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Quantitative Evaluation on Carbon Nanotube Distribution for Functional Ultra-High Performance Concrete

기능성 초고성능 콘크리트를 위한 탄소나노튜브 분산에 대한 정량적 평가

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Abstract

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This study covers two important design parameters, which are a uniformed dispersion of carbon nanotubes (CNTs) and their content, in developing multifunctional ultra-high performance concrete (UHPC) as an integrated system of repair/retrofitting and smart performance. Therefore, this study aims to seek viable dispersion methods incorporating highly concentrated CNT in UHPC and closely examine the rheological properties, mechanical strength, shrinkage, porosity, and electrothermal properties with various dispersion methods and CNT contents. Moreover, this thesis contributes to development of non-destructive evaluation of dispersion quality and CNT content in a relatively large area of hardened cementitious nanocomposites. To overcome the complexity and multi-scale characteristic of nanocomposites, confocal Raman micro-spectroscopy with high spatial resolution was adopted.

Dry mixing of CNT powder, silica fume, and silica sand before wet mixing was compared with macro-dispersed ultrasonicated suspension with superplasticizer (SP) and commercially available nano-dispersed suspension. In terms of the efficiency of improving the electrical conductance and the minimization of adverse effect on mechanical strength, dry mixing showed the best performance, up to 0.5wt% of CNT content. Unexpectedly, the incorporation of CNTs in the form of ultrasonicated suspension had an insignificant increase in electrical conductivity due to damages on CNT by sonication energy. Two methods significantly affected the rheological properties of UHPC. When 0.5wt% of CNT was added, fresh UHPC concrete had no more self-compacting properties, and therefore the vibration process was needed to fabricate specimens. On the other hand, samples manufactured with the commercial CNT suspension with shorter CNTs had better workability at a concentration as high as 6wt%, but the compressive strength significantly decreased, and the percolation threshold was found to be much higher than two other methods. It could be attributed to a much shorter length and poor interfacial bonding between CNTs and matrix due to the surfactant. The results indicated that dry mixing, which was more cost-effective and energy-efficient, can be used when CNT content near the percolation threshold (~0.3wt%) is required for specific performance.

The critical incorporation concentration for tailoring multi-functional UHPC was investigated with thorough examination on the pore structure, shrinkage, compressive strength, and multifunctional properties. The well-dispersed commercial suspension was used to minimize the reduction in flowability. At all concentrations, incorporating CNTs affects positively; in other words, no adverse effect was found at high CNT concentration. However, reduction in flowability could influence the porosity, leading to marginal increase or reduction in positive effect of CNT addition. The results confirmed that the multifunctionality of UHPC could be maximized by incorporating CNTs while mitigating autogenous shrinkage and utilizing superior mechanical performance and durability of UHPC. The CICs for various material properties were determined to 0.5 wt% considering percolation threshold and limited effect of CNTs on shrinkage and mechanical properties, a substantial reduction in volumetric heat capacity, and an increase in thermal diffusivity. When 6wt% of highly concentrated CNT suspension was used instead of mixing water, the electrical conductance was remarkably improved, and the electrical curing of UHPC instead of steam curing (heat treatment) was possible at a very low voltage of 19–23 V. There was no significant degradation due to electrical curing; the flexural strength was rather slightly increased with direct electrical curing.

Mapping of phases in hydrated cement sample was conducted using confocal Raman micro-spectroscopy (CRM) to overcome the limitation of conventional techniques such as electron microscopy that can be applied for the examination of hardened cement. It was found that CRM can be used to identify not only most of phases in cement-based material including clinkers, hydration products, and mineral additives, but also the presence of CNTs in the hardened matrix. When a well-dispersed stable CNT suspension was utilized, CNT was detected in almost the entire area despite a very low CNT content, which indicated that CNTs were uniformly distributed in the matrix. Raman imaging the submicron CNT aggregates below the resolution of optical microscope were spread in the matrix in the specimen fabricated with CNT suspension with ultrasonication applied. The distribution and dispersion efficiency of CNTs was quantitatively evaluated with the metrics proposed in this study. Hence, non-destructive investigation of nanocomposite without any sample preparation can be possible to compare the efficiency of various dispersion methods using high resolution CRM.

Quantitative Raman analysis was attempted to construct the calibration curve for the CNT concentration evaluation. To fully utilize the change in Raman intensity of phases in each measurement spot, the strategy for the normalization of CNT signal was to use the Raman sensitivity of material. The experimental Raman sensitivity was measured as the linear coefficient between the laser intensity and Raman intensity. Even though cement-based materials are multiphase and complex material, it was possible to quantitatively compare the Raman intensity of CNT between spectrums through the normalization. The average of normalized CNT signal, which represented the relative volume fraction in mapping area, non-linear logarithmic relation with volumetric concentration of CNT. In conclusion, the overall understanding of engineering properties with varying CNT concentration and dispersion methods will expand the application of UHPC/CNT composite by helping engineers to choose appropriate CNT dosage and efficient dispersion methods. Furthermore, the quantitative analysis framework will enable the comparison of dispersion quality and CNT quantity in hardened cement composite, which is not limited to cement/CNT system, but has lots of potential to investigate even more complicated phenomena of cement-based materials.

Keywords : Carbon nanotube, Ultra-high performance concrete, Dispersion, Functional concrete, Confocal Raman micro-spectroscopy, Nondestructive evaluation, Quantitative Raman analysis Student ID : 2017-23536

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List of Abbreviations

ABS	Absorbance				
AFM	Atomic force microscopy				
AR	Aspect ratio				
CC	Conventional concrete				
CCD	Charged coupled device				
CF	Carbon fiber				
СН	Calcium hydroxide				
CIC	Critical incorporation concentration				
CNF	Carbon nanofiber				
CNT	Carbon nanotube				
С–Ѕ–Н	Calcium silicate hydrate				
DC	Direct current				
DOD	Degree of dispersion				
EC	Electrical curing				
EMI	Electromagnetic interference				
EMP	Electromagnetic pulse				
FCR	Fractional change in resistivity				
HPC	High-performance concrete				
LD	Laser diffraction				
LOD	Limit of detection				
LOQ	Limit of quantitation				
MWCNT	Multi-wall CNT				
NF	Normalization factor				
PSD	Particle size distribution				

QP	Quartz powder					
SC	Steam curing					
SCC	Self-compacting concrete / self-consolidating concrete					
SEM	Scanning electron microscope					
SF	Silica fume					
SHM	Structural health monitoring					
SP	Superplasticizer					
SS	Silica sand					
SSA	Specific surface area					
SWCNT	Single-wall CNT					
TG	Thermogravimetric					
tpa	Tons per annum					
UE	Ultrasonication energy					
UHPC	Ultra-high performance concrete					
UHPFRC	Ultra-high performance fiber-reinforced concrete					
UTM	Universal test machine					
UV-vis	Ultraviolet-visible (light)					
VMA	Viscosity modifying agent					
w/b	water-to-binder					
w/c	water-to-cement					

Chapter 1. Introduction

1.1 Background

1.1.1 Smart concrete towards sustainable structures

Concrete is the most widely used material after water in the world, and its demand is hardly expected to decline during this century. The growth of urban population creates demand for construction material. Existing infrastructures need repair and expansion. Structures become more high-rise and long-span [1,2]. As shown in Figure 1-1, cement production has grown steadily to meet the demand in global urbanization and the maintenance of existing infrastructures and buildings [3,4]. Concrete has sufficient strength and durability and is moldable in esthetically pleasing shape. Its major component, cement, have been improved to satisfy various needs in construction sites over 200 years. Now, cement and concrete industries are anticipated to make significant contribution on meeting the goals of carbon neutrality [5]. As an indispensable building material, concrete must keep evolving to satisfy upgraded social demands.

Smart and multifunctional concrete has potential to address upgraded requirements regarding safety, longevity, and functions of advanced engineering structures. It is an integrated system of structure and function, such as self-healing, self-sensing, self-heating, photocatalytic, energy harvesting, and electromagnetic wave shielding [6]. Various types of materials are integrated in concrete to introduce new functionalities, and nanotechnology and biotechnology have played important roles on the advance in multifunctional concrete. For example, integrated materials in self-healing concrete are hollow fibers [7], micro encapsulations [8], expansive agents [9], and bacteria [10], and those in other

types of smart concrete can be found elsewhere [6]. These additional inclusions generally increase production costs, limiting large-scale application. Partially applying functional components to entire structures has significant social and economic advantages when considering high performance to price ratio and low life cycle cost.



Fig. 1-1 World production and apparent consumption of cement in the world [3].

Modifying electrical conductivity of concrete is one of the methods possessing high expandability to multiple functions owing to mechanoelectrical and electrothermal effect. The mechano-electrical effect can be used to structural health monitoring, traffic information processing, and military security service. Incorporating conductive fillers has been reported to have better sensing capability and structural integrity due to high compatibility with materials; thus, it has economic benefits by saving maintenance cost. The electrothermal effect can be more powerful because of the possibility of heating. It can be utilized to deicing of roads, bridges, and airports. The use of conductive concrete for this purpose not only enhances structural integrity, but also saves costs and labors for snow removal and reduces the use of salts harmful to reinforcing steel and environments.

1.1.2 Ultra-high performance concrete (UHPC) incorporating carbon nanotubes (CNTs)

Various types of conductive fillers have been introduced to modify the electrical conductivity of concrete: steel fiber, steel slag, carbon fiber (CF), carbon black, carbon nanotube (CNT), carbon nanofiber (CNF), and graphene nanoplatelets [11]. More attention has been paid to carbon nanomaterials due to some reasons. First, the electrical resistance change rate fluctuated over time when steel fiber was added even though steel fibers may have better sensing performance. Another problem of steel fiber was the possibility of corrosion promoted by applied current [11–13]. On the other hand, carbon-based materials have better chemical stability, and graphite nanomaterials such as CNT and CNF possess high mechanical strength and electrical/thermal conductivity. These nanoparticles provide a large specific surface area (SSA) for interacting with hydrate products and increase the packing density of composite with their fine geometry. When nano-sized material is added, the electrical conductivity of composite is expected to show the percolation behavior at a lower concentration of conductive fillers [14] (Figure 1-2).



Fig. 1-2 Illustration of CNT network percolation compared with carbon black

(from [14]).

CNT, which is discovered by Iijima [15], is one of intensively investigated nanofillers for cement-based composite to improve mechanical, electrical, and thermal properties. CNT is a tube made of layers of a two-dimensional hexagonal lattice of carbon atoms. It has a diameter typically measured in nanometers while having a length of a few micrometers, which makes an aspect ratio (AR) in range of 300 to 1000 on average. When several nested single-wall (SW) CNTs are weakly bonded together, it is referred to as multi-wall (MW) CNT (Figure 1-3). MWCNT is the dominant form in the market because it has better dispersibility and cost effectiveness than SWCNT [16]. Theoretical and experimental studies have revealed its remarkable physical properties. The tensile strength of a single layer of a multi-walled carbon nanotube can be as high as 100 times that of steel, and the graphene sheet (in-plane) is as stiff as diamond at low strain [17]. Also, its electrical conductivity (103–105 S/cm) is comparable to copper [18].



Fig. 1-3 Single and multi-wall CNT [19].

In fact, MWCNT is no longer a novel material but to say its market is currently experiencing growth in volume [20]. MWCNT is being used in conductive plastic application and battery of which market has the potential to grow rapidly due to the uptake of electric vehicles [21]. aTherefore, MWCNT can serve as the basis of next generation of multifunctional high-performance concrete [22].

When adding CNTs as conductive fillers, it is important to achieve

homogeneous dispersion of CNTs and proper interfacial bonding between CNTs and cementitious matrix. Researchers pointed out that a water-to-binder (w/b) ratio is an important factor which affects the CNT dispersion [23]. Typically, CNTs are dispersed in water before mixing with dry mixtures. They are much smaller than the particle size distribution of dry mixtures consisting of cement or mineral additives. Therefore, they initially exist in pore water and then comprising the composite matrix with micro-sized crystalline phases and amorphous hydrate products filling the pore as the hydration reaction progresses. If w/b ratio is high, CNTs can be agglomerated when excessive water in pore evaporates. Kim et al. experimentally demonstrated that by reducing the w/b ratio, the electrical performance and stability of the composite could be improved [24].

It is also important to select a suitable dispersant and optimize its dosage to achieve effective dispersion. CNTs easily agglomerates because van der Waals force between CNTs inevitably increases due to high SSA and AR. To physically separating CNTs, high local shear, commonly ultrasonication, is applied to CNTs in low viscous medium. After the mechanical dispersion, surfactants are used to improve the degree of dispersion and prevent re-agglomeration of CNTs in water due to their hydrophobic nature. Previous studies suggested that polycarboxylatebased superplasticizer, regularly used water reducer, was the most compatible dispersion agent without causing adverse effect on cement hydration [25]. Because homogeneous dispersion is the most important design parameter, various types of surfactants and mechanical mixing methods have been attempted to achieve effective dispersion and large-scale application (More detailed information in Chapter 2).

CNTs may not interact with cement matrix comprised of hydrate products and unreacted cement particles due to its geometry of nano-scale cross-section and micro-scale length. Inducing pozzolanic reaction would be beneficial because additional formation of nano-structured C–S–H can replace micro-sized crystals and fill the capillary pores making denser microstructures. Silica fume has high pozzolanic reactivity, and therefore can be hydrated by Ca^{2+} ions from cement and portlandite. Also, it has similar dimension to CNTs, of which particle size in range of 10–500 nm, can improve the dispersion of CNTs with its fine size and roundness. [26,27].

Lastly, double/ triple percolation behavior of electrical conductance of concrete should be considered when designing mix proportions (Figure 1-4) [28,29]. For the case of cement paste, there will be one type of percolation related to the continuity of fillers. Because concrete is a complex mixture of cement paste and aggregate, the continuity of conductive cement paste among aggregates can be influenced by sand-to-cement ratio. In this case, hybrid use of fillers with different scale can facilitate the electrical continuity and reduce the cost by incorporating macro fibers (e.g., carbon fiber and steel fiber) and carbon nanomaterials. Lee et al. concluded that cement-based composites containing both 0.1 vol.% CFs and 0.5 vol.% MWCNTs could achieve equivalent self-sensing performance at half the cost of cement-based composites with 1.0 vol.% MWCNTs. [30].

It is interesting that the mix composition of ultra-high performance concrete (UHPC) or ultra-high performance fiber-reinforced concrete (UHPFRC) satisfies the conditions aforementioned above. The mix proportion of UHPC is characterized by minimized w/b ratio, high content of superplasticizer (SP), use of silica fume, and optimized particle size distribution (PSD) [31]. Also, about 1– 2vol% of steel fiber is incorporated into UHPC, forming UHPFRC. UHPFRC is a class of high-performance materials that possess 6 to 8 times higher compressive strength, 10 times higher flexural strength, and superior ductility capable of deforming under excessive loads without rupture, 10 to 100 times higher durability than conventional/standard concrete [32]. Also, it is a type of viscous self-compacting concrete (SCC) that benefits the work environment by eliminating concrete vibration and related noise and the quality of concrete with

less voids and inhomogeneity, reducing the need for repairments. More slender and sophisticated forms with aesthetical surfaces can be realized with lighter and more durable materials having longer service lives and lower maintenance costs. Therefore, the optimized mix design of UHPC/UHPFRC can be an excellent starting point for smart concrete incorporating CNTs.



Fig. 1-4 Two types of percolation in (a) cement paste with conductive fillers and (b) concrete with conductive pastes [28].

One researcher might pose a question on the feasibility of multifunctional UHPC due to its high cost. If we simply consider the cost of constituents, UHPC has no competitiveness over conventional concrete. For example, the cost of ready mix concrete of C25 is about 135 USD/m³ while that of commercially available UHPC range from 1496 to 2843 USD/m³ [33,34]. However, UHPC can be a viable solution considering total installation cost and extended service life. Specifically, UHPC is a well-suited material for retrofitting and rehabilitation of beams and infrastructures owing to its high strength and stiffness, high compatibility with ordinary concrete, and high resistance to freeze-thaw cycles, water and chloride-

ion permeability, chemical attack, and carbonation [35,36]. Case study on the application of UHPC on bridge deck overlay approximated the cost of different overlay solutions for bridge deck replacement [37]. Ordinary concrete overlays range in thickness from 50 mm to 150 mm, while previous application of UHPC as an overlay have used its thickness between 25 mm and 50 mm [38,39]. Reduction in thickness not only leads to cost saving, but also minimizes additional dead load. As can be seen in Table 1-1 and 1-2, we can be expected to cost competitiveness in the field of repair and rehabilitation.

Therefore, this study suggests that UHPC composite can be the integrated system of repair, rehabilitation, and monitoring of infrastructures (e.g., bridges, buildings, and roads) as the next-generation advanced material. Instead of replacing the entire structure, only repairing damaged or weak parts can provide economic benefits. The parts requiring retrofitting are likely to be structurally important or vulnerable. In the case of roads and bridges, it is exposed to repetitive loads and severe weather, such as a low temperature and heavy snow, and causes economic and social expenses due to frequent maintenance, de-icing, and snow removal.

One of the crucial goals of manufacturing functional UHPC is to achieve designed performance while reducing CNT concentration by developing an effective dispersion method that requires less time and energy. UHPC has a very low w/b ratio of less than 0.2, and a higher concentration (> 5-6 wt%) of CNT suspension needs to be prepared than for the concrete having a normal w/c of 0.5. In this situation, SP-aided sonication, which has been readily adopted in the lab, may not be suitable for large-scale application because input energy increases the concentration of CNT and the volume of the suspension.

Multifunctional UHPC requires ~1.15 wt% of CNT by weight of cement, which corresponds to 9 kg of CNT per 1 m³ of UHPC, calculated under the assumption that the percolation (i.e., rapid increase in electrical conductivity due to the

formation of connected filler network) of cement-based materials occurs at a CNT concentration of 0.3-0.5 vol% [40]. Currently, the price of MWCNT tablets from a manufacturer in South Korea, which possess 6,100 tpa (tons per annum) facilities, is around \$50 per kg [41]. Based on this figure, \$270-450 costs for adding CNT in 1 m³ of UHPC. Therefore, achieving the required performance at a lower concentration by optimizing the dispersion method is essential to make it feasible.

It should be noted that the rheology of UHPC must be adjusted according to the application site. For example, when used for beam retrofitting, it should be formulated to have self-consolidating properties because it needs to fill the narrow space between the existing beam and the mold under gravity. On the other hand, UHPC applied to the deck overlay is formulated to have thixotropy because the bridge deck is not usually level. Like other nanomaterials, it aggregates easily, adsorbs large amounts of water, and provides additional reaction sites to promote hydration due to its hydrophobic nature and high AR and SSA. Therefore, CNT addition will significantly affect the rheological properties of UHPC. However, to the best of our knowledge, previous studies of functional UHPC have yet to deal with the effect of CNT addition and its dispersion method on the rheological properties and thixotropic behavior.

Orverlay, type	Overlay	Cost	
Overlay type	thickness (mm)	(USD/m^2)	
High performance concrete *	25-127	183–269	
Low slump concrete *	38-102	140-204	
Latex-modified concrete *	25-127	193–419	
Asphalt with membrane *	38-102	32-86	
Polymer-based *	3-152	107-183	
Non-proprietary UHPC	25-52	32–64 †	
Proprietary UHPC	25-52	97–184 ††	
Rehabilitation of the Chillon Viaduct (Switzerland)	40 **	015 **	
using a proprietary UHPC overlay	40	213	
Bridge deck replacement	Not applicable	462–570	

 Table 1-1 Approximate cost of different overlay solutions compared with bridge

 deck replacement (from [37]).

* Data collected from [39]. The costs shown reflect average values from low and high ranges.

** Data collected from [38]. Price reflects cost of material and installation.

[†] Price reflects material cost only, assumes UHPC cost of \$1,000 per cubic yard.

^{††} Price reflects material cost only, assumes UHPC cost of \$3,000 per cubic yard.

CFRP retrofitted with 1-2 layers							
Materials	Unit	Quantity	Unit price	Total	Remark		
CFRP sheet	m ²	1.09	67	73	Anchors AEC-S200		
Epoxy (A)	kg	1.2	6.7	8	Guosen		
Epoxy (B)	kg	0.6	10	6	Guosen		
Total cost	USD/m ²			87	(1 layer)		
	_			173	(2 layer)		
UHPC retrofitted with 3cm thickness							
Materials	Unit	Quantity	Unit price	Total	Remark		
Cement	kg	25	0.2	5			
Silica sand	kg	21	0.1	2.1			
Silica fume	kg	8.7	1	8.7			
Quartz powder	kg	7.2	0.1	0.7			
Steel fiber	kg	3	4	12			
Superplasticizer	kg	1.5	2	3			
Total cost	USD/m ²	_	—	31.5	1vol% steel fiber		
		_	_	43.5	2vol% steel fiber		

Table 1-2 Material cost of CFRP and UHPC reinforcement (from [36]).

1.1.3 Evaluation of CNT dispersion and concentration in hardened cement-based composites

One of the challenges in fabricating nano-enhanced cement composite is to evenly disperse nanomaterials in the matrix while avoiding. The CNT agglomerates (i.e., poor dispersion) can adversely affect final constitutive properties by increasing matrix defects such as porosity, stress concentration, and their premature debonding from the matrix. Therefore, during the past decades, researchers explored various dispersion methods such as ultrasonication, functionalization, ball milling, high-pressure homogenizer, and even in-situ synthesize of CNTs on cement surface [42–44].

The most widely used dispersion technique is ultrasonication and functionalization of CNT. Ultrasonication has been considered an inevitable process to disentangle as-received CNTs pellet or tablet (compressed form for storage and safety). It is an effective method for CNT dispersion in liquids having low viscosity. However, functionalization is required to retain the dispersion quality over time because the dispersed CNTs re-agglomerate after the ultrasonication process due to strong attraction. The commonly used functionalization is the treatment with oxidizing agents or the polymer/surfactant-aided ultrasonication. The former is called his covalent functionalization, which is used to attach COOH/OH functional group onto the surface of CNTs and this degradation could diminish the outstanding properties of CNTs. Therefore, polymer/surfactant-aided ultrasonication of pristine CNT is a preferred method.

If the uniform distribution of CNTs is ensured, CNT-dispersed cement paste can be simplified to a homogeneous matrix in analogous to the simplification of a well-hydrated cement paste as a homogeneous material neglecting the uneven distribution of solids and voids. It would enable the modelling and prediction of material behavior. Therefore, the most important design parameter can be a uniformed dispersion of CNTs in cement-based materials. Since the cement-based materials have complex hierarchy of structure with regards to pore structure, crystal structure, and intermixed of these two, the inclusion of nanomaterials which have characteristic length scale of sub-micron should add more complexity on the microstructure of cement-based materials. This leads a huge challenging to characterize the composite such as the evaluation of the degree of dispersion (DOD) of nanomaterials.

There has been a lack of discussion on the description of the term 'dispersion' and suitable methods for characterizing it despite of its importance. Image-based analysis using electron microscopy or atomic force microscopy (AFM), which have been considered as a standard method for CNT-reinforced metal or polymer composites, can observe only a small portion of samples (non-bulk). It may be inadequate for characterizing CNT suspension fabricated with polymer-aided ultrasonication of pristine CNTs. A complete nano-dispersion is hardly achieved due to its hydrophobic nature and strong van der Waals force between nanotubes with high specific surface area and aspect ratio, which could result in polydisperse suspension. It is time-consuming to observe enough number of particles in broad PSD from a statistical point of view. Also, most of research have shown the dispersion quality of CNTs in hardened cement composite with scanning electron microscope (SEM) images, but it is prone to bias in sampling and defects resulting from the sample preparation to observe in the vacuum condition.

The lack of quantitative evaluation on dispersion has made it difficult to systematically analyze considerable number of research showing high deviation in experimental results and conflicting conclusions. Without quantifying the dispersion, it can be difficult to separate the effect of dispersed CNTs and agglomerated CNTs. In addition, even if CNTs are well distributed in the matrix, they may adversely affect the microstructure (solids, voids, and water) of the

cement material, which may be mistaken for poor dispersion quality.

It is worth noting that dispersion state of nano-carbon materials varies in each manufacturing process. A well-dispersed CNT suspension is prerequisite for the fabrication of homogeneous nanocomposites but does not guarantee good dispersion in composites. It is because the distribution of CNT in composite can be affected by the compatibility between surfactant and highly alkaline pore solution in cement paste, the flocculation of cement particles, and the mix proportion of other components (amount of water and superplasticizer used).

Therefore, characterization of CNT dispersion for each production process can be considered as one of the essential steps of research and development on CNT/cement composite. The ability to properly anticipate and regulate CNT dispersion over fabrication process would be a tremendous practical benefit and it would facilitate the use of new generations of nano-enhanced cements and pave the way for robust mix design and admixture combinations.

1.2 Scope and objectives

The first part of this thesis is to seek viable dispersion methods incorporating highly concentrated CNT in UHPC. Smart UHPC should meet workability, strength, durability, and functionality requirements as an integrated solution for repair/retrofitting and functionality. Therefore, this study aims to closely examine the rheological properties, mechanical strength, shrinkage, porosity, and electrothermal properties with varying dispersion methods and CNT contents. Finally, this study targets to present an example of the multifunctional use of UHPC/CNT composite considering its economic feasibility.

The second part of this work is to study how the dispersion of CNT can be evaluated in as-is bulk samples and how the measured results can be quantitatively described. The dispersion and concentration of CNT are the most critical design parameters for tailoring the performance of nanocomposites. However, there has been a lack of research on proper methods for macroscopic investigation of CNT dispersion and quantitative methods for determining CNT concentration in hardened cement-based matrix. This thesis investigates the potential of studying nanocomposites using confocal Raman microspectroscopy and aims to provide information on the dispersion quality of CNTs in a relatively large area. Additionally, this work attempts to utilize Raman spectroscopy for quantitative evaluation of CNT concentration by adequately processing the Raman signal containing information on most clinkers, hydrates, and CNT.

1.3 Outline of the thesis

The manuscript is structured as follows:

Chapter 2 reviews previous studies on dispersion methods of CNT, techniques for characterizing CNT dispersion, and functional properties of UHPC incorporating CNT. Also, basics for the rheology of cement-based material and confocal Raman microscopy. The research hypothesis and strategy are established from the discussion of the existing studies.

Chapter 3 investigates the rheological, mechanical, and electrical properties of UHPC with varying CNT content and dispersion methods. Drying mixing for large-scale and highly concentrated CNT addition, commonly adopted SP-aided ultrasonication, and commercially available well-dispersed CNT suspension were compared, considering economic feasibility.

Chapter 4 presents the investigation of the poromechanical, autogenous shrinkage, compressive strength, and electrothermal properties of UHPC with varying CNT concentrations. The critical incorporation concentration is suggested for tailoring multifunctional UHPC. Commercial CNT suspension was adopted, targeting the application of an integrated system of structural retrofitting and monitoring. Additionally, the application of the electrical curing and crack sensing under flexural loading of UHPC/CNT composite was examined.

Chapter 5 focuses on visualizing the presence of CNTs in hardened cement composite using confocal Raman spectroscopy. Also, a quantitative index representing the dispersion efficiency and the heterogeneity of composite concerning CNT distributions is established.

Chapter 6 develops quantitative analysis techniques to fully utilize a large amount of information in a single Raman spectrum at each measurement. The
amount of CNT at each location can be compared without a quadrat-based approach. The effect of measurement and mapping conditions (e.g., laser power, mapping area, and mapping interval) on the quantitative evaluation of dispersion was investigated.

Chapter 7 presents the general conclusions and the future studies along with a summary of this study.

The graphical depiction of this manuscript is presented below, where the circles are the chapter numbers (Figure 1-5).

		Fur	nctional CNT/UHPC	Eva	aluation methods
Irameters	Dispersion quality	3	Dispersion methods and performance of composites	5	Visualization and quantification of spatial distribution
Design Pa	Concentration	4	Critical concentration for multifunctional application	6	Quantitative evaluation of CNT concentration

Fig. 1-5. Graphical summary of research objectives.

Chapter 2. Literature Review

2.1 Multifunctional application of UHPC

Design of multifunctional concrete should be different from conventional concrete. The application condition has to be identified first, and then target functionalities can be established [6]. Specific situations can be hypothesized where multifunctional UHPC is considered as a viable solution: (1) retrofitting of girder in buildings and infrastructures integrated with intrinsic self-sensing capability under flexural loading, (2) repair of bridge deck overlay with self-heating functionality, (3) reinforcement bridge connections with traffic detection system, and (4) electrical curing and self-heating of road, bridge, or parking lot exposed to cold weather. After appropriate range of CNT content ensuring the capabilities of sensing or heating is determined, examination on material properties and entire structural system will be followed. The addition of CNT fillers should not seriously compromise the structural function and durability. Therefore, some trials-and-errors may be required during design process, and the pre-optimized UHPC formulation may need some adjustment for the site situation.

In this chapter, previous studies on UHPC incorporating CNTs and hybrid with other fillers were examined. This chapter aims to provide examples for the practical range of CNT content specifically for self-sensing and self-heating. It is because the use of CNT inevitably undermines the cost-competitiveness of UHPC, and therefore marginal increase in mechanical performance with CNT addition may be not attractive and less efficient in construction industries.

2.1.1 Self-sensing UHPC

Self-sensing can be defined as the capability to sense the conditions of material itself (e.g., stress, strain, and crack) and environmental change (e.g., temperature and humidity). Concrete incorporated with functional fillers or sensing component (e.g., fiber optic sensors, strain gauges, and accelerometers) is referred to as intrinsic or non-intrinsic self-sensing concrete, respectively. The self-sensing concrete has developed for the fields of structural health monitoring (SHM), traffic detection, and military security. Here, only intrinsic self-sensing UHPC is covered.

Self-sensing capability is attributed to the change of inherit conductive network formed by functional fillers. Therefore, it is generally measured by volume resistivity of materials. The electrical resistivity of component will decrease as the distance between fillers decrease under the compression. On the other hand, the micro-crack formation attributed to flexural and tensile loading would lead to discontinuity of conductive path, increasing the electrical resistivity. The change in resistance can be quantified as a fractional change in resistance (FCR) in Eq. (1). For example, the gauge factor (i.e., strain sensitivity) is expressed as FCR/ $\Delta\varepsilon$, and the stress sensitivity can be expressed as FCR/ $\Delta\sigma$ in similar way. Detailed information can be found elsewhere [45].

$$FCR = \frac{\Delta\rho}{\rho_0} \times 100(\%) \tag{1}$$

Filler content is a critical factor tailoring the self-sensing capability of composites. Too high filler concentration does not ensure better sensing performance because the initially formed conductive pathway may be too stable to respond to the change in external environment.



Fig. 2-1. Dependence of the electrical conductivity of a composite with the concentration of carbon nanotubes (modified from [46]).

When CNT content is much lower than percolation threshold, the composite remains close to insulating material because the conductive path is hard to form, and the electrons are hard to move between CNTs (regime 1 in Figure 2-1). As filler concentration increases, the spacing between fillers decreases, leading to increase in the probability of electronic transition. Generally, percolation threshold refers to this regime where electrical conductivity rises sharply. When filler content is lower than the percolation threshold, the contacting conduction, tunneling conduction, and ionic conduction are all dominant factors in the electrical conductivity of the composite. It can be implied that free water content in the pore could affect the electrical conductivity due to the movement of ion. On the other hand, when the filler concentration exceeds the percolation threshold, the significance of ionic conduction decreases, and the tunneling conduction and the conduction with direct contact plays major roles. The tunneling conduction happens when the distance between fillers is less than approximately 10 nm. Therefore, we might expect that the electrical property would be more stable with the CNT content slightly higher than the percolation threshold. In regime 3, fillers are totally contacting each other showing very high electrical conductivity, and

additional incorporation of CNT marginally improves the electrical conductivity.

There are limited number of studies on UHPC embedded with CNTs for SHM (Table 2-1). From the research conducted by Yoo et al., and Lee et al., it can be concluded that relatively high content of CNTs ($0.5 \text{ vol}\% \simeq 1.1 \text{ wt}\%$) with hybrid of steel fiber can be used for prediction of tensile stress-strain behavior [47,48]. However, it was not sensitive to compressive stress because 0.5 vol% might be far beyond the percolation threshold with fillers forming stable conductive network.

The efficiency of CNT addition can be compared with studies utilizing other types of conductive filler (Table 2-2). UHPC containing steel fibers showed fine sensitivity to strain and stress under compression, tension, and flexural loading. However, it was significantly lower than that containing CNTs. Also, it should be noted that the use of micro-sized short steel fiber may have compromised the flexural strength considerably at approximately 50% comparing to conventional steel fibers having millimeter-scale length used in UHPC [49].

Deviewed	Conducti	ve filler	Londing	Sensing	
literatures	CNT	Steel fiber	condition	capability	Remarks
Yoo et al.,	0.5vol%	0,	Monotonic tension	GF: 136.3	Plain UHPC CNTs exhibited severe signal noise in the FCR and a high electrical resistance
2018 [48]		2vol%	(0.4 mm/min)	GF: 67.8	Pre- and post-peak tensile behavior can be predicted with FCR with 2vol% SF
Lee et al	0.5vol%	0, 2vol%	Monotonic compression (0.1 mm/min)	FCR: 0.6– 2.5%	Sudden increase in FCR can detect damage/failure
2018 [47]		0, 2vol%	Monotonic tension (0.4 mm/min)	GF: 36.5– 136.3	Shorter steel fiber is better for sensitivity
Lee et al., 2022 [50]	0.1, 0.2, 0.3, 0.5wt%	-	Cyclic compression (0.5–4Hz, 0–30 MPa)	Stress sensitivity: 1.03– 2.16 %/MPa	Stable FCR values were obtained over the percolation threshold (0.1– 0.2wt%)

Table 2-1 Summary of literatures related to UHPC with self-sensing capability embedded with CNTs and other .

Darierrat	Conduct	ive filler	Logit	Comain a	
literatures	Others	Steel fiber	condition	capability	Remarks
Dong et	SSSW (0, 0.5,	_	Cyclic compression (20 kN, 0.4 mm/min) Monotonic	GF: 2.66– 22.52	Percolation occurred
al. [49]	1.0, 1.5vol%)		compression (1.2 mm/min) Flexural loading (0.05 mm/min)	GF: 17.9– 94.9 GF: 3.5– 43.6	between 0.5 and 1.5 vol%.
	-	(0.6, 1.2vol%)	Cyclic compression (37.5, 56.3, 75.0	GF (cyc.): 3.7–26.6 GF (mono.): 17.7, 23.6	The relation between FCR and stress showed linear and non-linear stages.
Qiuet al. [51]	CCSF (0.6, 1.2vol%)	-	MPa, 0.4 mm/min, 0.05 Hz) Monotonic compression	GF (cyc.): 9.7–14.4 GF (mono.):	High electrical resistivity at 28 day $(\sim 10^6 \Omega \cdot cm)$
			(1.2 mm/min)	24.3, 28.2	Poor stress sensitivity in all samples (≤ 0.1 %/MPa) SSA was used instead of silica sand.
Le et al., 2020 [52]	SSA (50, 100 wt%)	(1, 2vol%)	Monotonic compression (1 mm/min)	Stress sensitivity: 0.1– 0.3 %/MPa	Finer SSA, 2vol% of steel fiber showed better FCR likely due to more uniform distribution.

Table 2-2 Summary of literatures related to UHPC embedded with other types of conductive fillers.

	FSSA (5, 10, 50 wt%) NA				FSSA was better than NA and CPA in terms of the cost and stress sensitivity.
Le et al., 2021	(10, 50 wt%) CPA (10, 50wt%)	(2vol%)	Monotonic compression (1 mm/min)	Stress sensitivity: 0.115– 0.41 %/MPa	CNT addition enhanced the electrical conductance and stress sensitivity significantly.
	MWCNT (0, 0.1w t%)				High electrical resistivity at 28 day $(10^5 \sim 10^6 \Omega \cdot cm)$

SSSW : short-cut super-fine stainless wire (8–20 μ m), CCSF : copper coated steel fibers, SSA : steel slag aggregate, FSSA : fine steel slag aggregates, NA : nickel aggregates, CPA : copper aggregates.

2.1.2 Self-heating of UHPC

The self-heating of functional concrete is attributed to Joule heating. By this process, the passage of an electric current through a material produces heat. The thermal performance of self-heating concrete can be derived as follows [53,54].

Under steady-static conditions, voltage has a linear relation to the electrical resistance of a material, where *I* is the electrical current, and *R* is the electrical resistance as shown in Eq. (2). The electrical resistivity (ρ) in Eq. (3) is a material property normalized by the conductive cross-sectional area (*A*) in the direction of current flow, and the distance between electrodes (*L*). The applied energy (*E*), a product of electric power (*P*) and operational time (Δt) is converted into the thermal energy in Eq. (4) [54].

$$V = IR \tag{2}$$

$$\rho = R \frac{A}{L} \tag{3}$$

$$E = P\Delta t = VI\Delta t = \frac{V^2}{R}\Delta t = \frac{V^2A}{\rho L}\Delta t$$
(4)

Eq. (4) indicates that higher applied voltage and lower electrical resistivity of composite achieve better efficiency for producing the same amount of heating energy. If we equate Eq. 4 and the thermal energy (Q) in Eq. (5), the increased temperature (ΔT) over operational time (Δt) can be evaluated as Eq. (6).

$$Q = cm\Delta T \tag{5}$$

$$\frac{\Delta T}{\Delta t} = \frac{V^2 A}{\rho Lmc} \tag{6}$$

where *m* is the mass, and *c* is the specific heat capacity of a material.

It has been suggested that a resistivity of less than 1,000 Ω · cm is required for self-heating concrete to prevent ice formation or to melt the accumulated [55,56]. The literature review indicates that the amount of macro-sized steel fibers or conductive aggregates used for self-sensing capability may not be adequate for achieving low resistivity for the use of self-heating (Table 2-2). This requirement of high dosage of conductive filler might be the reason for the lack of discussion on self-heating of UHPC.

Besides the potential of de-icing application, self-heating concrete can be utilized in fields of electrical curing (EC), which has more powerful impact specifically for UHPC. UHPC generally requires heat-treatment to achieve high mechanical strength by accelerating pozzolanic reaction. Heat treatment at high temperature (i.e., 90 °C) for 2 days ensured superior compressive strength (> 200 MPa) than that of the reference without heat treatment (160 MPa) [57]. Therefore, EC can be the alternative for heat treatment if it can produce the thermal energy enough for maintaining high temperature during the curing period.

Because fresh concrete contains a large amount of water in the matrix, it behaves as semiconductor, showing very low resistivity [58]. However, as hydration reaction continues, water is chemically bound to hydration products, and therefore the hardened matrix has significantly higher resistivity comparable to insulator. The rise in the electrical resistivity over curing age requires a high amount of power to produce enough thermal energy for electrical curing.

Several research has investigated the effects of electrical curing on structural degradation and the effectiveness of EC [59]. Cecini et al. reported that EC was feasible method for fiber reinforced concrete production. They fabricated samples the feasibility of ECTo achieve low electrical conductivity, steel fiber and CNT has been incorporated.

2.2 Methods for dispersing CNTs

CNT has superior properties such as mechanical strength, electrical and thermal conductivity, and therefore has been extensively investigated as electrical, thermal, and mechanical reinforcement. However, due to high SSA and AR, their fine size, it inevitably leads to agglomeration by van der Waals force, hydrophobic nature, and π - π stacking effect. Hence, overcoming this poor dispersion problem in solvents and composites is a first step for achieving target performance of CNT/cementitious nanocomposites.

2.2.1 Mechanical dispersion

Ultrasonication is the most used method for disentanglement of as-received CNT pallets. There are two types of sonication equipment: a probe (horn) or bath. The ultrasonic probe, also known as ultrasonicator, generates mechanical vibration resulting in the formation of cavitation bubbles through shear stress. These microscopic cavitation bubbles "unzip" or "peeling off" individual nanotubes at outer part of CNT bundles or agglomerates.

Design parameters of ultrasonication process are ultrasonication power (i.e., ultrasonication energy per unit time) and total time, which usually determined by the ultrasonication amplitude. Ramezani et al., developed useful relation between the ultrasonication amplitude and input energy per unit time for parameter design [60]. The higher amplitude can cause the damages to CNTs while a low amplitude increases the duration of sonication process. If total energy input exceeded a certain critical level, the damage and shortening of CNTs would be noticeable. The optimum sonication energy was found to be 50 J/mL per unit CNTs to suspension weight ratio that effectively improve the dispersion of surface functionalized CNTs with the aid of a polycarboxylate-based superplasticizer [61].

There are other mechanical dispersion methods such as dry mixing with fine minerals, ball milling, high speed stirring, and high pressure homogenizer [43]. Generally, mixing dry powders with CNTs is considered not efficient for CNT dispersion because ball milling process shortens the length of CNTs, which is detrimental to the load carrying capacity. It was observed that the average length of CNTs reduced from 50 μ m to 0.8 μ m by ball milling [62]. Also, Yazdanbakhsh reported that ball milling could result in high-water consumption, autogenous shrinkage, and thermal cracking [63].

The use of fine and round mineral additives such as silica fume and fly ash may improve the distribution of CNTs by physically separating them [26,27,64]. CNTs were mixed in dry mixture of cement and mineral additives or added in aqueous state with or without additional treatments. However, it appears that the energy generated by the collision with round particles during shearing mixing cannot sufficiently separate the CNTs aggregating by strong van der Waals force. In the scanning electron microscope image, of $2-3 \mu m$ of CNT lumps can still be seen in the specimen in which silica fume is mixed with the dry powder. As discussed in the literature, the dispersion of CNTs was improved to some extent in mixing with silica fume, but it was not possible to clearly distinguish the effect of improved dispersion and that of improved porosity and pozzolan effect on compressive strength [26]. The addition of 0.5 and 1% CNT by weight of binder would compensate the strength degradation occurred when ordinary Portland cement was replaced with fly ash. They discussed that CNTs acting as a filler resulting in a denser microstructure [27].

2.2.2 Functionalization

Ultrasonication is an effective method for CNT dispersion in liquids having low viscosity. However, functionalization is required to retain the dispersion quality over time because the dispersed CNTs tend to re-agglomerate due to strong attraction after mechanical dispersion.

2.1.2.1 Covalent functionalization

Functional groups enhance the dispersion of CNTs in solvents or solid matrices by improving the CNT hydrophilicity (i.e., degree to which the surface attracts water) [65]. CNTs and functional groups are covalently bonded on their surfaces. Hydrocarbyls (e.g., alkyls and alkenyls), halogens (e.g., fluoro and chloro), and oxygen (e.g., carboxyl [COOH] and hydroxyl [OH]) are the main functional groups. A comparison between COOH-functional groups and OH-functional groups suggests that OH-functional groups may have a greater effect on CNT wettability, thereby improving dispersion in the matrix [66].

CNTs are most commonly functionalized by oxidation. The process of oxidation involves treating CNTs with oxidizing agents (such as nitric acid, sulfuric acid, or hydrogen oxynitrate). The walls of MWCNTs with pristine surfaces have smooth surfaces, while the surfaces of MWCNTs with COOH surfaces have rough surfaces and contain acidic functions. In spite of this, some researchers have reported that short COOH/OH functional groups do not affect CNTs' dispersion stability [67]. Moreover, CNTs' outstanding properties may be diminished by acid treatment [68,69].

2.1.2.2 Non-covalent functionalization

It is generally preferred to use polymer/surfactant-assisted ultrasonication (noncovalent functionalization) in order to reduce the degradation of CNTs during covalent functionalization [70]. As a result of this technique, CNT suspensions have been found to be stable for several months without sedimentation [71]. CNTs, however, may exert a weaker force on polymer/surfactant molecules than do covalently functionalized CNTs, resulting in a weaker load transfer. When CNTs are functionalized non-covalently, polymers/surfactants are wrapped or adsorb onto their surfaces during ultrasonication [72]. As a result, the structure and properties of CNTs are not affected by polymers and surfactants.

For proper CNT dispersion, a wide range of ionic and nonionic surfactants has been investigated so far. Dispersing CNTs is primarily caused by electrostatic repulsion between the charges of the ionic surfactants' molecules, as well as by steric repulsion between nonionic surfactants' molecules. The commonly used modifier agents are as follows: sodium dodecyl sulfate [73], sodium dodecylbenzene sulfonate [74], polycarboxylate-based superplasticizers [25], Arabic Gum [75], Cetyltrimethyl ammonium bromide (CTAB) [76], Pluronic F-127 [74], and Triton X-100 (TX10) [75].

2.3 Evaluation of the quality of CNT dispersion

Although dispersion is the most important design variable, quantitative evaluation has not been performed. Among the studies conducted from 2015 to 2022, 73 studies were reviewed. It should be noted that these works utilized polycarboxylate superplasticizer, one of cement admixtures, as a CNT dispersant. Only 3 research quantitatively evaluated the dispersion quality, and about one-third (24 studies) did not present evaluation on the dispersion quality.

Table 2-3 Techniques for characterizing CNT dispersion quality and research adopted SP-assisted sonication as a dispersion method

Classification	Measurement	Bulk /non-bulk	Medium	References
	AFM	Non-bulk	Composite	
	TEM	Non-bulk	Suspension	[77]
	I EIVI	Non-bulk	Composite	
Direct		Non-bulk	Suspension	
observation	SEM	Non-bulk	Composite	Qualitative: [77–81] Quantitative: [82]
	LM	Bulk	Suspension	[61]
		Bulk	Composite	
Particle size	DLS	Bulk	Suspension	
distribution	LD	Bulk	Suspension	
Concentration	UV-vis	Bulk	Suspension	Qualitative: [43,61,83– 87] Quantitative: [88–91]
Stability	Zeta-potential	Bulk	Suspension	



Chracterization methods

Fig. 2-2 Characterization methods for CNT dispersion quality and observable scale

2.3.1 Direct observation

In transmission electron microscope (TEM) images, the adsorbed layer of polymers on the CNT sidewall and change in CNT surface roughness due to oxidation can be seen. Suspension is loaded on the grid, dried, and observed in vacuum condition. Due to the aggregation during preparation of the samples for observation by EM, particle size distribution of could not be determined by this direct method of measurement.

Scanning electron microscope (SEM) is another electron microscope having lower resolution than TEM. Using SEM, experimental evidence giving comprehensive sight into the reinforcing mechanism of CNTs in cement material has been obtained; for example, a pulled-out CNTs at fracture surfaces and hydration products nucleated onto the sidewall of CNTs. During the SEM analysis, energy dispersive X-ray spectroscopy (EDS) would be useful to distinguish the CNTs from needle-shaped cement hydrates (e.g., ettringite) based on the chemical composition [92]. To be imaged using SEM, the specimen needs a conductive surface and has to be inside the high vacuum environment. Thus, porous cement materials are required to be broken into small fragments or fine powders and properly dried. The surface of sample needs the sputter-coating, a thin layer of a conductive material, such as gold, silver, or platinum. It requires additional time, cost, and effort, and the surface of the specimen contains the coated material, not the original material. The additional thin layer of conductive material may hinder visualizing individual CNTs with diameter of a few tens of nanometer.

Light microscope (LM) is a fast and simple technique for morphological investigations of relatively large sample volumes. Due to the resolution of LM, aggregates smaller than the resolution limit (typically $< 1 \mu m$) are considered dispersed fillers [93]. If the contrast between agglomerates and matrix is clear, the area ratio of agglomerates can be easily evaluated by image processing. However, the fuzzy boundary between CNT and matrix is an obstacle to applying LM to the macroscopic investigation of CNT dispersion.

2.3.2 Batch particle measurement

Dynamic light scattering (DLS) is a non-invasive technique to measure the size of nanoparticles in a colloidal suspension. This method uses Brownian motion to measure the intensity of scattered light over time in a particle suspension. By analyzing the intensity variation of scattered light, the diffusion coefficient can be determined, and the particle size is obtained from this coefficient through the Stoke-Einstein equation.

The size characterization by DLS is a widely used method in laboratories due to its ease of use, the short duration of the measurements and the availability of accessible marketed apparatus. However, the determination of size of complex dispersion by DLS is problematic, while the method is powerful to evaluate size characteristics of monomodal dispersions with a high accuracy. This limitation comes from the fact that the intensity of scattered light depends on particle size being proportional to the power six of the particle diameter. Thus, intensity of scattered light due to large particles can hinder the detection of populations of particles having a smaller diameter.

Laser diffraction (LD) is also called static light scattering which enables to evaluate the radius of gyration of nanoparticles dispersed in liquid by measuring angular dependence of the intensity of scattered light. Larger particles scatter much light at small angles whereas smaller particles scatter light at greater angles. The scattered intensity is a function of detected angles which depends on particle size. The scattering pattern is deconvoluted to a series of individual number. The relative amplitude of individual number corresponds to the relative volume of equivalent spherical particles of that size.

2.3.3 Dispersion efficiency

UV-vis spectroscopy enabled the determination of the concentration of dispersed CNTs in suspension. The increase in absorbance peak of CNT indicates an increased dispersion efficiency. A small amount of CNT is put into water, and ultrasonication is performed until the UV-vis absorbance reaches the maximum achievable intensity. This solution is diluted to construct a calibration curve based on the Beer-Lambert law. The dispersion efficiency of the prepared suspension with known CNT content is quantified as the ratio between the theoretical maximum concentration and the concentration obtained by measuring the absorbance of the diluted suspension. Although this is a fast and simple bulk technique, the accuracy can be impaired. The dispersed CNT concentration can be overestimated when SP dosage is high because the absorbance of SP can overlap with that of CNTs. Also, the sonicated suspension is a complex mixture of individual, bundled, and aggregated particles, and the contribution of individual and bundled CNTs to the absorbance of non-centrifuged calibration samples is

unclear. Therefore, non-centrifuged calibration samples could cause inaccuracy; for the same reason, the reliability of the measured concentration could be undermined unless the contribution of individual and bundled CNTs and SP to the UV-vis absorption is clearly elucidated.

2.3.4 Dispersion stability

Smaller droplet sizes and higher surface charge (zeta potential) will typically improve suspension stability. Some studies show significant differences in CNT' stabilization depending on the surfactant's nature and concentration [12], [25]–[27]. Measurement of zeta potential depending on the pH value of the aqueous solution is commonly used in these studies. Mendoza et al. investigated the dispersion stability of functionalized multi-wall CNTs in alkaline environment [94]. It was found that the Ca(OH)₂ affects the stability of CNT dispersions identified using zeta potential and FTIR spectroscopy.

Chapter 3. Effects of Dispersion Methods on Fresh and Hardened Properties of UHPC

3.1 Introduction

One of the crucial goals of manufacturing functional UHPC is to achieve designed performance while reducing CNT concentration by developing an effective dispersion method that requires less time and energy. It should be noted that the rheology of UHPC must be adjusted according to the application site. For example, when used for beam retrofitting, it should be formulated to have selfconsolidating properties because it needs to fill the narrow space between the existing beam and the mold under gravity. On the other hand, UHPC applied to the deck overlay is formulated to have thixotropy because the bridge deck is not usually level. Like other nanomaterials, it aggregates easily, adsorbs large amounts of water, and provides additional reaction sites to promote hydration due to its hydrophobic nature and high AR and SSA. Therefore, CNT addition will significantly affect the rheological properties of UHPC. However, to the best of our knowledge, previous studies of functional UHPC have yet to deal with the effect of CNT addition and its dispersion method on the rheological properties and thixotropic behavior. Securing proper rheological properties can affect fiber dispersion and alignment with marked effect on UHPC performance. Therefore, fresh state performance plays an important role for the quality control of hardened properties of concrete. The main aim of this chapter is to compare the effect of various dispersion methods on the fresh and hardened properties and evaluate their efficiency for specific performance.

3.2 Experimental programs

3.2.1 Materials and methods

The raw materials used in this study to produce UHPC were Type I ordinary Portland cement (OPC, Union Cement Co., Ltd., Korea), silica fume (Grade 940U, Elkem, Norway), quartz powder (S-SIL 10, SAC, Korea, median particle size of $4.2 \mu m$), and silica sand (Saeron, Korea, particle diameters of 0.2-0.3 mm). The OPC and silica fume were utilized as binders, while the quartz powder and silica sand were used as the fine aggregate and inert filler, respectively. Polycarboxylate-based SP (solid content 30%, FLOWMIX 3000U, Dongnam, Korea) was used as a dispersant for cement and CNTs.

Pristine multi-wall CNT pallets (> 96%, LUCAN BT1003, LG Chem., Korea) and pre-dispersed multi-wall CNT suspension (Kumho Petrochemical, Seoul, Korea) consisting of 60 g of multiwall CNTs dispersed in 1 L of distilled water were purchased. The particle size distribution and zeta potential of the CNTs in commercially available suspension were measured using a laser scattering particle size distribution analyzer (LA-960, HORIBA, Japan) and nanoparticle analyzer (SZ-100, HORIBA, Japan), respectively. The mean particle size and zeta potential value were 0.41 μ m and -58.4 mV, respectively (Figure. 3-1). The CNTs in suspension were found to be stably dispersed considering their originally synthesized size.

Properties of CNTs in the form of powder and suspension are presented in Table 3-1 and 3-2, respectively. Note that the average diameter of CNTs in suspension is significantly shorter than that in the pallets.



Fig. 3-1 Particle size distribution (a) and zeta potential (b) of commercially available suspension.

Avg. diameter (nm)	Avg. length (µm)	Bulk density (g/cm3)	Purity (wt%)	Specific surface area (m2/g)
13	12	0.12	96	186

Table 3-1 Properties of pristine multi-wall CNT powder.

Table 3-2 Properties of multi-wall CNTs in commercial suspension.

Avg. diameter (nm)	Avg. length (µm)	Density (g/cm ³)	Purity (wt%)	Specific surface area (m ² /g)
1-8	0.1–5	0.15	> 95	180



Fig. 3-2 Silica sand mechanically blended with CNTs and silica fume.

3.2.2 Mixture proportion and sample preparations

The mixture proportion of samples is summarized in Table 3-2. The water-tocement (w/c) ratio was kept at 0.25. Three different dispersion methods were evaluated: dry mixing, SP-aided sonication, and commercial CNT solution. Samples were named with the mass percentage of CNT-to-cement ratio notated as CNTwt% and the suffixes of DM, US, and CS, representing dry mixing, ultrasonication, and commercial suspension, respectively.

Commercial pre-dispersed CNT suspension was diluted 1.875 to 15 times to adjust the CNT concentration. In preparation of the CNT suspension fabricated with ultrasonication, the sonication condition was determined based on the previous studies; the theoretic calculation and empirical results showed that optimum ultrasonication energy (UE) would be at around 200 J/mL for 0.1 wt% of pristine CNT in water while optimal UE for CNT with –COOH functional group was determined to be 75 J/mL [61,89,95]. In this study, the ultrasonication energy was determined as 65 J/mL for 0.1wt% pristine CNT suspension, considering adverse effect due to excessive power (i.e., damage and breakage of CNTs). Water, SP, and CNT powders were put into a jacketed beaker of which temperature was maintained below 5 °C to prevent overheating.

The process of preparing dry mixing sample was as follows: 1) dry mixing of powders and CNTs, 2) mixing with SP solution (i.e., mixed water and SP), and 3) placing and curing. Silica fume, silica sand, and CNTs were blended using a Hobart mixer fsor 5, 10, and 25 min. The sand particle can be used in place of a milling ball to mechanically separate the agglomerated silica fume and CNTs. Dry mixing time was increased in proportion to the amount of CNT. It was expected that silica fume could act as a buffer material which might prevent breakage of CNTs, and due to its very fine particle size (10–500 nm) similar to that of CNTs, they could intermix with CNT agglomerates. After dry mixing, the amount of silica fume clumps was significantly reduced compared to the as-is received state,

and sand particles were surrounded by silica fume and CNTs as shown in Figure 3-2. Then, cement and quartz powders were added together and mixed 5 more minutes. Water and SP were mixed before the contact with premixtures. Two third of dry mixtures was mixed with SP solution at a low speed, and the rest of them was poured slowly for 2 min. Then, the fresh concrete was further homogenized at a medium, high, and a low speed for 1 min, 2 min, and 30 seconds, respectively. The latter mixing with a low speed was to remove airs in the fresh samples.

Samples mixed with dispersed CNT suspension were prepared as follows: 1) preparing dry mixtures, 2) mixing with CNT suspension containing SP, and 3) placing and curing. Initially, silica fume and silica sand were poured and blended for 5 min to crush densified SF during storing. Cement and quartz powder were then added into the container and mixed for 5 more min. The mixing procedure of fresh concrete was the same as that of dry mixing sample.

As soon as the blending was completed, fresh sample was quickly transferred to a 3L container so that the rheological parameters was measured within 1 minute and 30 seconds. The rest of fresh concrete were casted in 5 cm cube molds for the measurement of compressive strength and electrical resistivity. The surfaces of the fresh cast mixtures were immediately covered with a vinyl sheet to prevent moisture evaporation, and the samples were cured for 24 h in an environmental chamber at 20°C and a relative humidity (RH) of 60%. The molds were then removed, and the samples were steam cured at 90°C for 2 days and stored in the chamber at 20°C and RH of 60% until testing.

Samples	WPC	SF	QP	SS	SP	CNT	Dispersion method
UHPC (Ref.)						0	-
CNT0.1_US						0.1%	Dry mixing for 5 min
CNT0.2_US						0.2%	10 min
CNT0.5_US						0.5%	25 min
CNT0.1_DM						0.1%	Ultrasonication 65 mL/J
CNT0.2_DM	1	0.25	0.35	1.1	0.04	0.2%	120 mL/J
CNT0.5_DM						0.5%	250 mL/J
CNT0.1_CS						0.1%	Commercial suspension diluted 15 times
CNT0.2_CS						0.2%	7.5 times
CNT0.5_CS						0.5%	3 times
CNT0.8_CS						0.8%	1.875 times

Table 3-3 Mixture proportion (by weight of cement).

3.2.3 Test methods

The flow curve was measured using a rotational rheometer (Viskomat XL, Schleibinger, Germany) equipped with a fishbone-shaped probe. Flow curves were fitted to Eq. (7) corresponding to a Bingham model by regression analysis to obtain dynamic yield stress and plastic viscosity.

$$T = g + h \cdot N \tag{7}$$

where g [Nm] and h [Nms] are rheological constants corresponding to Bingham yield stress and plastic viscosity, respectively. In this study, g is named dynamic yield stress. However, h can be presented in a physical unit of viscosity [Pas] by multiplying the calibration factor C_p (= 2.62) provided by the manufacturer. The static yield stress of samples was measured using a 6-blade vane-type probe. Time zero was defined as the point at which mixing was finished. The shear rate was as low as 0.3 rpm (0.005 /s) and maintained for at least 180 seconds until the maximum torque was achieved at each elapsed time (i.e., 15, 30, and 45 min after time zero). The examples of the flow curve and the test profiles are present in Figures 2-1 and 2-2, respectively. It should be noted that the shear ramp test was conducted for 3 times in a row and its profile was determined not to exceed the torque limit of 1200 Nmm for every fresh sample.



Fig. 3-3 Examples of flow curves of samples. a) Thixotropic loop test result to determine dynamic yield stress and plastic viscosity; b) constant shear rate test result to determine static yield stress.



Fig. 3-4 Test procedures for a single cycle of a) thixotropic loop and b) constant shear rate test.

The compressive strength was tested using a displacement-controlled universal testing machine (UTM) with a load cell capacity of 2000 tons based on ASTM C109 [96]. During the test, the applied loading rate was 0.02 mm/s. The compressive strength and elastic modulus were averaged from the three samples.

The electrical direct current (DC) resistance of the samples was measured at 2 days later after steam curing was finished. An LCR meter (LCR-6100, GW INSTEK, Taiwan) that measures the inductance (L), capacitance (C), and resistance (R) of a material was used. The measured DC resistance via the four-probe method was converted into electrical resistivity according to Eq. (3) in Section 2.1.1.

3.3 Results and discussion

3.3.1 Plastic viscosity and dynamic yield stress

Due to its low water-to-binder ratio (w/b) and high binder content, UHPC has superior mechanical properties and durability compared to conventional concrete (CC). The absence of coarse aggregates and use of fibers in UHPC also improve the homogeneity of mixture and enhances the mechanical properties, crack resistance, tensile strength, and ductility of the material. High dosage of SP is utilized to ensure high fluidity, which contributes to self-consolidating properties and improved dispersion of the binder system. Researchers have used other chemical admixtures in addition to SP to enhance the mechanical properties of UHPC. For example, Meng and Khayat reported that the fiber distribution uniformity and flexural performance of UHPC with 2% of micro steel fiber can be optimized by adjusting the plastic viscosity of suspending mortar and suggested the optimal plastic viscosity of 53 ± 3 Pa s and mini V-funnel flow time of 46 ± 2 s [97].

The models explain the relationship between the shear stress and shear rate. The flow curve was analyzed by regression using Bingham model. As shown in Figure 2-1a, all samples showed linear relation between shear stress and shear rate. However, it should be noted that the shear rate applied in this study was relatively low. The maximum shear rate and torque applicable using the equipment here was 80 rpm (= 1.33 s^{-1}) and 1200 N mm, respectively. Dils et al. observed a shear-thinning behavior of UHPC mortar using various types of cement [98]. However, as Feys et al. pointed out, the apparent viscosity might increase with increasing shear rate showing shear thickening behavior, and this shear thickening behavior should not be overlooked because high shear rate can occur in operations of mixing and pumping [99]. The maximum shear rate in various flow pattern can be found in [100,100]

During the induction period of cement hydration, the rheological behavior of UHPC is mainly controlled by the inter-particle interactions, which are influenced by the particle size distribution and fraction of particles. In the previous study, the hydration of cement retarded up to 12 h, measure by isothermal calorimetry and ultrasound pulse velocity [101]. There are a few probable explanations for the effect of CNTs; 1) decrease in free water due to absorption by the nanoparticles; 2) agglomeration of nanoparticles; and 3) filling of the gaps between cement grains by the nanoparticles [102]. The water absorption and agglomeration result in the increase of yield stress and viscosity of material, while the increase the viscosity of fresh concrete.

The plastic viscosity of reference UHPC was 20.86 Pa s, which was in relatively low range (Table 3-4). The plastic viscosity with increasing CNT content of 0.1 and 0.2% in samples fabricated by the dry mixing and the aids of ultrasonication increased exponentially (Figures 3-5, 3-6). When 0.5% of CNT was dispersed by those dispersion methods, the sample was too stiff to measure the rheological parameters. Care should be taken when interpreting the dynamic yield stress; the dynamic yield stress here is the slope, of which unit is N·mm·min, in Eq. (7), and therefore, it can be qualitatively compared with reference sample only in this study. The dynamic yield stress of samples fabricated by the dry mixing and the aids of ultrasonication shows steep rise with increase of CNT content. From the trend line in the Figures 3-5, and 3-6, it may be expected UHPC will no longer have the selfcompacting ability at a CNT concentration of 0.3% or more.

Table 3-4 Typical yield stress and plastic viscosity ranges for different concrete mixtures (adopted from [103]).

Rheological parameter	CC	SCC	HPC^*	UHPC
Yield stress (Pa)	500-2000	5-50	50-2000	10-100
Plastic viscosity (Pa·s)	50-100	100-400	50-550	20-200

* HPC: high-performance concrete.

It has been suggested that during the sonication treatment, not only water is adsorbed on the CNTs, but also that the less polar part of SP molecules aligns with the CNT walls, increasing the dispersibility of the CNTs (Figures 3-5, 3-6). In the case of dry mixing, the number of water molecules and SP molecules interacting with the CNTs was expected to be relatively lesser compared to the case of sonication treatment. It is because the ultrasonication treatment has been considered to be the most effective for disentanglement of CNT agglomerates among the mechanical dispersion methods. The better dispersion degree refers to the more individually dispersed CNTs, and therefore, the more water or SP molecules adsorbed onto the CNTs. Thus, it was envisaged that fresh samples with dry mixing method applied would show more flowability. However, both methods increased viscosity and yield stress to a similar extent.

In contrast, the viscosity and yield stress of samples incorporated with commercial suspension shows relatively gradual increase with the addition of CNTs. The viscosity of CNT0.1 CS slightly decreased compared to that of the reference sample, which may result from enhanced packing density of fresh concrete. Over this concentration, the effect of attractive force would be higher than that of particle packing, resulting in increased plastic viscosity and yield stress. However, it is worth noting that there exists significant difference in the degree of dispersion or agglomeration of CNTs in fresh UHPC. Also, the average length and diameter of CNTs are smaller in the form of aqueous solution than that of powder. The aspect ratio of CNTs in commercial suspension was ~600, while that of CNTs received as powder was ~ 1000 . In the squeeze flow test of CNT incorporated pastes, the increase in CNTs aspect ratio increased the viscosity and yield stress for an incorporation level of 0.05% and 0.1%. The yield stress and viscosity of the paste incorporating CNT with an AR of 900 were 10% and 28% higher than those of the paste incorporating CNT with an AR of 250 by 10% and 28%, respectively[104].



Fig. 3-5 Schematic drawing of PCEs (modified from [105]).



Fig. 3-6 Schematic drawing of dispersing mechanism of PCE (a) with cement

particles and (b) CNTs.



Fig. 3-7 Plastic viscosity of samples containing varying CNT content (% bwoc) with different dispersion methods applied.



Fig. 3-8 Dynamic yield stress at time zero containitng varying CNT content (% bwoc) with different dispersion methods applied.

Samples	Plastic viscosity (Pa·s)	Dynamic yield stress (N·mm·min)**
UHPC(Ref.)	20.86 (2.68)*	23.88
CNT0.1-DM	28.72 (3.49)	59.66
CNT0.2_DM	45.69 (4.06)	96.83
CNT0.1_US	27.26 (3.60)	39.88
CNT0.2_US	44.63 (4.33)	93.19
CNT0.1-CS	19.85 (1.89)	31.32
CNT0.2_CS	24.91 (2.08)	41.1
CNT0.5_CS	33.13 (2.92)	91.77
CNT0.8_CS	60.68 (4.95)	209.46

Table 3-5 Plastic viscosity and dynamic yield stress of samples from thixotropic loop test.

* Numbers in parentheses indicate standard deviation.** Dynamic yield stress in this study is presented for comparison with reference UHPC.

3.3.2 Structuration rate

Rheological properties are one of measures providing the mechanical properties of a material. It is particularly important for cement-based materials because the internal structure in fresh state is difficult to be directly observed [106]. The structuration or structural buildup of fresh concrete refers to the particle flocculation due to van der Waals interaction or the formation of irreversible bonds by hydration product between particles [100,107]. If the material has low bond strength of internal structure, it will be more susceptible to bleeding and segregation, which are the result of settlement of particles due to gravitational force.

It is important to control the structural buildup rate because it plays a crucial role on formwork pressure of self-consolidating concrete and maintaining high flowability in entire casting process.

For example, UHPC structural members often manufactured as precast concrete, which can accelerate construction time, minimize delays and disruptions to the community, extend service life of the structure, reproducibility of rheological and mechanical performance, and lower life cycle costs. For a large-scale precast beams measuring 0.91 m in depth and 23.9 m in length produces with UHPC of relatively low yield stress can secure high filling ability and reduce consolidation energy [108].

High-cost relative to CC is one of the major barriers to the use of UHPC. In some cases, it is unnecessary to use the UHPC in the whole specimen. Hybrid members with UHPC used in selected sections subjected to high levels of stress can be produced with the remaining sections cast with CC. During the multilayer casting, the evolution of static yield stress of both materials should be carefully considered to secure proper interlayer bond strength development [109,110]. High level of structural build-up at rest and extended waiting time before the casting
the UHPC layer onto an existing lift of concrete can significantly increase the permeability and hinder the development of adequate bond development [109,110].



Fig. 3-9 Structuration rate of samples as a function of CNT content.

It was clearly shown that the addition of CNTs increased the thixotropy of UHPC (Figures 3-9, 3-10, 3-11, and 3-12). The evolution of static yield stress of UHPC/CNT influenced by the dispersion method and the type of CNTs. Particularly, the length of CNT received as in the form of powder had about 2–1000 times longer than that of CNTs in pre-dispersed suspension. Therefore, attractive interaction of particles with longer CNTs could be higher resulting in increasing flocculation rate.

As the CNT content increased, deviations between flocculation rate of samples

containing same amount of CNTs also increased (Figure 3-9). The graph shows sharper rise of static yield stress with time in the samples fabricated with ultrasonicated CNT suspension. These higher structural buildup rate of CNT0.1_US and CNT0.2_US samples may be related to the hydration characteristics of the superplasticized cementitious material. It has been reported that nano-sized hydrates (C–S–H, ettringite) are formed in the very early-age cement paste containing superplasticizer. They are known to have high compatibility with SP, which hinder the nucleation and growth of nano-sized hydrates onto cement particles. Therefore, amount of free SP would have a considerable effect on the initial dispersion of cement grains. As shown in Figure 3-13, if the CNT suspension contacts with dry powders with the backbone of SP oriented towards the water, while the side chain aligned on the sidewall of the CNTs during the ultrasonication process, the dispersion effectiveness of the SPs on binder particles will be reduced.



Fig. 3-10 Evolution of static yield stress of samples with dry mixing applied.



Fig. 3-11 Evolution of static yield stress of samples with ultrasonication applied.



Fig. 3-12 Evolution of static yield stress of samples with commercial suspension

used.



Fig. 3-13 TEM images of CNT suspension; adsorbed SP layers are shown.

3.3.3 Compressive strength

The w/c of the reference UHPC was 0.25, which is relatively higher than commonly adopted water content (w/c = 0.22-0.23) in the previous studies [57]. It was determined to compare the samples under the same conditions, considering the free water absorption of CNTs. Nevertheless, the reference sample showed compressive strength of 175 MPa on average without steel fiber owing to high packing density and self-compacting characteristic.



Fig. 3-14 Compressive strength of samples as a function of the content of CNT with different dispersion methods applied.

It was shown that the compressive strength of UHPC/CNT decreased overall with CNT addition (Figure 3-14). This reduction was much greater for samples incorporating commercial suspension. The lowest strength was 119 MPa when 0.2wt% of CNT was incorporated, and then recovered to 136 MPa as the CNT

content increased up to 0.8wt%. When ultrasonication or dry mixing was applied for CNT dispersion, the degradation due to CNT addition of 0.1% was negligible; compressive strengths of CNT0.1_US and CNT0.1_DM were 173 and 171 MPa, respectively. It can be inferred that the reinforcing effect CNT addition might overwhelm the adverse effects of CNT incorporation between 0.2–0.5wt%.

It was difficult to expect a reinforcing mechanism of CNTs in the UHPC matrix with a w/c ratio of 0.25, despite of superior dispersion quality of commercial suspension. This can be due to the dispersants and short length of CNTs, ironically enhancing the degree of dispersion. Probable explanation for decrease in compressive strength is weak interfacial bond between cementitious matrix and dispersed CNTs in commercial suspension of which polymeric dispersant may act as air entraining agent and be incompatible with cement hydration. The impact of CS on the rheological properties was much lower than other methods, as shown in Section 3.3.1, it is suitable for the fabrication of conductive concrete that requires a high content of CNT.

The compressive strength of dry mixed UHPC/CNT samples is slightly higher than that of samples with sonicated CNT suspension. It can be inferred that the macroscopic dispersion quality might be comparable in both methods. The reason for the decrease in strength may be due to entrained air during SP-aided sonication or entrapped air due to reduced flowability. Also, incomplete disentanglement of agglomeration by dry mixing could lead to mechanical defect because the bond between individual CNTs in clumps can be much weaker than that between CNT and cement matrix.

The dry mixing and the ultrasonication of CNT would be better when a relatively low content of CNT is required, given the degradation of mechanical performance. Particularly, dry mixing has the potential to minimize damage to CNTs compared to ball milling or ultrasonication. It has been reported that ball milling process reduces the aspect ratio of CNTs by shortening their length [68].

Pierard et al. observed a reduction in the average length of CNTs from 50 μ m to 0.8 μ m [62]. More highly dispersed CNTs usually entails shorter CNT length due to the simultaneously exerted separating and scissoring forces during ultrasonication [111]; therefore, their load carrying capacity is reduced. Also, regarding economic and environmental impact, dry mixing is considered efficient because ultrasonication is more time-consuming, laborious, and energy consuming (i.e., ultrasonication and cooling). Therefore, it is worth investigating the effectiveness of dry mixing methods, particularly for situations where a low content of CNT is desirable, such as mitigating autogenous shrinkage, antispalling effect, durability, and as tensile reinforcing nanofibers [112].

3.3.4 Electrical resistivity

CNT incorporated cement-based material exhibited the gauge factor, which is the fractional change in electrical resistance per unit strain, of up to 130, while the gauge factor of common strain gauges is approximately 2 [45,113]. The piezoresistivity can be achieved through two main mechanisms of percolation threshold and electron tunnelling effect. The distance between CNTs changes during loading cycles, and the closer the CNTs are, the easier the electrical current can flow. The change in electrical resistivity is reversible in the elastic range. In view of this, the sensitivity of CNT/cement-base material to compressive strain would show the highest performance near the percolation threshold of electrical conductivity, where conduction begins to occur in disorderly mixed conductive materials above a certain concentration in the matrix.



Fig. 3-15 Electrical resistivity of samples as a function of the content of CNT with different dispersion methods applied.



Fig. 3-16 Electrical conductivity of samples as a function of the content of CNT with different dispersion methods applied.

It can be seen that the percolation threshold of UHPC mixed with commercial suspension was relatively higher than samples mixed in the form of CNT powder (Figure 3-17). In the previous studies suggested that the percolation threshold of electrical resistivity of UHPC having w/c ratio of 0.23 was near 0.9 wt%, which was in line with this result [114]. It can be attributed to that a larger amount of shorter CNTs is required to form a connected network than longer CNTs. In addition, the dispersant sufficiently wrapping the CNTs can act as an obstacle hindering the contact between CNTs as Yu suggested [115].

Contrary to expectations, this study did not find a significant decrease in electrical resistivity in CNT0.5_US (Figure 3-16). The electrical resistivity of samples incorporated in sonicated CNT suspension gradually decreased until CNT added up to 0.2wt%, then slightly increased with a CNT content of 0.5wt%. It should be noted that the samples CNT0.5_US and CNT0.5_DM no longer had

SCC properties, and the casting of samples required subsequent tamping. Therefore, a decrease in the workability of CNT0.5_US might negatively affect the formation of a conductive network by increasing air content. Also, the ultrasonication energy emitted from the tip may not be effectively delivered to the entire quantity of CNTs because the viscosity of the suspension would increase with higher CNT concentration. If the suspension with high viscosity were not circulated well despite the magnetic stirring, energy would be intensively transferred to CNTs near the tip, which may have induced damage to the CNT and poor dispersion quality.

What is interesting in the result is that samples fabricated with dry mixing have much lower resistivity than other samples containing the same CNT content despite of reduced workability. It could be hypothesized that nano-sized silica fume crushed by sand particles enhanced the dispersion of CNTs. Also, those two nanomaterials coated onto sand particles further synergistically improved the macro distribution of CNTs. This method can alleviate the extent to which agglomeration occurs when the as-received CNT powder is mixed with dry powder in contact with water.



3.3.5 Future studies and direction

Fig. 3-17 Rheograph of CNT incorporating UHPC (Diamond symbol represents τ_0 and μ of the reference UHPC).

Dry mixing is more energy efficient and economic method, but the rheological properties of fresh UHPC should be adjusted when the target concentration is 0.5wt% [116]. Figure 3-17 clearly showed that the addition of CNT significantly increased the static yield stress and plastic viscosity of UHPC, which makes UHPC/CNT be inapplicable without the aid of vibration or compaction. Based on the previous studies on the effect of constituents on the rheological properties of concrete (Figure 3-20), the two simplest steps are to add water, air, or SP. However, adding air can adversely affect the strength and the electrical and thermal conductivity by increasing porosity.



Fig. 3-18 Principal illustrations showing the effect of adding different constituents to a reference mix (from [116])

3.4 Summary

Depending on the purpose of application, the appropriate concentration of CNT may vary. In many cases, about 0.1% of CNTs are incorporated for the purpose of improving durability or mechanical performance, 0.2-0.5% for piezoresistive material, and close to 0.5-0.8% CNT to produce conductive concrete. However, the percolation threshold also varies with the geometric characteristic of CNTs and adopted dispersion methods.

The most adopted dispersion method is polymer-aided ultrasonication. Due to very low w/c of UHPC, pre-dispersing CNTs in water might be very difficult to achieve by sonication. CNT concentration of suspension is obtained by dividing CNT/c ratio with w/c ratio. For example, if the target CNT/c is 0.1, 0.5, and 1.0 wt% with w/c given as 0.24, required CNT content in water will be as high as 0.42, 2.08, and 4.17%. The viscosity of the suspension increases with higher amount of CNT incorporated, and thus the effectiveness of sonication decreases. Therefore, the sonication process is one of the biggest limitations in practical application of cement-based sensors for large structures.

The commercial dispersion had superior dispersion quality, so there was no difficulty in casting and placing even at a high dosage of 0.8 wt%. The viscosity and yield stress were also within the range of the rheological parameters of typical UHPC. Nevertheless, the compressive strength decreased the most, and the percolation threshold of electrical conductivity was relatively high because it contained relatively short CNTs and an additional dispersant.

The rheological parameters of fresh UHPC applied with dry mixing and sonication showed similar trends. It was found that the decrease in workability was not significant for CNT incorporation of less than 0.2wt%. Interestingly, dry mixed specimens had better performance in terms of electrical conductivity and compressive strength than sonication applied samples.

Chapter 4. Critical CNT Concentration for Functional Application of UHPC

4.1 Introduction

Ultra-high performance concrete (UHPC), an advanced cementitious composite, exhibits exceptional compressive strength (> 150 MPa), high flowability, and excellent durability due to very fine admixtures (e.g., silica fume and quartz powder), lack of coarse aggregates, high-range superplasticizer, and dense packing of particles with a low water-to-cement ratio (w/c; range 0.2–0.25) [1-3]. Recently, it has been reported that incorporation of carbon materials can improve various material properties of UHPC. Meng and Khayat evaluated the effect of two types of graphite nanoplatelet (GNP) and one type of carbon nanofiber (CNF) on various properties of UHPC and compared four dispersion methods to secure the homogeneity of the composite [4]. They reported that carbon nanomaterials increased autogenous shrinkage and reduced total porosity. Lim et al. showed that CNFs were uniformly dispersed in the UHPC matrix by sonication and effectively improved the compressive strength and compensated for the autogenous shrinkage of UHPC [5]. Viana et al. investigated the behavior of UHPC, incorporating carbon nanotubes (CNTs) under thermal load, and found that the inclusion of CNTs reduced the occurrence of explosive spalling [6].

Among functional carbon materials, CNTs have received great attention in the construction sector due to their superior mechanical, electrical, and thermal properties [7]. Because of its high aspect ratio, high surface area, and nanosized characteristics with multifunctionalities, CNTs have been reported as an effective

reinforcement, improving the engineering properties of CNT/cement composites when uniformly dispersed into the matrix [8-12]. Like CNT-reinforced cement, UHPC incorporating CNTs can potentially be used in smart materials capable of electromagnetic interference (EMI) shielding or self-sensing for structural health monitoring (SHM) [13]. As an example, Lee et al. examined the hybrid effects of steel fiber and CNT on the self-sensing capability of UHPC under tension [14]. Additionally, they reported the effect of CNT concentration on the self-sensing capability of UHPC beams reinforced with 2% steel fibers under flexure [15]. Mung et al. investigated the crack-sensing capability, mechanical properties, and electrical curing efficiency of UHPC/CNT [16]. Moreover, it was evidenced by thorough probes that CNT inclusion modified the microstructures of UHPC hydrates stiffer, denser, and more complicated [13, 17-19].

However, examination of the effect of CNT addition on other key properties of UHPC is still in progress. While the enhancement of mechanical and electrical properties with CNT addition was demonstrated in the above studies, research on the shrinkage and thermal properties of the UHPC/CNT composite has not been explored. Moreover, prior research has focused on the designated properties; therefore, an investigation into the influence of CNT concentration on overall engineering properties and the side effect of an excessive load of CNTs on specific performance must be carried out before a multifunctional composite material can be designed. Meanwhile, the importance of combining nanosized materials in cementitious composites with various dispersion methods—such as high-shear mixing, ultrasonication, a surfactant, ozone-treated water, and the combination of the aforementioned treatments—has been considered in previous studies [9, 13-15, 20]. However, the sonication process limits the practical application of CNT/cementitious materials on a large scale, and the efficiency of sonication is also limited above a certain value of CNT content [8, 21].

In this study, the effect of CNT concentration on the mechanical, electrical,

shrinkage, and thermal properties of UHPC are evaluated when the content of CNTs is increased from 0 to 0.8% by mass of cement. Well-dispersed commercial CNT suspensions are utilized to improve the dispersion quality of CNTs even in higher concentrations. The side effects of excessive CNTs, such as degradation of properties, high costs, and fluidity reduction, are discussed. Moreover, the critical incorporation concentration (CIC) for applying CNTs to UHPC for practical applications is determined. The main goal of this study is to experimentally verify that a single CIC concept can be used due to the correlation of engineering properties and give insights for tailoring various aspects of engineering performance while maintaining the superior mechanical properties and durability of UHPC.

4.2 Experimental programs

4.2.1 Materials

The raw materials used in this study to produce UHPC were Type I ordinary Portland cement (OPC, Union Cement Co., Ltd., Korea), silica fume (Grade 940U, Elkem, Norway), quartz powder (S-SIL 10, SAC, Korea, median particle size of $4.2 \mu m$), and silica sand (Saeron, Korea, particle diameters of 0.2–0.3 mm). Smooth steel fibers (length of 13 mm, aspect ratio of 65.0, elastic modulus of 200 GPa, tensile strength of 2788 MPa) were incorporated to fabricate UHPFRC. The OPC and silica fume were utilized as binders, while the quartz powder and silica sand were used as the fine aggregate and inert filler, respectively.

A predispersed multiwall CNT suspension (Kumho Petrochemical, Seoul, Korea) consisting of 60 g of multiwall CNTs dispersed in 1 L of distilled water was used; this suspension was selected because uniformly dispersing CNTs in cementitious materials is challenging due to their hydrophobic characteristics, high specific surface area and aspect ratio, and strong van der Waals force [22, 23].

The particle size distribution and zeta potential of the CNTs were measured using a laser scattering particle size distribution analyzer (LA-960, HORIBA, Japan) and nanoparticle analyzer (SZ-100, HORIBA, Japan), respectively (Fig. 3-1). The mean particle size and zeta potential value were 0.41 μ m and -58.4 mV, respectively. The CNTs in suspension were found to be stably dispersed considering their originally synthesized size.

4.2.2 Sample preparation

The mixture design is listed in Tables 4-1 and 2, and the mineralogical compositions of the binders can be found in the authors' previous work [24, 25]. The w/c and water to binder ratio (w/b) were maintained at 0.24 and 0.23, respectively. For samples containing CNTs, part of the water was replaced with the dispersed CNT suspension, as listed in the mixture design. Initially, OPC, silica fume, quartz powder, and silica sand were uniformly blended using a Hobart mixer for 5 min. Then, water and the dispersed CNT suspension were added to the dry mixture along with a polycarboxylic acid–based superplasticizer and mixed for 10 min. The fluidity of fresh mixtures according to the American Society for Testing and Materials (ASTM) C1856 [26], which was used for directly comparing the samples, is shown in Figure 2. The fluidity of the UHPC, which was 23 cm, was significantly reduced with the addition of CNTs due to their adsorption of water molecules and high aspect ratio and specific surface area.

The fresh mixture was cast into cubic molds to determine compressive strength, electrical resistance, and thermal properties $(50 \times 50 \times 50 \text{ mm3})$ and into prismatic molds to measure autogenous shrinkage $(40 \times 40 \times 160 \text{ mm3})$. In the cubic samples, two copper plates with dimensions of 20 (W) × 60 (H) × 0.4 (T) mm3 were embedded as electrodes to determine electrical resistance [27]. The area of each copper plate that contacted the samples was coated with silver paste to ensure continuous contact between the concrete surface and the electrode [28-30]. In the prismatic samples, adhesive Teflon sheets were attached to the molds to allow deformations, and a thermocouple and strain gauge (PMFL-60-2LJRTA, Tokyo Sokki Kenkyuio Co., Ltd., Japan) were inserted in the center of the sample without constraints.

The surfaces of the fresh cast mixtures were immediately covered with a vinyl sheet to prevent moisture evaporation, and the samples were cured for 24 h in an environmental chamber at 20°C and a relative humidity (RH) of 60%. The molds

were then removed, and the samples were cured under the same conditions until testing. To prevent volume reduction due to moisture evaporation, the prismatic samples were sealed with aluminum foil. A schematic illustration of the samples is presented in Figure 4-3. The UHPFRC samples were cured using either SC at 90 °C and RH of 95 % or EC at low DC voltages of 19–23 V applied by DC power supply under the same RH condition for a period of 48 h. Subsequently, the specimens were held at 20 °C and RH of 60 % for 25 d, for a total curing period of 28 d.

Table 4-1 Mixture proportions of UHPC without steel fibers (wt% of cement).

Specimen	w/c (w/b)	Water	CNT suspension	OPC	SF	QP	SS	Super- plasticizer
CNT0.0 (Ref.)	0.24 (0.19)	0.24	-	1	0.25	0.35	1.1	0.05
CNT0.2		0.21	0.03					
CNT0.5		0.16	0.08					
CNT0.8		0.11	0.13					

Table 4-2 Mixture proportions and material properties of UHPC containing steel fibers (wt% of cement).

	Mix proportions						Material properties		
Specimen	w/c OPC	SF	QP	SS	SP	Steel fibers	Curing Method	Compressiv strength (MPa)	e Elastic modulus (GPa)
UHPC_SC	0.24 1	0.25	0.35	1.1	0.05	2 (vol%)	SC	181.1 (3.0)	44.5 (2.1)
UHPC_EC							EC	-	-
UHPC/CNT_SC							SC	191.1 (3.8)	49.2 (2.2)
UHPC/CNT_EC							EC	196.6 (2.3)	52.1 (3.7)

Note: Material properties of UHPC_EC have not been measured due to the inefficient curing. Red numbers in parentheses represent the standard deviation.



Fig. 4-1 Flow table test results of (a) UHPC, (b) CNT0.2, (c) CNT0.5, and (d) CNT0.8 without steel fibers.



Fig. 4-2 Flow table test results of (a) UHPC, (b) UHPC/CNT containing steel fibers.







(b) Prismatic sample for autogenous shrinkage test

Fig. 4-3 Schematic illustration of the samples: (a) cubic sample to measure electrical resistance and (b) prismatic sample to test autogenous shrinkage.

4.2.3 Test methods

The autogenous shrinkage and the internal temperature of the samples were measured after 28 days of curing (d) every 5 min after casting; these measurements were recorded by gauges linked with a data logger. This method has shown almost perfect repeatability under room temperature conditions in previous studies [25, 31]. The pore size distribution of the samples was analyzed with mercury intrusion porosimetry (MIP) using an Autopore VI 9500 (Micromeritics, USA). The samples were cut into $5 \times 5 \times 5$ mm³ cubes for the test, and the cubes were immersed into isopropanol to remove internal water and then dried at 40°C. The test variables for mercury intrusion and extrusion pressure, surface tension, and contact angle were 0–420.58 MPa (0.1–61,000 psia), 0.485 N/m, and 130°, respectively.

The compressive strength was tested using a displacement-controlled universal testing machine (UTM) with a load cell capacity of 2000 tons based on ASTM C109 [32]. During the test, the applied loading rate was 0.02 mm/s. Two strain gauges connected to the data logger and attached to the surface of each side of the samples were used to measure the strain under load. Additionally, the elastic modulus was calculated according to ASTM C469 [33]. The compressive strength and elastic modulus were averaged from the three samples.

The electrical DC resistance of the samples was measured at 24 h and 28 d via the four-probe method using an LCR meter (LCR-6100, GW INSTEK, Taiwan) that measures the inductance (L), capacitance (C), and resistance (R) of a material. The measured resistance was converted into electrical resistivity according to Eq. (3) in Section 2.1.1.

The thermal properties of the samples were measured at 20°C using a thermal constants analyzer (TPS-500S, Hot Disk, Sweden). A flat Kapton sensor, which acted as both a heater and detector of temperature increase, was placed between

the two cubic samples, as presented in Figure 4-4. Then, by recording the temperature against time, the thermal conductivity and thermal diffusivity were measured, and the volumetric specific heat was evaluated based on the power input and time-dependent variation for the transient plane source (TPS).





Fig. 4-4 Schematic description of thermal properties test.

When the specimens were under load during mechanical tests, the change in electrical resistivity was synchronously measured using the LCR meter and recorded in a computer to evaluate the crack sensing capability (Figure. 4-3). The FCR induced by loading was calculated following the Eq. (1):

A hard rubber plate with 1 mm thickness was attached at the interface between the specimen and UTM during compressive strength test to prevent undesirable flow of electricity. In addition, the pins of the center-point load component used for flexural strength test were wrapped with a plastic vinyl sheet to eliminate the unexpected effect of the metal device on the FCR of the specimens.



Fig. 4-5 Experimental set-up for measuring FCR during mechanical tests: (a) compressive strength test, (b) flexural strength test.

4.3 Critical concentration of CNT for tailoring multifunctional properties of UHPC

4.3.1 Poromechanical properties

Figures 4-6 and 4-7 show the effect of CNT addition on the pore distribution on UHPC and the change in volume of each pore type classified based on pore diameter at different CNT concentrations [34, 35]. The pore structure of UHPC completely changed, and the volume fraction of each type of pores changed differently when the amount of incorporated CNT varied. The mesopores (4.5-25 nm) and micropores (< 4.5 nm) were significantly reduced at all samples; these pores were physically filled with CNTs of similar sizes, as indicated in Table 4-1. While micropores steadily decreased from 1.94% to 1.32%, the mesopores slightly increased when 0.8 wt% of CNTs added. This suggests that individual CNTs effectively fill the nanopores in C-S-H gel even at 0.8 wt%; however, such in high concentration and high packing density, owing to van der Waals forces between the nanotubes, CNTs more likely to form the bundles or agglomerates, increasing in the size and volume of the capillary pores [36, 37]. Note that the entrapped air voids formed at 100-25 µm increased at all concentrations, especially at 0.8 wt% CNT content, even though the total porosity was still lower than that of the reference sample. The increased air voids were ascribed to the reduced fluidity of the samples with CNT incorporation (Figure 4-1); it is well reported that low fluidity in a fresh concrete mixture increases the ratio of air voids in the hardened matrix [38]. The presence of CNTs did not affect the volume fraction of macropores, and it is known that UHPC does not have large capillary pores (>50nm in diameter) due to the optimally designed particle size distribution of fine fillers such as silica fume and quartz powders [3].



Fig. 4-6 Pore size distribution of the samples at 28 d: (a) log differential intrusion and (b) cumulative pore volume.



Fig. 4-7 Pore volume distribution of the samples at 28 d (the red numbers on the bars indicate the total porosity).

4.3.2 Autogenous shrinkage

Figure 4-8 summarizes the autogenous shrinkage of UHPC that occurred during 28 d for CNT content. By incorporating 0.2–0.8 wt% of CNTs, the shrinkage at 3 d and 28 d was decreased by 17-39% and 16–34%, respectively. The addition of CNTs was as effective as using 1-2% of shrinkage-reducing admixture (SRA) by mass of cement that reduced 10-30% of the autogenous shrinkage of UHPC [39, 40].

The autogenous shrinkage is caused by chemical shrinkage and self-desiccation shrinkage. Since the water was replaced by CNT suspension to maintain the w/c ratio, the effective water for hydration was reduced, leading to lower hydration degree and chemical shrinkage. Moreover, excessive CNTs can be reagglomerated and cover the surfaces of the binder and hydrates and inhibit hydration reaction, as reported in [41]. Besides, dispersed CNTs can act as a nucleating agent on C-S-H gel and provide sites for hydration [42, 43]. This accelerated formation of C-S-H and stress-resistant microstructure can finally induce the termination of early shrinkage [31].

The self-desiccation induced shrinkage develops in proportion to the number of fine pores because it is induced by tensile stress in the pore solution [44]. Thus, CNTs reduced the fine pores in the matrix (Figure 4-7), mitigated capillary stress, and resulted in lower shrinkage strains. Additionally, the stress resistance of the microstructure was likely enhanced with the addition of CNTs, as evidence of denser, stiffer, and more complex hydrates have been reported [17-19].

However, the additional CNTs over 0.5 wt% had a limited effect on mitigating autogenous shrinkage. As shown in Figure 4-8, the extra reduction in shrinkage of 0.8wt% CNT sample was as few as 35 um/m. The increase in mesopores of the sample with 0.8 wt% CNTs was a reasonable cause for this marginal effect, and it appears that 0.8 wt% of CNTs can be an excessive load for the amount of cement



concerning its re-agglomeration and hindrance of hydration.

Fig. 4-8 Autogenous shrinkage of the samples (a) and obtained values at 3 and 28 d

(b).

4.3.3 Compressive strength and elastic modulus

The compressive strength and elastic modulus of UHPC reinforced with increased CNT content are presented in Figure 4-9. As anticipated, the UHPC/CNT composites showed enhanced performance at all concentrations compared to the reference. The samples with 0.2–0.5 wt% CNT content showed 4.1–14.2% higher compressive strength and 17.5–23.6% higher elastic modulus than those of the UHPC sample. The reinforcing mechanism of CNT has been reported as combining the following effects: the bridging effect, the pore filling effect, the role of CNT as a nucleating agent, and the modification of hydrate microstructures [8, 17, 45-47]. The results suggested that these reinforcing effects compensated the increase in air voids, which affect the strength of a material adversely.

For 0.8 wt% CNT addition, the compressive strength and elastic modulus increased by only 9.2% and 11.5%, respectively, showing insufficient results compared to 0.5 wt% CNT addition. Similarly, previous studies have reported the side effect of excessive CNTs on mechanical properties on CNT-reinforced cementitious materials [9, 48]. They suggested the re-agglomeration and poor quality of dispersion of CNTs as a probable cause of this marginal enhancement. However, the possibility of collision between the particles of silica fume, micro sand, and agglomerated CNTs is very high in UHPC/CNT composites due to a low w/b and high packing density. Moreover, incorporating an appropriate amount of silica fume, the binder of UHPC, has been shown to enhance the CNT dispersion in the matrix [48, 49]. Furthermore, stabilized CNT suspension and high shear mixing process were utilized in this study. In these respects, it appears that the marginal effect at 0.8 wt% CNT content was associated with increasing entrapped air voids and medium capillaries rather than poor dispersion of CNTs.



Fig. 4-9 Compressive strength test results: (a) summary and (b) compressiveaverage strain curves.

4.3.4 Electrical resistivity

The electrical resistivity of UHPC for CNT content at 24 h and 28 d is shown in Figure 4-10. The results demonstrated excellent conductivity of UHPC/CNT composites and indirectly showed the quality of dispersion of CNTs in the matrix. After 24 h, all specimens showed a low resistivity of 4.48–7.8 Ω ·m. At an early period, electrical conduction in cementitious material occurs mainly due to the movement of ionic charges dissolved in the pore solution [50]. As pore water is consumed by hydration and evaporation, ionic conduction is no longer available, leading to increased electrical resistivity. While the electrical resistivity of UHPC increased substantially to 116 k Ω ·m at 28 d, the electrical resistivity of samples with 0.2, 0.5, and 0.8 wt% CNT content reached 15.7 k Ω ·m, 242, and 27.4 Ω ·m at 28 d, respectively; all values were significantly lower than that of UHPC. These results indicated that the conduction mechanism in the UHPC/CNT composite changed from ionic to electronic, owing to the network of CNTs [51]. The dispersed CNTs formed conductive pathways and enabled the electrons to move regardless of the water content in the matrix (Figure 4-10).

Note that the electrical resistivity steadily and dramatically decreased with the addition of CNTs, unlike the changes of aforementioned mechanical properties. If the dispersion quality of CNTs deteriorates at a higher concentration, it is expected that the drop in electrical resistivity gradually decreases. Thus, this reduction indirectly suggested that CNTs are uniformly incorporated in the matrix. Additionally, the percolation threshold of UHPC was determined at around 0.5 wt% as a large decrease in resistivity of the composite was observed. Kim et al. suggested 0.3-0.5 vol% of CNTs for the percolation threshold value of cementitious materials, and it is equivalent to 0.16-0.26% by total mass and 0.42-0.71% by mass of cement in UHPC [52]. Thus, by incorporating 0.5 wt% of CNTs, UHPC can be utilized for self-heating, electrical curing, and SHM [14-16, 52, 53].



Fig. 4-10 Electrical resistivity of UHPC with respect to the CNT content: (a) at 24 h and (b) at 28 d (red numbers on the symbols represent the average resistivity of the samples).

4.3.5 Thermal properties

Figure 4-11 shows the thermal properties of the UHPC/CNT specimens with varying CNT content. Using the TPS method, the thermal diffusivity and thermal conductivity were measured from three samples, and volumetric heat capacity, which is the thermal conductivity divided by the thermal diffusivity, was obtained. As CNTs were incorporated, the thermal conductivity increased gradually (Fig. 11a). The thermal conductivity showed a one-hundredth order of magnitude increase with increasing CNT content, while the electrical resistivity followed a percolation transition, dramatic change at percolation threshold (Figure 4-10b). This difference in trend could be attributed to the influence of the interfacial thermal resistance and the different physical origin of thermal transport [54-57]. The heat transfer can be improved by increasing the number of thermal pathways, thereby allowing the heat to transfer mainly through this pathway by utilizing the high thermal conductivity of CNT [58]. It can also be improved by reducing the thermal resistance between the CNTs and the UHPC/CNT interface.

Meanwhile, the thermal diffusivity and volumetric heat capacity changed reversely. The thermal diffusivity, a rate of heat transfer of material, increased from 1.12 to 1.32 mm²/s until 0.5 wt% of CNT incorporated, then dropped to 1.10 mm²/s at 0.8 wt% CNT content, lower than that of UHPC. Conversely, the volumetric heat capacity decreased from 1.97 to 1.74 MJ/m³K, then appreciably increased to 2.12 MJ/m³K, higher than that of UHPC. The considerable decline in thermal diffusivity of the specimen with 0.8 wt% CNT content was attributed to the deterioration of the thermal conductive network by increased air voids and increased interfacial thermal resistance due to re-agglomeration. This is undesirable for heat dissipation media where high thermal conductivity and diffusivity are required, such as self-deicing road systems and nuclear power plants [59, 60]. Moreover, further enhancement of thermal conductivity will be insignificant because degradation of workability and re-agglomeration of CNTs is inevitable in higher concentrations.

It is worth mentioning that there was an anomalous reduction of volumetric heat capacity near the percolation threshold. These anomalous trends have not yet been studied in CNT/cementitious composites, but some cases have been reported in CNT/polymer composites [61]. Exploring the universal validity of the observed phenomenon would be worthwhile in future studies in terms of thermal property modification of cementitious composites.



Fig. 4-11 Thermal properties of the UHPC with respect to CNT content.
4.4 Applications on electrical curing and crack-sensing

4.4.1 Changes in the temperature and electrical resistivity during curing process

As shown in Figure 4-12, the results for the prismatic specimens were similar to those of the cubic specimens. The resistivity of the UHPC was initially 2.5–5.4 Ω m but dramatically increased during 2 d of curing to 552.2 Ω m under SC and 50 Ω ·m under EC. For UHPC EC, the low voltage of 23 V was insufficient to increase the temperature of the specimens to 90 °C because of the high resistivity. In contrast, for the UHPC/CNT, there was little variation in the electrical resistivity, which ranged from 0.27–0.46 Ω ·m during curing irrespective of the curing method. In particular, for UHPC/CNT EC, even with a low voltage of 23 V, the temperature of the specimens increased to almost 90 °C within 3 h and remained at that level until the completion of curing. However, the temperature varied by up to 8 °C depending on the location in the specimen. The temperature in the middle of the specimen rose the fastest and remained the highest whereas the temperature of the right side of the specimen where the anode (+) was applied rose rapidly and remained at the level close to that of the center of the specimen. However, the temperature of the left side of the specimen where the cathode (-)was applied remained in the range of 81-85 °C.

The large variation in the measured electrical resistivity between the UHPC and UHPC/CNT specimens was attributed to the change in the dominant electrical conduction mechanism in the UHPC matrix incorporated with the CNTs. In general, electrical conduction can be classified as either ionic or electronic [49]. Ionic conduction is caused by the motion of the ionic charge whereas electronic conduction occurs due to the movement of electrons in the conductive pathways. The increase in the number of charges transferred can cause an increase in temperature [50]. For the UHPC in this test, ionic conduction was the dominant conduction mechanism. Specifically, the matrix was surrounded by water prior to

the initiation of curing, and the ions in the water (i.e., pore solution) could carry current between the steel fibers. Thus, the electrical resistivity was initially low and a conductive pathway in the matrix was constructed. However, as the curing progressed, the ionic feature of the pore solution and ions in the matrix decreased because of the hydration reaction and evaporation, thus weakening the strength of the conductive pathways between steel fibers. As a result, the resistivity increased significantly and low voltages of 19–23 V were not enough to increase the temperature of the specimens. Therefore, it is insufficient for EC. In contrast, for the UHPC/CNT, the conduction mechanism changed from ionic to electronic when the CNTs were incorporated. Specifically, the dispersed CNTs that were uniformly distributed throughout the matrix formed strong conductive pathways along which the electrons could move rapidly by building connections with the steel fibers regardless of the water content in the matrix. For this reason, the initial resistivity was considerably lower than that of the UHPC. In addition, the reduction in the number of ions in water as the curing progressed had little effect on the degree of the electrical resistivity of the matrix. Thus, the resistivity remained unchanged during curing. Furthermore, even with low voltages of 19-23 V, it was possible to increase the temperature of the matrix to 90 °C, at which point EC was quite effective. For the prismatic specimen, it was found that the differences in the rates of temperature increase and the variation in the maximum temperatures at various points in the specimen were attributable to the direction of current that flowed from the anode (+) to the cathode (-).



Fig. 4-12 Changes in temperature and resistivity for prism specimens during curing: (a) UHPC_SC, (b) UHPC/CNT_SC, (c) UHPC_EC, and (d) UHPC/CNT_EC.



Fig. 4-12 (Continued) Changes in temperature and resistivity for prism specimens during curing: (a) UHPC_SC, (b) UHPC/CNT_SC, (c) UHPC_EC, and (d) UHPC/CNT_EC.

4.4.2 Flexural strength and crack-sensing capability

The flexural strength of UHPC_SC, UHPC/CNT_SC, and UHPC/CNT_EC were 40.36, 33.38, and 34.38 Mpa, respectively. The flexural strength of the UHPC/CNT was higher than that of the UHPC. The lowest flexural strength of 30.5 MPa was obtained for the UHPC_SC, while the highest flexural strength of 34.4 MPa was obtained for the UHPC/CNT_EC. The relative increase in the strength of the UHPC/CNT_SC and UHPC/CNT_EC specimens were 9.6 % and 12.9 %, respectively.

The flexural stress and FCR behaviors of the specimens with respect to time are shown in Figure 4-13. The flexural stress-time response curves of all specimens were similar to the general flexural stress-strain curves for the UHPC except for approximately 180–300 s from the beginning of the loading where the load did not significantly increase due to the displacement control. Thus, the response curves were classified into three zones: a linear elastic zone (I), a deflection hardening zone (II), and a crack opening zone (III). The flexural stress increased almost linearly until the first cracking stress (σ_{fc}) was reached in zone (I). After this point, the flexural stress in zone (II) gradually increased compared with that in the elastic zone (I) until the stress reached the maximum post cracking stress (σ_{pc}). After this point, the stress gradually decreased as the crack width increased, which is called crack localization, in zone (III) [57].

The σ_{fc} for all specimens was similar and in the range of 28–30 MPa. This is because the effect of nano-micro scale fibers on the first cracking stress was small [15, 62]. However, in the deflection hardening zone (II), the UHPC/CNT exhibited significantly improved strain hardening behavior regardless of the curing method in comparison with that of the UHPC. In addition, beyond the σ_{pc} , the stress decreased slightly for the UHPC/CNT whereas that of the UHPC decreased relatively more rapidly. This indicates that the CNTs with a high aspect ratio favorably affected the strain hardening and multiple cracking behavior due to the bridging effect as shown in Fig. 7e–f. Fibers smaller than micro size increase the strain hardening and post cracking behavior rather than increasing the first cracking stress in the UHPC [62].

The FCR of the UHPC could not be used to accurately estimate the flexural state or crack sensing timing under deflection. The FCR of the UHPC increased slightly to 0.65 as the stress increased until the σ_{pc} was exceeded, then abruptly increased in the crack opening zone (III). However, the value of the FCR was still below 1.5, which was not large enough to use for the crack sensing. In addition, the point at which the first crack occurred did not match the point at which the FCR rapidly increased. Therefore, it was difficult to recognize the point of first cracking and whether the specimen had yielded or not. In contrast, the measurement of the FCR enabled the detection of cracking in the UHPC/CNT. The FCR of the UHPC/CNT was close to zero until the σ_{fc} was reached regardless of the curing method. However, after first cracking, the FCR rapidly increased up to about 25 and fluctuated wildly. In addition, the FCR gradually increased and fluctuated as the crack width increased. Thus, it is possible to determine whether the specimens had cracked or not based on the obtained FCR data. Moreover, since the multiple cracks gradually progressed from the bottom to the top of specimen, the disconnection between the CNTs also progressed slowly. Therefore, the FCR significantly increased at the point of first crack because some of the CNTs became disconnected and then began to fluctuate as this increased.

The GF was calculated at the point of the first crack to evaluate the crack sensing capability of the UHPC and UHPC/CNT under deflection as Eq. (3). Note that the ε of the specimens was not measured under the flexural strength test; however, since the stress-time response based on displacement control was quite linear until the σ_{fc} was reached, ε could be calculated as follows:

$$\varepsilon = -\frac{My}{EI} \tag{8}$$

where M is the flexural moment (kNm), y is the distance from the specimen to the tension surface (m), E is the elastic modulus (GPa), and I is the moment of inertia of the cross-section (m⁴) of the specimen. The GF of the UHPC_SC was calculated as 295.7, whereas those of the UHPC/CNT_SC and UHPC/CNT_EC were calculated as 2957.9 and 2133.4, respectively, which were approximately 10.0 and 7.2 times higher. Thus, it can be confrmed from the GF value that the crack sensing capability of the developed UHPC/CNT under deflection improved enough to determine the yielding point.

To assess the crack-sensing performance of UHPC/CNT composites in this study, the gauge factors obtained from the reported literature [19, 22, 63-67] is provided in Table 4-3. It is found that the sensitivity of UHPC/CNT composites was at least 11 and 15 times higher in the case of under compression and deflection, respectively. As reported in [68], different dosages of CNTs used in cementitious materials may modify their electrical conductivity and mechanical performance. In terms of self-sensing capability, the compression sensor using piezoresistive effect have shown better performance with CNTs of concentration under the percolation threshold [63], while previous studies have reported that nanomaterial concentration above threshold was favorable of sensing tension [69]. In this study, crack-sensing capability of UHPC improved with the CNT content of 1.2 wt%, which also enabled EC of UHPC.



Fig. 4-13 FCR behaviors with respect to time: (a) UHPC_SC, (b) UHPC/CNT_SC, and (c) UHPC/CNT_EC.



Fig. 4-13 (Continued) FCR behaviors with respect to time: (a) UHPC_SC, (b) UHPC/CNT_SC, and (c) UHPC/CNT_EC.

	Conductive filler				Reference
Cementitious material	Kind Content (by weight of cement)		Load type	Gauge factor (GF)	
Cement	CNT	0.3, 0.6 wt%	Deflection	148.66, 194.32	Naeem et al. [19]
Cement	CNT	0.1 wt%	Compression	50	Han et al. [65]
Cement	CNT	0, 0.05, 0.1, 0.25, 0.5 wt%	Compression	65, 240, 180, 110, 140	Camacho- Ballesta et al. [63]
Cement	CNF / CNT	0.1 wt% / 0.05 wt%	Compression	228 / 189	Sasmal et al. [64]
Cement / Mortar / Concrete	CNT	1.0 wt%	Compression	130 / 68 / 23	D'Alessandro et al. [22]
ECC	CNT	0, 5, 10 wt%	Direct tension	102.0, 540.4, 344.8	Yang and Qian [66]
UHPC	SF / CNT	3.0 vol% / 0.5 vol%	Direct tension	Straight: 67.8, 46.4, 36.5 Twisted: 39.0	Lee [67]

Table 4-3 Gauge factors of cementitious materials with conductive fillers.

Note: CNT-Carbon nanotube, CNF-Carbon nano fiber, SF-Steel fiber, ECC-Engineered cementitious composites

^a The values indicate the content of CNTs by weight of PE fiber.

4.5 Summary

Prior works have investigated the effect of CNTs on the electrical and mechanical properties of UHPC and discussed its applications, such as EMI shielding, self-heating, and piezoresistivity. However, the thermal properties, and shrinkage of UHPC/CNT have not been studied much in the UHPC/CNT composite. The overall understanding of engineering properties for CNT concentration will expand UHPC/CNT as a smart and multifunctional composite.

Thereby, this study examined the mechanical, autogenous shrinkage, electrical and thermal properties of CNT-reinforced UHPC and determined the CIC of CNTs for designing engineering performance of UHPC. The well-dispersed CNT solution was used, and the stable dispersion of CNTs in the matrix was indirectly confirmed by the consistent and dramatic decrease in electrical resistivity of the composite. At all concentrations, incorporating CNTs affects positively; however, the fluidity of UHPC decreased significantly due to high surface area and reagglomeration of CNTs, which affects the poromechanical properties of UHPC significantly. The total porosity was reduced due to a decrease in micro-and mesopores filled with CNTs, but the volume fraction of entrapped air was increased. Furthermore, CNTs showed marginal enhancement on overall properties when over 0.5 wt% was included. The autogenous shrinkage, electrical resistivity, and thermal conductivity barely increased at 0.8 wt% of CNT content, and mechanical properties and thermal diffusivity were even degraded. This limited effect was explained by the deteriorated workability and change in pore size distribution.

The results confirmed that the multifunctionality of UHPC could be maximized by incorporating CNTs while mitigating autogenous shrinkage and utilizing superior mechanical performance and durability of UHPC. The CICs for various material properties were determined to 0.5 wt% considering percolation threshold and limited effect of CNTs on shrinkage and mechanical properties, a substantial reduction in volumetric heat capacity, and an increase in thermal diffusivity. Moreover, these findings confirmed experimentally that a single CIC concept could be usefully applied to tailoring engineering properties of UHPC.

On the other hand, application of UHPC in field construction is limited owing to the particular requirements of SC. In this study, successful incorporation of CNTs in UHPC was reported for practical manufacture of UHPC via EC as well as multi-functionality as crack sensitive structural material.

Based on these results, the production of UHPC structures in field construction by applying EC on UHPC/CNT composites is feasible. This is possible because the resistivity of a material is not affected by its geometry [12] and the temperature of the actual structure can be effectively increased with even a low voltage. In this way, the proposed approach uses significantly less energy than that required for traditional UHPC production to accelerate curing and achieve target performance. Lastly, it was found that the UHPC/CNT composites could be also used as a SHM structural sensor with high crack sensing capability. Future studies should be focused on using large scale specimen or structure and improving workability for producing UHPC/CNT composite on-site efficiently.

Chapter 5. Non-destructive Evaluation of CNT Dispersion Using Confocal Raman Mapping

5.1 Introduction

In recent years, there has been significant interest in utilizing the extraordinary properties of carbon nanotubes (CNTs) to improve the material properties of cementitious materials and to fabricate building materials with novel functionalities, such as structural health monitoring, electromagnetic shielding, and self-heating [92,114,117-119]. Despite the extensive investigation, experimental data conflict and show large deviations, making it challenging to apply CNT to building materials in practice. This inconsistency is attributed to the variance in dispersion methods used and the dispersion quality of CNT in ongoing studies [120]. Although CNT dispersion is a crucial factor affecting composite performance, discussion of the description and methods of measuring CNT dispersion is still lacking. The conventional characterization methods, transmission/scanning electron microscopes (TEM/SEM), are commonly used for direct observation of CNTs in bulk samples, but they have some limitations in cementitious material. The observable sample size is small compared to the particle size of raw materials, and preparing fine powder is destructive and timeconsuming.

On one hand, researchers have often characterized CNT dispersion in suspension to compare the effectiveness of the dispersion method. The absorbance of ultraviolet and visible light (UV-vis) has been used to compare the CNT dispersion according to total ultrasonication energy [61]. It is difficult to utilize UV-vis absorbance as an indicator of CNT dispersion when comparing results with the different types and amounts of dispersants used, because the absorbance of the dispersant can overlap with that of CNTs [121]. Additionally, the particle size distribution (PSD) of CNTs in suspension has been measured by dynamic light scattering or laser diffraction [122]. Although it can be inferred that the smaller the CNT size in suspension, the better the dispersion of CNTs in the matrix, few consistent empirical pictures have been presented to support this inference. Moreover, this approach, limited to the suspension state, cannot capture either the uneven distribution of CNT due to various particles accounting for about 40% of volume or the dispersion stability issue in a complex alkaline environment [91,94,123].

On the other hand, several studies have attempted to indirectly evaluate CNT dispersion by measuring composite constitutive properties (e.g., mechanical strength, electrical conductivity) [124–127]. Using these properties as a dispersion gauge can hinder systematic research on CNT/cement composites because other variables (e.g., porosity, moisture content, mix proportions) can significantly influence composite properties [60,127,128]. Moreover, the bulk properties cannot be used as dispersion indicators when developing a prediction model, because they are generally the final target performance. Nonetheless, it is indisputable that proper measurement and quantified indicators to characterize CNT dispersion in cement composites are strongly required to understand the contribution of CNT dispersion to the final properties of a composite and to compare the efficiency of different fabrication methods.

Therefore, this study aimed to describe and quantify CNT dispersion in a cement matrix by introducing two indices: the dispersion efficiency and the unevenness in spatial distribution. We report the use of confocal Raman microspectroscopy (CRM) as a practical and complementary tool equipped with a light microscope (LM) to visualize the spatial distribution of CNTs in the *as-is* hardened composite. LM is a fast and simple method for morphological

investigations of relatively large sample volumes. However, the fuzzy boundary between CNT and matrix is an obstacle to applying LM to the macroscopic investigation of CNT dispersion. CRM enabled a more elaborate evaluation of CNT distribution by mapping the localized chemical and crystallographic properties with high spatial resolution [129]. In this study, we quantified and compared the CNT dispersion in *as-is* hardened composites with different dispersion states and CNT contents. The phase maps obtained by CRM showed the uneven distribution of CNTs induced by unreacted clinkers. The experimental evidence showed that the dispersion state of CNTs in composites was associated with that in suspensions. Overlapped definitive maps of primary phases illustrated how increased CNT content began to fill pores, and the possibility of using easy and fast light micrography for dispersion evaluation was discussed.

The quantifying indices and CRM measurement suggested in the study will be a key step toward introducing quantitative standards for the practical application of CNT/cement composites. A more systematic study of CNT/cement composites will be possible by quantifying the CNT dispersion in cement composites using different dispersion methods by adopting the evaluation methods suggested herein.

Few innovative approach, such as small-angle X-ray scattering (SAXS), has been introduced for evaluation of macro-dispersion of CNTs in as-is hardened cement matrix [130]. The SAXS plots for the poorly-dispersed samples showed substantial variation in intensities at each measurement location, while the intensities of the reference specimen without CNTs and the well-dispersed CNT/cement specimen were almost identical for all measuring points.

The main objective of this chapter is to visualize the distribution of CNTs in 2D over a large area using confocal Raman spectroscopy, in addition to obtaining the additional information such as distribution of unreacted clinkers and hydrates. The resolution of this mapping reaches $\sim 0.8 \ \mu m$ per pixel giving an accurate picture of carbon nanotube dispersion. The development of a broadly applicable

dispersion quantification metric will provide a better understanding of reinforcement mechanisms and effect on performance of large-scale composite structure.

5.2 Characterization of dispersion of carbon nanotubes using confocal Raman spectroscopy

5.2.1 Description of the dispersion of CNTs in cement composites

Primary particle, aggregate, and agglomerate

Certain terminologies require clarification before main discussion. In this study, "primary particle" refers to one nanotube, and "aggregate" is used to signify a few nanotubes that are strongly bundled together and cannot be broken down through additional physical/chemical treatment. "Agglomerate" is a cluster of aggregates loosely bonded due to the bridging effect and van der Waals force, which may be broken down through shearing power and collision with solid particles (Figure 5-1).

One researcher might point out that the diffraction limit spot size of CRM is larger than a CNT diameter of tens of nanometers, and therefore, CRM is not adequate for specifying the precise location of a CNT. When referring to "welldispersed" CNTs in a cement composite, it is not likely to indicate strict nanodispersion of individual CNTs because complete separation into each nanotube is time-consuming, non-economical, and unnecessary for most applications. Therefore, "better dispersion" is used in the sense of smaller aggregates that exhibit a more uniform spatial distribution.

Evaluation of dispersion using a device with a lower resolution than the size of primary particles implies that aggregates in the range below the resolution are considered to belong to dispersed fillers. That is, the resolution of LM (typically < 1 µm diameter) and the diffraction limit of CRM (~ 0.7 µm when N.A. = 0.45, λ = 532 nm) determines the size criteria of dispersed filler [93,131]. At that point, it is more important to discuss if the presence of clumps below a certain size can be tolerated or whether the assessment of dispersion based on this assumption is plausible for investigations into specific applications rather than pinpointing the location of individual CNTs. Although it is beyond the scope of this study, it should be addressed in future work.

Yazdanbakhsh et al. showed that the distance between neighboring CNTs with a diameter of 10 nm and a length of 1 μ m would be approximately 440 nm in uniformly dispersed cement paste with a water-to-cement ratio (w/c) of 0.35 and CNT-to-cement ratio (CNT/c) of 0.5% [63]. We reasoned that Raman signals obtained from CRM with submicron resolution would be sufficient to detect the presence of CNTs in a cement matrix with practical CNT concentrations, as multiple CNTs are expected to be present in the interaction volume of CRM measurements [132].



Fig. 5-1 Schematic drawing of a) primary particle and its equivalent spherical diameter, b) aggreage, and c) agglomerate of CNT.

Degree of dispersion of nanomaterials

'Nano-dispersion' can be defined as splitting aggregates into individual, nonbundled CNT. A complete nano-dispersion, therefore, refers to a state where all CNTs are suspended in the form of primary particle. The degree of nanodispersion could have several conceptually different definitions [133]:

- 1) the fraction of dispersed CNTs (bundle or individual)
- 2) the reciprocal of the average number of CNTs per bundle
- 3) the fraction of CNTs that are unbundled

The functionality of nanocomposite generally depends on the dispersion of individual CNTs rather than just CNT bundles. The dispersion of small CNT bundles can be called 'macro-dispersion.' The distinction between nano- and macro-dispersion is important because the frequently used term "well-dispersed" can refer to either.

Therefore, depending on which concept the researcher has in mind, 'better dispersion' means a higher fraction of individual nanotubes (i.e., better nanodispersion) or a smaller aggregate and less agglomerate (i.e., better macrodispersion). There remains uncertainty in the definition of dispersion of CNTs. This uncertainty ultimately stems from the fact that there are multiple ways for CNTs to be poorly dispersed, and a variety of structured networks may form at non-dilute concentrations.

When referring to "well-dispersed" CNTs in a cement composite, it is not likely to indicate complete nano-dispersion of individual CNTs. Even though the higher degree of dispersion improves the target properties of the composite for the application, complete separation into each nanotube is time-consuming, noneconomical, and unnecessary for most applications; it is considered even incapable at high concentration. Dispersion is an issue of practical relevance since the required dispersion state of CNTs in cement matrix depends on each intended application. When CNTs are incorporated as a reinforcing agent, appropriate interfacial adhesion between the matrix and nanotube should be made. The hydrates that form nuclei on the CNT surface act as an adhesive between the unreacted particles and the CNT and fill the pores. Better dispersion indicates more contact area between CNTs and matrix, thus reducing the amount of CNTs required for the same reinforcing effect. On the other hand, when CNTs are used as a conductive filler, generally much higher amount of CNTs would be incorporated to achieve percolation network. CNTs should be distributed so that the distance between CNTs is close enough to enable electron hopping, or a connected conductive pathway of CNTs is formed. Some theoretic approaches shown that the waviness and agglomeration of CNT play a crucial role in the conductivity of cement-based composites, and complete separation of individual CNTs induced by other nanoparticles may adversely affect electrical conductivity [134,135].

From an engineering point of view, determining what level of bundling/aggregation to consider a dispersed entity would be the first step in quantitatively measuring the degree of 'macro-dispersion' in cement composite.

Spatial distribution of nanomaterials

It is worth noting that the term 'dispersion' is used to indicate not only separation into smaller particles but also uniform spatial distribution in composite. However, the concept of uniform distribution could be overlapped with the definition of agglomerate (Figure 5-2). Some researcher defined agglomerate as a continuous region where nano-particles spaced less than a characteristic particle diameter [136].



Fig. 5-2 Schematic drawing of spatial distribution of nano-particles: a) uniform dispersion/distribution, b) some CNT particles clustered, c) an agglomerate with spacing between particles less than a particle diameter (reproduced from [136]).

In the case of cement-based composite, even if the degree of dispersion in suspension is high enough, uneven distribution of CNTs in the composite can occur during fabrication. The probable causes are:

- Because the large host particles (i.e., cement grain and mineral additives) can result in non-uniform distribution of large host particles. It is referred to as geometry dependent clustering, which occurs when host particles are much larger than the nano-particles. The geometric dependent clustering exacerbates as the concentration of nano-particle increases (Figure 5-3).
- Also, dispersed CNTs can significantly agglomerate in an alkaline pore solution after mixing. It is related to the dispersion stability of CNT suspension and the compatibility of surfactant with cement-based materials.
- Due to inappropriate rheology, bleeding can / vertical direction. This can be prevented fine and coarse aggregate.

For these reasons, a well-dispersed CNT suspension may not guarantee the quality of dispersion in composite matrix.



Fig. 5-3 Schematic drawing of a geometric dependent clustering: a) relatively uniform dispersion with low CNT concentration, and b) with high CNT concentration.

5.2.2 Dispersion efficiency of CNT in cement composites

When conducting a macroscopic inspection in polymer composites using light microscopy, the degree of dispersion (DOD) was quantified by the volume fraction of dispersed CNTs. The volume fraction of non-dispersed CNTs (i.e., the product of the packing density of CNT agglomerate and its volume fraction) was subtracted from 1 [93]. However, the contrast between agglomerates and matrix became vague in micrographs of cement composites with ultrasonication treatment even in white Portland cement (Figure 5-4). Furthermore, a valid assumption about the packing density of CNTs in agglomerates can hardly be made because preparing a very thin section of cement composite is nearly impossible [93]. Therefore, the dispersion efficiency (I_{DE}) that can be measured using CRM is introduced as a substitute for DOD.

$$I_{DE,Raman} = \frac{V_{CNT}}{V_{Total}} = \frac{N_{CNT}}{N_{Total}}$$
(9)

The calculation is simple, but care must be taken when interpreting this metric. V_{CNT}/V_{Total} is computed by counting the number of points where the

characteristic Raman signal of CNT is identified (N_{CNT}). This indicates the volume fraction of the CNT-affected region, not the volume fraction of dispersed CNTs. Because the detection of the CNT signal can only confirm the presence of CNTs in the interaction volume, it does not provide information about how CNTs are dispersed in the region. Nevertheless, it is reasonably presumed that the matrix in the region can be regarded as a CNT-affected region, given that the length of a CNT is several micrometers, and an interaction volume is less than 1 μ m³.

When inferring the increased proportion of dispersed filler from a higher I_{DE} , a condition must be satisfied: a large I_{DE} should not be achieved by significant agglomeration of CNTs present in the scanning area nor by dosing high CNT content. Because CRM is equipped with LM, visually proving the presence or absence of substantial agglomerates is easy. Samples with different CNT content can be compared by normalizing I_{DE} to a specific concentration. The range of I_{DE} is 0 to 1, with a value close to 1 indicating better dispersion efficiency.



Fig. 5-4 Optical micrographs obtained with 20x objective of (a) cement paste, (b) CNT/cement paste containing 0.2 wt% CNTs without ultrasonication treatment, and (c) CNT/cement paste containing 0.2 wt% CNTs dispersed with ultrasonication treatment.

5.2.3 Heterogeneity of CNT in cement composites

Even if the dispersion efficiency is evaluated as high, there is still a possibility that the composite is highly heterogeneous. This could be induced by non-uniform distribution of host particles and/or significant agglomeration of CNTs in an alkaline pore solution. Therefore, the heterogeneity metric (I_{HT}) is introduced to describe how CNTs are distributed in the composite.

 I_{HT} is modified to be suitable for cement material based on the quadrat approach [136]. The binary map of CNT is subdivided into quadrats (squares), and the number of pixels containing CNT is counted. If CNTs are uniformly distributed, each quadrat will contain the same number of CNT pixels. With the observed CNT distribution probabilities \bar{q}_i , the probability of finding CNTs in the i-th quadrat is defined in Eq. (11).

$$\bar{q}_i = \frac{q_i}{\sum_{i=1}^n q_i}, \qquad q_i = a_i/A \tag{10}$$

where a_i is the number of CNT pixels, and A is the area of a quadrat. The denominator normalizes the probability over the total number of quadrats so that the sum of p_i is to unity. For example, the probability of a uniform distribution \bar{p} is calculated as 1/n using Eq. (10). The heterogeneity can be presented as the distance between a uniform distribution P and particular nano inclusion distribution Q using Kullback–Leibler divergence (relative entropy).

$$D_{KL}(P||Q) = H(P,Q) - H(P)$$
(11)

where H(P,Q) is the cross-entropy of the distributions P and Q. Kullback– Leibler divergence always has a value greater than or equal to zero. Relative entropy is zero when the two probability distributions are identical, and a larger value indicates that the distribution Q differs more from a standard distribution P. The heterogeneity index I_{HT} is computed using Eq. (12):

$$I_{HT} = \sum_{i=1}^{N} (-\bar{p}_i \log \bar{q}_i + \bar{p}_i \log \bar{p}_i) + \sum_{i=1}^{M} (-\bar{p}_i \log \bar{p}_i)$$
(12)

where N and M are the number of quadrats with and without CNTs, respectively.

Examples of the calculation of probability for specific cases are presented in Figure 3. Note that there is a case where a finite value is not yielded (Figure 5-5b). Because the cross-entropy term $\bar{p}_i \log \bar{q}_i$ does not give a finite value, the quadrat where $\bar{q}_i = 0$ was penalized by subtracting the entropy of uniform distribution ($\bar{p}_i \log \bar{p}_i$).



Fig. 5-5 Examples for calculating the probability of the presence of CNT.(a) A binary image of CNT. (b) A quadrat where CNT is not detected.(c) A quadrat where CNT is detected.

The heterogeneity index decreases as spatial uniformity increases and becomes 0 in the case of perfectly uniform distribution. In the binary image of CNT, I_{HT} will be 0 when the number of CNT pixels is the same in all quadrats. The maximum value of heterogeneity depends on I_{DE} and N_{Total} . As an extreme example, I_{HT} will always be 0 if $I_{DE} = 1$. If the number of measuring points

 (N_{Total}) increases (i.e., the observation area is wider or the resolution is higher), the maximum achievable inhomogeneity will increase. Therefore, a significant comparison of I_{HT} can be made between specimens with a similar I_{DE} . Also, it would be possible to evaluate the CNT distribution by comparing I_{HT} and $I_{HT,max}$, calculated with the given I_{DE} and N_{Total} .

5.3 Experimental program

5.3.1 Materials and sample preparation

Type I white Portland cement (WPC; Union Corporation, Seoul, Korea) was used to fabricate cement paste samples, and the mineral composition of WPC was obtained with X-ray diffraction/Rietveld refinement (Table 5-1). The CNT suspensions were prepared with three different dispersion states: commercially available CNT suspension (Kumho Petrochemical, Seoul, Korea), multi-wall CNT powder in the form of a tablet (LUCAN BT1003, LG Chem Ltd., Seoul, Korea), and polycarboxylate superplasticizer (Dongnam Co. Ltd., Pyeongtaek, Korea). The commercial CNT suspension consisting of 26.1 g of multi-wall CNTs dispersed in 1 L of distilled water by a small amount of surfactant (≤ 5 g) was used a well-dispersed suspension. The macro-dispersed suspension was as manufactured following the process of placing water and CNT powders in a jacketed beaker at a temperature of 10 °C and dispersed with an ultrasonic processor (Sonoplus; Bandelin, Berlin, Germany) at a power rate of 2 kJ/min and ultrasonic energy of 350 J/mL. Then, the superplasticizer was poured and stirred with a magnetic bar for 20 min to be absorbed into the CNTs. In preparation for poorly dispersed suspension, CNT powder, superplasticizer, and water were poured into a beaker and stirred with a magnetic bar for 30 min. Samples fabricated with well-, macro-, and poorly dispersed suspensions were named with the prefixes W-, M-, and P-, respectively, and the mass percentage of CNT-tocement mass was notated as CNT_{wt%}. The mix proportions and dispersion methods for the sample preparations are summarized in Table 5-2. Note that the superplasticizer was added to all samples as a dispersant of cement and/or CNTs because cement particle dispersion influences the CNT distribution in a composite. The PSDs of the cement and dispersed CNTs were measured using a laser diffraction particle size analyzer (LA-960; HORIBA, Ltd., Kyoto, Japan), as shown in Figure 5-6.

Cement was added to a bowl with CNT suspension, giving a w/c of 0.3, and was blended using a homogenizer with vertical blades at 300 rpm. The resulting cement paste was transferred to a cylindrical holder with a diameter of 25 mm. The surface of the paste was covered with a plastic sheet to prevent moisture evaporation, and the specimen was cured for 24 hours at 20 °C and relative humidity of 60%. Then, the mold was removed, and the specimen was cured using steam curing at 90 °C for 2 days. The sample was cut using a diamond blade at 1200 rpm, then immersed in isopropyl alcohol and cleaned with an ultrasonic treatment.



Fig. 5-6 Particle size distribution of cement and CNT in suspensions.

Alite (monoclinic)	46.79
Alite (triclinic)	6.94
β-Belite	2.19
γ-Belite	1.38
Anhydrite	0.61
Aluminate	0.88
Amorphous	6.38
Calcite	21.38
Dolomite	12.36
Gypsum	1.09
Total	100

Table 5-1 Mineralogical composition of WPC (mass %).

Table 5-2 Mix proportions for sample fabrication (by weight of cement).

Samples	WPC	Water	SP (%)	CNT (%)	Dispersion method
W-CNT _{0.025}		0.3	0.8	0.025	
W-CNT _{0.05}			0.8	0.05	
W-CNT _{0.1}	1		0.8	0.1	Commercial suspension
W-CNT _{0.2}			0.8	0.2	-
W-CNT _{0.4}			0.8	0.4	
M-CNT _{0.05}			0.85	0.05	Sonication 350 J/mL
P-CNT _{0.05}			0.85	0.05	Magnetic stirring 30 min

5.3.2 Confocal Raman microspectroscopy (CRM)

Raman spectra were collected using a CRM system (NOST, South Korea) equipped with a 532 nm laser using an excitation power of 13 mW and a 1200 g/mm grating and a charged coupled device (CCD). The first peak of Si was used to calibrate the excitation wavelength. The lateral and depth resolution for $20 \times$ objective used in the air (n = 1.0) is constrained by the diffraction limit [131].

$$\Delta_{\text{lat}} = \frac{0.61\lambda}{(N.A.)} = \frac{0.61 \cdot 532}{0.45} \sim 721 \ nm \tag{13}$$

$$\Delta_{\rm dep} = \pm \frac{4.4\lambda n}{2\pi (N.A.)^2} = -\pm 1840 \ nm$$
(14)

The step size of X/Y direction and the scan area were determined to be 0.7 μ m and 105 × 105 μ m², respectively, concerning the lateral resolution of the equipment. Raman maps of a 105 × 105 μ m² scan area (150 × 150 points) were acquired with an accumulation time of 1.0 s per point (total 6.25 hours per sample).

5.3.3 Data analysis and map construction

MATLAB software and Raon-Vu (NOST, South Korea) were used for preprocessing, data analysis, and visualization. Cosmic ray was removed from the raw data, and the noise level of each point was computed using the arPLS method by averaging the fluctuations in the background region [137].

The basis spectra of the initial primary phases (i.e., alite, belite, calcite, dolomite, and gypsum) and hydration products (i.e., portlandite and ettringite) were obtained from a large dataset and were normalized to utilize as basis spectra. A linear combination of basis spectra was fitted to the Raman spectrum obtained from each point. The coefficients were calculated by minimizing the error between the obtained spectrum and a superposition of multiple bases. Then, the images containing coefficients of each phase were processed with a thresholding value of five times of noise at each location to obtain definitive phase maps (Figure 5-7) [138,139].



Fig. 5-7 Schematic representation of the data acquisition and analysis procedure.

5.4 Results and discussion

5.4.1 Phase identification and construction of phase map using CRM

Recent studies have applied Raman imaging to quantify the chemical composition of cement and utilized *in situ* CRM to monitor the phase transformations and hydration kinetics [140,141]. The possibilities for localization and characterization of phases may open more opportunities for the examination of heterogeneous cement nanocomposites using CRM.

One researcher might point out that the diffraction limit spot size of CRM is larger than a CNT diameter of tens of nanometers, and therefore, CRM is not adequate for specifying the precise location of a CNT. Evaluation of dispersion using a device with a lower resolution than the size of primary particles implies that aggregates in the range below the resolution are considered to belong to dispersed fillers. That is, the resolution of LM (typically < 1 µm diameter) and the diffraction limit of CRM (~ 0.7 µm when N.A. = 0.45, λ = 532 nm) determines the size criteria of dispersed filler [93,131]. At that point, it is more important to discuss if the presence of clumps below a certain size can be tolerated or whether the assessment of dispersion based on this assumption is plausible for investigations into specific applications rather than pinpointing the location of individual CNTs.

Yazdanbakhsh et al. showed that the distance between neighboring CNTs with a diameter of 10 nm and a length of 1 μ m would be approximately 440 nm in uniformly dispersed cement paste with a water-to-cement ratio (w/c) of 0.35 and CNT-to-cement ratio (CNT/c) of 0.5% [63]. We reasoned that Raman signals obtained from CRM with submicron resolution would be sufficient to detect the presence of CNTs in a cement matrix with practical CNT concentrations, as multiple CNTs are expected to be present in the interaction volume of CRM measurements [132].

The experimental basis spectra obtained from the basis analysis are presented and annotated with vibrational modes in Figure 5-8a. Clinkers (alite, belite, and gypsum) and other initial phases (dolomite and calcite) were detected, and corresponding hydrates (portlandite, ettringite, and monosulfate) were identified. The basis spectra obtained in this study accorded with the external database and previous research. Alite and belite are distinguished by the SiO₄ v_1 band (800– 870 cm⁻¹). Although sulfate phases accounted for a small weight portion of the WPC (Table 5-1), the intensive $SO_4^{2-} v_l$ peak confirms the presence of ettringite $(\sim 990 \text{ cm}^{-1})$ and gypsum ($\sim 1008 \text{ cm}^{-1}$). It should be noted that the spectrum of monosulfate is referenced in the literature [141]. This is because acquiring a clear basis spectrum was difficult due to overlapping of the peak profiles assigned to monosulfate and those of other phases. However, the existence of monosulfate could be identified from the Al(OH)₆ v_1 peak near 530 cm⁻¹ (Figure 6b). The strong $CO_3^{2-} v_l$ peak identifies the carbonate phases of calcite (~ 1086 cm⁻¹) and dolomite (~ 1098 cm^{-1}). CH is identified with the lattice vibration (LV) peak of \sim 360 cm⁻¹. The weak broad band at around 680 cm⁻¹ was assigned to CH, while a narrower Raman signal at a lower wave number of $\sim 660 \text{ cm}^{-1}$ is distinctive to the broad CH band and appeared in the spectrum of the hydrated sample [142]. This signal was assigned to the symmetrical bending (SB) vibration of the Q^2 of C–S–H. The broad LV peak in the range of $130-300 \text{ cm}^{-1}$ was also assigned to the basis spectrum of C-S-H. It has been reported that tobermorite-like fresh (nonsynthetic) C–S–H had the characteristic peaks of the SB vibration at $\sim 670 \text{ cm}^{-1}$ and strong LV in the range of 100–350 cm⁻¹ [142,143]. CNT was identified by the presence of G and D bands that did not overlap with other phases. The G band (~ 1580 cm^{-1}), a common peak in graphite-related materials, was derived from the in-plane phonon mode, and it broadened due to bond inhomogeneity in defective or amorphous carbon materials. The D band (~1350 cm^{-1}) was derived from inelastic scattering on the defect point [144,145].

The peak positions of the average spectrum (mean of 22,500 spectra of P-CNT_{0.05}) are in agreement with the basis spectrum used in this study (Figure 5-8b). The fitting results at specific locations of P-CNT_{0.05} show the combination of basis spectra composing the entire Raman signal (Figure 5-8c). It can be seen that the intensity of the Raman signal of each phase varies depending on the measurement point in heterogeneous cement composites. The phase maps can be constructed according to the process described in Section 5.3.3. As expected, unreacted clinkers remained, and hydrates were found filling the matrix (Figure 5-9b). The spatial distribution of mineral additives (e.g., calcite and dolomite) and hydration products of sulfates are visualized in the phase map (Figure 5-9c, d). The spatial analysis of these phases is an essential subject in cement material but is beyond the scope of this paper. In the data presented in the following sections, only a CNT map was used for the quantification of dispersion.



Fig. 5-8 Basis spectra and the examples of fitting result.

 (a) Basis spectra with vibrational modes annotated. (b) Average Raman spectrum of P-CNT_{0.05} with characteristic peak positions marked. (c) The examples of fitting result at specific locations of P-CNT_{0.05}.



Fig. 5-9 Optical micrograph and phase maps of P-CNT_{0.05}.

(a) Optical micrograph (Note that the focuses of the light and the 532 nm laser are not perfectly aligned). (b) Phase map of main clinker phase and hydration products.

(c) Phase maps of mineral fillers and CNTs. (d) Phase map of sulfate phase and

hydration products.

5.4.2 Comparison of the effectiveness of dispersion methods

The spatial distributions of CNTs, major clinkers, and hydrates are presented in the second, third, and fourth columns of Figure 5-10. The black indicates the absence of the particular phases. Based on these maps, the definitive maps were obtained with a thresholding value of five times of noise at each location. These binary images overlapped and are shown in the fifth column of Figure 5-10, where the black, gray, and scarlet denote the presence of CNTs, clinkers, and hydrates, respectively. The points designated as CNTs were counted, and the total was divided by the total number of points (i.e., 225,000). The total area of $105 \times 105 \,\mu\text{m}^2$ was subdivided into small quadrats ($3.5 \times 3.5 \,\mu\text{m}^2$ /quadrat, 900 quadrats in total) to compute the observed CNT distribution probabilities.

The optical micrograph and CNT definitive map indicated that CNT-affected regions can be elaborately separated using CRM (Figure 5-10a). With ultrasonication treatment, the size of the CNT clump in M-CNT_{0.05} was reduced, and its boundary was indistinct compared to that of P-CNT_{0.05} (Figure 5-10b). The Raman signal of CNT was identified not only near the black spots, but also in the speckle-free regions, indicating that dispersed CNT fillers were increased by ultrasonication. The boundary between the CNT and the matrix is no longer clear in W-CNT_{0.05}, and the CNT-detected area is significantly wider than other samples. This qualitative observation is quantified as I_{DE} (Figure 5-11a). I_{DE} varies in poorly dispersed samples whenever the scanning region changes, and the dispersion efficiency could be constructed incorrectly when a large I_{DE} is obtained due to the presence of substantial agglomerates. In this case, the agglomerates in the micrograph and the unevenness of spatial distribution of CNT (I_{HT}) will prevent the misinterpretation (Figure 5-11b). It should be noted that the poorly dispersed sample exemplified here is not for practical application. It is apparent in this illustration that the smaller the particle size of CNT in a suspension, the broader the region where CNTs are detected.
The definitive map of CNT observed in samples with low CNT content is presented in Figure 5-12. The non-uniform state containing the same number of white pixels is shown, and their I_{HT} was computed. The I_{HT} index reflects the improvement in CNT distribution. In P-CNT_{0.05}, there was no change in I_{HT} , compared to the severely agglomerated example. In contrast, the I_{HT} of M-CNT_{0.05} was reduced by 20% from the extreme case. M-CNT_{0.05} and W-CNT_{0.025} suggested that dispersion using sonication with a superplasticizer has room for further improvement. More work is required to determine that CNT is well-dispersed in the CNT/cement composite fabricated by ultrasonication.

It should be noted that there are no agreed-upon criteria for choosing a quadrat size. If we set the quadrat size too large, a clustered distribution could be recognized as uniform because each quadrat is likely to have a similar number of CNTs, producing the same effect as a microscope with low magnification. The quadrat size of 3.5 μ m implies that the CNT distribution in this region is averaged to the normalized probability, and the variations on a scale above the quadrat size are quantitatively calculated. Therefore, I_{HT} can be interpreted appropriately, presented with the quadrat size. The quadrat-based approach can be considered a scale-sensitive measurement, like alternative indices such as L_f , free-space length, and L_a , agglomeration length [136].



Fig. 5-10 Optical micrographs, spatial maps of major components, and overlapped binary images of (a) P-CNT_{0.05}, (b) M-CNT_{0.05}, (c) W-CNT_{0.025}, (d) W-CNT_{0.05}, (e) W-CNT_{0.1}, (f) W-CNT_{0.2}, and (g) W-CNT_{0.4}.



Fig. 5-11 (a) The dispersion efficiency (I_{DE}) and (b) the heterogeneity index (I_{HT}) of the samples.



Fig. 5-12 Observed CNT binary image and corresponding non-uniform state containing the same number of CNT pixels of the samples for the computation of maximum heterogeneity index (I_{HT}). (a) P-CNT_{0.05}, (b) M-CNT_{0.05}, and (c) W-CNT_{0.025}.

5.4.3 Dispersion of CNTs with varying concentrations in cement composites

When comparing the micrograph with the CNT map of M-CNT_{0.05}, the CNTidentified region was limited to the black spot and its surroundings. In contrast, in W-CNT_{0.025}, the CNT signal was abundant in dark areas and remaining spaces except where the clinker was aggregated. Therefore, the I_{DE} of W-CNT_{0.025} (0.79) is about 3 times higher than that of M-CNT_{0.05} (0.26), despite having half the CNT content. This result showed that CNT aggregates less than 1 µm were uniformly distributed to some extent of the expectations (Figure 5-6). This suggests the importance of the smaller size of CNT aggregates in preparing a suspension for better dispersion. Quantifying the mass or volume portions of CNT aggregates less than a specific size could be an alternative method for presenting the DOD of a CNT/cement composite.

The overlapped binary maps provided supplementary information regarding CNT distribution. At lower CNT contents, unreacted clinkers existed in the scanning area, and CNTs filled the remaining space. For the W-CNT_{0.025} and W-CNT_{0.2} specimens, the I_{DE} and the maximum achievable I_{HT} were similar. The presence of clinkers gathered in the center affected the dispersion of CNTs (Figure 5-10c), and therefore, the I_{HT} of W-CNT_{0.025} had a higher value than that of W-CNT_{0.2}. As CNT addition increased, the overlapping area between CNT and other phases expanded. Because the penetration depth of CRM is greater than the lateral resolution and the PSD of CNTs, the final map can be considered a planar projection of the section with a thickness of the depth resolution rather than a planar image. The CNT region generally overlaps with hydrate phases in all samples, which is consistent with previous findings that CNTs provided the nucleation site, whether in dispersed or agglomerated forms [128,146].

The I_{DE} increased from 0.79 to 0.90 as the CNT concentration doubled from 0.025 wt% to 0.05 wt%. Above this concentration, the I_{DE} was maintained

around 0.90 (Figure 5-11). The relatively low I_{DE} of W-CNT_{0.2} (0.78) can be explained by the presence of large clinkers at the bottom left (Figure 5-10f). In the cement paste with w/c = 0.3, water was initially occupying about 50% of the paste volume, which corresponds to the volume fraction where CNTs can be dispersed [147]. At a CNT content of 0.05 wt% or more, CNT signals were detected at more than 90% of the measurement points. It can be inferred that CNTs are fully filling the pore space with a distance less than the resolution of CRM.

5.4.4 Limitations and future studies

Concerning the proposed quantifying technique, some important weaknesses need to be acknowledged. Due to the spatial resolution, the dispersion efficiency index I_{DE} did not represent the exact fraction of dispersed CNT. Nevertheless, it was possible to compare the dispersion efficiency of various dispersion methods using the index, compensating for the limitations of conventional techniques, such as electron and light microscopes. Besides the resolution issue, only the presence or absence of CNT was determined with a threshold of the signal-to-noise ratio of 5. Accordingly, the relative quantity of CNTs in the interaction volume has been ignored in this study. Even though this study did not focus on the normalization of the Raman signal of CNT to quantify the relative concentration at each measured location, future research should address a more precise characterization of the dispersion state at each interaction volume. If the relative amount of CNT present at each measurement can be compared, subdividing the entire area into small quadrats will not be necessary for calculating the heterogeneous index I_{HT} . This study provided a useful method that can be applied to quantitatively evaluate the dispersion of any non-cementitious inclusion considering micro- and nanoscale issues. The spatial distribution of nanoparticles can be quantified using the proposed method. These results can be used to systematically analyze the influence and importance of the dispersion state of nanomaterials on constitutive

properties or more complicated kinetics of hydration, carbonation, and deterioration of a cementitious system incorporating nanomaterials. Finally, a long scan time was required to obtain Raman spectra with a good signal-to-noise ratio. Deep learning can be applied to determine the presence of a single phase (e.g., CNT in this study) in a multiphase Raman spectrum with a high noise level to reduce mapping time.

5.5 Summary

Previous studies described the dispersion of nano-sized particles in heterogeneous cement composites because dispersion is the critical feature influencing the performance of composites [63,123]. Despite ongoing studies on CNT/cement composites, research on the measurement of CNT dispersion in heterogeneous and complex cement composites is still lacking due to the small sample size and destructive sample preparation of conventional evaluation techniques. A few studies have included factors related to CNT dispersion in developing the prediction model for mechanical properties of CNT/cement composite [60,148]. However, instead of quantified metrics reflecting the dispersed state of CNTs in a matrix, indirect parameters, such as dispersion procedure (e.g., CNT initial pre-wetting, sonication time, and energy), have been considered. Therefore, this study utilized CRM equipped with LM for macroscopic inspection of CNTs was quantified from the definitive map of CNT.

We found that CRM can be used to identify the presence of CNTs in the hardened matrix. Despite a very low CNT content, CNT was detected in almost the entire area in W-CNT $_{0.025}$, which indicated that CNTs were uniformly distributed in the matrix when using a well-dispersed stable CNT suspension. Raman imaging confirmed not only that the CNT agglomerates were visible in micrographs, but also that the nano-sized CNT aggregates below the LM resolution were spread in the matrix in M-CNT_{0.05} with ultrasonication applied. The qualitative evaluation in LM images was quantified with the dispersion efficiency I_{DE} and the heterogeneity I_{HT} . These simple metrics can be used to compare samples with different dispersion methods and CNT contents. In summary, these results enable the quantification of CNT dispersion in a heterogeneous multiscale composite and the evaluation of the efficiency of dispersion techniques, especially ultrasonication with incorporated superplasticizer.

However, some limitations are worth noting. The indices were developed based on the presumption that CNT aggregates less than a diffraction limit can be considered dispersed fillers. The micrographs could partly support the binary image of CNT, but not other phases. A more elaborate validation could be made by elemental mapping using an energy dispersive X-ray spectrometer [140,149]. Raman imaging directly identified CNT by its characteristic peaks, but it is still time-consuming in the current experimental setup. Future studies should therefore include fast and accurate phase detection using CRM.

Chapter 6. Quantitative Evaluation of CNT Concentration in Hardened Cement Composite

6.1 Introduction

Studying nanocomposites using confocal Raman microspectroscopy (CRM) may be beyond the equipment's abilities, given the spatial resolution. However, in the past decade, CRM has immensely contributed to the advances in our understanding of the application of nanomaterials and technology in various fields, including materials, bioscience, pharmaceutics, and chemical engineering [150]. CRM, complementary to conventional methods, can give useful information on materials containing nanoparticles by describing the location, distribution, and quantity of nanomaterials, implying the potential impacts of using CRM in cementitious nanocomposites. For example, CRM has been a practical tool for identifying and localizing intracellular nanoparticles, enabling studies on cytotoxicity, delivery, and degradation of nano-sized inclusions [151–153]. CRM was also found to be effective for the evaluation of nanocomposites. The dispersibility of nanofillers in polymeric matrices was examined using 2-D Raman maps, and the prediction model of constitutive properties could be updated with the mapping results [154,155]. Moreover, micro-Raman mapping has been conducted to analyze solid dispersion with electron microscopy techniques combined. The size and spatial distribution of domains where the drug existed as molecularly or nanodispersed could be examined, and the quality of solid dispersion could be characterized [156,157].

Recent years have seen renewed interest in utilizing CRM in cement chemistry. It was possible to visualize and monitor phase transformation during hydration and carbonation *in situ* (without sample processing) and *operando* (reflecting the real condition) and to quantitatively analyze the spatial distribution of various phases using the Raman map [141,158,159]. Moreover, quantitative Raman analysis has been attempted in cement-based materials. 4 principal phases and 8 secondary phases present in cement clinkers have been quantified with a high degree of confidence in 11 types of commercial cement [140]. Also, the progress of carbonation in hardened cement paste was quantitatively analyzed using the correlation between CO_3^{2-} concentration and Raman peak intensity [159]. These results demonstrated the versatility of CRM, having a high impact on the cement and concrete society, and were reported in prestigious journals.

In Chapter 5, a definitive map was constructed to visualize the spatial distribution of phases constituting the matrix of cement-based material. Because the Raman signal contains unwanted information, which is noise, a threshold value of 5 times of the noise is used to determine the existence of a specific phase. This approach is conservative and safe, but valuable information is lost during the process. The definitive map is only expressed as 0 or 1 (referring to the absence or presence), the implicit information contained in peak intensity is neglected. Even though the major phases such as unreacted clinkers and hydrates could be clearly identified as seen in Chapter 5, the strong advantage of Raman spectroscopy was not fully utilized. Therefore, this chapter aims to convert a large amount of information in a single Raman spectrum into quantitative value indicating the concentration at a specific point; then, the distribution of CNTs can be evaluated without using quadrat-based approach.

6.2 Normalization of Raman signal for quantitative analysis

6.2.1 Basic for Raman scattering intensity

There is a large quantity of information about interaction volume in a Raman spectrum. The intensity of Raman scattered light from the sample, $I(v)_R$ is given by Eq. (15) [160].

$$I(\nu)_{\rm R} = \frac{2^4 \pi^3}{45 \cdot 3^2 \cdot c^4} \cdot \frac{h I_L N(\nu_0 - \nu)^4}{\mu \nu (1 - e^{-h\nu/kT})} \times [45(\alpha_a')^2 + 7(\gamma_a')^2]$$
(15)

where c is the speed of light, h is the Planck's constant, I_L is the excitation intensity, N is the number of scattering molecules, v_0 is the molecular vibrational frequency [Hz], v is the laser excitation frequency [Hz], μ is the reduced mass of the vibrational atoms, k is the Boltzmann constant, T is the Absolute temperature, α_a' is the mean value invariant of the polarizability tensor, and γ_a' is the anisotropy invariant of the polarizability tensor.

Equation (15) explains sufficient Raman signal of CNTs despite the incorporation of very small volume fractions. The Raman signal is a result of a molecular vibration causing a change in polarizability of the molecule. And typical strong Raman scatterers are moieties with distributed electron clouds, such as carbon-carbon double bonds. Also, it provides the information that the Raman scattering intensity is proportional to the number of molecules (N) in the interaction volume being measured by Raman equipment and the intensity of the excitation source.

Eq. (15) can be expressed in simpler way as presented in Eq. (16).

$$I_i = C \cdot I_0 \cdot n_i \cdot \sigma_i \tag{16}$$

where C is a constant, I_0 is the laser intensity, n_i is the number density (mole fraction) of a *i*-th molecule (phase), and σ_i is the Raman cross-section. The Raman cross-section can be considered as the Raman sensitivity of each vibrational mode [141].

There is unwanted intensity generated by the sample. One of the most important examples is the fluorescence. Because the product of the constant in Eq. (15) is a very small number, the Raman signal is vulnerable to being obscured by more efficient optical processes such as fluorescence. It has been shown that the background in the 532 nm spectra was markedly higher than in the 785 nm spectra [161]. This background can be attributed to the autofluorescence of mineral phases in cement and this effect will be greater at short excitation wavelength with higher excitation energy [162].

What is important for us to recognize here, is that the intensity of the Raman signal is not only related to the number of molecules in interest but is also a result of, change in the polarizability of molecules, excitation energy, or even fluorescence. Therefore, it is necessary to properly normalize the signal to represent the volumetric concentration.

6.2.2 Raman intensity of hardened cement-based material

As can be seen in Figure 5-8, Raman spectra of cement composite contains enough information to address most of phases in raw material verified from XRD (Table 5-1). In addition, Raman bands of CNTs are well resolved from common phases in cement composite. Because the Raman scattering cross-sections are very small, we can analyze the Raman spectrum based on the principle of linear superposition of these bases. It is expected that the probability of a Raman scattered photon being lost due to another Raman scattering interaction is essentially zero [160].

However, the spectra are usually on different non-zero baseline. Previous studies claimed that showed that the fluorescence-induced background was markedly higher when using lasers with shorter excitation wavelength [161]. Figure 6-1 shows the histogram of relative fraction of background level in each measurement spot of samples, W-CNT0.05, M-CNT0.05, and W-CNT0.05, analyzed in Chapter 5. The total number of measured points were 225,000. Almost two-thirds of intensities account for the background level on average. That makes the removal of the baseline is undoubtedly an essential step in increasing the reliability of spectral interpretation. Baseline removal requires special attention in the case of hydrated cement samples. It can be seen that the shape and height of baseline varies with the major component in measurement volume (Figure 6-2). The least squares polynomial subtraction may be sufficient for single phase analysis. However, humps in the low range of Raman shift may contain broad lattice vibration of poorly crystalline hydrates such as calcium-silicate-hydrate (see C–S–H basis in Figure 6-3) or information on the type of minerals in cementbased materials. Therefore, in the analysis of cement pastes containing several amorphous hydrates, subtracting polynomial function can remove these kinds of data and significantly impair accuracy. Various types of humps make difficult to differentiate the Raman signal from the baseline.

Therefore, we made basis spectra for common form of humps in hydrated cement paste and some peaks from fluorescent light to use for baseline correction (Figure 6-3). The common humps were included in I_{bgd} in Eq. (17). Therefore, the relative fraction of the phases of interest was analyzed for the I_{signal} .

$$I_0 = I_{signal} + I_{bgd} = \sum_i I_{phase_i} + I_{bgd}$$
(17)



Fig. 6-1 Relative fraction of background level in a Raman spectrum of samples W-

CNT0.05, M-CNT0.05, and W-CNT0.05.



Fig. 6-2 Examples of Raman signals on the baseline with different shape and height.



Fig. 6-3 Basis spectra used for phase identification.



Fig. 6-4 Basis spectra used for baseline correction.

6.2.3 Normalization of Raman spectrum of cement-based material

From Eq. (15) and (16), we may infer that the concentration of CNT in interaction volume is proportional to the integrated intensity of a Raman band. The Raman band area can be calculated by a summation of the measured intensity over the wavenumber range of the Raman band after the baseline intensity is subtracted. If the band shape does not change, the integrated band area is proportional to its height. Measuring band height would give better accuracy when there is partial overlap between the analytical band and another band in the spectra. However, generally including more photons by integrating the whole Raman band can reduce the signal-to-noise (S/N) ratio when the main source of noise is random noise in the baseline. Another way to improve upon simple band integration or height measurement is to use curve fitting by using additional information about the Raman band. In lower region, there are many of overlapping phases as seen in Figure 6-1. Therefore, basis analysis was preceded carefully including broad humps to fully utilize the detected photons in Raman spectra.

The experimental variables are not constant unless Raman spectra is collected in single measurement in the laboratory. If experimental variables change, quantitative analysis is possible by measuring the change and applying a correction to the measured signal, that is, normalization.

The bands that do not change with the concentration of the analyte are a type of noise. This type of noise is potentially useful information, as they can be used as internal standards. The benefit of using an internal standard is that it can be obtained without adding a foreign material homogeneously to the sample.

Common matrix materials, such as water and glass have weak Raman signal, and therefore relatively little interference is occurred during measurement. However, it is almost impossible to add external standards in highly heterogeneous cement-based materials. Also, the phase comprising hardened cement material is highly complex, including capillary pores, unreacted cement and crystalline (e.g., portlandite, ettringite, and gypsum) as well as amorphous hydration products (e.g., calcium-silicate-hydrate), and their relative volume fraction changes with hydration reaction.

As can be seen in Figure 6-5, the volume fraction of CNTs did not change with the age of specimen while space initially occupied with water got filled with the hydrates. If the Raman band is well normalized, it should not change with the curing age, mix proportion, carbonation, or measurement condition.



Fig. 6-5 Schematic presentation of (a) fresh CNT/cement paste and (b) hardened CNT/cement composite.

Instead, we can consider modifying the Eq. (15) and (16) with respect to the concentration of analyte. The Raman spectrum of a mixture is equal to the weighted sum of the Raman spectra of the components that make up the mixture. If the Raman cross-section of each phase is known, we may be able to quantify the mole fraction X_i and even the volume fraction f_i .

$$X_i = \frac{n_i}{\sum_k n_k} = \frac{I_i / \sigma_i}{\sum_k I_k / \sigma_k}$$
(18)

$$f_{i} = \frac{V_{i}}{\sum_{k} V_{k}} = \frac{I_{i} \left(\frac{M}{\rho\sigma}\right)_{i}}{\sum_{k} \left(I_{k} \left(\frac{M}{\rho\sigma}\right)_{k}\right)}$$
(19)

, where X_i and f_i are the mole fraction and the volume fraction of i-*th* molecule, respectively. M_i is the molar mass, and ρ_i is the density of the material. Then, the normalization factor (NF) can be defined as

$$NF = \frac{M}{\rho\sigma} \tag{20}$$

It would be an intriguing task to calculate the polarizability tensors in Eq. (15) theoretically or precisely measuring the Raman cross-section in Eq. (16) of each phase. However, it will be very challenging to accomplish in cement composites due to their complexity and intrinsic heterogeneity. Instead, the bold assumption of this chapter is that a single normalized value proportional to the concentration could be obtained if we know the relative ratio of the Raman cross-section between materials. Therefore, the Raman sensitivity of raw materials was measured by changing the laser power. Then, it was corrected with the volume fraction of each material in interaction volume. Using the relative ratio between Raman sensitivity, each phase's Raman intensity could be normalized for any experimental setup or sample age. The more Raman sensitivity data of substances constituting the cement-based composite is obtained, the more reliable the normalization result is expected.

6.3 Experimental programs

6.3.1 Materials and sample preparation

The pure materials (> 95-98%) in powder form were prepared to measure the relative intensities of Raman cross-section. C3S-triclinic and C2S-beta were purchased from Sukyung (Korea), and calcium hydroxide (CH), calcium carbonate (CC), calcium sulfate dihydrate were purchased at Daejung (Korea). A commercial CNT solution (Kumho Petrochemical, Seoul, Korea) was used.

C3S-triclinic was hydrated to synthesize C-S-H with water-to-C3S ratio of 0.55 and cured at a temperature of 60°C for 3 days. Hardened paste was cut using a diamond blade at 1200 rpm, then immersed in isopropyl alcohol and cleaned with an ultrasonic treatment to remove the lubricant oil. Before the measurement, it was dried in oven at 40°C for a few minutes to remove isopropyl alcohol on the surface.

CNT incorporated cement paste samples for calibration were fabricated using commercial CNT suspension. The w/c ratio was fixed at 0.3, and CNT/c ratio was 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.8, considering the typical content of CNT as a reinforcing or conductive nanofiller. Then, it was converted to volumetric concentration using the true density of MWCNT and the density of cement paste. Water and CNT suspension was mixed with a homogenizer with a small fourblade impeller. Then, cement powder and diluted CNT suspension was put into the stainless container and mixed for 3 min at 300 rpm. The curing process of the paste samples was the same as in Section 5.3.1.

Specimens under various conditions were prepared for experimental validation: uncarbonated (freshly cut), carbonated (stored in a thermo-hygrostat for a few days), and CNT/cement composites containing varying CNT content and dispersion methods.

6.3.2 Confocal Raman microspectroscopy

Raman spectra were obtained using a CRM system (NOST, Korea) equipped with a 532 nm laser, a 1200 g/mm grating, and a CCD. The excitation wavelength was calibrated with the first peak of silicon. The lateral and depth resolution were 721 nm and 1.84 μ m (See section 5.3.2).

Powders were put into cylindrical stainless holder with a diameter of 28 mm and a height 3 mm. They were tapped and the surface was flattened with a glass plate. The measurement time was fixed at 1.0 s while the laser power was varied from 0.42 mW to 30.21 mW. The height of the characteristic peak according to the laser power was measured. It should be noted that the laser power here is measured with the optical power meter at the sample surface with changing the value of neutral density filter (ND filter), not the power of laser beam (Figure 6-6).



Fig. 6-6 Laser power at the sample surface as a function of ND filter.

CRM mapping was conducted for samples with various preparation conditions (dispersion methods, carbonated, uncarbonated, and age of specimen) and measurement conditions such as the step size of X/Y (0.7, 1, 2, 5, and 10 μ m) and the scan area (100×100 to 400×400 μ m²).

6.3.3 Data analysis

To obtain the Raman sensitivity of single raw material, the characteristic peak of each phase was chosen as the highest peak in the base spectrum. In single phase analysis, the baseline was corrected using the arPLS algorithm in Matlab software. The spectrum was fitted with basis spectrum to minimize the influence of noise. The noise level was calculated by the root mean square value of the noise on the background signal after baseline correction according to ASTM E579-04 [163].

More than three locations were measured and averaged for each phase. Because the interaction volume of measurement (less than 1 μ m³) is relatively smaller than a crystalline phase, we assumed that the measurement volume is full of crystalline phase. Therefore, the peak intensity to the laser power ratio was calculated for each point, and significantly low values were excluded for the analysis.

For the construction of phase maps, baseline was not corrected by arPLS algorithm; instead, humps and linear functions were used (Figure 6-4) to enhance the accuracy of curve fitting. A linear combination of basis spectra was fitted to the Raman spectrum while minimizing the error between the obtained spectrum and a superposition of multiple bases. This method showed better performance.

6.4 Results and discussion

6.4.1 Raman sensitivity of synthesized materials as a function of laser power

It can be assumed that the ratio of the characteristic peak intensity to the laser power is proportional to the product of number density and the Raman scattering cross-section (Eq. (21)). The molar mass and the density of pure materials were presented in Table 6-1, adopted from the literature [140]. It should be noted that the chemical composition and density of C–S–H varies with Ca/Si ratio and their drying condition. The chemical formula and density of C–S–H presented here is $(CaO)_{1.7}(SiO_2)(H_2O)_{1.80}$, and 2.604 Mg m⁻³, followed the numbers in [164]. In fact, we don't need to compute the exact Raman cross-section for normalization of Raman signal, because the linear coefficient is the inverse of normalization factor in Eq. (20) when the volume fraction is 100%.

$$\frac{I_i}{I_0} : \frac{I_{CNT}}{I_0} = \left(\frac{\rho\sigma}{M}V\right)_i : \left(\frac{\rho\sigma}{M}V\right)_{CNT} = \left(\frac{V}{NF}\right)_i : \left(\frac{V}{NF}\right)_{CNT}$$
(21)

The characteristic peak intensity to the laser power was computed after fitting the basis spectra to the raw spectrum. In the case of hydrated C3S-t specimen, this procedure is necessary because it contains at least three phases (i.e., unreacted C3S-t, CH, and C–S–H) (Figure 6-7). It is worth noting that water has weak Raman signal in the spectral region of 150 - 2700 cm⁻¹. If the spectral region is extended to ~ 4000 cm⁻¹, the relative amount of water can also be evaluated. There was no characteristic peak appear to be related to the surfactant in commercial suspension used (Figure 6-8).

Raw materials	Molar mass (g/mol)	Density (g/cm3)	
C2S	172.24	3.30	
C3S	228.32	3.18	
СН	74.09	2.26	
CC	100.09	2.71	
Gypsum	172.20	2.32	
C–S–H	134.18	2.60	
CNT	12.00	1.90	

Table 6-1 Molar mass and the density of materials [140,164].

The crystalline phases, such as C3S, C2S, CH, CC, and gypsum, show the linear relation between the peak intensities and the laser power (Figure 6-9). C–S–H tends to increase exponentially with increasing laser power; however, a linear relationship is confirmed within power range of common Raman measurement (< 15 mW). It should be noted that the average linear coefficient of CNT was calibrated by volume fraction in CNT suspension using known CNT concentration and the density of suspension (34 g/L \approx 17.8 vol%). As mentioned above, the volume fraction of other phases is assumed to be 100 vol%. Once the normalization factor of C3S and CH was obtained, relative amount of C–S–H could be estimated by subtracting the portion of C3S and CH in measurement volume. The NF obtained as the inverse of the coefficient of linear regression between peak intensity and laser power is presented in Table 5-2. Now we can calculate normalized intensity of CNT related to the volumetric density in interaction volume by fully utilizing all information in a Raman spectrum following the Eq. (22).

$$\overline{I}_{CNT} = \frac{I_{CNT}}{\sum_{i} NF_{phase_i} I_{phase_i}}$$
(22)

It is noteworthy that the accuracy of this approach can be influenced by the amount of free water in the measured spot, and this is an important issue for future research.



Fig. 6-7 Illustrative example of basis analysis of hydrated C3S-t (three phase system).



Fig. 6-8 Raman spectrum of commercial CNT suspension with the concentration of 34 g/L (laser power = 13 mW, exposure time = 1.0s,).

Table 6-2 Computation results of normalization factors with respect to CNT of synthesized constituents of hydrated cement-based materials.

Raw materials	Average linear coefficient (-)	Standard deviation	Normalization factor (-)
C2S	135.34	9.69	1.27
C3S	32.03	4.26	5.38
CH	14.37	1.31	11.99
CC	CC 384.15		0.45
Gypsum	271.28	11.19	0.64
C–S–H	38.31	6.37	4.50
CNT	172.35	2.07	1.00



Fig. 6-9 Characteristic peak intensities as a function of laser power. (a) C3S, (b) C2S, (c) Gypsum, (d) CC, (e) C-S-H, (f) CH, and (g) CNT.

6.4.2 Quantitative relation between normalized peak intensity and concentration

We calculated the average of normalized CNT peak in all regions for samples with varying CNT content. The range of mapping area and step size were $105 \times 105 - 200 \times 200 \ \mu\text{m}^2$ and $0.7 - 2 \ \mu\text{m}$, respectively.



Fig. 6-10 Average of normalized CNT peak as a function of CNT content (wt%).

Figure 6-10 clearly shows that Raman spectroscopy can detect a very low amount of CNTs in a hardened cementitious matrix. A huge Raman cross-section of CNT has been mentioned in many papers [165]. If the normalization is perfectly performed in calibration samples where CNTs are dispersed uniformly, the concentration versus the average of normalized CNT peak should be linear. However, the curve shows a clear logarithmic relationship. This could be due to rough assumptions on the Raman scattering cross-section of dolomite and other sulfate phases. Another probable explanation is the change in the microenvironment with CNT concentration, which can alter Raman sensitivity of vibration interaction of other phases with their micro-environment.

The logarithmic relation presents realistic predictions; when where normalized peak intensity of CNT reaches 1, 70 vol% of CNT concentration is expected. This value indicates that over 70 vol% of CNT content, the peak intensity of other phases may be marked by strong Raman signal of CNT. However, care must be taken to interpreting this model because workable CNT concentration is much less than 70 vol%.

CNT	Normalize	Normalized peak intensity		Measurement condition			
content (vol%) Mean		Standard	Step size	Mapping	Curing age		
		deviation	(µm)	area (µm²)	(day / C)		
0.017	0.02	0.0212	2	200x200	1d (20), 2d (90)		
0.021	0.0746	0.0661	0.7	105x105	1d (20), 2d (90)		
0.043	0.1016	0.0709	0.7	105x105	1d (20), 2d (90)		
0.043	0.0571	0.0407	2	200x200	1d (20), 2d (90)		
0.043	0.0597	0.0462	1	150x150	1d (20), 2d (90)		
0.043	0.0434	0.0328	2	200x200	3d (20)		
0.085	0.1941	0.1238	0.7	105x105	1d (20), 2d (90)		
0.085	0.1451	0.0896	1	150x150	1d (20), 2d (90)		
0.170	0.2604	0.1811	0.7	105x105	1d (20), 2d (90)		
0.170	0.2288	0.1325	1	150x150	1d (20), 2d (90)		
0.255	0.3637	0.1691	0.7	105x105	1d (20), 2d (90)		
0.340	0.3714	0.1589	0.7	105x105	1d (20), 2d (90)		
0.424	0.4108	0.1812	0.7	105x105	1d (20), 2d (90)		
0.424	0.3391	0.2006	0.7	105x105	1d (20), 2d (90)		

commercial CNT suspension with various measurement conditions.

Table 6-3 Normalized peak intensity of 14 calibration samples fabricated with

Reference sample (i.e., paste without CNTs) was scanned for 6 times; the mapping area was $50 \times 50 \ \mu\text{m}^2$ with the step size of 1 μm . The measurement spot was chosen randomly. The limit of detection (LOD) and the limit of quantitation (LOQ) can be calculated as three and ten times the standard deviation of the mean concentrations of blank sample [166]. However, it cannot be applied to this logarithmic prediction curve because the model gives negative concentration with a very low value of average of normalized peak height. (Table 6-4). Instead, three and ten times the standard deviation of the normalized peak height can be used as a criterion of presence/absence of CNT.

Table 6-4 Average of normalized intensity of CNT of reference paste sample without CNT.

Number of measurements	Average of normalized intensity of CNT	Predicted CNT concentration	
1	7.21E-06	-0.95	
2	0	NaN	
3	0.0013	-0.33	
4	7.63E-06	-0.94	
5	4.73E-04	-0.45	
6	1.38E-05	-0.87	
Mean	0.0003	-	
Standard deviation	0.00052	-	
Mean + 3× Standard deviation	0.00187	-	
Mean + $10 \times$ Standard deviation	0.00554	-	

6.4.3 Determination of measurement condition

The LOD and LOQ can also be evaluated using signal-to-noise ratio (SNR). In general, LOD is determined where SNR is in the range of 2:1~3:1, and LOQ is determined where SNR is 10:1.

The correlation between laser power and SNR of main phases are presented in Figure 6-11. Increase in laser power significantly enhanced SNR. In samples expect for CNT and CC, the increase rate of noise intensity gradually decreases and converges to a certain value. The noise levels obtained from the mapping results were within $5\sim12$, which was comparable with the upper limit of the value obtained in the measurement of the synthesized pure materials here.

Based on the results, the volume fraction at which each phase can be sufficiently identified at the measurement volume can be predicted with respect to the laser power (Table 6-5). The LODs of CH and C–S–H are relatively lower than other phases because their characteristic peaks in the spectral range ~2700 cm⁻¹ are weak; their strong Ca–OH vibrational band exist at 3610–3617 cm⁻¹. Therefore, it can be inferred that the reliability of detection of CH, C–S–H, and other sulfate hydrates can be further improved when using 600 grating with a little low spectral resolution.

C3S, CH, and C–S–H show 6-10 times higher LOD than that of CNT, and other crystalline materials show LODs that are better than or close to that of CNT. These results suggest that measurement conditions such as laser power and accumulation time should be determined based on if detection of CNTs is possible in the very condition. This is because the volumetric fraction of CNT is very small compared to other phases on average. Therefore, the identification of other constituents can be conducted sufficiently with the laser energy density that can discriminate CNT.



Fig. 6-11 SNR and background noise level of raw materials as a function of laser power. (a) C3S, (b) C2S, (c) Gypsum, (d) CC, (e) CH, and (f) CNT.

Table 6-5 Calculation results of LOD and LOQ as volumetric concentration at laser power of 5, 10, and 15 mW taken accounted with based on experimentaly measured Raman sensitivity of each phase. Note the that accumulation time is fixed at 1 s.

	Raman sensitivity (A.U./mW)	Noise level (A.U)	Laser power (mW)	Expected peak intensity (A.U)	LOD (vol%)	LOQ (vol%)
C3S	32.03	3.65	5	160.15	4.56	22.79
		4.19	10	320.30	2.62	13.09
		4.51	15	480.45	1.88	9.39
C2S	135.34	9.81	5	676.71	2.90	14.50
		10.74	10	1353.43	1.59	7.93
		11.64	15	2030.15	1.15	5.73
СН	14.37	2.75	5	71.87	7.65	38.23
		3.30	10	143.74	4.59	22.94
		3.54	15	215.61	3.28	16.42
CC	384.15	8.83	5	1920.73	0.92	4.60
		10.95*	10	3841.46	0.57	2.85
		11.85*	15	5762.2	0.41	2.06
Gypsum	271.28	2.53	5	1356.41	0.37	1.87
		2.69*	10	2712.83	0.20	0.99
		2.77*	15	4069.25	0.14	0.68
C-S-H	38.31	5.71	5	191.56	5.96	29.80
		6.92	10	383.13	3.61	18.07
		9.13	15	574.69	3.18	15.89
CNT	172.35	3.71	5	861.76	0.86	4.31
		8.36	10	1723.52	0.97	4.85
		11.72	15	2585.29	0.91	4.53

* The asterisk denotes a predicted result based on the Figure 5-10, not a measured value.

Raman spectra of a cement paste containing 0.025 wt% of CNT is presented in Figure 6-12. Agglomerates were not found at the measurement spot. It is possible to hypothesize that the number of photons detected at CCD is proportional to the energy density (kJ/cm²) input, which is the product of the laser power and accumulation time (or exposure time) over the irradiated area. The results show that increasing the laser power or increasing the exposure time improves the SNR. There are two options when determining the experimental conditions: the measurement time can be shortened by using stronger laser power, or the exposure time should be increased when the laser power is controlled to avoid the degradation.


Fig. 6-12 (a,b) cement composite containing 0.025 wt% of CNTs.

6.4.4 Quantitative analysis of CNT distribution using normalized peak intensity

In Section 5.2.2., the heterogeneity index was developed based on quadratbased approach. Because the presence of CNT was expressed in a binary, we had to use larger area (quadrat) than one pixel and calculate the difference in the relative proportion of CNTs in each quadrat. As mentioned in Section 4.4, the limitation of this approach was that the size of quadrat affects the quantified index suggested as I_{HT} .

Now the pixel contains the information on the relative quantity of CNT, we use the number of pixels vs. normalized peak intensity, instead of quadrat-based approach. Figure 6-13 shows samples containing various quantity of CNTs with different dispersion methods.

The probability of CNT distribution (q_i) in the quadrat (number of CNT detected pixel over a few tens of pixel) is now replaced with the normalized CNT peak intensity at a single pixel indicating the volume fraction(f_i) of CNT in the irradiated volume using obtained empirical relationship in Figure 6-10. Also, we can visualize the number of pixels with respect to CNT volume fraction as shown in Figure 6-13.



Fig. 6-13 Visualization of relative CNT content. (a) CNT 0.021vol%, (b) CNT 0.043vol%, (c) CNT 0.085vol%, (d) CNT 0.17vol%, (e) CNT 0.255vol%, (f) CNT 0.34vol% (continued)



(g) CNT 0.424vol%, (h) CNT 0.043vol% (sonication),

- (i) CNT 0.085vol%, w/c = 0.22 (sonication),
- (j) CNT 0.085vol%, w/c = 0.24 (sonication)
- (k) CNT 0.085vol%, w/c = 0.26 (sonication)

6.5 Summary

Since the volume fraction of free water will be significant under in-situ measurement conditions, the accuracy of the analysis can be improved by considering the amount of water by extending the spectral range to 4000 cm⁻¹.

The results of this study confirmed the possibility of precise calculation of the amount of CNT incorporation and spatial distribution if a sufficiently wide area was mapped at intervals of less than 1 μ m.

The recommended settings are applicable to mortars containing siliceous aggregates, even though the quartz fines are sometimes mixed with other crystalline minerals such as calcite, feldspar and mica. In any case, the presence of these phases is not expected to interfere with the detectability of cement hydrates and clinker minerals in the cement paste matrix. For mortars and concretes containing high aggregate volume fraction however, a small mapping step size should be used corresponding to the thinner cement paste regions between aggregate particles.

If the approximate concentration of CNT is known, measurement conditions can be determined considering CNT content because CNT has high Raman sensitivity. When a very small amount of CNT is mixed, the laser power must be sufficiently increased or the measurement time must be lengthened, but there is a possibility of damage to cement matrix and CNT.

Chapter 7. Conclusions

7.1 Summary and concluding remarks

Concrete is the most consumed material with sufficient strength and durability and is moldable in a pleasing shape. As an indispensable building material, concrete must keep evolving to satisfy upgraded social demands. Ultra-high performance concrete (UHPC), an advanced construction material, possesses superior compressive strength, flexural strength, ductility, and durability, having longer service life and low maintenance costs. It has been widely adopted to repair and retrofit existing buildings and infrastructure due to its exceptional strength and resistance to weathering action and chemical attacks.

Smart and multifunctional concrete has potential to address upgraded requirements regarding safety, longevity, and functions of advanced engineering structures. Carbon nanotube (CNT) is one of the most extensively investigated nanofiller for multifunctional composites due to its exceptional mechanical, electrical, thermal, and chemical properties. UHPC has optimized mix proportion, characterized by a low water-to-binder ratio, high content of superplasticizer, and high volume of silica fume, which is suitable for incorporating CNTs. CNT embedded UHPC can be the next generation construction material as an integrated system of repair/rehabilitation and functional properties, such as structural health monitoring, self-heating, and electrical curing.

The most important design parameters can be a uniformed dispersion of nanomaterial and its content for achieving target performance in developing cement-based smart nanocomposite. However, there has been lack of discussion on the quantitative techniques for evaluating the dispersion quality and the concentration of nano inclusions in hardened cementitious matrix. This challenge is attributed to complex hierarchy of structure regarding pore, crystal structure, nano-sized amorphous hydrates, and unreacted clinkers in the matrix.

Therefore, this study aims to seek viable dispersion methods incorporating highly concentrated CNT in UHPC and closely examine the rheological properties, mechanical strength, shrinkage, porosity, and electrothermal properties with varying dispersion methods and CNT contents. Additionally, this thesis contributes to development of non-destructive evaluation of dispersion quality and CNT content in a relatively large area of hardened cementitious nanocomposite. To overcome the complexity and multi-scale characteristic of nanocomposites, confocal Raman micro-spectroscopy with high spatial resolution was adopted as a non-destructive technique for bulk samples. The major finding can be summarized as follows.

In chapter 3, dry mixing of CNT powder, silica fume, and silica sand before wet mixing was compared with superplasticizer-aided ultrasonication. In terms of the efficiency of improving the electrical conductance, dry mixing showed the best performance, up to 0.5wt% of CNT content. The electrical resistivity of the specimen with 0.5wt% CNT by dry mixing reached ~1,000 Ω -cm, which is the requirement for self-heating concrete suggested in previous studies. Unexpectedly, the incorporation of CNTs in the form of ultrasonicated suspension had an insignificant increase in electrical conductivity despite better macro-dispersion in a cement matrix. Two methods significantly affected the rheological properties of UHPC. The plastic viscosity, yield stress, and structuration rate rise abruptly with the addition of CNTs. When 0.5wt% of CNT was added, fresh UHPC concrete had no more self-compacting properties, and therefore the vibration or compaction process was needed to fabricate specimens. On the other hand, samples manufactured with the commercial CNT suspension with shorter CNTs

had better workability with highly concentrated CNT addition. Unfortunately, the percolation threshold was found to be much higher than that of dry mixed specimens. Also, the compressive strength was considerably lower than dry mixed and sonicated specimens. It could be attributed to a much shorter length and poor interfacial bonding between CNTs and matrix due to the surfactant. The results indicated that dry mixing, which was more cost-effective and energy-efficient, can be used when CNT content near the percolation threshold (~0.3wt%) is required for specific performance. However, adjustment of water and/or superplasticizer was required to achieve self-heating capability because of the adsorption of superplasticizer and entrapment of water of CNTs with hydrophobic nature and high specific surface area.

In chapter 4, the critical incorporation concentration for tailoring multifunctional UHPC was investigated with thorough examination on the pore structure, shrinkage, compressive strength, and multifunctional properties. The well-dispersed commercial suspension was used to minimize the reduction in flowability. At all concentrations, incorporating CNTs affects positively; in other words, no adverse effect was found at high CNT concentration. However, reduction in flowability could influence the porosity, leading to marginal increase or reduction in positive effect of CNT addition. The results confirmed that the multifunctionality of UHPC could be maximized by incorporating CNTs while mitigating autogenous shrinkage and utilizing superior mechanical performance and durability of UHPC. The CICs for various material properties were determined to 0.5 wt% considering percolation threshold and limited effect of CNTs on shrinkage and mechanical properties, a substantial reduction in volumetric heat capacity, and an increase in thermal diffusivity. When 6wt% of highly concentrated CNT suspension was used instead of mixing water, the electrical conductance was remarkably improved, and the electrical curing of UHPC instead of steam curing (heat treatment) was possible at a very low voltage of 19–23 V. There was no significant degradation due to electrical curing; the

flexural strength was rather slightly increased with direct electrical curing.

In chapter 5, mapping of phases in hydrated cement sample was conducted using confocal Raman micro-spectroscopy (CRM) to overcome the limitation of conventional techniques such as electron microscopy that can be applied for the examination of hardened cement. It was found that CRM can be used to identify not only most of phases in cement-based material including clinkers, hydration products, and mineral additives, but also the presence of CNTs in the hardened matrix. When a well-dispersed stable CNT suspension was utilized, CNT was detected in almost the entire area despite a very low CNT content, which indicated that CNTs were uniformly distributed in the matrix. Raman imaging the submicron CNT aggregates below the resolution of optical microscope were spread in the matrix in the specimen fabricated with CNT suspension with ultrasonication applied. The distribution and dispersion efficiency of CNTs was quantitatively evaluated with the metrics proposed in this study. Hence, nondestructive investigation of nanocomposite without any sample preparation can be possible to compare the efficiency of various dispersion methods using high resolution CRM.

In chapter 6, quantitative Raman analysis was attempted to construct the calibration curve for the CNT concentration evaluation. To fully utilize the change in Raman intensity of phases in each measurement spot, the strategy for the normalization of CNT signal was to use the Raman sensitivity of material. The experimental Raman sensitivity was measured as the linear coefficient between the laser intensity and Raman intensity. Even though cement-based materials are multi-phase and complex material, it was possible to quantitatively compare the Raman intensity of CNT between spectrums through the normalization. The average of normalized CNT signal, which represented the relative volume fraction in mapping area, non-linear logarithmic relation with volumetric concentration of CNT.

7.2 Future research

The rheological and thermal properties, and shrinkage of UHPC/CNT have not been studied much in the UHPC/CNT composite. The overall understanding of engineering properties with varying CNT concentration and dispersion methods will expand the application of UHPC/CNT composite by helping engineers to choose appropriate CNT dosage and efficient dispersion methods. However, to realize the integrated system of repair/retrofitting and smart functions, the prerequisites for field conditions, should be considered when design multifunctional concrete. Now, more effort is needed for the empirical study with detailed requirements given, such as the target smart capability, mechanical performance, and service life. Additionally, the cost and environmental impact of UHPC/CNT should be reduced. For example, the use of different materials such as fly ash, limestone powder, and rice husk ash can be used to reduce the content of cement, silica fume, quartz powder, and silica sand. Partial or full replacement with different material will affect not only the workability, durability, and mechanical performance, but also the structures in micro-level interacting with CNTs. Therefore, with the demand for carbon reduction in construction sector, the interaction mechanism between by-products, natural aggregates, and CNTs should be systematically examined for the feasibility of smart UHPC.

Furthermore, along with the sustainability issue on cement, there is increasing attention on the mineralization of carbon dioxide in the form of carbonates in cement and concrete. Hence, revealing the carbonation mechanism of cement and quantitative evaluation of captured carbon dioxide is one of the main topics in cement and concrete research. CRM can in-situ monitor the phase transformation in operando condition. Combined with quantitative Raman analysis, in-situ mapping of carbonation of cementitious composite under various composition and curing condition will pave a path toward sustainable concrete development.

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초 록

기능성 초고성능 콘크리트를 위한

탄소나노튜브 분산에 대한 정량적 평가

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이 논문은 우수한 역학적 성능과 내구성, 작업성을 보유한 초고성능 콘크리트 (Ultra-high performance concrete, UHPC)에 독특한 전기적, 열적 특성과 화학적 안정성을 지닌 탄소나노튜브 (Carbon nanotube, CNT)를 혼입하였다. 이를 통해 보수/보강과 동시에 발열 양생, 융설/융빙, 균열 감지, 교통흐름 감지 등의 기능성을 통합한 차세대 건설 재료의 개발이 가능하다.

이에 CNT의 농도와 분산을 주요 변수로 하여 UHPC의 레올로지 특성, 역학적 성능, 전기 및 열적 특성을 조사하였다. 물-바인더 비가 매우 낮은 UHPC에 고농도의 CNT를 효율적으로 분산하는 방법으로 건식 혼합이 제안되었다. 미세한 크기의 실리카 흄, CNT, 모래를 일정 시간 혼합하여 모래에 실리카 흄과 CNT로 얇게 코팅하였다. 기존의 초음파 분산 처리에 비해 더 낮은 침투 임계점을 달성할 수 있고, 초음파 분산 및 상용 분산액에 비해 강도 저하를 최소화할 수 있어, 경제적이고 에너지 효율이 높은 방식으로 평가되었다. 그러나 임계 농도 이상에서 CNT의 물과 감수제 흡수로 인해 작업성 확보가 어려우므로 시멘트 중량 대비 0.5%에서는 물과 감수제의 비율 조정이 불가피한 것으로 판단되었다.

침투 임계점 이상의 CNT를 상용액을 이용하여 균일하게 분산시킨 경우 시멘트 중량 대비 0.8%까지 첨가하였을 때, 공극률, 자기 수축, 압축 강도, 전기 및 열적 특성이 모두 기존 UHPC에 비해 향상되었다. 그러나 침투 임계점 농도에 해당하는 0.5% 이상에서는 작업성 저하와 과도한 CNT의 일부 응집으로 인해 향상 정도가 미미하였다. 시멘트 중량 대비 1.4%의 고농도 CNT의 첨가는 UHPC의 전기저항을 현저하게 낮추어 20V 내외의 저전압에서 발열 양생이 가능했으며 기존 성능의 저하는 발견되지 않았고 오히려 압축강도, 휨 변형 경화 등의 기계적 성능이 향상되었다. 또한, 휨 응력 하에서 뛰어난 균열 감지 능력을 발현하여 보수/보강과 스마트 특성의 통합이 실현될 수 있음을 보였다.

경화된 시멘트 매트릭스 내부의 CNT 분산 품질 및 농도의 비파괴 검사법 개발을 위해 공초점 라만 현미경 (confocal Raman microspectroscopy, CRM)을 활용하였다. 수백 나노미터의 매우 높은 공간적 분해능으로 수백 마이크로미터의 영역을 스캔하여 각 지점의 라만 신호를 획득하였다. 기저 분석을 통해 다상의 수화한 시멘트 페이스트 내부에 존재하는 미반응 클링커와 수화물을 구별할 수 있었으며 높은 감도로 CNT의 존재를 탐지할 수 있었다. 이를 상대 엔트로피 개념을 적용하여 CNT의 공간적 분포를 정량적으로 평가하는 지표를 개발하여 다양한 분산 방법의 평가법을 제시하였다.

개개의 탄소나노튜브 다발로 존재하는 잘 분산된 상용액을 여러 농도로 첨가하여 시편을 제조하고 동일 방법으로 라만 맵핑을 수행하였다. 또한 주요 클링커 및 수화물의 라만 산란 민감도 (Raman sensitivity)를 레이저 강도를 높여가며 실험적으로 산정하였다. 이를
통해 한 지점에서 획득한 라만 신호에서 각 상의 라만 산란 민감도를 반영하여 CNT의 부피 농도를 나타내는 라만 신호 정규화를 시도하였다. 넓은 영역에서 정규화 된 CNT 라만 신호의 평균값과 CNT 첨가 농도는 로그 관계를 가졌으며 높은 상관계수를 보였다. 이를 이용하면 경화된 시멘트 내부의 CNT 농도 정량이 가능하다.

결론적으로 목적에 따라 적절한 양의 CNT를 UHPC에 혼입하면 노후화된 건물과 기반 시설의 일부를 보수/보강함과 동시에 현장 발열 양생, 균열 감지 등의 스마트 구조체로 활용이 가능하다. 또한 CRM을 이용한 라만 정량 분석을 통해 CNT의 첨가 농도와 분산 품질의 비파괴 정량 검사가 가능하여, 향후 현장에서의 품질 관리 및 검사법으로 활용이 가능하다.

주제어 : 초고성능 콘크리트, 탄소나노튜브, 분산, 기능성 콘크리트, 공초점 라만 현미경, 비파괴 검사, 라만 정량 분석.

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