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Original Article

Moisture dependence of electrical resistivity in under-percolated cement-based composites with multi-walled carbon nanotubes

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ABSTRACT

Cement-based piezoresistive composites have attracted significant attention as smart construction materials for embedding self-sensing capability in concrete infrastructure. Although a number of studies have been conducted using multi-walled carbon nanotubes (MWCNTs) as a functional filler for self-sensing cement-based composites, studies addressing the influence of the internal moisture state on the electrical properties are relatively scant. In this study, we aim to experimentally investigate the effect of internal moisture state on the electrical resistivity of cement-based composites containing MWCNTs as an electrically conductive medium to raise a need for calibration of self-sensing data considering the internal moisture state. To this end, the moisture dependence of electrical resistivity in under-percolated cement-based composites was mainly evaluated, along with other material properties such as strength, shrinkage, and flowability. Results revealed that the electrical resistivity increased almost linearly as the internal relative humidity (IRH) decreased, and the increase was more pronounced below the percolation threshold. In addition, it was found that the strength gained by the microfiller effect of MWCNTs was significantly reduced particularly in under-percolated mixtures, leading to overall strength reductions. Furthermore, this study showed that the more the MWCNT was added, the smaller the flowability was obtained due to the increased viscosity of the mixture. The findings of this study are expected to provide pivotal information for accurate and reliable interpretations of self-sensing data generated by MWCNT-embedded cement-based composites.

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1. Introduction

Many in-service civil infrastructure assets that have reached their service lives require extensive repair and rehabilitation to keep them safe and functional [1,2]. For proper decision-making related to prioritization and selection of projects that need maintenance, it is crucial to accurately assess the structural conditions of the infrastructure efficiently and sustainably. A self-sensing cement-based composite is a stimuli-responsive material that is engineered to function on a pressure-driven stimulus, namely piezoresistivity [3]. Taking advantage of the piezoresistivity, a concrete element itself can act as a sensor because its electrical resistivity changes depending on the magnitude and direction of the applied stress [4]. Such self-sensing materials have recently attracted significant attention as they can be potentially implemented for intelligent structural health monitoring and advanced damage detection in various concrete infrastructures without the installation of any specific or high-cost sensors, devices, and accessories [5–7].

To embed the piezoresistive capabilities of cement-based materials, highly electrically conductive media, such as carbon nanotubes [8], chopped carbon fibers [9], carbon blacks [10], and graphene [11] are generally added. In such cement-based composite systems dispersed with highly electrically conductive media, the total electrical conductivity relies on the following: (1) contact conductivity via a connected network of conductive phases [12], (2) tunneling conductivity via isolated conductive media [13], and (3) ionic conductivity via pore solution in the matrix [14]. In particular, the pore solution is a good source of electrolytes, which substantially contributes to the formation of electrically conductive pathways in the matrix of the composites. This implies that variations in internal moisture content may have a considerable effect on the piezoresistive responses of the composites [7,15]. Concrete structures generally lose their pore solutions over time due to prolonged drying over the service life, which in turn may noticeably reduce the ionic conductivity [16–18]. In addition, the environmental interactions in concrete structures may lead to continuous changes in the moisture state of materials [19]. Therefore, to implement MWCNT-embedded composites as sensing materials for long-term monitoring of actual field structures, it is crucial to quantitatively evaluate the effect of moisture state on its electrical properties.

Nonetheless, only a few studies address the influence of the internal moisture state on the electrical characteristics of self-sensing composites. Han et al. [20] reported that the water content in multi-walled carbon nanotube (MWCNT)/cement composites under uniaxial compression is a key factor influencing the piezoresistivity of the composites. Song et al. [21] fabricated the cement composites containing 0.5% MWCNTs, showing that the piezoresistive responses such as initial electrical resistivity, amplitude of resistivity change, and piezoresistive sensitivity increased as the internal moisture state decreased. Jang et al. [22] examined the effect of water ingress on the electrical conductivity of CNT/cement composites, indicating that the water ingress significantly affected the electromechanical sensing responses. Several other studies also analyzed the effect of water content changes depending on exposure conditions such as ambient humidity, temperature, and curing regime on the piezoresistive properties of cement-based self-sensing composites [7,23,24]. Although these former studies investigated the influence of the internal moisture state on the electrical characteristics, the moisture state was mostly characterized by the weight changes of a specimen, of which only a few studies adopted internal relative humidity (IRH) as an indicator to present the internal moisture state. The water content can be calculated by measuring the weight changes of a sample using a digital scale [20,23], but this may lead to measurement errors (sample loss, readability, operator, etc.) and poor accuracy. Also, the moisture content can be estimated based on IRH using desorption isotherms that relate IRH to the evaporatble moisture content in the pores [25,26]. However, measuring IRH is a more reliable means because it depends entirely on the internal moisture state without any interference from other factors [21]. Therefore, a systemic study using IRH as an indicator is needed for better identification of the relationship between moisture state and electrical property. In addition, studies evaluating the moisture dependence of electrical resistivity below a percolation threshold are lacking. Most previous studies have investigated the changes in electrical properties above the percolation threshold [3]. However, since the relationship between internal moisture state and electrical property may not be consistent at different levels of MWCNT content, an investigation is essentially required for a reliable interpretation of data generated by self-sensing cement-based composites with different contents of electrically conductive media.

The primary aim of this study is to identify the effect of internal moisture on the electrical resistivity of MWCNT-embedded cement-based composites. To this end, the composites with different additions of MWCNTs (0.1–1.0% by mass of cement) were fabricated, and the percolation threshold was determined by measuring the electrical resistivity. In addition, a simple method capable of determining the percolation threshold in cement-MWCNT composites was proposed. Following that, two MWCNT contents leading to under-percolated MWCNT networks in the matrix (i.e., 0.3% and 0.5%) were investigated to observe the impact of the

Table 1 – Chemical composition and physical properties of cement.

Chemical composition (%)								Fineness (m^2/kg)	Specific gravity (–)
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O		
19.7	5.33	2.90	61.5	3.81	2.54	0.86	0.18	370	3.15

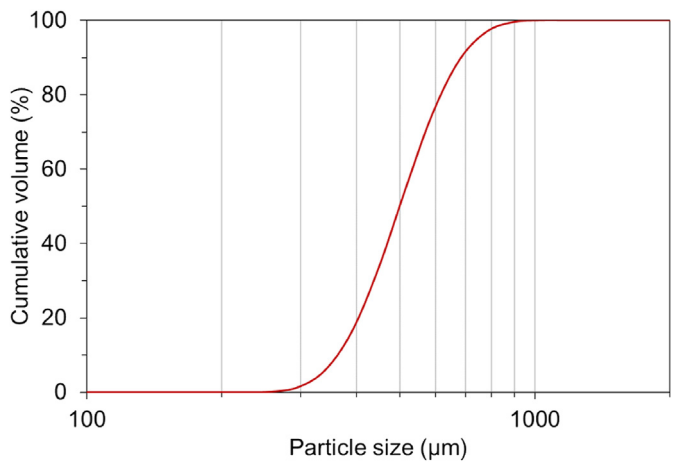

Fig. 1 – Cumulative particle size distribution of standard sand used.

internal moisture state on the electrical resistivity as over-perlocated mixtures would have a non-significant internal moisture effect. The moisture state in the specimens was quantified by measuring the IRH. Additionally, the effects of MWCNT content on the strengths, shrinkage, and flowability of the composites were comprehensively investigated.

2. Experimental

2.1. Materials

Type I Portland cement per ASTM C150 was used, and its chemical composition and physical properties are listed in Table 1. The phase compositions of the cement computed based on the Bogue equation were 60.65% C3S, 10.72% C2S, 9.22% C3A, and 8.82% C4AF. Standard sand with a specific gravity of 2.65, fineness modulus of 2.87, absorption capacity of 1.02%, SiO_2 content of 98.4%, and median diameter (D50) of 533 μm were used as fine aggregates. Fig. 1 shows the particle size distribution of the standard sand measured using a particle size analyzer (Hydro 2000S; Malvern Instruments, USA).

A chemically functionalized multi-walled CNT (MWCNT) was used as an electrically conductive medium (K-Nanos SWT300; Kumho Petrochemical, Korea). The MWCNT used in this study was in the form of a suspension, which was dispersed in water using a sodium dodecyl sulfate-based chemical surfactant. Tables 2 and 3 present the properties of the MWCNT suspension and those of the MWCNT, respectively. In addition, Fig. 2 shows a scanning electron microscope (SEM) image of the MWCNT used in this study.

2.2. Methods

2.2.1. Percolation threshold of MWCNT

Cement-MWCNT composite specimens with dimensions of 50 × 50 × 50 mm^3 were fabricated with varying amounts of MWCNT ranging between 0.1% and 1.0% (by mass of cement) with a 0.1% interval to determine the percolation threshold. To assess the percolation threshold of the MWCNT irrespective of the internal moisture state, the electrical resistivity was measured for up to 28 days while the specimens were continuously dried at 30 ± 0.5 °C and 40 ± 1% RH. Two duplicates were tested to ensure the reliability and repeatability of the data. A water-to-cement (w/c) ratio of 0.45 and a fine aggregate-to-cement (a/c) ratio of 2.4 were consistently used to formulate the cement-MWCNT mixtures. Kostrzanowska-Siedlarz [27] reported that a w/c of 0.45 was most commonly used in cement-MWCNT composites through a statistical analysis of 39 studies. In addition, previous studies have revealed that an increase in w/c improved the piezoresistivity of cement-MWCNT composite [28], while the change in the w/c had a limited influence on the percolation threshold [29]. In consideration of the general mixture proportions with enhanced piezoresistivity, a w/c of 0.45 was chosen in this study. An s/c of 2.4 was employed to obtain the target flowability (210 mm) of the control mixture [30]. The mixing water content was adjusted according to the water content in the CNT suspension. A 5-L Hobart-type mixer was used to mix the cement-MWCNT composites in accordance with the following procedures:

- Mix dry cement and fine aggregate for 1 min with a mixing intensity of 140 rpm

Table 2 – Properties of the MWCNT suspension.

Color	MWCNT contents (%)	CNT type	Suspension base	Viscosity (cps)	Surface resistance (Ω/□)	pH
Dark black	3.0	MWCNT	Water	<300	<300	7–8

Table 3 – Properties of the MWCNT.

Type	Bundle diameter (μm)	Bundle length (μm)	Diameter (nm)	Purity (%)	Crystallinity (IG/ID)	Bulk density (g/mL)
Bundle	2.4–3	27	8–15	>95	0.80	0.015–0.030

- Add a mixture of water and CNT suspension for 30 s with a mixing intensity of 140 rpm
- Mix for another minute with a mixing intensity of 285 rpm
- Scrap the mortar from the wall and manually mix for 1 min
- Final mix for 1 min with a mixing intensity of 285 rpm

As electrodes to measure the electrical resistivity of the cement-MWCNT specimen, four thin copper plates with dimensions of 25 (W) × 50 (H) × 0.8 mm (T) were inserted at a constant spacing of 10 mm. The embedment depth of the electrodes was 40 mm. In this study, an LCR meter (LCR-821; GW Instek, Taiwan) operating on an alternating current (AC) voltage source was employed to monitor the electrical resistivity based on the Wenner 4-point method because the 2-point method using a direct current (DC) voltage source can lead to the polarization of the pore solution over time, resulting in unstable electrical resistivity outputs. Additionally, because the outputs generated based on the Wenner 4-point method do not include the effect of contact resistance between the electrode and surrounding material, more reliable results can be collected compared to the method using the 2-point circuit layout. Fig. 3 shows the specimen used to determine the percolation threshold of MWCNT.

2.2.2. *Internal relative humidity on electrical resistivity*

Twenty pairs of under-percolated cement-MWCNT specimens were produced with dimensions of 50 × 50 × 50 mm^3 to measure the IRH of the cement-MWCNT composites and the corresponding electrical resistivity at those IRH levels. To see the dramatic effect of IRH on the electrical resistivity of cement-MWCNT composites, two under-percolated mixtures (ten pairs with 0.3% MWCNT and the other ten pairs with 0.5% MWCNT) were tested. As with the percolation threshold testing, a w/c ratio of 0.45 and a/c ratio of 2.4 were used to fabricate the cement-MWCNT mixtures, as shown in Table 4.

A capacitance-type humidity sensor (HYT-939; IST AG, Switzerland) with a diameter of 9.8 mm and a data logger (MSHTDL-16; Japan) were used to measure the IRH of cement-MWCNT composites at the geometric center of the specimen. The accuracy and response time of the humidity sensor was ±1.8% RH and 10 s, respectively. To protect the humidity sensors against direct water contact, they were treated with an impermeable thin-walled hollowed plastic tube capped with an engineered fabric that permitted effective vapor transmission before embedded in the cement-MWCNT composites as illustrated in Fig. 4.

Four thin copper plate electrodes with dimensions of 25 (W) × 50 (H) × 0.8 mm (T) were embedded at a constant spacing of 10 mm and embedment depth of 40 mm to measure the electrical resistivity using the 4-point method. Fig. 5 shows a pair of IRH (left) and resistivity (right) specimens tested in this study.

To identify the effect of IRH on the electrical resistivity, humidity sensors and electrodes were installed at the designated locations as soon as the mixture was cast into the molds. Subsequently, the specimens were stored in dual airtight plastic bags and cured for 24 h in an environmental chamber maintained at 23 ± 0.5 °C and 98 ± 1% RH. After demolding, each specimen was tightly wrapped with adhesive-backed aluminum foil and then stored in the environmental chamber for 5 weeks at 23 ± 0.5 °C and 98 ± 1% RH. To prevent possible leakage of vapor through the gap between the plastic tube and composite, a sealant was applied around the plastic tube of the IRH specimens. After 5 weeks, all the specimens were simultaneously dried at 30 ± 0.5 °C and 40 ± 1% RH, as shown in Fig. 6(a). Each pair of IRH and resistivity specimens was treated precisely the same to maintain identical moisture conditions during the drying process. Once any pair of specimens reached the target IRH level, the pair was sealed using aluminum foil to achieve moisture

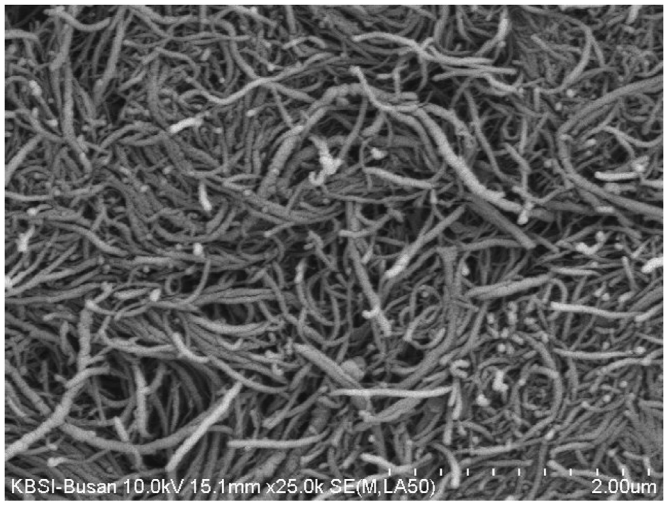

Fig. 2 – SEM image of the dry MWCNT used in this study (magnification: ×25.0 k).

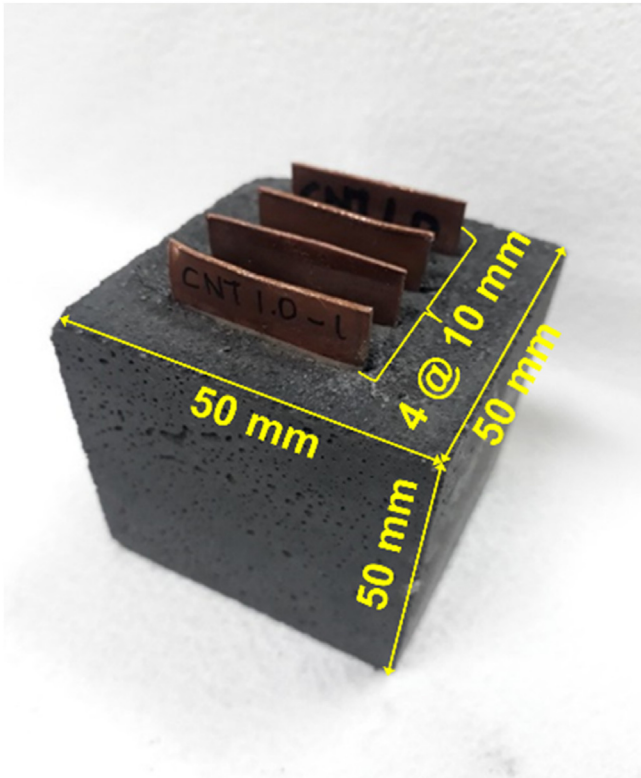

Fig. 3 – Cement-MWCNT composite specimen used in percolation threshold test embedded with 4 equally spaced copper plates.

equilibrium within the specimens. Fig. 6(b) shows the typical IRH behavior of the specimen before drying, while drying, and subsequent sealing for equilibrium measured from three different IRH specimens. Immediately after the moisture equilibrium was obtained, the electrical resistivity was measured using an LCR meter, as illustrated in Fig. 6(c).

2.2.3. *Flexural and compressive strengths*

Three replicate prismatic specimens with dimensions of $40 \times 40 \times 160$ mm^3 were fabricated with 0, 0.2, 0.4, 0.6, 0.8, and 1.0% MWCNT by mass of cement. The specimens were cured at 23 ± 0.5 °C and 98 ± 1% RH until the specified test ages, i.e., 1, 3, 7, and 28 days. Flexural strength was measured as per ASTM C348 (Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars) using a center–point loading scheme with a load rate of 50 N/s. ASTM C349 (Standard Method for Compressive Strength of Hydraulic-Cement Mortars Using Portions of Prisms Broken in Flexure) was adopted for compression tests. Six parallel specimens were tested for each mixture with a load rate of 2400 N/s. The load-bearing area for the compression test was 40×40 mm^2. A 200-kN universal testing machine (UTM) was employed for the strength measurements.

2.2.4. *Shrinkage*

Freshly mixed cement-MWCNT mixtures with 0, 0.2, 0.4, 0.6, 0.8, and 1.0% MWCNT by mass of cement were poured into molds with inner dimensions of $50 \times 50 \times 300$ mm^3 in two layers to produce shrinkage specimens. Each layer was vibrated for 30 s using a vibrating table after manually compacting 25 times using a tamping rod. A vibrating-wire strain gage (VWSG) (Model 1240; ACE Instrument Co., Ltd.) with a capacity of 3000 με, gage length of 153 mm, and resolution of 0.5 με was longitudinally embedded between the layers (at the geometric center of the cross-section) to measure the bulk shrinkage strain. Before placing the mixture, a double layer of polyethylene sheets was placed onto the mold to minimize the friction between the specimen and mold. The specimen was demolded after 24 h and then tightly sealed with adhesive-backed aluminum foil to prevent moisture loss. Subsequently, all the specimens were stored in an environmental chamber set at 23 ± 0.5 °C for 14 days to measure the autogenous shrinkage. After 14 days, the aluminum foil was removed, and the specimens were consistently exposed to 30 ± 0.5 °C and 40 ± 1% RH for up to 90 days to measure the free drying shrinkage (see Fig. 7).

2.2.5. *Flow*

The flowability of fresh cement-MWCNT mixtures was measured based on ASTM C1437-20 (Standard Test Method for Flow of Hydraulic Cement Mortar) using a motorized automatic flow table. Eleven mixtures with an MWCNT content between 0.1% and 1.0% (by mass of cement) with a 0.1%

Table 4 – Mixture proportions of cement-MWCNT composites for determining percolation threshold.

Mixture	Effective w/c	Weight per unit volume (kg/m^3)			
		Cement	Fine aggregate	Water	MWCNT suspension[a]
Control	0.45	597.7	1434.4	269.0	0.0
CNT 0.1%		597.3	1433.6	249.5	19.9
CNT 0.2%		597.0	1432.7	230.0	39.8
CNT 0.3%		596.6	1431.9	210.6	59.7
CNT 0.4%		596.3	1431.0	191.2	79.5
CNT 0.5%		595.9	1430.2	171.8	99.3
CNT 0.6%		595.5	1429.3	152.5	119.1
CNT 0.7%		595.2	1428.5	133.1	138.9
CNT 0.8%		594.8	1427.6	113.8	158.6
CNT 0.9%		594.5	1426.8	94.5	178.3
CNT 1.0%		594.1	1425.9	75.3	198.0

[a] Note: The MWCNT content in the suspension was 3.0 wt.%.

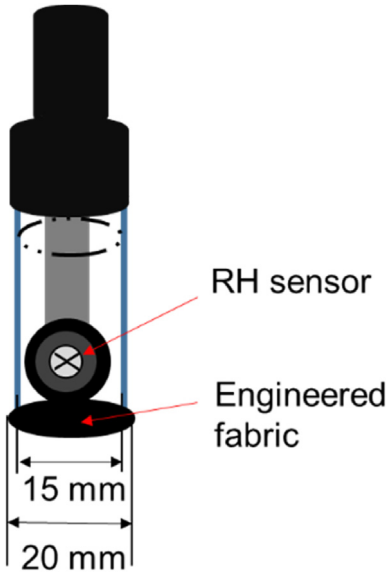

Fig. 4 – Schematics of IRH sensor treated with hollowed plastic tube and engineered fabric for internal moisture measurement.

interval were produced. The mixture was placed into a mold in two 25-mm thick layers. Each layer was tamped 20 times with a tamping rod. Excess mortar was cut off using a straight edge of a trowel across the top of the mold to produce a flat top surface. Subsequently, the mold was lifted, and the table was dropped 25 times in 15 s through a height of 12.5 mm. The flow was defined as a percentage of the spread average diameter to the original base diameter.

3. Results and discussion

3.1. *Determination of percolation threshold of MWCNT*

Fig. 8 shows the effect of the MWCNT content on the variations in electrical resistivity over time. Similar to the results of many previous studies, the electrical resistivity tended to decrease dramatically as the MWCNT content increased [3]. This tendency can be well described by the fact that the increased amount of MWCNT particulates creates better dispersed electrically conductive pathways/networks in the matrix, mostly via direct contact of the MWCNTs and their tunneling [3]. An increase in the electrical resistivity over time was also noted for several mixtures with lower MWCNT contents (<0.5%). This result is understandable because the continued loss of internal moisture due to expedited drying gradually reduced the ionic conductivity of the cement-MWCNT composites. It should also be mentioned that the electrical resistivity was rarely affected by age and internal moisture state, particularly when more than 0.5% MWCNTs were added.

The percolation threshold is defined as the minimum filler content that can ensure a continuous conductive pathway by forming a contact between adjacent conductive particles in the composite matrix [31]. The most common practice to determine the percolation threshold in MWCNT-embedded composites is to relate a conductive medium content to electrical resistivity and to find the point at which a sudden change in the slope occurs on the curve [32]. However, because the shape of the curve significantly varies depending on the age and corresponding moisture state, as shown in Fig. 8(a), it is more reasonable to define the percolation threshold as the lowest MWCNT content where the electrical resistivity hardly changes over time and moisture state. Rooted in this fact, the percolation threshold of MWCNT was determined to be 0.5%, as little change in the electrical resistivity over time was observed above this content as a result of the interconnected MWCNT networks in the matrix as shown in Fig. 8(b). The percolation threshold determined in this study fell within the range of 0.3–0.6 wt.% reported by Kim et al. [33].

3.2. *Effect of internal relative humidity on electrical resistivity*

The effect of IRH on the electrical resistivity of the under-percolated cement-MWCNT composites (0.3% and 0.5%) is shown in Fig. 9. Again, the 0.5% series overall showed lower electrical resistivities because denser electrically conductive networks with a higher degree of redundancy were established as a result of increased MWCNT content. In addition, it is important to note that the electrical resistivity increased almost linearly with a decrease in IRH for both MWCNT contents. As discussed earlier, the reduced ionic conductivity due to the loss of internal moisture (i.e., pore solution) appears to be the key reason for this trend. The electrical resistivity of the 0.3% series increased by approximately 5.5 times when the IRH decreased from 98% to 50%, while that of the 0.5% series approximately doubled with the same IRH drop. This result indicates that the moisture dependence of the electrical resistivity was greater for the 0.3% series than for the 0.5% series. This result is valid because the 0.3% series contains fewer MWCNT particulates sparsely distributed in the matrix, and thus its electrical conductivity relies more on the internal moisture than the direct contact of MWCNTs and their tunneling effect. Based on these findings, it can be concluded that the internal moisture state is a crucial factor that affects the overall electrical resistivity of the under-percolated cement-MWCNT composites. Because the so-called "self-

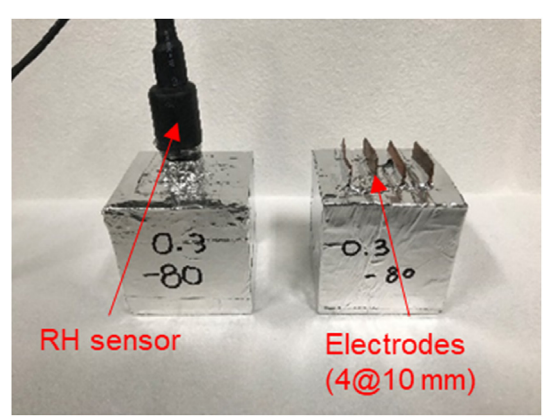

Fig. 5 – Specimens for IRH (left) and resistivity (right) measurements used in this study (aluminum foil wrapped for equilibrium).

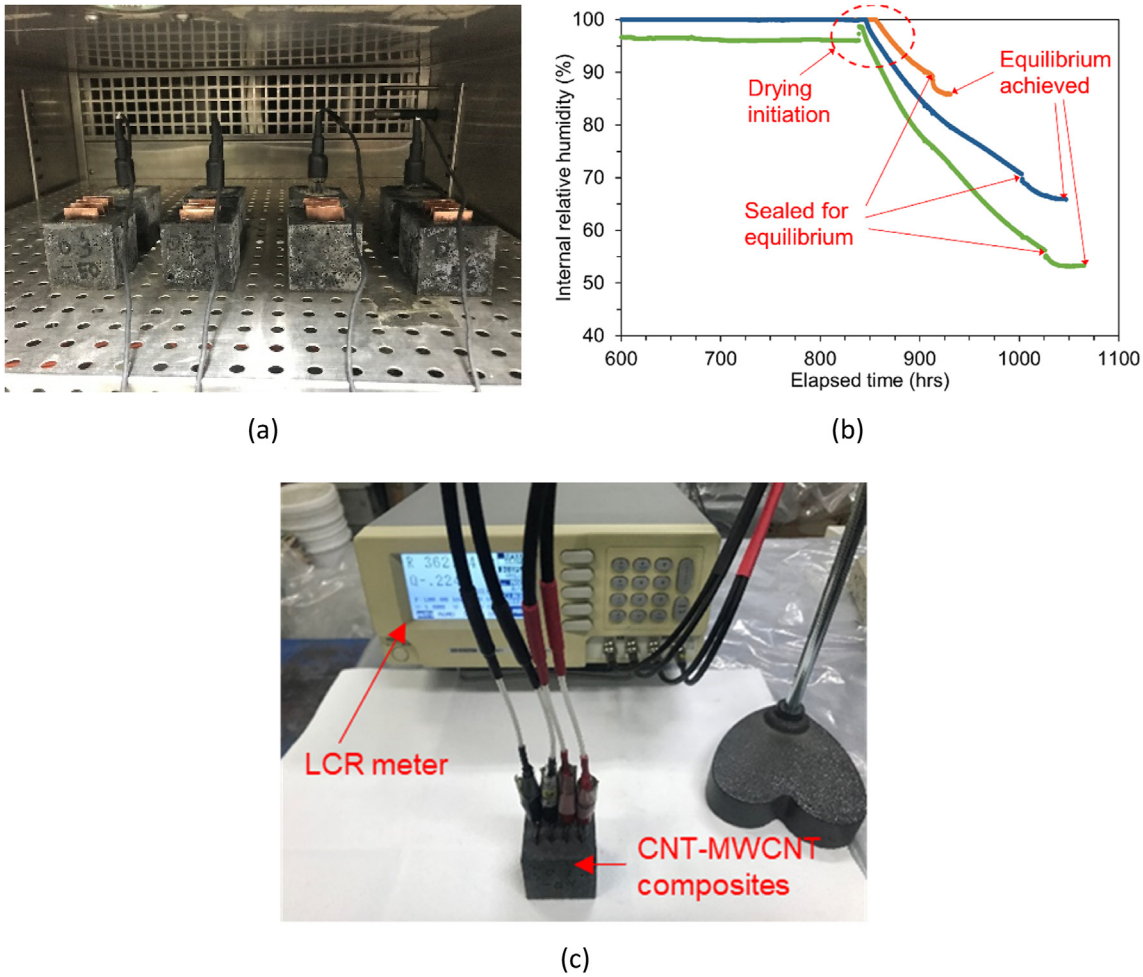

Fig. 6 – Experimental procedure: (a) IRH and resistivity specimens while drying in environmental chamber; (b) data samples showing the changes in IRH before drying, while drying, and subsequent sealing; (c) electrical resistivity measurement using LCR meter and 4 independent probes.

sensing smart concrete structures" use electrical resistivity as an indicator to detect damages and structural conditions, such as stress, deflection, cracking, and steel corrosion, the moisture state should be essentially taken into account for accurate and reliable interpretations of self-sensing data.

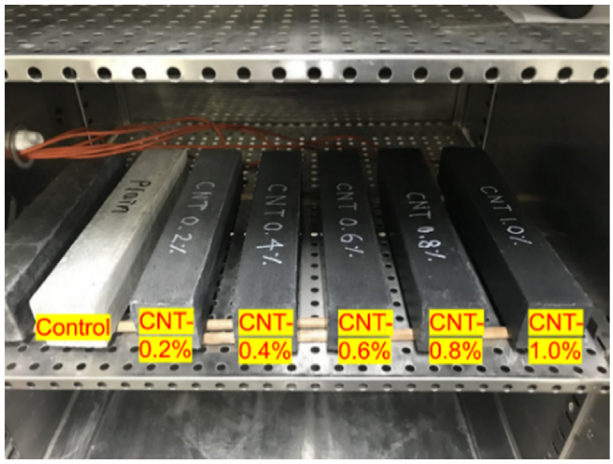

Fig. 7 – Cement-MWCNT specimens subjected to drying in environmental chamber.

3.3. *Effect of MWCNT content on strengths*

Fig. 10 presents the effect of MWCNT additions on the flexural strength and compressive strength of cement-MWCNT composites, respectively. Compared to the control mixture, both the flexural and compressive strengths overall decreased with additions of MWCNT. While several former studies [3,34] reported that the addition of MWCNT generally leads to an increase in strengths thanks to its excellent stiffness and strength, adverse results were obtained in this study. Some previous studies [35–38], however, also showed quite similar results to the present study. Naqi et al. [35] reported that the compressive strength of cement-based composites incorporating less than 0.05% of MWCNT increased in proportion to the MWCNT content and was higher than that of the reference mixture without MWCNTs. For the higher MWCNT contents, however, the cement-MWCNT composites showed lower strengths than the reference mixture, and the strengths even decreased further as the MWCNT content increased. Morsy et al. [36] found that the strength of cement-MWCNT

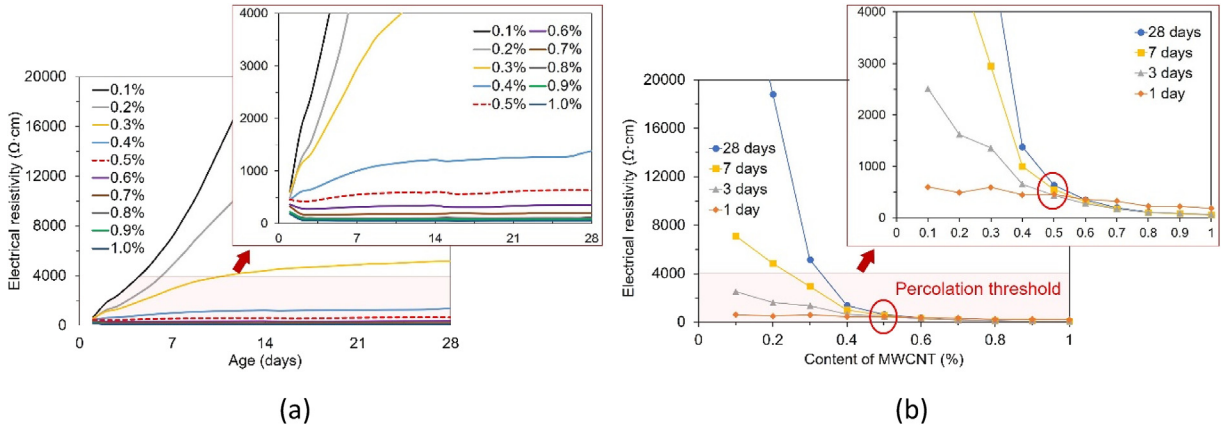

Fig. 8 – Variations in electrical resistivity of cement-MWCNT composites as a function of: (a) age; (b) MWCNT content.

composites gradually decreased with an increased MWCNT, particularly when the content exceeded 0.02%. In addition, Tragazikis [37] reported that the mortar specimens containing less than 0.8% of non-vacuumed MWCNT suspensions exhibited lower flexural strengths compared to those of the control specimen without MWCNTs. Furthermore, Choi et al. [38] reported that the compressive strength of MWCNT mortar was higher than that of the reference mortar when the w/c was 0.4, but it was comparable to or lower than that of the reference mortar when the w/c was greater than 0.4.

Based on the findings of former studies, the results shown in Fig. 10 may be attributed to the use of non-vacuumed MWCNT suspension with a chemical surfactant for dispersing MWCNT particulates in water, as it leads to excessive air entrapment in the matrix [37]. In addition, it is well identified that overdose of chemical surfactant in cement-based materials yields the degradation of concrete strength [39]. The agglomerated/tangled MWCNT particulates due to their poor dispersion may be another possible reason that caused the lower strengths because the agglomerates create weakness zones in the matrix [40,41] and weaken the bond between the carbon nanotubes and hydration products [42]. Moreover, the strength losses may be associated with inadequately wetted MWCNT because it allows the MWCNT to be pulled out due to weak bonding with the matrix, which might result in formation of microcracks [43]. However, as with the results of the aforementioned studies, as the MWCNT content increased from 0.2 to 1.0%, there was a general tendency that both the flexural and compressive strengths increased, although there was inconsistency in compressive strength between 0.2 and 0.4%, as shown in Fig. 10. This reserved trend may be explained by the fact that, in the surfactant-rich under-percolated mixtures (<0.5%), the air entrapment in the matrix due to the presence of MWCNTs was more dominant than the microfiller effect provided by MWCNTs, which resulted in lower strengths than that of the control mixture [37]. In contrast, in the over-percolated mixtures, the density enhancement effect was greater than the air entrapment effect, thereby leading to an increase in strengths [34], as shown in Fig. 10. Further elaborate studies are required in this regard.

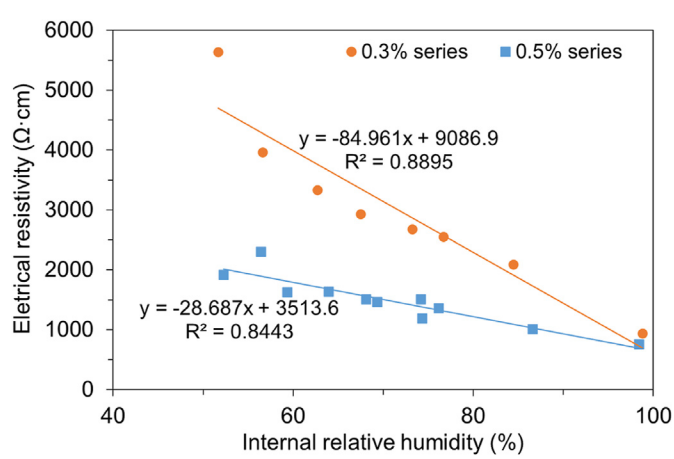

Fig. 9 – Effects of IRH on electrical resistivity of cement-MWCNT composites for two different MWCNT content (0.3% and 0.5% by mass of cement) with linear regressions.

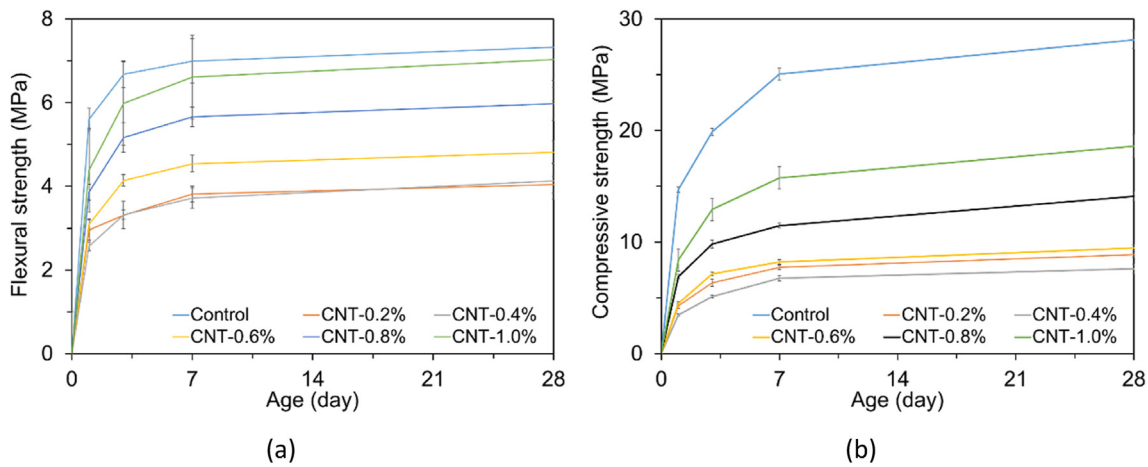

Fig. 10 – Effect of MWCNT content on the strengths of cement-MWCNT composites: (a) flexural strength; (b) compressive strength.

3.4. *Effect of MWCNT content on shrinkage*

Fig. 11(a) displays the effect of MWCNT content on both autogenous and subsequent drying shrinkage developments of cement-MWCNT composites. Fig. 11(b) shows the development of the autogenous shrinkage for approximately 14 days after the final set drawn based on Fig. 11(a). There were minor discrepancies among the mixtures over the entire measurement period, with the maximum strain difference of 5 με at 14 days found between 0.6 and 1.0%. The non-significant differences were presumably attributed to the high w/c ratio of the mixtures because autogenous shrinkage becomes significant at a low w/c generally less than 0.30 [44]. Removal of water held by capillary tension in small capillaries

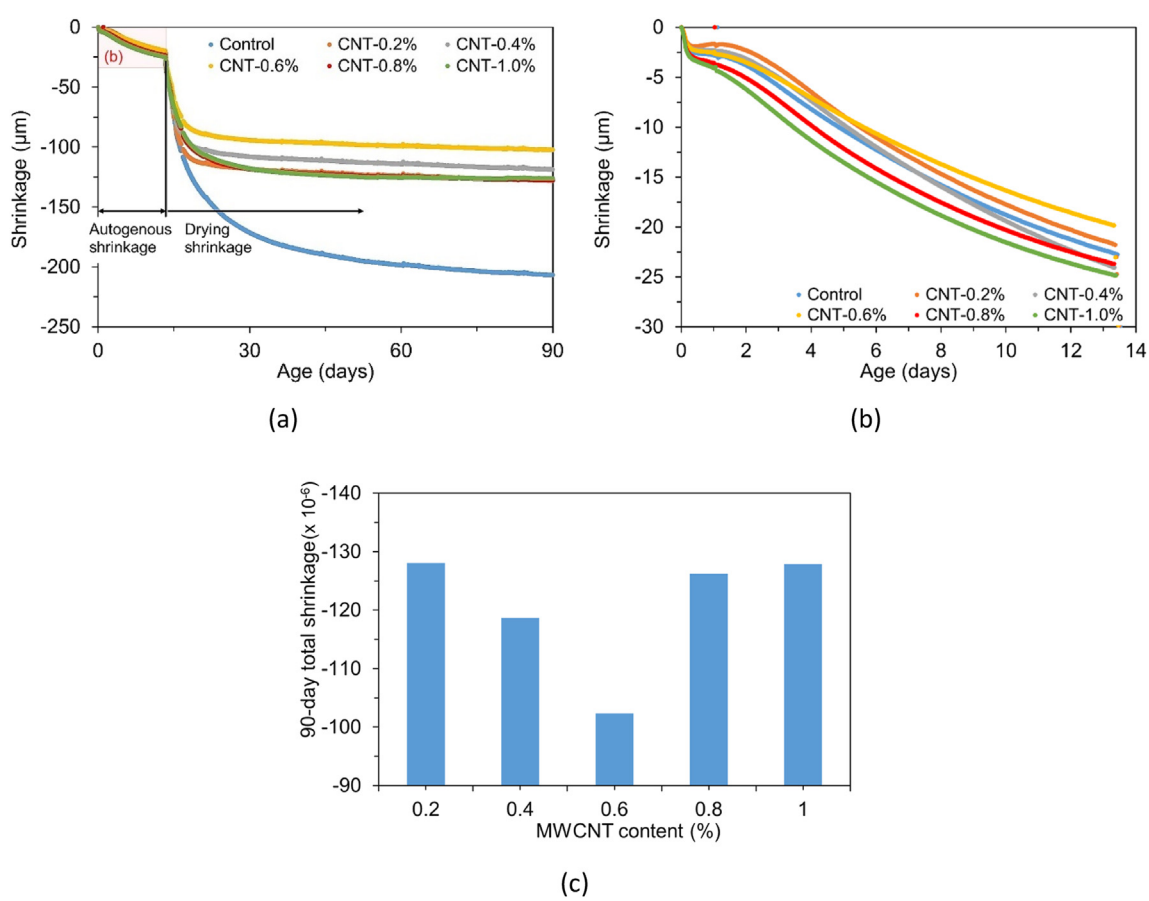

Fig. 11 – Effect of MWCNT content on shrinkage developments of cement-MWCNT composites: (a) total shrinkage (autogenous shrinkage + drying shrinkage); (b) autogenous shrinkage (taken from (a)); (c) comparison of total shrinkage measured at 90 days.

Table 5 – Measurement of spread diameter for different MWCNT contents.

MWCNT content (%)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Flow (mm)	207	199	195	188	189	179	171	168	164	156

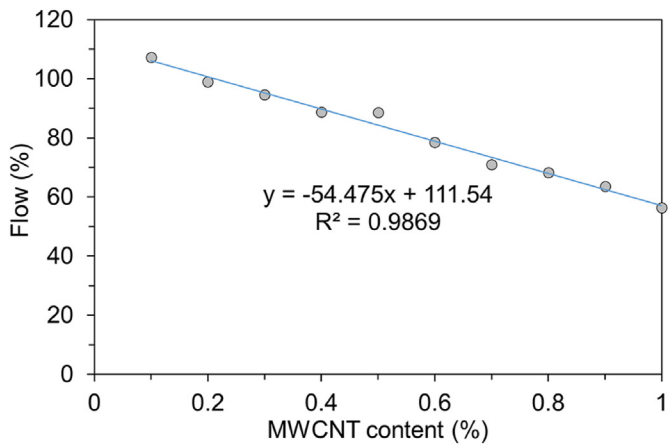

Fig. 12 – Effects of MWCNT content on flow value.

(5–50 nm) causes (autogenous) shrinkage of cement pastes [45]. Nochaiya and Chaipanich [46] reported that the addition of CNTs in cement paste decreases the amount of mesopores (<50 nm) up to 1 wt.%, which possibly decreases the autogenous shrinkage of mortar slightly along with the restraint effect.

The drying shrinkage developments in cement-MWCNT composites by up to 90 days are included in Fig. 11(a). Note that the drying shrinkage was reduced by approximately 50% with the incorporation of MWCNT. This result seems to be attributed to the hydrophobic characteristic of the chemical surfactant dissolved in the MWCNT suspension, reducing the surface tension and forming stable bubbles in the matrix [47]. Also, it appears that densification of the matrix due to MWCNT addition played a role. Among the MWCNT-embedded mixtures, the total shrinkage (i.e., superposition of autogenous and drying shrinkage) was greatest for 0.2% and was least for 0.6%, with a non-significant difference of approximately 24 $\mu\epsilon$. Fig. 11(c) shows that the 90-day total shrinkage tended to decrease almost in proportion to the MWCNT content by up to 0.6%, while it was reversed when more than 0.6% MWCNT was added. As aforementioned, the result appears to be related to the effect of MWCNT addition on the pore characteristic; in surfactant-rich under-percolated mixtures, the presence of MWCNT causes air entrapment in the matrix, resulting in a smaller negative pore pressure build-up upon drying and, in turn, less drying shrinkage. However, in over-percolated mixtures, greater pore pressure can develop when dried since the addition of MWCNT helps form a number of finer pores in the matrix.

3.5. *Effect of MWCNT content on flowability*

Table 5 presents the variations in spread diameter after 25 drops in 15 s taken for each mixture. It was evident that the flow diameter gradually decreased with an increase in MWCNT content. As can be seen in Fig. 12, the flowability almost linearly decreased as the MWCNT content increased from 0.1 to 1.0%, with a rate of −54.5%/wt.% MWCNT. The obtained result was consistent with that of many former studies, which reported that incorporating MWCNT reduces the flowability of cement-based composites mixtures. Skripkiunas et al. [48] showed that a 0.25% dose of MWCNTs added by weight of cement increased the plastic viscosity by about 29.59%. Moreover, existing works by Kim et al. [49], Ha et al. [50], Manzur and Yazdani [40], and Collins [51] reported the reductions in flowability with an increase in MWCNT content. The gradual loss of flowability appears to be associated with the increased viscosity of mixtures since an increased MWCNT concentration reportedly increases the agglomeration of MWCNT particulates [40]. Also, the significantly large specific surface area of MWCNT could be another reason that caused the reduced flowability because it facilitates high absorption of water molecules in MWCNT, thereby reducing the free water content available for the lubrication of mixtures [52].

4. Conclusions

In this study, a series of laboratory experiments was carried out to quantify the effect of internal moisture state on the electrical resistivity of multi-walled carbon nanotube (MWCNT)-embedded cement-based composites. Moreover, a new method to determine the percolation threshold in MWCNT-embedded cement-based composites was proposed. Additionally, the compressive and flexural strengths, shrinkage, and flowability of cement-MWCNT composites with different contents of MWCNT were investigated. Based on the findings obtained in this study, the following conclusions can be drawn:

1. A simple method to determine the percolation threshold in MWCNT-embedded cement-based composites was proposed. The method finds an MWCNT content of which electrical resistivity does not change with time, which was proven to be quite effective and reasonable.
2. It was established that the electrical resistivity of MWCNT-embedded cement composites significantly depends on the internal relative humidity (IRH) level. Such internal moisture effects, therefore, should be considered for an accurate and reliable analysis of self-sensing data generated by MWCNT-embedded cement-based composites with self-sensing capability.
3. As more MWCNT was added to cement-based mixtures, both flexural and compressive strengths tended to increase, although the strengths of cement-MWCNT composites were overall lower than those of the control mixture due to the air entrapment effect caused by the surfactant dissolved in the CNT suspension used.
4. Additions of MWCNT significantly reduced the shrinkage of cement-based mixtures by up to approximately 50% compared to the control mixture.
5. As the MWCNT content increased, the flowability of cement-based mixtures was almost linearly lowered due to the absorption of free water in MWCNT and resulting reduction of free water content available for lubrication.

Declaration of Competing 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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