Piezoresistive/piezoelectric intrinsic sensing properties of carbon nanotube cement-based smart composite and its electromechanical sensing mechanisms: A review

Abstract: Structural health monitoring (SHM) technology based on the mechanical–electrical sensing effect of various intrinsic smart materials has a good application prospect. Carbon nanotube (CNT) has excellent electromechanical properties and hence can be doped into cement by appropriate dispersive means to produce CNT-modified cement-based smart material (CNTCS) with excellent electromechanical (piezoresistive/piezoelectric) capacity. CNTCS can be developed into a static/dynamic intrinsic sensor for SHM after effective packaging and calibration. Based on the characteristics of CNT, the dispersion methods and the dispersity characterization techniques of CNT in the water/cement matrix are summarized, and then the influence laws of various factors on piezoresistive and piezoelectric sensing behaviors of the corresponding CNTCS are also discussed. The full-frequency domain sensing mechanism of CNTCS is analyzed by combining its finite element model and electromechanical coupling theory, and the practicability of applying CNTCS as an SHM static/dynamic intrinsic sensor is further investigated.

Keywords: structure monitoring, electromechanical sensing effect, carbon nanotubes, cement-based intrinsic smart materials, static/dynamic sensing performance

1 Introduction

With the development of engineering technology, structural health monitoring (SHM) technology has been widely used in some major engineering fields. SHM is used to continuously monitor and evaluate the service condition of structure by measuring stress, displacement, strain, and other data that reflect the real-time condition of structure through various sensors. The sensing signals of local damage monitoring and health warning in SHM are previously acquired by various types of attached or embedded sensors such as fiber optical grating, shape memory alloy, and resistance strain gauge; however, these traditional sensors often have short life, poor anti-interference capacity, and poor compatibility with concrete [1]. Therefore, the research and development of cement-based sensors with intrinsic piezoresistive and/or piezoelectric self-sensing capability have crucial engineering significance for better achievement of SHM.
Since first documented in 1990, carbon nanotube (CNT) has become a research hotspot on serving as a reinforcing phase of varied composites owing to its excellent mechanical, electrical/thermal conductive, wave-absorbing properties, etc. [2–5]. Li et al., Han et al., Luo et al., and Kim et al. reported that CNT-modified cement-based smart material (CNTCS) has superior stress/strain sensitive behavior and piezoresistive response. Meanwhile, due to the outstanding electrical conductivity of CNT, insulative piezoelectric cement-based composite (PCM) doped with some CNTs can be polarized at low voltages, and its piezoelectric performance can be significantly enhanced.

Actually, the piezoresistive or piezoelectric sensing characteristics of CNTCS favor the development of CNTCS into an intrinsic sensor for concrete structure. Ubertini et al. [6] used CNTCS as a concrete embedded sensor for the identification of intrinsic frequency of foot-print-reinforced concrete beams; Metaxa et al. [7] employed CNTCS as the cementitious sensor for repair works, and its piezoresistive response under stress changes was captured which could provide an early warning failure; Tareen et al. [8] developed a CNTCS sensor two-end wire connected with a pair of lead zirconate titanate (PZT) wafers and evaluated the feasibility of a nondestructive monitoring method for concrete strength detection; Zhang et al. [9] established an intelligent traffic monitoring through embedded CNTCS sensors, which can be used for vehicle weighing and traffic flow detection under high speed movement.

Unfortunately, the aforementioned two types of CNTCS sensors cannot detect static and dynamic loads/deformations simultaneously, which are often encountered in the process of SHM. It is noted that the frequency response of piezoresistive sensors is relatively low, just suitable for the detection of (quasi-)static signals at low frequency; whereas the frequency response of piezoelectric sensors mainly consisting of piezoelectric elements can reach dozens of thousand hertz and be suitable for the detection of dynamic signals at high frequency. In-service structures are frequently subjected to static/dynamic complicated loads or deformations; thus, it is necessary to develop a new type of intrinsic electromechanical sensor with high-sensitivity, wide-frequency response that integrates piezoresistive and piezoelectric sensing characteristics for SHM in the full frequency domain.

Chen et al. [10] developed a piezoresistive/piezoelectric composite flexible sensor using CNT and ZnO nanowire as piezoresistive and piezoelectric phases, respectively, with polyvinyl alcohol as matrix, and verified its static and dynamic sensing feature with wide frequency responses. Sanati et al. [11] exploited a nanocomposite sensor by incorporating CNT into polyvinylidene fluoride matrix, which could achieve strain detection in a wide frequency range (0–10 kHz) based on the integration of piezoresistive and piezoelectric sensing mechanisms. Although the aforementioned studies have achieved the combination of piezoresistive and piezoelectric sensing mechanisms, to the best of our knowledge, no scholars have yet been found to use cement concrete as a matrix to study the piezoresistive/piezoelectric compound sensing performance of CNTCS and develop it as a structural intrinsic sensor with wide frequency response.

As known, as a nanofiller, there are still great challenges in CNT dispersion among diversified matrix. The large aspect ratio and surface energy of CNT makes it easy to entangle and agglomerate in aqueous system, and poorly dispersed CNT will greatly affect the performance of composite. On this account, only when CNT has a good but stable dispersion in the cement matrix, an intrinsic CNTCS sensor with superior sensitivity and self-monitoring capacity of concrete structure can be effectively achieved when embedded or attached.

Here, based on the review of dispersion and dispersity characterization methods of CNT, the current experimental results, numerical and physical model analysis, and sensing mechanism discussions are analyzed from the perspective of piezoresistive and piezoelectric sensing performance of CNTCS, respectively. Hereafter, an CNTCS intrinsic sensor is studied by detecting static/dynamic signals simultaneously, and the electromechanical sensing mechanism of CNTCS and a fundamental concept of full frequency domain structure intrinsic monitoring are clarified and established.

2 Dispersion of CNT in aqueous system

2.1 CNT dispersion methods

Composites are multifunctional materials made of two or more materials with different properties, which can be regarded as two parts: matrix and functional phases. A good dispersion of added phase in the matrix is a key prerequisite to ensure the functionality of composites [12]. Therefore, it is necessary to identify the practical means of dispersion to ensure good dispersion of CNT in the cement matrix to implement the functionality of composites [13]. The current dispersion methods for CNT mainly include mechanical stirring, ball milling,
ultrasonic treatment, electric field induction, surfactant treatment, strong acid oxidation, etc. [14].

Mechanical stirring and ball milling methods are both mechanical dispersion, which achieve the dispersion and homogenization of materials through external forces such as shear and friction. Mechanical stirring can break up CNT in the solvent initially, but the dispersivity is not good if CNT and cement matrix are mixed directly [15,16]. Wan and Huang [17] found that the ball milling of CNT using a low-speed ball mill should be controlled with suitable time, too long ball milling time will cause more agglomeration. Ultrasonic treatment is the use of the strong cavitation of vibration wave propagation to produce a large number of micro bubbles in liquid medium. The change in frequency causes the bubbles perturbed: some bubbles are compressed to produce high temperature while others burst to produce shock waves, that CNT can be well dispersed in solution under the action of high temperature and shock waves [18,19]. The action of DC or AC produces directional electric field force, which makes CNT be along the direction of electric field line directional arrangement to achieve the effect of dispersion, namely, electric field induction method [20]. Surfactant decoration is a non-covalent modification method, in which the active agent can be adsorbed on the CNT surface to reduce its surface energy and weaken the inter-tubular adsorption that help it disperse better [21]. In contrast, strong acid oxidation is a covalent modification method, which opens the covalent bonds on the CNT surface by strong acid modification and introduces functional groups to improve hydrophilicity and dispersibility.

Many scholars have conducted research on CNT dispersion in aqueous systems, yet there is not much control on the initial dispersion of water into the cement system. In situ growth of CNT on cement or mineral admixture particles may be a feasible idea [22]. Analyzing the reasons that CNT is prone to agglomeration, three conditions are necessary to achieve homogeneous dispersion: reduction of aspect ratio, weakening of inter-tube adsorption, and stabilization of dispersion state [23]. All the above proposed dispersion methods are difficult to meet the three conditions alone, so the synergistic work of multiple methods needs to be considered. For example, a weak oxidant such as Fenton can be combined with ozone or UV irradiation treatment that covalently modifies CNT to a certain extent, and then concrete superplasticizer can be used as a surfactant to ensure the stability of its dispersion in concrete associated with ultrasonic treatment. The integrity of the electronic structure of CNT can be guaranteed to the greatest extent in this way, which can ensure the superior mechanical and electromechanical sensing properties of CNT in the concrete system.

2.2 Evaluation of CNT dispersivity

The characterization methods for the dispersion of CNT suspensions include incubate observation, high-speed centrifugation, UV-Vis spectroscopy, Raman spectroscopy, and so on [24]. Both the incubate observation and high-speed centrifugation are used to initially evaluate the dispersivity by duration of suspension delamination or sedimentation time, which can also be used as a basis for judging the stability of CNT suspensions [25]. UV-Vis spectroscopy is based on the Lambert–Beer law, where the absorbance of suspension at the specific wavelength is proportional to the solute present alone in suspension [26,27]. Jiang et al. [28] and Yu et al. [29] have also confirmed through experiments that the dispersion effect of CNT at specific wavelength was related to the absorbance, as shown in Figure 1, and the longer ultrasonic treatment time resulted in a better dispersion of CNT and the corresponding absorbance was at a higher quantitative value. Raman spectroscopy is a method that can effectively identify the microstructure of nanocarbon-based materials and be widely used to determine the size and distribution of CNT [30,31]. The number of defects on CNT can be determined by the intensity ratio of D-peak to G-peak in spectrogram, and the concentration of CNT can be further characterized by the adsorption of surface reactive groups through thermal weight loss analysis [32]. Gong et al. [33] conducted an interesting study. They established a 3D percolation model to quantitatively reflect the effect of CNT agglomeration on the piezoresistive properties of the corresponding composite.

![Figure 1: UV-Vis images of CNT suspensions under different ultrasonic treatment durations](image)
The good dispersion and stability of CNT is still an important factor limiting its popularization and application. Poorly dispersed CNT will cause agglomeration and entanglement in the cement matrix, which will affect the workability, mechanical, electrical, and electromechanical properties of cement paste. Consequently, the dispersion effect of CNT can also be evaluated by measuring the aforementioned properties [34].

In addition, the in-scale blending process needs further consideration in practical application. D’Alessandro et al. have carried out the above work with preliminary results [35]. According to the existing research results, on the basis of certain functional modification of CNT surface, further combination of non-covalent modification of concrete superplasticizer and ultrasonic treatment of synergistic dispersion technology can be used as an effective means of industrial preparation of CNT dispersions.

3 Experimental study on electromechanical sensing performance of CNTCS

3.1 Piezoresistive behavior of CNTCS

The piezoresistive behavior refers to the phenomenon of change in resistivity under external loading and can also be defined as the relationship between resistivity and stress/strain. On the basis of excellent mechanical and electrical properties of CNT, the high sensitivity and stable linearity of the piezoresistive properties of CNTCS have been widely proven [36]. It is expected to be used as an embedded piezoresistive sensor to detect the subjected stress/strain of concrete structure in real time. Luo et al. [37] synchronously collected the resistance and stress/strain under the load of CNTCS based on Wheatstone half-bridge connection (as shown in Figure 2) and further identified the feasibility of CNTCS as an intrinsic sensor from the perspectives of cost, reusability, and scalability.

In practical application, the piezoresistive behavior of CNTCS for SHM should consider the influence of various factors, such as moisture content, load conditions, CNT parameters (content, surface treatment), and hybrid other conductive fillers.

3.1.1 Moisture content effect

The variation of moisture content of CNTCS is mainly reflected in two aspects: water–cement ratio and ambient humidity, which are the primary problems faced by CNTCS applied in engineering structures. According to the existing research results, the effect of moisture content on the piezoresistive performance of CNTCS is extremely obvious [38,39].

Cha et al. [40] tested the piezoresistive properties of CNTCS specimens under different moisture conservation and drying conditions, as shown in Figure 3. Compared to the specimens without CNT doping in Figure 3(d), the CNTCS specimens maintained in dry air have good piezoresistive properties (better correlation between resistance

![Figure 2: Wheatstone-based data acquisition system: (a) piezoresistive testing of CNTCS and (b) Wheatstone half-bridge connection principle (R₁, R₂ are the standard resistances)](37).
and load), while the specimens maintained in a humid environment did not have a significant piezoresistive response. Although the specimen in Figure 3(c) was cured under humid conditions, the piezoresistive response was more obvious after being fully dried. Han et al. [41] studied the effect of different moisture contents on the piezoresistive performance of CNTCS. By comparing the initial resistivity, resistance amplitude change, and piezoresistive sensitivity of CNTCS with different moisture contents, it was found that the conductivity of CNTCS increased with the moisture content. However, the piezoresistive sensitivity did not show a linear increase, but instead decreased after the moisture content was greater than 3.3%, as shown in Figure 4. In addition, other scholars such as Kim et al. [42], Wang et al. [43], and Zhang et al. [44] have also concluded that the effect of moisture content on the piezoresistive properties and sensing stability of CNTCS is extremely remarkable.

Certainly, the CNT incorporation can improve the pore structure of cement matrix [45]. The moisture content will be reduced due to the decrease of porosity, which will lead to the improvement of electrical conductivity of CNTCS specimens [46].

The influence of moisture content on the piezoresistive response is mainly reflected in two aspects: one is electrical conductivity, the internal moisture content of the porous composite has a significant impact on its initial resistivity, which in turn affects the piezoresistive
behavior of composite by increasing the polarization effect. The second is the field emission effect between the reinforcement nanotube end. The increase in moisture content reduces the internal resistance of cement matrix, which enhances the field emission effect between the nanotube end and the electrical conductivity of composite [47]. Besides, the tunneling barrier decreases when the specimen is deformed by compressive load, resulting in a high susceptibility to field emission-induced tunneling effects. Therefore, the CNTCS composite exhibits high electrical conductivity and piezoresistive behavior inside with high moisture content. However, excessive moisture content leads to a significant decrease in resistivity, making the composites to be also less sensitive to applied stress [48].

### 3.1.2 Load condition effect

The load situation of the SHM with CNTCS is complex and diverse, mainly including load amplitude, rate, and time, which have great impact on the piezoresistive properties of CNTCS.

Zhang et al. [49] found that the piezoresistive behavior was more sensitive to the stress amplitude in the elastic scope, and the resistivity change rate could reach 16.0, 22.1, and 25.4% for the stress amplitude of 6, 8, and 10 MPa, respectively, as shown in Figure 5. This is mainly because the higher load amplitude produces larger deformation of CNTCS specimens, and the spacing of functional fillers became smaller that was more prone to tunneling effect, which made the resistivity of CNTCS decrease and the corresponding piezoresistive response was more obvious accordingly. This was also confirmed by Han et al. [50] and Wang et al. [51].

![Figure 5: Change of resistivity of CNTCS with different load amplitude [49].](image)

Wang et al. [51] studied the influence of different load rates on the piezoresistive response. It was found that the maximum resistance change of the CNTCS specimen increased from 6 to 14% with the increase of load rate from 50 to 500 N/s. Nevertheless, some scholars reported that the load rates have limited effect on the piezoresistive behavior of CNTCS, and there is divergent in the effect of load rates. According to Han’s experimental research, when the load rate was less than 0.20 cm/min, the piezoresistive response was almost unaffected, but it would have a significant effect on the piezoresistive performance when the load rate exceeded 0.20 cm/min [52].

CNTCS must serve for a long time as the embedded sensor for SHM, so the fatigue and creep conditions of CNTCS must be considered [53]. Kim et al. [54] estimated the long-term resistivity of CNTCS by effective medium theory and verified by experiments, all of which found that the resistivity of the composite would gradually increase with serving time in a dynamic change process. As shown in Figure 6, the resistivities of different CNTCS specimens over dynamic times have non-negligible gaps between the theoretical estimation and experimental results. Therefore, during the in-real service of CNTCS sensors, the dynamic correction of resistivity with time should be considered [55].

As mentioned above, almost all load factors have non-negligible influences on the piezoresistive responses of CNTCS. The higher load amplitude gives the composite a lower contact resistance, resulting in lower resistivity and more pronounced piezoresistive response of CNTCS. The impact on the piezoresistive performance gradually increases after the load rate exceeds a certain limit. In practical application, CNTCS for SHM should be served in

![Figure 6: Comparison of test data with predicted resistance and time responses of CNTCS [54] (Ex. – test value; Pred. – predicted value; N5F1-50 = 5 g CNT + 1 g CF + 50 g fine aggregate, the rests are similar).](image)
the elastic deformation phase guaranteeing sufficient strength, modulus, and durability of CNTCS.

3.1.3 Effect of CNT content and surface treatment method

As a reinforcement, the influence of own factors of CNT on the piezoresistive response of CNTCS is also extremely significant, which mainly includes the CNT content and its surface treatment methods.

The CNT content is one of the most direct factors affecting the piezoresistive performance of CNTCS. Yu and Kwon [56] compared the piezoresistive response of specimens with CNT content of 0.06 and 0.1 wt%, respectively, and found that superior piezoresistive sensitivity could be obtained with 0.1 wt%. Han et al. [57] chose 0.05, 0.1, and 1.0 wt% CNT content for the piezoresistive tests, and the CNTCS in all three levels showed stable and regular compressive resistance responses. However, in terms of the amplitude of resistance change under the same compressive stress, the largest amplitude of CNTCS occurred for 0.1 wt% CNT content, while the smallest amplitude occurred for 1.0 wt%. This indirectly indicates that the piezoresistive sensitivity of CNTCS does not increase linearly with the CNT content. To date, the explanation for this phenomenon is relatively unified as follows: the resistance of CNTCS is mainly composed of innate resistance of CNT and the contact resistance between the nanotube end. Since the piezoresistive performance of CNTCS is almost tested in elastic phase and the deformation is small, the innate resistance of CNT can be negligible. The spacing between the nanotube ends distributed in the matrix is large when the CNT content is low (0.05 wt%), and the contact resistance formed between the nanotube ends is limited even under compressive deformation. When the CNT content increases a certain value (0.1 wt%), the contact spacing is effectively reduced under compression deformation, the resistance of CNTCS is reduced significantly since a large number of CNTs form a contact resistance between the nanotube ends that are prone to cause electrical tunneling. However, when the CNT content continues to increase (1.0 wt%), it is difficult to increase the number of conducting contact points even with compression deformation because there already forms a stable conductive network with sufficient CNT contacts in the matrix [58].

The high aspect ratios and the large van der Waals forces on the surface of CNTs render them be very apt to entangle and agglomerate. The surface treatment is an effective means of dispersion in matrix which mainly includes strong acid oxidation and surfactant modification [59]. Li et al. [60] prepared CNTCS with acid-treated CNT and compared its piezoresistive properties with unacidified specimens, and found that both could exhibit stable piezoresistive properties, but the former had a higher piezoresistive sensitivity. As observed by microstructure that the acid-treated CNT was covered by C-S-H in the matrix, there were fewer contact points. In contrast, the untreated CNT with smooth surfaces had more obvious contact points and agglomerates, as shown in Figure 7. Yu and Kwon [56] compared two modification methods of acidification and surfactant treatment and also confirmed that acidification treatment gave CNTCS a higher piezoresistive response and signal-to-noise ratio, whereas the surfactant would wrap on the surface of CNT and hinder the contact between conductive CNT ends, thereby affecting the piezoresistive response of CNTCS [61]. Besides, Gao et al. [62] achieved uniform dispersion of CNT in cement matrix by preparing CNT suspension and CNT suspension coated sand, respectively, and compared the effects of two treatments on the piezoresistive properties of CNTCS accordingly, and found that the CNT suspension coated sand mortar possessed superior stress sensitivity, linearity, and stability. This indicates that the sand medium can favor CNT attached to form more tough and stable conductive paths. Liu et al. [63] used nickel-coated CNT to achieve it precisely aligned in a magnetic field, which brought out the strain sensitivity of CNTCS reaching 993 when the CNT content was 1.2 vol%.

3.1.4 Effect of CNT mixed with other conductive fillers

Some scholars have considered mixing CNT with other conductive fillers to further improve the piezoresistive response, sensitivity, stability, and linearity of composite. Luo [64] investigated the piezoresistive performance of CNTCS mixed with carbon fiber (CF) or carbon black (CB). It was found that the hybrid CF did not have a significant optimization effect on the piezoresistive performance of CNTCS, while hybrid CB not only had superior piezoresistive performance but also had a higher sensitivity coefficient. The phenomenon was similarly corroborated by Zhang et al. [65] that maximum resistivity change and stress/strain sensitivity coefficient of CNTCS doped with 1.41 vol% CNT/CB can reach 13.4%, 3.21%/MPa, and 521, respectively. Qin [66] reported the case of mixed CF, CB, and CNT, the composite hybrid with 0.2% CF/1.5% CNT/1.0% CB could achieve a resistance change of 9.5% enhancement compared to that of CNTCS, and the sensitivity coefficient could reach 42. Liu et al. [67] blended 3D
graphene–CNT into cement paste and tested that the stress/strain sensitivity coefficients of the composites could reach 2.3%/MPa and 291, respectively, with significantly improved piezoresistive properties. Han et al. [68] prepared CNT/nanocarbon black (NCB) composite fillers by electrostatic self-assembly technique, and their synergistic effect significantly improved the piezoresistive response of CNTCS. Zhang et al. [69] used electrostatic self-assembly method to combine CNT with micron-scale TiO2 to develop CNTCS. It was found that the maximum resistivity change and stress/strain sensitivity coefficient of the CNTCS could reach 9.5%, 1.18%/MPa, and 317, respectively, which is attributed to the excluded volume effect produced by the incorporation of micron-scale TiO2 in CNTCS which increased the effective content of CNT.

Hybrid mixing conductive microfibers or nanofillers can improve the field emission effect of CNT and enhance the tunneling conducting capability of leaping the barrier [70]. Yet, mixing hydrophobic materials with large aspect ratio or high surface energy into cement matrix at the same time may substantially increase the possibility of entanglement; therefore, we should consider varied compounding materials with great mutual independence in doping process and strong complementarity in function [71]. In addition, allowing for the mixing between multiple nanoscale materials, higher requirements of the dispersion process are also put forward.

The content of CNT has an extremely significant effect on the piezoresistive behavior of CNTCS. Besides the piezoresistive response, the sensitivity, stability, reversibility of CNTCS should be paid attention, as well as to the electrolysis caused by ion conduction [72]. Although acidification treatment is beneficial to the piezoresistive behavior, some researchers believe that acidification treatment may jeopardize the electronic structure of CNT [73], which is detrimental to its performance. Therefore, suitable dispersion need to be selected, and the influence of innate properties of CNT such as tube length and diameter on the piezoresistive behavior should be further carried out.

3.2 Piezoelectric behavior of CNTCS

The piezoelectric behavior means that the piezoelectric medium is polarized by compressive strain, and opposite bound charges will appear on its opposite surface, which is called the positive piezoelectric effect [74]. The inverse piezoelectric effect indicates that the piezoelectric medium will be deformed when an electric field is applied along the direction of piezoelectric medium polarization. Piezoelectric

Figure 7: SEM images of CNTCS: (a and b) arrows are the morphology of CNT after acidification and (c and d) arrows are the morphology of untreated CNT [60].
materials mainly include piezoelectric ceramic, piezoelectric polymer, and piezoelectric composite material. Piezoelectric ceramic has the advantages of high piezoelectric strain constant \( (d_{33}) \), dielectric constant, and electromechanical coupling coefficient \( (K) \), but low piezoelectric voltage constant \( (g_{33}) \) and poor toughness leading to low durability; piezoelectric polymer possesses higher \( g_{33} \) and superior flexibility, but its \( d_{33} \) and \( K \) are on the low side. Piezoelectric composite, which dopes piezoelectric ceramic component within the matrix, can overcome the shortcomings of the above two by varying the dosage to adjust the performance of bulk composite [75]. Among them, polymer-based piezoelectric composites still cannot solve the compatibility problems with concrete systems in terms of acoustic impedance, deformation coordination, and interface bonding. If piezoelectric composites are prepared using cement as a matrix and embedded in concrete structures as sensors, it is expected to realize piezoelectric intrinsic sensing of structures and solve the compatibility problem between sensors and concrete structures. Li et al. [76] verified the feasibility of PCM through experiments first. Zhang et al. [75] discussed three aspects of compatibility, composite preparation, polarization, and also concluded that the application of PCM in SHM is reasonable.

However, 0-3 type PCM still suffers from the problem of difficult polarization. The reason is the piezoelectric particles are independent and discontinuous in cement matrix, and the impedance of the matrix is much higher than the piezoelectric functional phase. So even if the applied polarization voltage is very high \( (100–200 \text{ kV/cm}) \), the electric field acting on piezoelectric particles is still low and cannot generate a sufficiently high polarization voltage \( (10–30 \text{ kV/cm}) \). Blindly increasing the external polarization voltage will cause changes in the microstructure of cement system and even breakdown the materials [77]. An effective solution is to introduce conductive phases such as CB [78,79] and CNT [80] into the composite material to create continuity of electric flux between piezoelectric particles so that the external polarization voltage can effectively act on the piezoelectric ceramic particles and improve the bulk polarization efficiency.

This section summarizes and analyzes the effect of CNT content on piezoelectric performances of PCM, involving piezoelectric properties, dielectric properties, and dielectric losses.

### 3.2.1 Effect of CNT content on piezoelectric strain constant of PCM

Piezoelectric effect is the conversion capacity between mechanical and electrical energy, which can be effectively characterized by the most important parameter \( d_{33} \) [81]. The addition of conductive CNT has a significant improvement effect on \( d_{33} \). The incorporation of CNT forms a conductive path in 0-3 type PCM, which helps to form an effective polarization electric field on the piezoelectric phase and improve the polarization efficiency [82]. In addition, some scholars believe that the doping of third-phase CNT creates a parallel resistance within the bulk composite, which reduces the overall resistance of the system and likewise increases the effectiveness of polarization voltage [81]. Table 1 shows the piezoelectric behavior results of 0-3 type PCM with varied content of CNT \( (\varphi_{\text{CNT}}) \). CNT dosage can increase the \( d_{33} \) of 0-3 PCM up to about 60 pC/N. Zhang et al. [83] further adjusted the polarization temperature, polarization voltage, and polarization time, to render the \( d_{33} \) of 0-3-1 type PCM to be as high as 122 pC/N.

Yet, the enhancement of piezoelectric behavior of PCM dosage by CNT is limited, its \( d_{33} \) will show a decreasing trend when \( \varphi_{\text{CNT}} \) exceeds a certain value, which is called the percolation threshold \( (\varphi_c) \). The \( \varphi_c \) is related to CNT treatment, substrate type, and even deformation [89]. The \( d_{33} \) of composite is extremely sensitive when the CNT content is close to \( \varphi_c \), the composite becomes a conductor when \( \varphi_{\text{CNT}} \) exceeds \( \varphi_c \), and its piezoelectric phase will have difficulty in polarization, so the \( d_{33} \) will be accordingly reduced.

| Piezo phase | \( \varphi_{\text{Piezo phase}} \) | \( \varphi_{\text{CNT}} \) | \( d_{33}/(\text{pC/N}) \) | Enhancement/\( \% \) | Authors |
|-------------|-------------------------------|-----------------|-----------------|-----------------|--------|
| PZT         | 75.0 wt%                      | 1.0 wt%         | 50.6            | 18.5            | Luo et al. [84] |
|             | 50.0 vol%                     | 0.7 vol%        | 122.0           | 159.6           | Zhang et al. [83] |
|             | 70.0 vol%                     | 0.3 vol%        | 62.0            | 41.0            | Gong et al. [85] |
|             | 34.1 wt%                      | 0.6 vol%        | 13.0            | 420.0           | Zhao et al. [86] |
|             | 50.0 vol%                     | 0.7 vol%        | 19.7            | 140.0           | Kim et al. [87] |
| BNBK\#       | 50.0 vol%                     | 1.0 vol%        | 58              | 41.5            | Potong et al. [88] |

\#BNBK is referred to as lead-free bismuth sodium titanate–bismuth potassium titanate–barium titanate.
3.2.2 Effect of CNT content on relative dielectric constant of PCM

The relative dielectric constant ($\varepsilon_r$) is defined as the performance of medium’s ability to store charges, which can comprehensively reflect the polarization behavior and quality of the piezoelectric medium [90]. When the $\varphi_{\text{CNT}}$ is below and close to $\varphi_c$, the function of CNT is equivalent to a micro-electronic storage layer, which induces charge storage at the interface between CNT and PCM matrix [91]. This has significant improvement effect on the dielectric properties of composite material and the relationship between $\varepsilon_r$ and $\varphi_c$ is as follows:

$$\frac{\varepsilon_r}{\varepsilon_m} = \left| \frac{\varphi_c - \varphi_{\text{CNT}}}{\varphi_c} \right|^q,$$

(1)

where $\varepsilon_m$ is the dielectric constant of the substrate; $q \approx 1$ [92].

As shown in equation (1), the lower $\varphi_c$ of CNT has a positive effect on the higher $\varepsilon_r$ of composite material, as also proved by experimental studies. W. Wei [93] first synthesized nanoscale PZT powder by optimizing the reaction time, calcination temperature, pH value, and thereby prepared 0-3 type PCM dosing with 1.0 wt% CNT, whose $\varepsilon_r$ reached 412. Gong et al. [94] explored the influence of $\varphi_{\text{CNT}}$ on the dielectric properties of PCM on the basis of 70 vol% PZT content, the $\varepsilon_r$ showed a continuous upward trend up to more than 165 in the $\varphi_{\text{CNT}}$ range (0–1.3 vol%) with an increase of 38.78%, but it was accompanied by an increase in dielectric loss. This phenomenon was also observed by Zhao et al. and Kim et al. in their experiments [86,87].

Some scholars argue that using chemical modification to disperse CNT in PCM matrix will destroy its dielectric properties. Higginbotham et al. [95] found that the $\varepsilon_r$ of the composite could be varied within a certain range just by adjusting the ratio of pristine CNT to modified CNT under constant $\varphi_{\text{CNT}}$, and higher $\varepsilon_r$ could be achieved with an increase in the ratio of pristine CNT.

There is an upper limit for the enhancement of $\varepsilon_r$ by CNT dosage, the dielectric loss phenomenon will occur when $\varphi_{\text{CNT}} \geq \varphi_c$, which is detrimental to the dielectric properties of composite. Yao et al. [96] and Dang et al. [97,98] obtained a high dielectric but low-loss material, which has important engineering applications in the fields of radiation protection and electromagnetic shielding if it can be applied to concrete structure.

3.2.3 Effect of CNT content on dielectric loss factor of PCM

The loss part during electrical energy transferring into heat energy of piezoelectric particles in the electric field is called the dielectric loss ($\tan \delta$). Piezoelectric particles convert mechanical energy into electrical energy in the polarized state and dissipate it in the form of thermal energy through the conductive network formed by the conductive network, exhibiting the piezoelectric damping phenomenon [99]. Only a small portion of energy can be consumed through intermolecular viscoelasticity and interfacial friction between piezoelectric particles with a low order of magnitude of $\tan \delta$ if only rely on piezoelectric particles [100]. However, existing conductive phase is a crucial factor to realize energy dissipation and damping reinforcement.

The lower $\varphi_c$ of CNT-doped PCM enhances piezoelectric damping performance, because CNT can form a conductive network at a lower content level, allowing the electrical energy generated by the piezoelectric effect to be effectively dissipated [101]. We have found in the related literature of CNT/PCM that $\tan \delta$ increases slowly when $\varphi_{\text{CNT}}$ is low (as shown by the circle in Figure 8). But the effect of $\varphi_{\text{CNT}}$ on $\tan \delta$ is intensified when exceeds a

Figure 8: The dielectric loss of CNT/PCM: (a) ref. [86], (b) ref. [87], and (c) ref. [94].
certain threshold. This is due to the fact that CNT exists independently in the matrix when $\varphi_{\text{CNT}}$ is low, the polar-ization charge cannot be converted into other energy consumption, and the mechanical energy can only be consumed through the friction at the interface between CNT and other phases [102].

Polarization also has a certain effect on $\tan \delta$. Carponcin et al. [103] compared the $\tan \delta$ value of CNT-reinforced piezoelectric composites before and after polarization and found that the $\tan \delta$ value of pre-polarized composites was increased by about 20%. The polarization is more like an “activation” process, ensuring the mechnoelectrical conduction mechanism of the piezoelectric phase. If the effect of CNT-reinforced piezoelectric damping can be applied to concrete structures, it will have profound engineering implications, just as the structural vibration reduction and energy consumption.

In summary, the effects of CNT dosage on the piezo-electric behavior of PCM are closely related to $\varphi_c$, especially $d_{33}$, $\varepsilon_r$, and $\tan \delta$ are extremely sensitive to changes in $\varphi_{\text{CNT}}$ when near $\varphi_c$. Then, the determination of $\varphi_c$ is rather vague at present because it is affected by various factors such as piezoelectric phase, treatment method of CNT, and aspect ratio of CNT. Furthermore, the current research studies on the piezoelectric properties of CNT-reinforced PCM have only focused on the variable of CNT content and the influence of multiple factors such as the bond interface between CNT and matrix, the coupling effect with the piezoelectric phase need to be further considered.

Subsequent works would focus on the effects of concrete shrinkage creep, temperature difference, durability degradation, and other factors on piezoresistive and piezoelectric properties of CNTCS allowing for its actual application conditions.

### 4 Electromechanical sensing efficiency model of CNTCS

Analytical models help to evaluate and predict material properties. At present, the establishment of CNTCS piezoresistive model mainly includes physical and numerical simulation, and there are four types of piezoelectric models or methods: series-parallel model, variational boundary method, analytical method, and finite element method.

#### 4.1 Piezoresistive sensing model

Wen and Chung [104] first proposed a piezoresistive theoretical model of carbon fiber-reinforced cement-based composite (CF/CBC), which was based on the pulling-in/out assumptions of CF within the matrix, and believed that the good piezoresistive behavior of CF/CBC comes from the half-lap behaviors between fibers. The spacing between the half-lap fibers becomes smaller and tends to full lap when composite material is compressed, and the contact resistance decreases at this time showing the piezoresistive behavior. When unloaded, the bridging fibers are slightly pulled out, the inter-fiber spacing increases, and the contact resistance springs back. In the simulation process, the total resistance change rate of the composite material is considered to be the weighted sum of the resistance change rates in the $x, y, z$ directions, as shown in equation (2).

$$\Delta R^{3D} = w_x\Delta R^{3D}_x + w_y\Delta R^{3D}_y + w_z\Delta R^{3D}_z,$$

where $\Delta R^{3D}$ is the total resistance change of the specimen, $\Delta R^{3D}_x$, $\Delta R^{3D}_y$, $\Delta R^{3D}_z$ are the resistance changes in the $x, y, z$ directions, respectively. $w_x$, $w_y$, $w_z$ are the weighting factors that contribute to the total resistance change in the $x, y, z$ directions.

As a basic theoretical physical model, the above model has a good guide role in the piezoresistive sensing model establishment of CNTCS. Seidel and Lagoudas [105] used a composite column model as a representative volume unit to establish a micromechanical model to simulate electron leap behavior in the form of a continuous interfacial layer, and the change of aspect ratio of representative volume elements to simulate conductive network formation. The simulation results show that the barrier width of the energy and the aspect ratio of CNT have obvious effect on the piezoresistive behavior. However, this model can only qualitatively describe the piezoresistive behavior of the composites. In order to carry out deeper quantitative analysis, it is necessary to obtain more constitutive information through nanoscale characterization. Sanati et al. [11] took into account the non-uniformity of the composite material when model established, randomly dispersed CNT formed conductive paths in the matrix. The carriers also chose the path from high to low potential according to the probability, which could obtain resistivity of the network by summing up the current and voltage at each node, as shown in Figure 9. Furthermore, D’Alessandro et al. [106] developed an equivalent circuit model to evaluate the piezoresistive response of CNTCS, which took into
account including the internal resistance, contact resistance, and electrodeposition.

Wang and Ye [107] systematically analyzed the mechanism and characteristics of piezoresistive behavior of CNT composites with numerical simulation. The effective resistive network of matrix was composed of the nanotube segment resistance \( R_N \) and the tunneling junction resistance \( R_J \), but the simulation results revealed that \( R_J \) played a dominant role in the conductive network and the resistivity change was a net effect of the gap change. Based on the above findings, the average gap variation (AJGV) was introduced to quantitatively describe the piezoresistive behavior of composites, and the effects of CNT parameters (CNT conductivity \( \sigma_{CNT} \), aspect ratio \( AR \), diameter \( D \)), matrix parameters (elastic modulus \( E \), Poisson’s ratio \( \nu \)), and preparation process (CNT orientation \( \theta \), \( \varphi_{CNT} \)) on AJDV were quantitatively characterized by numerical model, and found that \( D, \nu, \theta \), and \( \varphi_{CNT} \) played crucial roles in the piezoresistive effect.

The piezoresistive model of CNTCS has been constructed based on numerical analysis with different factors. For example, Behnam and Ural [108] superimposed several 2D nanotube layers to build a 3D model and investigated the effects of the ratio of contact resistance to tube resistance, density, length, and arrangement of CNT on the resistivity of constructed model using the Monte Carlo simulation method. Li et al. [109] used a percolation model to investigate the influence of wave patterns of CNT on the conductivity of composite materials and found that the electrical conductivity of wave-shaped nanotube composites was much lower than that of straight nanotube composites. Yang et al. [110] parametrized the bending and winding distribution of CNTs and predicted the effective conductivity of CNTCS by combining micromechanical models. In addition, numerical models have been used to analyze the effects of nanotube orientation [111], geometry [112], waviness [113], measurement orientation [114], and tunneling resistance [115] on the resistivity and its variability under mechanical strain. The change in volume fraction of CNT due to specimen strain, CNT orientation during cement hydration, and tunneling resistance were the main constituents of piezoresistive response [116].

Compared with the traditional physical model, numerical model has realized the leap from qualitative to quantitative analysis. The piezoresistive behavior performance and mechanism analysis of CNTCS can be more systematic and objective by further combining with the supporting experimental data. However, some assumptions made during the numerical simulations are different from actual situation, for example, assuming that CNT is a rigid, straight cylinder, ignoring the corrugated and bent CNT in matrix. The random distribution assumption ignores the van der Waals forces between nanotubes and does not consider the effects of overlap and agglomeration of CNT. The nanotube contact resistance is considered to be zero when the axis spacing of CNT is less than or equal to the diameter, which is inconsistent with the experimentally observed phenomenon. Therefore, a lot of research studies are needed to realize the accurate construction and quantitative analysis of piezoresistive model of CNTCS.

### 4.2 Piezoelectric sensing model

For multi-phase composite reinforcement materials, the first series-parallel model regards the materials as the composite of each phase material in series or parallel. It is a relatively simple mixing rate rule with large errors in prediction results. The second is the variational boundary method represented by Hashin and Shtriman, which can solve the upper and lower boundaries of effective properties for two-phase composites using mathematical simulation equations [117,118]. Walpole [119] and Willis [120] introduced higher-order functions to propose an improved variational boundary method, which can be
applied to multi-phase composites. The third is the analytical method, which is based on Eshelby’s theory and can be used to predict multi-phase composites with non-homogeneous media and has a certain universality, but there are problems of large number of parameters and difficult to find solution. The last is the finite element method, which compared to the analytical method can be solved using direct numerical calculations, and the process is relatively simplified [121].

García-Macías et al. [122] developed an equivalent circuit model of the piezoelectric response for CNTCS. Although it did not consider the intervention of piezoelectric particles, they proposed the capacitive phenomenon caused by the dielectric properties, which was the most significant feature of piezoelectric particles. The sensing unit of this electromechanical model consisted of contact resistance \( R_{ip} \) and capacitance \( C_{gap} \) in parallel (as shown in Figure 10), and the strain of the substrate caused changes in both. The authors have modeled the above equivalent circuit using MATLAB software and verified it experimentally. It was found that the model can better represent the mechanical response under dynamic loading.

Due to the difference in materials and acoustic impedance of each functional phase and the matrix, there will be a problem of interfacial transition zone (ITZ) at the interface bond. The performance fault in ITZ is a key factor affecting the effective performance of PCM [123,124]. Modeling analysis is an effective means to quantify the parameters influencing the ITZ, while it is difficult to control the performance index of each interface via experiment. Wang et al. [125] developed a model with imperfect interface using modified micromechanics, which enables the continuity of strain and potential at the interface. Wang [126] considered the weak bonding between piezoelectric phases and cement matrix and modified the traditional fine mechanics model according to the generalized spring interface model. The simulation results found that the effect of weak interface can be ignored when the volume fraction of piezoelectric phase is lower than 20%, but the presence of weak interface will significantly reduce the electromechanical coupling performance of composite when the volume fraction is higher. In fact, both CNT and piezoelectric phase surfaces will have weak bond with the matrix leading to non-perfect interfaces, and the resulting displacement discontinuities and modulus discontinuities have significant perturbations on the properties and structure of composite [127,128].

In a further review, we found that numerical modeling analysis for more precise piezoelectric effective performance of CNT-enhanced PCM is missing. More often, the polymer-based matrix [129–133]. Related studies have been carried out extensively and intensively, which have certain reference significance for the analytical model build of PCM.

5 Electromechanical sensing mechanism of CNTCS

Mechanism analysis helps explain the macroscopic performance of materials. The piezoresistive and piezoelectric performance mechanisms of CNTCS are summarized and analyzed to lay a theoretical foundation for the establishment of CNTCS electromechanical sensing mechanism.

5.1 Piezoresistive mechanism analysis

The piezoresistive behavior can be simply understood as the behavior of resistivity changes under load which is a conductive property. As a functional filler, CNT is

![Figure 10: Microscopic model diagram of CNTCS composed of resistors and capacitors in parallel [122].](image-url)
incorporated to improve the conductivity of cement matrix to give it piezoresistive characteristics. There are currently three main mechanisms for explaining this phenomenon: percolation theory, field emission effect, and effective medium theory.

5.1.1 Percolation theory

Percolation theory can be explained by the formation of conductive paths [134]. When the content of conductive phase in the matrix increases and exceeds a certain threshold, a stable conductive path (network) will be formed in the matrix, which can be depended for the migration of carriers, and the resistivity of composite material is greatly reduced, at which time the volume fraction of conductive phase is \( \phi_c \) [135]. Predictions were made very early on using Monte Carlo statistics, and it was found that the \( \phi_c \) of CNT in the cement matrix was about 1.0 vol% [136,137] or fluctuating around this [138]. The \( \phi_c \) depends on many factors including conductive phase itself, the nature of substrate material, and its distribution in the substrate. Han et al. [139] concluded that the \( \phi_c \) was strongly influenced by geometry of conducting phase that small dimensions and high aspect ratios of CNT were conducive to reduce the \( \phi_c \) of CNTCS, especially the aspect ratio.

When the content of CNT exceeds \( \phi_c \), a stable three-dimensional contact network structure is formed in matrix (Figure 11). Most of the CNTs have overlapped each other or the space is close enough to tunnel before loading, and the resistivity of CNTCS is relatively stable and not sensitive to changes in loading [140]. There exists a certain piezoresistive behavior while CNTCS is under external loading, but the maximum resistance change rate is not large with relatively low piezoresistive sensitivity.

Percolation theory can explain the piezoresistive behavior and the sudden change of resistivity near \( \phi_c \) according to the formation of conductive paths. It is believed that conductive particles can only be in contact with each other to produce conductivity, but percolation theory cannot explain the phenomenon that discontinuous conductive particles in some media still give the composite material conductive or piezoresistive behavior.

5.1.2 Field emission effect

CNT has a unique field emission effect that can cause quantum tunneling phenomenon [141], which gives a better explanation for the presence of electrical conductivity of some uncontacted conducting particles. The theory believes that there is a potential energy barrier between uncontacted conduct particles, and some electrons will overcome the potential energy barrier and undergo a directional transition if there is a potential energy difference and the space is small, which leads to the conductive phenomenon when conductive particles not lap each other or the gap is close to 1 nm [142]. Hu et al. [143] combined the 3D resistance network model and 3D fiber reorientation model to simulate the resistance variation and field emission effect of composite material, and combined with the SEM to provide a more visual representation, as shown in Figure 12. After verification by experiments, it was concluded that tunneling effect caused by field emission effect is the main conduct mechanism when the content of CNT is below and close to \( \phi_c \). Simmons [144] proposed an equation for the tunneling effect,

\[
J = \frac{3(2\pi m)^{1/2}}{2S^2}\left(\frac{e}{\hbar}\right)\exp\left[-(4\pi S^2 m^2)^{1/2}\right],
\]

where \( J \) is the current density; \( \varphi \) is the gap barrier; \( S \) is the gap width; \( m \) is the single electron mass; \( e \) is the single electron charge; and \( \hbar \) is the Planck constant.

From equation (3), it can be seen that tunneling current density \( J \) is the exponential row of gap width \( S \).

Figure 11: 3D contact network diagram of CNT in cement matrix [140].
Therefore, it can be considered that a smaller gap width is necessary for the tunneling effect to occur. Lutwyche and Wada [145] suggested that the tunneling effect of CNT in matrix could only occur if the gap distance reached the nanoscale. Han et al. [139] believed that the tunneling current caused by the field emission effect of CNT has limited improvement in the conductivity of composite compared to the contact conductivity, but has a significant enhancement of the piezoresistive properties. This is mainly due to the fact that the particle gap is too large for field emission effect to occur when the conductive filler concentration is low. If the composite material is compressed and deformed, the particle gap decreases to the nanometer scale, the tunneling effect is significantly enhanced, and the resistivity is significantly reduced, showing a strong piezoresistive response.

5.1.3 Effective medium theory

Both cement matrix and the corresponding composites are essentially non-uniform media with defects, and the effective medium theory is to consider each particle in the non-uniform composite as an effective medium with the same conductivity, which explains the conductive behavior in discontinuously distributed system. Effective medium theory can be divided into two types: Bruggeman uniform effective medium and nonuniform effective medium [146].

Effective medium theory can better simplify the analysis model of composite conductivity, but the application is based on the premise that the conductive particles in any range can be completely filled with a certain defined medium, which requires the conductive particles in matrix meet at least three requirements: (a) wide enough distribution; (b) sufficient numbers; (c) small enough size. Actually, it is difficult to fill all of the above requirements in practice [147]. Therefore, the effective medium theory has certain errors and defects in the application of binary system.

The three aforementioned theories are widely used in analyzing the piezoresistive behavior of CNTCS, and the actual simulation process should not be analyzed by single theory alone, but be comprehensively considered and interconnected. Effective medium theory can homogenize the discontinuous and heterogeneous medium, which can better link the microstructure and macroscopic properties of composite materials [148]. This model simplification process can be well combined with percolation theory and field emission effects. The percolation and field emission effect are continuous transition processes and constitute the main mechanism of piezoresistive response of CNTCS [149], as demonstrated in Figure 13. When the conductive phase content is low, the gap

![Figure 12: Schematic diagram of CNTCS tunneling effect (J stands for tunneling current): (a) SEM image of possible CNT tunneling and (b) tunneling model diagram [143].](image)
between conductive particles is large and no tunneling effect occurs without overlap (Figure 13(a)); the conductive phase content increases which leads to the spacing of conductive particle to be smaller, although not lapped but the field emission effect can break through the barrier and undergo transitions, the resistivity is reduced (Figure 13(b)). If the conductive phase content reaches near the percolation threshold, a conductive pathway will form and a sudden change in resistivity occurs, but it does not mean that the tunneling effect does not exist (Figure 13(c)). The conductive phase content continues to increase, where the resistivity comes to plateaus (Figure 13(d and e)).

5.2 Piezoelectric mechanism analysis

CNT mostly appears in PCM as piezoelectric enhancement phases, and the piezoelectric behavior of the composite is closely related to \( \varphi_c \). Therefore, the enhancement mechanism of piezoelectric behavior by CNT/PCM can still be explained by the percolation theory.

To ensure the efficient realization of piezoelectric behavior, a sufficient effective polarization electric field is required to act on the piezoelectric phase. But cement matrix is almost insulated and the piezoelectric phase is isolated and cannot be effectively polarized. The low \( \varphi_{CNT} \) can build part of the conductive path in cement matrix (as shown in Figure 14), which reduces the resistance of matrix while greatly improving the efficiency of polarizing electric field. Some results showed that CNT doping could reduce the polarization voltage of PCM by about 50% [81]. The increase in polarization efficiency leads to effective activation of the piezoelectric activity of piezoelectric phase, and the composite exhibits a more efficient electromechanical conversion efficiency, with a consequent increase in \( d_{33} \). Meanwhile, the incorporation of CNT will create a new interface in the three-phase system, and the conductive layer can act as an electronic micro-reservoir on the basis of increasing the polarization efficiency and inducing the generation of dipoles, inducing charge storage at the CNT–substrate interface and causing the enhancement of dielectric properties. However, all above are based on the premise that \( \varphi_{CNT} < \varphi_c \). The conductive network of the composite material is completely formed when \( \varphi_{CNT} \) exceeds \( \varphi_c \), where a large amount of leakage current and dielectric loss will occur, which will have an extremely negative impact on the piezoelectric and dielectric properties.

Lower \( \varphi_c \) achieved by CNT conducting effect makes it have wide application prospects in piezoelectric damping materials. On the basis of improving the piezoelectric and dielectric properties of CNT, there must be dielectric loss due to the formation of conductive paths. The conductive network is completely formed when \( \varphi_{CNT} \) reaches \( \varphi_c \), the piezoelectric composite material will convert the mechanical

![Figure 13: Schematic diagram of resistivity change with varied conductive phase doping [135].](image)

![Figure 14: Conductive pathway constructed by CNT nanofibers in PCM matrix (yellow arrows are CNT): (a) bridging fibers between cracks; (b) pull-out fibers from PCM matrix (yellow arrows are CNT) [85].](image)
energy bearing into electric energy, in addition to leakage current and dielectric loss at this time, the electric energy will be dissipated by transforming into heat energy through the conductive network, achieving the energy dissipation of mechanical–electricity–heat transformation, and the damping reinforcement effect [150].

Although the percolation theory can give a systematic explanation of the enhancement mechanism of CNT affecting the three piezoelectric performance parameters of $d_{33}$, $\varepsilon_r$, and $\tan \delta$, the theory cannot explain the effect of electron jumping behavior on the piezoelectric performance other than the conducting pathway. When $\varphi_{\text{CNT}} < \varphi_c$, a CNT piezoelectric enhancement mechanism with tunneling effect as the main effect and percolation theory as a supplement should be considered. Finally, the percolation theory enhanced CNT piezoelectric effect should be considered when $\varphi_{\text{CNT}} \geq \varphi_c$.

The enhanced electromechanical sensing performance of CNTCS mainly relies on the construction of CNT conductive network. The distributed conductive fibers forms composed by field emission or contact mechanism will vary with the CNT spacing, accordingly the CNTCS exhibits piezoresistive properties. The formation of conductive networks improves the polarization efficiency of piezoelectric particles and enhances the piezoelectric properties of PCM. Hence, the enhancement mechanisms of CNT on the piezoresistive and piezoelectric sensing properties of PCM are interlinked.

We should focus on the enhancement mechanism of CNT on the piezoresistive and piezoelectric properties of CNTCS to lay the electromechanical sensing mechanism of the CNTCS and establish a unified accurate quantitative analysis model as a basis for the development of piezoresistive/piezoelectric CNTCS, which can improve the compatibility of intelligent structures with environmental signals. At the same time, multi-scale research and analysis of CNTCS should be considered to establish cross-scale analysis mechanisms to promote the in-scale application of CNTCS.

6 Conclusions

Based on the characteristics of CNT, this article summarizes and analyzes some of the existing research results from the following three aspects: experimental study, model analysis, and mechanism discussion for the electromechanical (piezoresistive/piezoelectric) sensing effect of CNT-reinforced composites, which draw the following conclusions:

1. The dispersion of CNT in aqueous system is still a major challenge limiting its application. According to the available research results, CNT is first weakly covalently modified and then combined with surfactant ultrasonic dispersion treatment it seems to be the optimal choice; UV-Vis spectroscopic analysis is an effective means to rapidly and quantitatively characterize the effect of CNT dispersion.

2. Regarding the piezoresistive behavior of CNTCS, moisture content, load conditions, CNT content, surface treatment methods, and the effect of CNT mixed with other conductive fillers are focused on. The research results proved that the aforementioned factors had significant impacts on the piezoresistive behaviors. Incorporation of CNT will have a significant impact on the piezoelectric, dielectric, and dielectric loss properties of piezoelectric composite, especially when $\varphi_{\text{CNT}}$ is closely related to $\varphi_c$.

3. The enhancement mechanism of CNT on the piezoresistive and piezoelectric properties of CNTCS is analyzed and discussed by model building and mechanism discussion, respectively. For the establishment of the piezoresistive model there are mainly two methods: physical simulation and numerical simulation. The numerical model has achieved a leap from qualitative to quantitative analysis. As yet, there are limited studies on the prediction and evaluation models for the effective performance of CNT-reinforced PCM, and the available studies are not sufficient to establish a full-framework performance evaluation system. However, model analysis is still an effective tool for studying multifunctional composites that related studies need to be carried out in depth. Percolation theory, field emission effect, and effective medium theory can be used as complementary mechanisms to effectively interpret the piezoresistive response mechanism of CNTCS under different $\varphi_{\text{CNT}}$. The enhancement mechanism of piezoelectric behavior of CNTCS by CNT as a piezoelectric enhancement phase can be explained by percolation theory, but the current discussion of this enhancement mechanism is not comprehensive enough and other theories need to be further considered.

4. This article can be used as a reference review model for CNTCS, which has theoretical support significance.

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