- Technical Paper -

EVALUATION ON THE MECHANICAL PROPERTIES OF HOOK-SHAPED STEEL FIBER-REINFORCED CEMENT-BASED COMPOSITES WITH CNTs

Byungcheol CHOI [*1], Gyuyong KIM[*2], Hyeonggil CHOI[*3] and Jeongsoo NAM[*2]

ABSTRACT

This study examined the mechanical properties of fiber-reinforced cementitious composites (FRCC) using hooked-shaped steel fiber (HSF) with deposited multi-walled carbon nanotubes (MWCNTs) for MWCNTs dispersion. The results showed that the fiber deposition method exhibited the best mechanical performance compared to the ultrasonic dispersion and dispersant methods. Also, within the scope of this study, an MWCNTs incorporation ratio of 5 wt.% was found to be optimal for HSF at 1.5 vol.%, and the fiber deposition method was confirmed to have the potential to enhance MWCNTs dispersion.

Keywords: multi-walled carbon nanotubes, fiber deposition method, dispersion, mechanical properties, hook-shaped steel fiber, fiber reinforced cementitious composites

1. INTRODUCTION

In order to prevent brittle fracture and improve the mechanical performance of fiber reinforced cementitious composites (FRCC) with high tensile strength and ductility, and to impart performance such as crack detection, some FRCC research using smart materials has been conducted [1-2]. Among smart materials, nanomaterials are characterized by the ability to adapt to the environment by sensing and judging stimuli from the external environment and exhibiting intelligent behavior, unlike conventional materials that have the limitation of passively responding to environmental changes. In particular, carbon-based nanomaterials such as carbon nanotubes (CNTs) have been utilized to build management systems using magnetic sensing, crack detection, etc. [3-4].

On the other hand, CNTs tend to agglomerate, which hinders their uniform distribution in the matrix when incorporated into cementitious composites [5]. In addition, the agglomeration and incorporation of CNTs degrades the mechanical properties of cementitious composites. Against this background, most of the previous studies on the application of CNTs in cement composites have used dispersed CNTs [6-7]. The dispersion methods of CNTs generally include physical dispersion and chemical dispersion [8-10]. In the physical dispersion method, ultrasonic dispersion and chemical dispersion method using dispersant are mainly used. The types of dispersants include sodium deoxycholate (DOC), sodium dodecyl sulfate (SDS), and polycarboxylate (PCE). Among them, PCE-based dispersants are easily adsorbed on the surface of CNTs, which are hydrophobic materials, and have been reported in previous studies to have better dispersibility than other dispersants [11-12]. In addition, the application of dispersed CNTs to cement composites can improve the mechanical properties of cement composites.

Zhang, Jinyuan, et al. evaluated the dispersion mechanism and performance of multi-walled carbon nanotubes (MWCNTs) in cement paste containing well-dispersed MWCNTs. Two types of dispersants (SDS and PCE) were used for MWCNTs dispersion. The results showed that the mechanical properties of the cement paste using PCE-based dispersant were higher than those using SDS dispersant. It was also reported that the mechanical properties (compressive strength, flexural strength) and electrical properties (electrical resistivity) of the cement paste improved as the content of MWCNTs increased based on PCE-based dispersant [6]. Konsta-Gdoutos et al. reviewed the rheological properties, mechanical properties, and nanostructure of nanocomposites incorporating MWCNTs. The results showed that effective dispersion can be obtained by applying ultrasonic energy and using a dispersant. They also reported that the weight ratio of dispersant and MWCNTs should be close to 4.0 for effective dispersion of MWCNTs. Therefore, maintaining the dispersion through uniform dispersion of MWCNTs is of utmost importance to utilize MWCNTs as building materials [7].

However, in the case of ultrasonic dispersion, quantitative dispersion is difficult due to differences in researcher skill and equipment. In addition, excessive ultrasonic dispersion can damage CNTs particles due to overheating of the equipment. Furthermore, a previous study reported that the optimal sonication period of CNTs in terms of mechanical properties of cement composites is still a challenge, although many studies have been conducted [12]. As for the dispersant, it was reported that the strain transfer efficiency is low at the interface between the cement matrix and the nanomaterials due to the weak link formed between the

*1 Ph.D Course, Dept. of Architectural Engineering, Chungnam National University, Rep. of Korea, JCI Member
*2 Prof., Dept. of Architectural Engineering, Chungnam National University, Rep. of Korea, JCI Member
*3 Prof., Dept. of Architectural Engineering, Kyungpook National University, Rep. of Korea, JCI Member

CNTs and the molecules of the dispersant used [5].

On the other hand, to improve the mechanical properties of fiber-incorporated cementitious composites, studies have been conducted using nanomaterials such as CNTs to coat the fiber surface to strengthen the interface between the fiber and the cement matrix [13-19]. He et al. developed strain hardening ultra-high performance concrete (SHUHPC) by surface coating carbon nanotube fiber (CNF) on polyethylene (PE) fiber to enhance the interfacial transition region and strengthen the interfacial tribological bond between fiber and cement-based matrix. The results showed that the compressive strength was increased by more than 150 MPa, the tensile strength was improved by 15%, the tensile strain capacity was improved by 20%, and the crack spacing was reduced. In addition, through the pull-out test, the interfacial friction bond strength of CNF-coated PE fibers increased by 22%, which can improve the mechanical properties of cementitious composites [13].

In addition, the method of coating CNTs on fibers can not only improve the interfacial bonding of fibers and matrix, but also improve the aggregation of CNTs. Yang, F., & Qian, S. reviewed the mechanical properties and piezoelectric properties of CNTs-coated PE fibers and engineered cementitious composites (ECC) incorporating CNTs. The results showed that the performance of compressive strength, tensile strength, and electrical resistivity of CNTs-coated PE fibers was improved compared to the plain without CNTs. In addition, it was reported that some agglomeration of small CNTs was present on the surface of CNTs-coated PE fibers, but no agglomeration of large CNTs was present [14]. Thus, although there are studies that applied ultrasonic dispersion of CNTs and coating of CNTs on fibers without using dispersant, the studies were concentrated on improving the fiber-matrix interfacial bonding force to improve the mechanical properties of cementitious composites or to impart conductivity. In other words, there are no studies that concentrated on improving the dispersibility of CNTs using fiber coating method.

Therefore, this study examined the mechanical properties of FRCC using hooked-shaped steel fiber (HSF) with deposited MWCNTs for MWCNTs dispersion. In addition, MWCNTs methods utilizing ultrasonic dispersion and dispersant were also evaluated for comparative analysis. The definition of MWCNTs dispersion using the fiber deposition method is limited to the scope of this study, and the mechanism is that when MWCNTs-deposited HSF is mixed in the FRCC mixing process, MWCNTs are dispersed similarly to the dispersion of HSF according to the dispersion degree of HSF. However, since MWCNTs are simply deposited on the surface of HSF without complex heat treatment and chemical treatment during the deposition process, the adhesion is weak and some MWCNTs are peeled off from the surface. The peeled off solidified MWCNTs are evenly dispersed inside the FRCC. In order to derive the optimal incorporation rate of MWCNTs when the fiber incorporation rate is 1.5 vol%, MWCNTs incorporation rates of 3% and 5% by weight of cement were selected to examine the optimal incorporation rate of MWCNTs.

2. EXPERIMENTAL PLAN AND METHOD

2.1 Materials

For the preparation of FRCC, ordinary portland cement (OPC), class-C Fly ash (FA) was used as binder and its chemical composition is shown in Table 1. Silica sand (SS) with particle size of 0.18-0.25 mm and density of 2.65 g/cm^3 was used as aggregate. HSF was used as the fiber and the mechanical properties and morphology are shown in Table 2 [20]. In addition, a Polycarboxylate (PCE) based high-performance superplasticizer (SP) was used to reduce the workability due to HSF incorporation. For CNTs, liquid MWCNTs were used. The physical properties of the liquid MWCNTs used in this study are described in Table 3. The dispersant used was an aqueous dispersant based on polyethyleneimine (PEI), and its physical properties are described in Table 4.

Table 1 Chemical composition of the binder, sand

Chemical composition (%)	OPC	FA	SS
CaO	66.79	26.19	-
SiO_2	16.14	38.84	83.00
Al_2O_3	4.40	19.52	9.76
MgO	2.47	0.43	-
Na_2O	0.08	0.87	-
K_2O	1.18	1.84	-
SO_3	3.23	-	0.55
Fe_2O_3	3.83	2.87	-
TiO_2	0.34	-	-

Table 2 Physical properties of HSF

Parameters	Values
Diameter (mm)	0.50
Length (mm)	30
Tensile strength (MPa)	1,140
Aspect ratio (L/D)	60

Table 3 Physical properties of MWCNTs

Parameters	Values
Outer diameter (nm)	30-80
Length (μm)	<10
Specific surface area (m^2/g)	>60
Purity (wt%)	>98

Table 4 Physical properties of dispersant

Parameters	Values
Active ingredient (%)	38-42
Solvent	Water
Density (20°C)	1.02-1.06
Amine value (mg KOH/g)	10

Table 5 Mix proportions

W/B	Matrix ID	OPC	FA	SS	Water	SP (wt.%)	HSF (vol.%)	MWCNTs (wt.%)	Dispersant (wt.%)
0.32	Plain	0.85	0.15	0.35	0.32	0.4	1.5	3	-
	U							3	-
	D 0.5							3	0.5
	D 1.0							3	1.0
	CHSF 3							3	-
	CHSF 5							5	-

2.2 Mix Design

Table 5 shows the mix design for preparing FRCC by MWCNTs dispersion method. The water-binder ratio was 0.32 and MWCNTs were used at 3% and 5% by weight of cement. For the 3% case, it was selected to examine the mechanical properties depending on the MWCNTs dispersion methods (ultrasonic dispersion, dispersant use, and fiber deposition). In contrast, the 5% MWCNTs was used only when depositing on the fibers. This is because, as shown in Fig. 1, when 3% MWCNTs was used, it was less uniformly deposited on the fibers compared to the 5% case, resulting in partial exposure of the HSF surface. Through this, the deposition differences depending on the MWCNTs content were identified, and the MWCNTs dosage was adjusted to achieve a more uniform deposition. The dispersant was selected at 0.5% and 1.0% by weight of MWCNTs. The incorporation rate of high-performance water-reducing agent is 0.4% by weight of cement.

Among the Matrix IDs, Plain is FRCC with MWCNTs without any dispersion method. U is FRCC incorporating ultrasonically dispersed MWCNTs. D is FRCC with MWCNTs incorporated using a dispersant. Also, the number after the dispersant indicates the dispersant incorporation rate. CHSF is FRCC with HSF deposited with MWCNTs. The number following the CHSF is the percentage of dispersant.

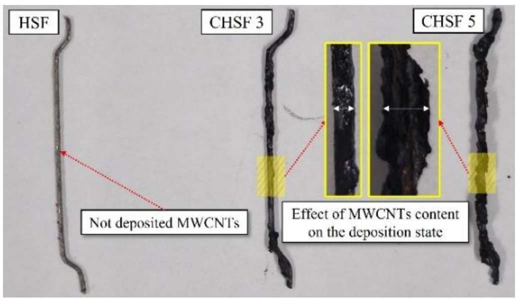

Fig.1 HSF with/without deposited MWCNTs and deposition differences by MWCNTs content

2.3 Dispersion Methods for MWCNTs

For the ultrasonic dispersion of MWCNTs, prepare the MWCNTs, superplasticizer, and water used in the fabrication of U according to the mixture proportion. Then, the MWCNTs are mixed with the superplasticizer and water. After that, the ultrasonic equipment's amplitude (AMPL) was performed for 30 minutes at 65% intensity. AMPL means ultrasonic amplitude power. The ultrasonic run time was set to 5 seconds and the pause time was set to 2 seconds and repeated. As a result, Fig. 2 shows the SEM images of MWCNTs before and after ultrasonic dispersion.

The first step of the dispersion method using dispersant is to prepare MWCNTs and PCE-based dispersant in a mixture proportion. Then, the PCE-based dispersant is added at the time of compounding.

For fiber deposition, HSF required for FRCC manufacturing was prepared, as shown in Fig. 3. MWCNTs were then prepared at 3% and 5% by weight of cement, respectively. The prepared HSF was mixed with MWCNTs to ensure even deposition. Finally, the deposited HSFs were evenly spread out and dried at room temperature (20±2°C) for more than 24 hours. However, the fiber deposition method in this study resulted in a surface-deposited state rather than a strongly bonded deposition of MWCNTs onto the HSF surface. Previous studies have reported that when hydrophobic fibers and hydrophobic MWCNTs are placed in an aqueous solution, they tend to adhere to each other due to hydrophobic interactions, leading to MWCNT attachment on the fiber surface [14]. In this study, however, MWCNTs were deposited onto HSFs without any additional treatment. As a result, MWCNTs were deposited on the fiber surface, as shown in Fig. 1. Furthermore, Fig. 4 presents SEM images comparing the surface conditions of deposited and non-deposited HSF, confirming that MWCNTs were successfully deposited on the HSF.

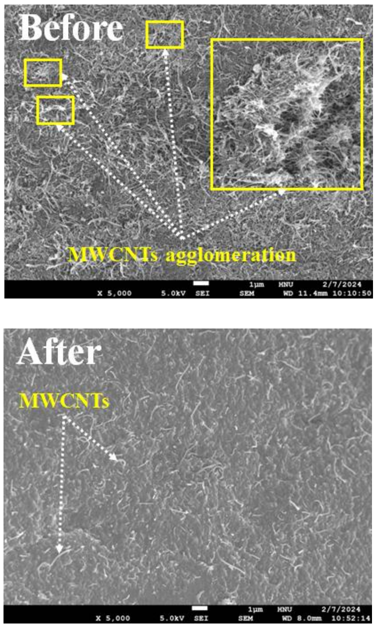

Fig.2 SEM image of MWCNTs before and after ultrasonic dispersion

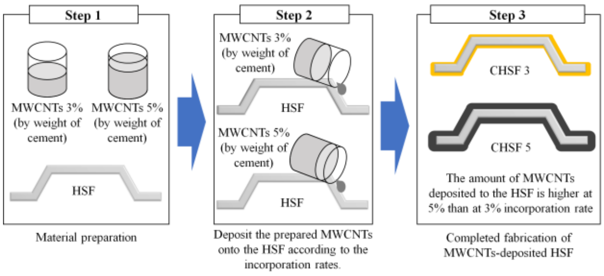

Fig.3 Manufacturing method of CHSF with deposited MWCNTs

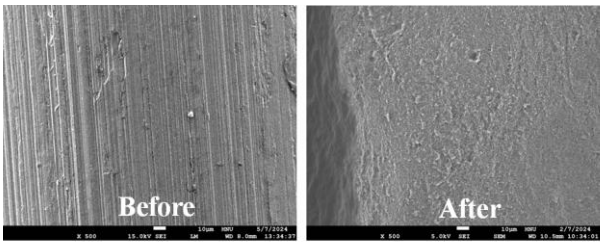

Fig.4 SEM images of HSF surfaces with and without MWCNT deposition

2.4 Matrix Preparation and Experimental Method

The common step in the preparation of FRCC was dry mixing of binder (OPC, FA) and silica sand at a speed of 10 rpm for 30 seconds. In the case of incorporating ultrasonically dispersed MWCNTs, a mixture of MWCNTs, superplasticizer, and water was prepared. Then, MWCNTs with water and superplasticizer were added to the dry mixture and the first wet mixing was performed for 180 seconds at 30 rpm. Finally, HSF was added and a second wet mixing was performed for 90 seconds at 30 rpm.

When using a dispersant, water and superplasticizer were first added to the dry mixture, followed by wet mixing at 30 rpm for 150 seconds. Then, HSF was added and wet mixing was performed for another 30 seconds at 30 rpm for a total of 180 seconds. Finally, MWCNTs and dispersant were added and a second wet mixing was performed at 30 rpm for 90 seconds.

For fiber deposition, deposited HSF, superplasticizer, and water were added to the dry mixture and wet mixing was performed for 210 seconds at 30 rpm. The FRCC mixture mixed according to the dispersion method was thoroughly mixed and poured into the molds. After 24 hours, the prepared matrix was demolded from the mold and cured under constant temperature and humidity (20±2℃, 60±5%) until 27 days, and the flexural strength and compressive strength were measured on 28 days. The measurement method was carried out according to ISO 679.

3. RESULTS AND DISCUSSION

3.1 Direct Tensile Stress-Strain Behavior Curve

Fig. 5 presents the strain-hardening and strain-softening regions observed in the direct tensile stress–strain behavior of each matrix. Strain-hardening behavior occurred after the formation of initial cracks, induced by the bridging effect between the HSF and the matrix, which led to an increase in tensile stress. In contrast, strain-softening behavior was characterized by a gradual decrease in strain as the fibers were progressively pulled out from the matrix [21].

For the Plain matrix, the strain-hardening behavior persisted up to a strain of 0.244%, after which it transitioned into the strain-softening stage. In comparison, matrices incorporating MWCNT dispersion methods exhibited strain-hardening behavior in the range of 0.411%–0.587% strain, indicating that the duration of strain-hardening was approximately 1.6 to 2.4 times longer than that of the Plain matrix.

As shown in Fig. 6, the peak stress of the Plain matrix was measured at 2 MPa, whereas CHSF 5, which employed the fiber coating method, recorded the highest peak stress of 3.58 MPa among all matrices and was the only one to exceed 3 MPa. The peak stresses of the other matrices were 2.48 MPa for D 0.5, 2.82 MPa for D 1.0, 2.65 MPa for U, and 2.97 MPa for CHSF 3. These results indicate that the mechanical performance of FRCC varies depending on the MWCNT dispersion method, with the CHSF series exhibiting relatively superior tensile performance.

In fact, the peak stress increased by approximately 24% to 79% compared to the Plain matrix, and CHSF 5 showed the highest performance with a value approximately 1.79 times greater. This improvement is attributed to the effective dispersion of MWCNTs, which enhanced both the tensile strength and strain capacity. These findings suggest that the fiber deposition method is a promising approach to significantly improve the dispersion efficiency of MWCNTs.

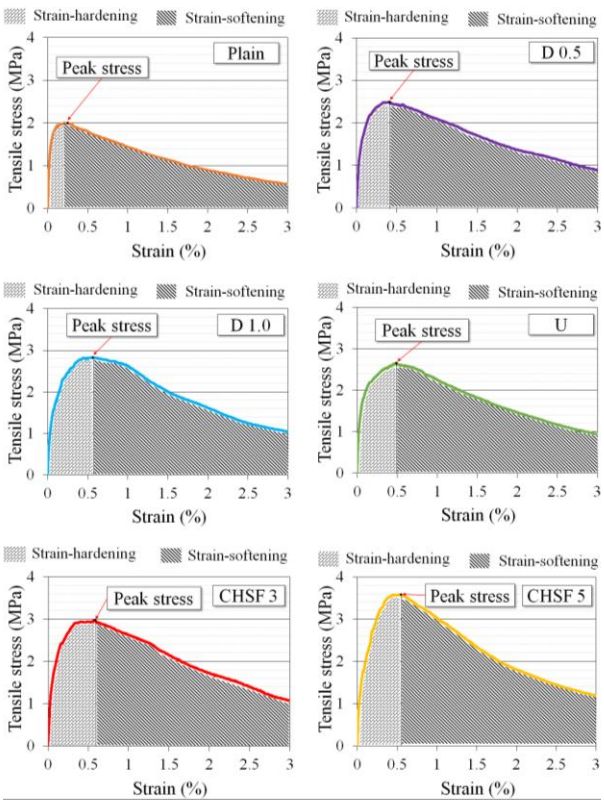

Fig.5 Strain-hardening and strain softening in the direct tensile stress-strain behavior curve

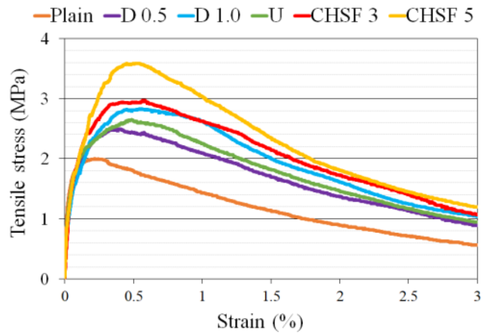

Fig.6 Direct tensile stress-strain behavior curve

3.2 Flexural and Compressive Strength

With the dispersant, the flexural strength of D 0.5 and D 1.0 increased by 20% and 25%, respectively, and the ultrasonic dispersion (U) increased by 30%, as shown in Fig.7. For the matrix incorporating MWCNTs-deposited fibers, CHSF 3 showed a 40% increase in flexural strength and CHSF 5 showed a 65% increase in flexural strength. Compressive strength increased by 12% and 17% for D 0.5 and D 1.0 with dispersant, respectively, and ultrasonic dispersion (U) improved by 21%, as shown in Fig.8. In the matrix containing MWCNTs-deposited fibers, CHSF 3 showed a compressive strength improvement of 48% and CHSF 5 showed a 70% improvement.

The mechanism of dispersant use is to control the surface tension of MWCNTs to reduce the contact angle and disperse the MWCNTs to prevent re-aggregation by reducing the contact angle. Previous studies have shown that the higher the amount of dispersant incorporated into MWCNTs, the more bridging aggregation can occur between the molecules of the dispersant. On the other hand, it was reported that the lower the amount of dispersant incorporation, the fewer the dispersant molecules, which cannot play a sufficient role in preventing aggregation [11]. Based on this, it is concluded that the amount of dispersant used is appropriate as the flexural and compressive strengths are improved compared to the plain.

Overall, both the ultrasonic dispersion, dispersant, and fiber-deposited matrices showed higher flexural and compressive strengths than the plain matrix without dispersion. This indicates the importance of MWCNTs dispersion, i.e., dispersed MWCNTs can positively affect mechanical properties by improving flexural and compressive strength when mixed with cement. This is similar to the results of previous studies. Previous studies have reported that mechanical properties are improved by the fiber bridging effect, in which various components of the cement hydration product are combined, or by the packing effect, in which MWCNTs act as fillers and fill the interstitial space of the hydration product [10], [22], [23].

Among them, the matrix using the fiber deposition method showed the highest flexural and compressive strengths compared to the matrix using ultrasonic and dispersant, including plain. In particular, CHSF 5 showed about 17% higher flexural strength and 14% higher compressive strength compared to CHSF 3. This is because the MWCNTs were uniformly deposited at 5% by weight of cement when the fiber incorporation rate was 1.5%, as mentioned in Section 2.2.

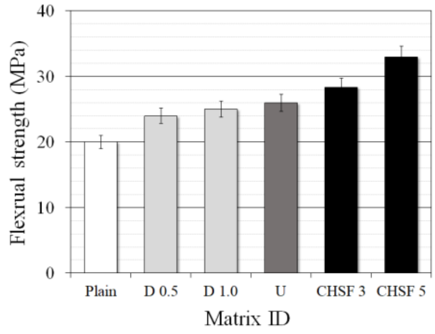

Fig.7 Flexural strength

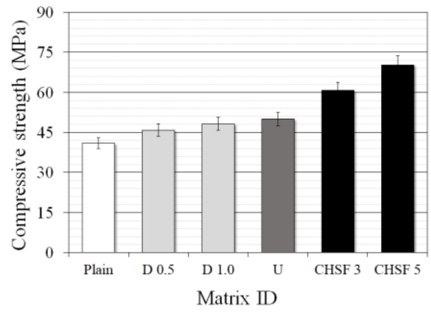

Fig.8 Compressive strength

4. CONCLUSIONS

This study investigated the mechanical properties of fiber-reinforced cementitious composites using deposited hook-shaped steel fibers for MWCNTs dispersion. In addition, MWCNTs methods utilizing ultrasonic dispersion and dispersant were also evaluated for comparative analysis. The main contributions of the study can be summarized as follows.

(1) Based on the experimental results of flexural strength, compressive strength, and direct tensile stress-strain behavior curves, it was confirmed that when MWCNTs are uniformly dispersed, regardless of the dispersion method, the mechanical properties improve compared to when they are not well dispersed.

(2) Among the dispersion methods for MWCNTs, the fiber deposition method exhibited the best performance in terms of flexural strength, compressive strength, and direct tensile stress-strain behavior curves compared to the ultrasonic dispersion and dispersant methods. In particular, CHSF 5 recorded the highest performance among all experimental groups.

(3) Based on the findings of this study, it was indirectly confirmed that the fiber deposition method has the potential to enhance the dispersibility of MWCNTs. Furthermore, within the scope of this study, it was determined that an MWCNTs incorporation ratio of 5 wt.% is an appropriate amount for fiber deposition when the HSF incorporation ratio is 1.5 vol.%. However, since this study was conducted using only a single type of fiber, additional analysis is required to examine the optimal MWCNTs

incorporation ratio and the changes in the mechanical properties of FRCC depending on different types of fibers. Additionally, further microscopic analysis is necessary to visually and directly confirm the degree of MWCNTs dispersion.

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