover, the CNT clusters as the indicator of non-uniform dispersion, had the same detrimental effect as defects and imperfections causing stress concentration and reduction in bond between CNTs and surrounding cement [49], [50].

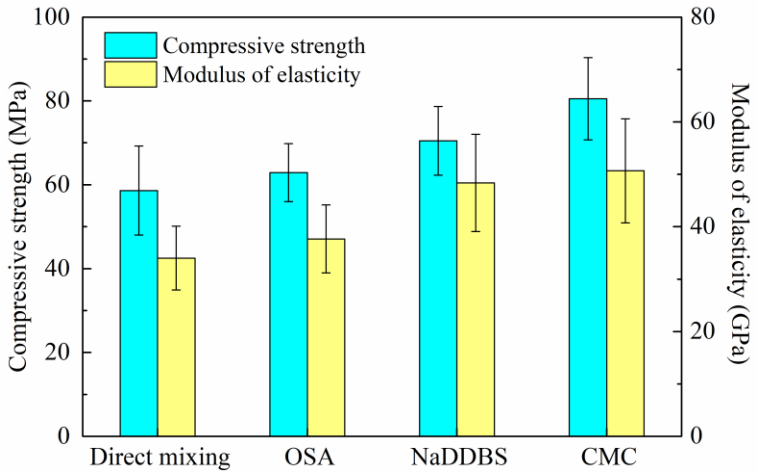


Figure 9. Comparison of compressive strength and modulus of elasticity with different dispersion methods.

Poisson ratio also plays a crucial role in the mechanical properties of cementitious materials. The Poisson coefficient was calculated from the ratio between the longitudinal strain in the loading direction and the lateral strain of the test sample. Figure 10 displays the Poisson ratio of CNT reinforced cementitious composites with different dispersion methods. For direct mixing method, the Poisson coefficient was estimated to be 0.151, which was consistent with previous research [51]. For OSA modified tapioca starch and NaDDBS functionalization, the Poisson ratios increased to 0.161 and 0.169 with the increments of 6.6% and 11.8% respectively. For CMC treatment method, a notable (21.2%) improvement was obtained producing the Poisson ratio of 0.183. The difference in Poisson ratio of

CNT reinforced cementitious composites with different dispersion methods could be attributed to the same mechanism as the earlier discussion of compressive strength and modulus of elasticity. Better CNT dispersion contributed to the improvements of loading capacity and deformability of CNT reinforced cementitious composites, while CMC functionalization method was able to achieve more desirable mechanical properties.

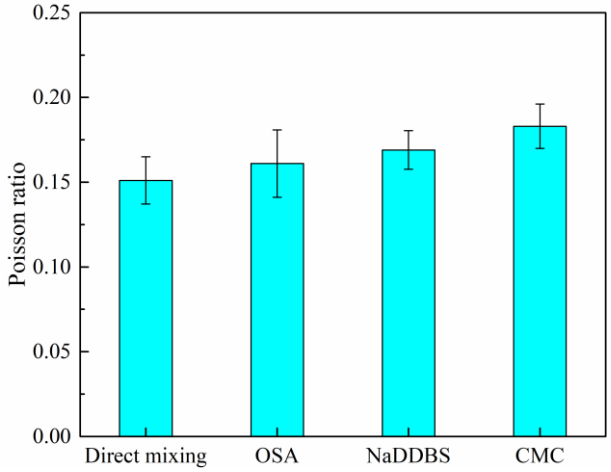


Figure 10. Comparison of Poisson ratio with different dispersion methods.

3.4 Piezoresistive properties

One of the major applications of CNT reinforced cementitious materials is smart concrete with self-sensing ability. CNTs with outstanding electrical properties are promising to provide cementitious materials with piezoelectricity with which the stress or strain of concrete structures could be measured and monitored by their electrical parameters such as electrical resistance, capacitance or impedance [33], [34]. In this study, the piezoresistive response was the change in the electrical resistance of CNT reinforced cementitious composites as an indication of compressive stress. Figure 11(a-d) presents the typical piezoresistive responses of CNT reinforced cementitious composites with different dispersion methods throughout the compression period. It was obvious that the piezoresistive response of CNT reinforced cementitious composites by direct mixing was rather limited, with the electrical resistance change of only 0.1114 Ohm. Considerable improvements were seen for cementitious composites with CNT functionalization, with the piezoresistive responses of OSA modified tapioca starch, NaDDBS, and CMC functionalization reaching 0.4194 Ohm, 0.6018 Ohm, and 1.0802 Ohm, respectively.

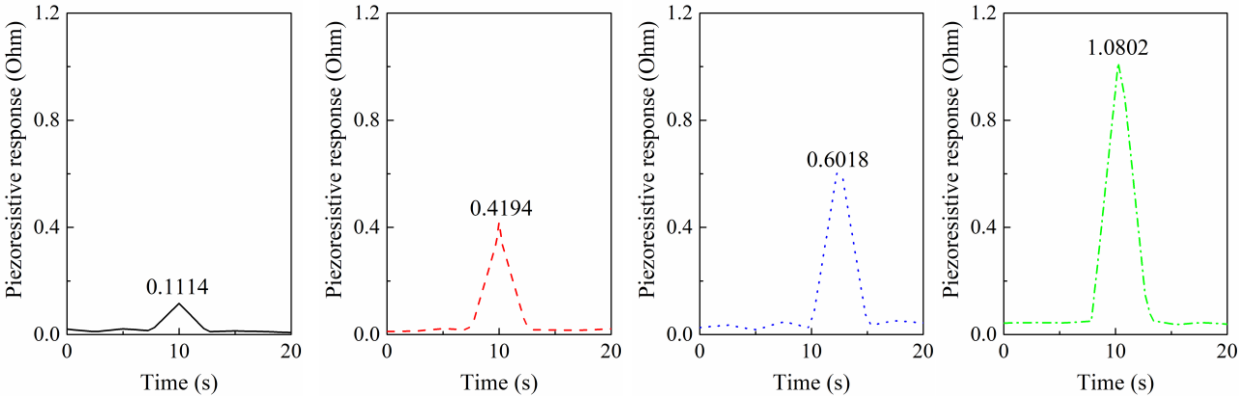


Figure 11. Piezoresistive responses of CNT reinforced cementitious composites with different dispersion methods: (a) direct mixing; (b) OSA modified tapioca starch; (c) NaDDBS; (d) CMC functionalization.

Since different cementitious composites experienced different stress during the compression, in order to fairly evaluate the piezoresistive properties among different dispersion methods, the piezoresistive sensitivity (S) was specified as the relative electrical resistance change with the change of stress [30], [52]:

$$S = \frac{\Delta R}{\Delta \sigma} = \frac{R - R_0}{\sigma - \sigma_0} \quad (1)$$

In this study, R_0 and σ_0 were both zero before the composites being compressed, while R_p and σ_p were the peak electrical resistance and peak stress (compressive strength). Thus Equation 1 was expressed as:

$$S = \frac{R_p}{\sigma_p} \quad (2)$$

A higher piezoresistive sensitivity indicates a larger electrical resistance change with unit change of stress indicating better piezoresistive properties for more attractive sensing applications in the field. Figure 12 shows the piezoresistive sensitivities of CNT reinforced cementitious composites with different dispersion methods. The piezoresistive sensitivity of CNT reinforced cementitious composites with direct mixing was rather low with merely 1.901×10^{-3} Ω/MPa. It was found in the previous sections that directly mixed CNTs usually did not provide a uniform CNT dispersion. Since a sound piezoelectricity requires a uniform dispersion of CNTs within the composite matrix so that the CNTs could build up a continuous and extensive conductive network [53], agglomerated CNTs by direct mixing failed to provide a robust conductive network for an acceptable piezoresistive property. For OSA modified tapioca starch and NaDDBS dispersion methods, the piezoresistive sensitivities increased significantly reaching 6.667 $\times10^{-3}$ Ω/MPa and 8.542 $\times10^{-3}$ Ω/MPa, respectively. It was highlighted that CNT reinforced cementitious composites with CMC treatment method achieved a significantly higher piezoresistive sensitivity of 13.423 $\times10^{-3}$ Ω/MPa.

Compared to the other three dispersion methods, it was 101.3% and 57.1% improvements as those of OSA modified tapioca starch and NaDDBS methods respectively, besides more than 7 times as that of direct mixing.

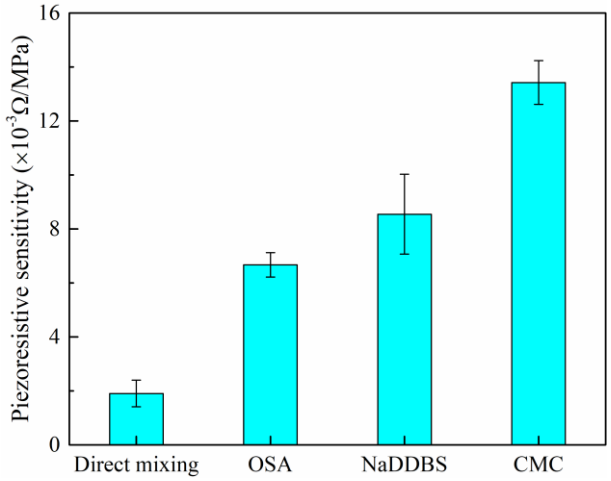


Figure 12. Comparison of Piezoresistive sensitivity with different dispersion methods.

As discussed previously, there was no doubt that the well-dispersed CNTs promoted piezoresistive properties of CNT reinforced cementitious composites. It is also worth highlighting that CNTs functionalized with carboxyl group (OSA modified tapioca starch, NaDDBS, and CMC) and hydroxyl group (CMC method only) have distinct physical properties and are more hydrophilic in comparison with non-functionalized CNTs (direct mixing method) [34], [54], [55]. Such functionalized CNTs are more prone to develop strong chemical bond with the surrounding cement matrix. In addition to better CNT dispersion, the superior mechanical and piezoresistive properties of CNT reinforced cementitious composites with CMC treatment method could also be interpreted by the distinctive functional groups of the CMC.

4. Conclusions

This study systematically investigated the dispersion, mechanical, and piezoresistive properties of CNT reinforced cementitious composites using the CMC dispersion method compared to traditional direct mixing, noncovalent functionalization using OSA modified tapioca starch as a polymeric additive, and NaDDBS as a well-established surfactant. It was shown by FTIR and TEM analyses that the CMC treatment method on CNTs was a physical or noncovalent surfactant as OSA modified tapioca starch and NaDDBS. TEM analysis and zeta potential measurement further indicated that the CMC treatment method was more effective in CNT dispersion modification, followed by NaDDBS and OSA modified tapioca starch methods, while direct mixing as the last. For the mechanical properties, the compressive strength, modulus of elasticity, and Poisson ratio of CNT reinforced cementitious

composites with CMC dispersion method attained significant improvements, compared to the direct mixing method. The corresponding improvements of OSA modified tapioca starch and NaDDBS dispersion methods were less remarkable than CMC method. Regarding piezoresistive properties, the CNT reinforced cementitious composites with CMC treatment method have shown superior piezoresistive sensitivity over the other three dispersion methods, which could be interpreted by the more uniformly dispersed CMC functionalized CNTs and the functional groups (carboxyl and hydroxyl groups) of the CMC. These investigations may assist the related industries for more consistent field applications of the CNT reinforced cementitious composites. Further field applications of the CNT reinforced cementitious composites using the CMC treatment method can be the potential future work of this study.

CRediT authorship contribution statement

Leonard Chia: Data curation, Formal analysis, Investigation, Writing - original draft. **Ying Huang**: Project administration, Methodology, Funding acquisition, Supervision, Writing - review & editing. **Wenjie Xia**: Supervision, Writing - review & editing. **Pan Lu**: Funding acquisition, Supervision, Writing - review & editing. **Dawei Zhang**: Methodology, Formal analysis, Investigation, Writing - review & editing.

Declaration of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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