

Preparation and Smart Properties of Carboxylated Carbon Nanotube Reinforced Cement-Based Composites

Xinhui Jiang *, Jiahui Luo, Xiaochen Su, Wenping Li, Dehui Song, Lin Wei

University of Science and Technology, Anshan Liaoning, 114100, China

* Corresponding author: Xinhui Jiang

Abstract: This study investigated the influence of the outer diameter of carboxylated carbon nanotubes (CNTs) on the electrical conductivity and piezoresistive characteristics of cement-based composites. Specimens incorporating CNTs of varying outer diameters were prepared using ultrasonic dispersion technology. Under a constant pressure of 10 MPa, the relationship curve between CNT outer diameter and the rate of resistivity variation was analyzed, revealing that the composite's state governs its piezoresistive response characteristics. The experimental results demonstrate that the outer diameter of the CNTs significantly affects the stability of both the electrical resistance and the piezoresistive performance of the composites. When the CNT outer diameter falls within the range of 25-35 nm, the material exhibits optimal comprehensive performance, achieving both a stable conductive network and high-sensitivity piezoresistive response simultaneously.

Keywords: Electrical Resistivity; Piezoresistance; Cement-based Composites; Carbon Nanotubes.

1. Introduction

In recent years, with the large-scale construction and continuous improvement of intelligent buildings and new infrastructure in China, the construction industry is ushering in a new stage of rapid development and technological innovation. Some large-scale infrastructure projects have put forward more stringent requirements for building materials, attracting widespread attention. However, during the service life of buildings, the quality problems of cement-based materials have become increasingly complex. The key issue lies in the obvious shortcomings in key electrical energy indicators such as real-time monitoring and intelligent early warning of building structural health status, which have hindered the multi-functional and intelligent development of building materials and their impact on engineering quality has become increasingly prominent. At the same time, frequent natural disasters and material aging often lead to various safety accidents, resulting in significant property losses and casualties. As the core material of modern buildings, cement-based materials are required to have not only high strength, high toughness, durability, workability, volume stability, and sustainable environmental protection, but also smart characteristics. Thus, conductive cement-based composites have emerged as the times require, opening a new chapter in the intelligence of building materials. Conductive cement is a composite material that makes the cement matrix conductive by incorporating conductive materials (such as carbon fiber); piezoresistivity refers to the characteristic that its resistance changes with stress, which can be used for structural self-monitoring. Therefore, by endowing traditional building materials with conductive and piezoresistive properties, conductive cement realizes structural health self-monitoring and intelligent early warning, significantly improving building safety and durability.

Nowadays, many scholars have proposed various solutions to address the issue of "difficulty in implementing health monitoring of building structures" using conductive cement.

Initially, scholars commonly used materials such as steel slag and carbon black to produce conductive cement.

Peng Jia et al. [1] prepared conductive cement bricks by compounding steel slag and steel shavings. The results showed that with the increase of steel shavings content, the variation law of resistance was related to the change of contact resistance of the electrode mesh and the thermal expansion effect of steel shavings. With the deepening of research, the types of conductive fillers have become rich, including steel fibers, carbon fibers, metal fillers, and some highly conductive nanomaterials. Jiang Yongsheng [2] used carbon fibers and nano-carbon black to prepare composite cement-based materials. The research results indicated that the addition of carbon fibers or nano-carbon black would have a significant impact on the fluidity and electrical conductivity of cement-based materials.

Among them, nanoscale fillers (such as graphene and carbon nanotubes) have opened up new paths for the large-scale production of smart cement due to their characteristics of high strength, durability, versatility, high electrical conductivity, and low specific surface area. Carbon nanotubes are nanoscale hollow tubular structures composed of carbon, with high strength, high electrical conductivity, and unique physical and chemical properties. Some researchers have conducted studies on nanotube-modified cement-based materials. Guo Miaocai et al. [3] prepared carbon nanotube (CNT)-modified and CNT/multi-layer graphene (MLG) co-modified fabrics and their composite materials using a coating method. Conductivity studies showed that the conductivity of CNT-hybridized and CNT/MLG co-hybridized fabrics was significantly improved, and the corresponding composite materials showed significant increases in through-thickness electrical conductivity (σ_z) and in-plane electrical conductivity, respectively. Lou Xiaoqiang [4] et al. studied the effects of different contents (0.1% and 0.5%) of carbon nanotubes and graphene nanoplatelets on the pore structure of cement-based composite materials. The pore structure was analyzed using the nitrogen adsorption test NLDFT model

and compared with the traditional BET and BJH models. The results showed that the composites doped with CNT and GNP could improve the compressive strength and reduce the pore volume of the cement matrix.

With the in-depth research on nanotubes in the field of cement-based materials, many researchers have found that functionalized nanotubes are more suitable for the needs of conductive cement. Carboxylated nanotubes (COOH-functionalized nanotubes) are a type of functionalized nanomaterial prepared by introducing carboxyl (-COOH) functional groups on the surface of carbon nanotubes (CNTs), which significantly improve the dispersibility, reactivity, and biocompatibility of the nanotubes, and promote the solution to the problem of easy agglomeration of nanomaterials in cement-based materials. Zhao Weidong [5] oxidized carbon nanotubes with concentrated sulfuric acid and concentrated nitric acid, observed the dispersion of carbon nanotubes and the structure of the material by transmission electron microscopy and scanning electron microscopy, then studied the mechanical and thermal properties of the material, and discussed its influence on the structure and properties of the composite material. The experimental results showed that the oxidized CNTs were well dispersed in the matrix, had good compatibility between the two phases, the mechanical properties of the material were improved, and the longer the carbon nanotubes were acidified, the better the high-temperature resistance.

Jia Hui [6] et al. prepared a carboxyl-functionalized carbon nanotube dispersion using a dilute acid oxidation process to verify the effect of carboxyl-functionalized carbon nanotubes on improving the mechanical properties of cement paste. The results showed that carboxyl functionalization could reduce the particle size of carbon nanotubes by 89.71% and convert hydrophobic materials into hydrophilic materials. At the same time, the dispersion stability of carboxyl-functionalized carbon nanotubes in water was improved by 100%; 0.005% addition of carboxyl-functionalized carbon nanotubes increased the compressive strength of cement paste by 16.05%, flexural strength by 25.82%, and tensile strength by 18.07%.

Zhu Zhongbo [7] successfully prepared a carbon nanotube-copper hybrid (CNTs-Cu) with superhydrophobic properties by surface modifying hydroxyl multi-walled carbon nanotubes and nano-copper powder. Studies have shown that the coating exhibits excellent anti-biofouling performance and corrosion resistance (corrosion current density as low as 9.55×10^{-8} A/cm²), providing a new high-performance coating solution for the field of metal corrosion protection.

Li Lixiang [8] et al. oxidized carbon nanotubes using mixed acid, air, nitric acid, and potassium permanganate respectively to introduce functional groups on their surfaces, and then studied the effect of surface functional groups on the electrochemical properties of carbon nanotubes. The results showed that the obtained carbon nanotubes had similar specific surface areas and pore structures. Carbonyl and carboxyl groups contributed the most pseudocapacitance, and in particular, the carbonyl content was proportional to the capacitance of the carbon nanotubes. Since carbonyl and carboxyl groups have lower charge transfer resistance than hydroxyl groups, they facilitate rapid Faraday reactions, thereby introducing pseudocapacitance. Lu Yang [9] et al. studied fly ash@multi-walled carbon nanotubes (MWCNTs) core-shell heterojunctions and their piezoresistive sensitivity in conductive cement, proving that fly ash@MWCNTs

heterojunctions can effectively improve the sensing performance of conductive cement composites.

At present, carboxyl carbon nanotube-reinforced cement-based materials are one of the current hotspots in the interdisciplinary field of nanomaterials and civil engineering. Due to their excellent dispersibility and interface bonding properties with the cement matrix, they show good application potential in cement-based composites. Studies have shown that carboxyl nanotubes can effectively improve the mechanical properties and durability of cement-based materials. Zhao Jingwei [10] studied the influence of carbon nanotubes and graphene on the mechanical and electrical properties of cement-based materials. The results showed that the ability of the cement-based composites to form a conductive network internally was enhanced, indicating that nanomaterials have a significant improvement effect on the mechanical properties and electrical conductivity of cement-based composites. However, the influence on their electrical conductivity and piezoresistive properties has not yet been systematically studied, especially the influence of the diameter and length of carboxyl carbon nanotubes on electrical conductivity remains unclear. In view of this, this paper aims to systematically study the influence of the diameter and length of carboxyl nanotubes on the electrical conductivity and piezoresistive properties of cement-based composites, in order to provide key theoretical basis for the design and development of functional cement-based materials.

2. Methodology

(1) Raw Materials and Instrument

Cement, standard sand; Graphene oxide; Carboxylated multi-walled carbon nanotube powder, produced by Suzhou Tanfeng Graphene Technology Co., Ltd.; Water reducer: A mixture of sodium dodecyl sulfate and methylcellulose in a mass ratio of 5:1 was used as a dispersant, with the concentration of SDS added being 2.0 g/L and the concentration of MC added being 0.4 g/L; Stainless steel mesh; Ultrasonic disperser; Magnetic stirrer; Electronic balance; Multimeter; Press machine.

(2) Preparation of Experimental Materials

1) Pretreatment of Composite Cement-Based Materials

Five groups of materials were weighed respectively: 450g of cement, 1350g of sand, 225g of water, and 0.9g of water reducer. Additionally, 0.36g of nanotube water reducer with the same total weight but different tube lengths and diameters was prepared. The water-cement ratio was 0.5, the cement-sand ratio was 1:3, and the water reducer dosage was 0.2%.

	Cement/g	Sand/g	Water/g	Water-reducing agent/g	CNT/g
C0	450	1350	225	0.9	0
C1	450	1350	225	0.9	0.36
C2	450	1350	225	0.9	0.36
C3	450	1350	225	0.9	0.36
C4	450	1350	225	0.9	0.36

Fig 1. Mix proportion of cement mortar.

2) Preparation of Aqueous Nanomaterial Dispersion.

First, polycarboxylate superplasticizer was added to water and magnetically stirred (300 r/min for 2 min followed by 2000 r/min for 5 min). Then, nanotube dispersant was added, and magnetic stirring was repeated. After uniform dispersion in water, nanotubes were slowly added and stirred at low speed for two minutes. The mixture was then subjected to

ultrasonic dispersion for 30 min. To prevent evaporation and control temperature, the beaker mouth was covered with plastic wrap during the entire stirring and ultrasonic process to prevent evaporation, and the mixture was cooled in a water bath after ultrasonication.

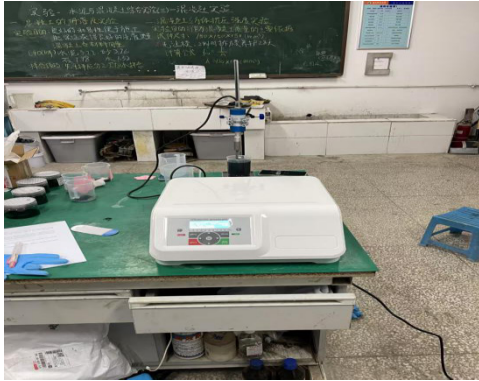


Fig 2. Schematic diagram of dispersion by ultrasonic disperser.

(3) Specimen Preparation Process

First, the mixing bucket was cleaned and thoroughly dried. The weighed cement and sand were put into a cement mortar mixer and dry-mixed for 2 minutes. Then, the room-temperature nanomaterial dispersion was slowly added into the mixing pot, followed by stirring at low speed (120 r/min) for 60 seconds and then at high speed (280 r/min) for 120 seconds in sequence.

1) Casting and vibration

The inner walls of the 40mm×40mm×160mm specimen molds were oiled to prevent adhesion. After pouring the cement mortar, the molds were placed on a cement mortar vibrating table and vibrated for 1 minute. Subsequently, the surface was smoothed to ensure density and flatness, and finally covered with plastic wrap to prevent moisture loss.

2) Placing the electrodes

After the initial vibration was completed, two pieces of 40mm × 60mm 10-mesh stainless steel mesh were inserted in parallel along the midline of the specimen as electrodes using the four-electrode method. The spacing between the inner electrodes was 60mm, the spacing between the outer electrodes was 100mm, and they were placed in parallel with a burial depth of 40mm. Subsequently, secondary vibration was performed to compact the mortar around the electrodes.



Fig 3. Physical picture of the insertion position of the steel mesh by the four-probe method.

3) Demolding, curing and drying

The molds containing the cement paste were placed in a standard curing chamber at a temperature of $20.0 \pm 2^\circ\text{C}$ and a relative humidity of 95%, and left to stand for 24 hours before demolding. The specimens were then placed in room-temperature water for natural curing until 48 days, after which the surface moisture was wiped off. They were then placed in an oven to dry to a constant weight, and subsequently cooled

to room temperature in a desiccator.

Compression Test on Cement-Based Composite Specimens

The change in resistance is an important parameter for evaluating the effect of adding nanotubes with different lengths and diameters. Therefore, the five prepared groups of specimens were each subjected to a pressure of 10 MPa to observe the range of resistance change.

A press machine was used to apply pressure to the specimens. The specimens were placed vertically in the center of the test bench, ensuring that the upper and lower surfaces were vertically aligned with the center of the indenter to prevent uneven force or instability. A multimeter and a computer were connected for real-time data collection of current and voltage.

The circuits were checked to confirm all connections were correct. The press machine, multimeter, and computer were debugged to ensure normal data transmission. After that, electrical pre-treatment was performed, and pressure was applied only after the multimeter data stabilized.

After starting to apply pressure, the press machine data, multimeter current values, and voltage values were recorded synchronously to monitor the relationship between stress and resistance in real-time. After the test, the data was saved, and the next group of experiments was conducted.



Fig 4. Compression test of composite material specimens.

3. Experimental Results and Analysis

The measurement results are shown in the figure. By comparing the effects of carboxylated carbon nanotubes with different outer diameters on the electrical and piezoresistive properties of cement mortar, an attempt was made to explore the relationship between the microstructural characteristics of nanotubes and the macroscopic electrical response. In Fig. 6, the initial resistivity of the control group C0 specimen is as high as $6097.55 \Omega \cdot \text{m}$. Its piezoresistive property originates from the limited adjustment of contact points of inherent pores inside the cement matrix. Under external pressure, although the resistance shows a monotonous decrease, the resistivity only decreases by $212.39 \Omega \cdot \text{m}$ to $5855.16 \Omega \cdot \text{m}$, corresponding to a low rate of change of $0.03 \Omega \cdot \text{m}^{-2}$. This phenomenon reflects the inherent weak electrical conductivity of traditional cement-based materials and also indicates that pure cement mortar does not exhibit piezoresistive properties. This is due to the severe lack of carrier transport paths in the unmodified system. Its conduction mechanism mainly relies on the combined effect of ionic migration and contact conduction, and the high impedance characteristic dominated by ionic migration leads

to hysteresis in the piezoresistive response, with external loads having no significant impact on the resistance value of

the specimen.

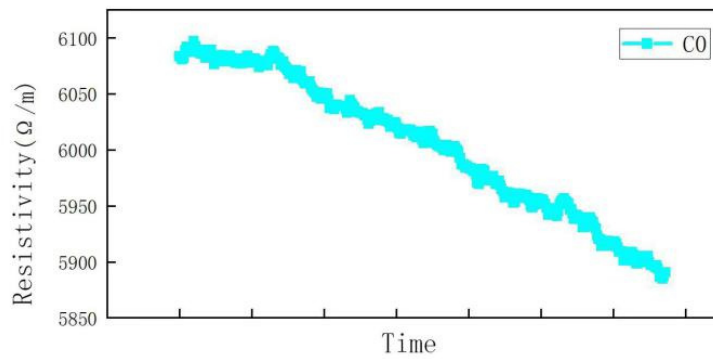


Fig 5. Effect of non-added carboxylated carbon nanotube powder on resistance change.

The experimental data in Fig.7 shows that the modified specimens with carboxylated carbon nanotube powder exhibit superior electrical conductivity and piezoresistive properties. Among the experimental group specimens, the maximum initial resistivity of C1 is 3461.59 $\Omega\cdot m$, while the initial resistivity of C2 is further reduced to 1120.29 $\Omega\cdot m$, a decrease of 43.23% compared with the control group, indicating a

significant improvement in electrical conductivity. Under pressure, C1 and C2 show excellent piezoresistive responses, with resistance changes as high as 2341.30 $\Omega\cdot m$ and 2287.74 $\Omega\cdot m$, respectively; the resistance changes of C3 and C4 are the next, 1629.44 $\Omega\cdot m$ and 1241.87 $\Omega\cdot m$, respectively, still significantly better than the control group.

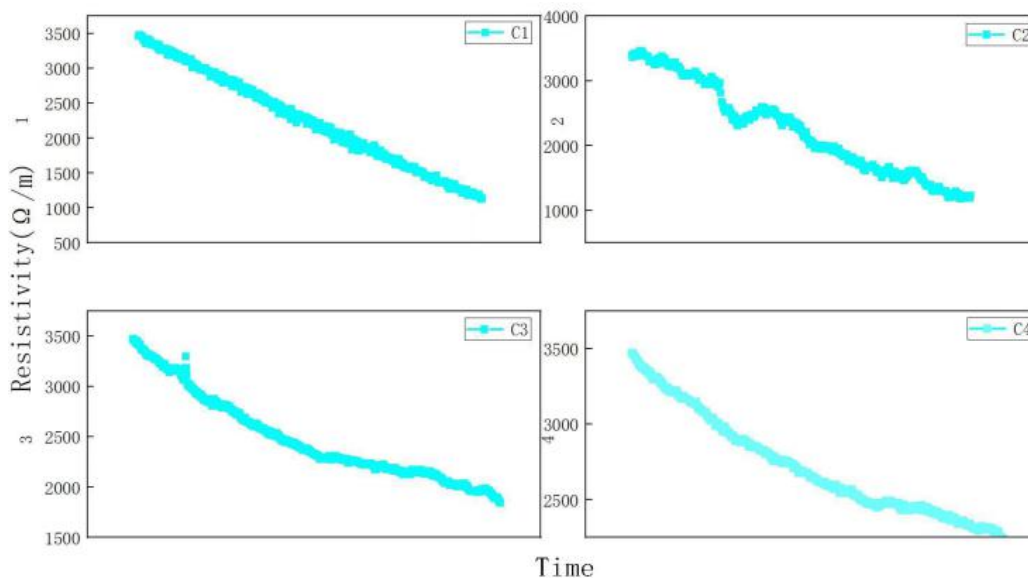


Fig 6. Effect of carboxylated carbon nanotube powders with different tube diameters and lengths on resistance change.

	Cement/g	Sand/g	Water/g	Water-reducing agent/g	CNT/g
C0	450	1350	225	0.9	0
C1	450	1350	225	0.9	0.36
C2	450	1350	225	0.9	0.36
C3	450	1350	225	0.9	0.36
C4	450	1350	225	0.9	0.36

Fig 7. Resistance change values of cement-based materials with carbon nanotubes of different outer diameters

By comparing the resistance change rates in Fig. 8, it can be more clearly found that the performance of specimen C1 is the most prominent, with a change rate of 0.68 $\Omega\cdot m^{-2}$; C2 is next, at 0.66 $\Omega\cdot m^{-2}$; C3 and C4 are 0.47 $\Omega\cdot m^{-2}$ and 0.36 $\Omega\cdot m^{-2}$, respectively. This series of data indicates that the addition of carboxylated carbon nanotubes not only significantly improves the conductivity of the material but also greatly enhances its piezoresistive response characteristics. Among them, specimen C1 exhibits the most excellent comprehensive performance, with both the resistance change

amount and change rate being the highest among the four experimental groups. Conclusion: Within the scope of the current study, the resistance change rate decreases with increasing outer diameter. This may be because, at the same mass fraction and same length, nanotubes with smaller outer diameters have more particles, increasing the chance of forming a conductive network.

The experimental results on the differences in piezoresistive properties further reveal the influence law of nanotube outer diameter on the microstructural stability of

composite materials. Among them, specimen C1 (outer diameter 10-20 nm) exhibits the most excellent piezoresistive

performance, with a resistance change rate of $0.68 \Omega \cdot m^{-2}$.

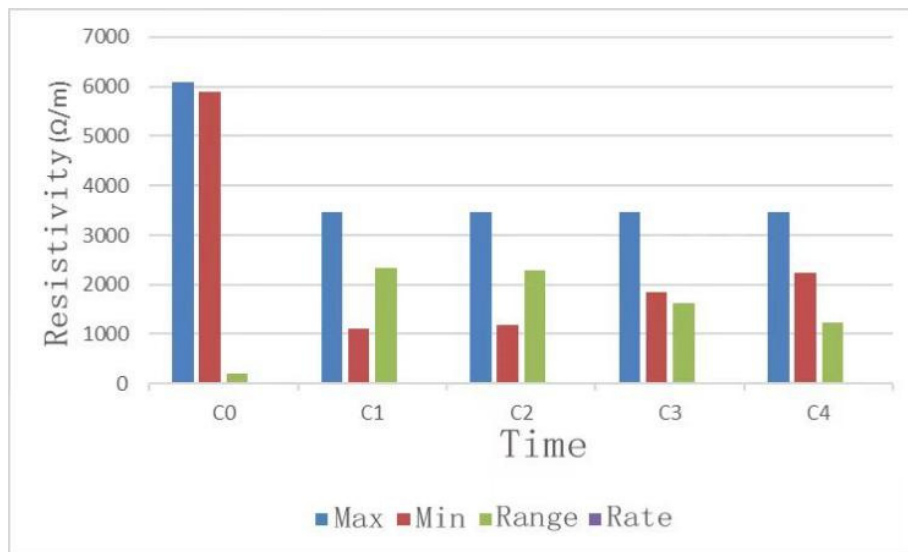


Fig 8. Effect of carbon nanotubes with different outer diameters on the resistance variation of cement-based materials.

This outstanding performance originates from its moderate outer diameter design: while ensuring the structural strength of the nanotubes themselves, it maintains good deformation sensitivity. Under a pressure of 10 MPa, its conduction mechanism shows a dual effect: the contact resistance caused by the compression of nanotube spacing decreases exponentially, and the piezoresistive effect of the tube itself contributes about 40% of the resistance change. In contrast, although specimen C2 (outer diameter 8-15 nm) has a smaller outer diameter, it brings higher initial conductivity, with a minimum resistance of $1175.02 \Omega \cdot m$. However, the smaller outer diameter leads to a significant increase in specific surface area, exacerbating the secondary agglomeration tendency of nanotubes. Under cyclic stress, the agglomerates are prone to cause irreversible contact loss, resulting in its piezoresistive stability being significantly lower than that of specimen C1. This clarifies the decisive influence of differences in outer diameter on the stability of piezoresistive properties from the perspective of microstructure.

It is worth noting that specimens C3 (outer diameter 20-30 nm) and C4 (outer diameter 30-50 nm) with larger outer diameter nanotubes show obvious performance degradation, with their change rates dropping to $0.47 \Omega \cdot m^{-2}$ and $0.36 \Omega \cdot m^{-2}$ respectively, confirming that the nanotube curvature radius is a key parameter regulating the efficiency of interface stress transfer. Their performance degradation mainly stems from two mechanisms: on the one hand, the elastic modulus mismatch, where the increased difference in elastic modulus between nanotubes and the cement matrix results in the dissipation of about 30% of the stress energy during interface slip; on the other hand, the enhanced random orientation of large-sized nanotubes significantly reduces the density of effective conductive paths. This microstructural feature also explains the mechanical-electrical coupling mechanism reflected by their relatively lower resistance changes (C3: $1629.44 \Omega \cdot m$, C4: $1241.87 \Omega \cdot m$).

In summary, the outer diameter of carboxylated carbon nanotubes has an influence on the electrical conductivity and piezoresistive properties of cement-based composite materials. The experimental results show that within the scope of the current study, when the outer diameter of the nanotubes is in the range of 25-35 nm, the material can

construct a stable conductive network and ensure high piezoresistive sensitivity.

4. Conclusion

Studies have found that nanotubes with an outer diameter of 25-35 nm can endow composite cement-based materials with the best electrical conductivity and piezoresistive properties. Based on this, this study selects carboxylated carbon nanotubes as functional modification materials, and by applying pressure to composite specimens, successfully verifies the effectiveness of this material system in real-time monitoring of the structural health status of cement-based materials.

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