Transport and Communications Science Journal, Vol. 71, Issue 1 (01/2020), 46-55

Transport and Communications Science Journal

REINFORCING CEMENTITIOUS MATERIAL USING SINGLE-WALLED CARBON NANOTUBE - NYLON 66 NANOFIBERS

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ARTICLE INFO

TYPE: Research article
Received: 24/12/2019
Revised: 25/01/2020
Accepted: 30/01/2020
Published online: 31/01/2020
https://doi.org/10.25073/tcsj.71.1.6

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Abstract. Based on the increase in tensile strength and toughness (43% and 30%, respectively), the feasibility of the hybrid nanofibers containing Single-walled carbon nanotubes and Nylon 66 on reinforcing cementitious materials has been clarified. The well-linking effect of nanofibers in the microstructure of hardened cement pastes has been found by scanning electron microscope (SEM) analysis and well-explained for the increase in mechanical strengths. Besides, field emission transmission electron microscope (FE-TEM) analysis has also been conducted to analyze the properties of the hybrid nanofibers.

Keywords: Nanofibers, Nylon-66, carbon nanotubes (CNTs), cement, tensile strength, toughness.

1. INTRODUCTION

Cement, a commonly used material in worldwide construction. Studying on cement matrix has gained the attention of research community. Up to now, several studies enhancing the strength of cementitious material by adding additives, admixtures or short fibers have been published [1-6]. Recently, enhancing the strength of the cement matrix using nanofibers has become a new trend in this field. Saleh et al. [7] studied the effect of iron slag and titanate nanofibers on cement to produce an anti-radioactive material. Brown and Sanchez [8] clarified the performance of carbon nanofibers in cement pastes under the sulfate environment.

Li et al. [9] and Rocha et al. [10] studied the influence of carbon nanotubes (CNTs) on the mechanical performance of cementitious materials.

Since found in 1991 by Iijima [11], the mechanical and physical properties of CNTs were clarified by many researchers. According to Treacy et al. [12], Walters et al. [13] and Yu et al. [14], the tensile strength and elastic strain of CNTs were 100 times and 60 times higher than those of steel, respectively. Due to these characteristics, CNTs became a promising reinforcing agent not only for cement-based material but also for other materials or nanofibers [15-17]. However, the problem when incorporating CNTs in cementitious materials was the poor dispersion of CNTs in the aqueous solution due to the strong Van der Waals binding associated with the CNT aggregates. To solve this problem, the effect of sonication as well as surfactants were proposed in some recent researches. Then using the aqueous solution to prepare the cement pastes [18] or drying them to treat the surface of CNTs and mix with cement [9] or to prepare the powder of cement particles coated with CNTs [10]. In this study, another indirect approach to incorporate CNTs into cement pastes was presented. The new hybrid nanofibers including Nylon 66 [19, 20] and CNTs were fabricated by electrospinning (e-spinning) technique [21-23], then combined together with cement powder by an improved collector that was presented in the previous study [24]. By this approach, CNTs act as reinforcement for Nylon 66 nanofibers, and these as-hybrid nanofibers act as reinforcement for cement pastes. It should be noted that according to previous studies, CNTs were grown directly on the cement matrix and showed the good results in enhancing the mechanical strengths of hardened cement pastes [9, 10, 18]. The approach in this study is another manner to incorporate CNTs into cementitious materials and shows their effectiveness and comparative to the results from former studies of CNTs applications to cement.

Above all, in this study, cement pastes were reinforced by hybrid nanofibers containing Nylon 66 nanofibers (N66) and single-walled carbon nanotubes (SWCNT-N66 NFs). The mechanical properties of modified cement pastes were clarified by the tensile and compressive strength tests. The microstructural characteristics of the modified cementitious materials were also analyzed by the scanning electron microscope (SEM) and field emission transmission electron microscope (FE-TEM) methods.

2. MATERIALS AND SAMPLES PREPARATION

2.1 Materials

A type I Ordinary Portland Cement (OPC) compliance with ASTM C150 [25] from Ssangyong Co, Korea was utilized for cementitious materials in this study. The chemical components and physical characteristics of OPC were presented in **Table 1**.

Table 1: Chemical composition and physical properties of cement.

CaO	Al_2O_3	SiO_2	SO_3	MgO	Fe_2O_3	Ig. loss	Specific surface area (cm^2/g)	Compressive strength, 28-day (MPa)
61.33	6.40	21.01	2.30	3.02	3.12	1.40	2800	42.5

Two main precursors for fabricating nanofibers in this study were Single-walled carbon nanotubes (SWCNTs, grade: MKN-SWCNT-P1; Mknano, Canada) and Nylon 66 pellets ($C_{12}H_{26}N_2O_4$; Sigma-Aldrich Co, USA) (See **Fig. 1**). Besides, chloroform ($CHCl_3$; Daejung, Korea) and formic acid (HCOOH; Daejung, Korea) were utilized as the solvent for preparing the dope solutions. All chemicals were used as received.

(a) (b)

Figure 1. *a) Single-walled carbon nanotubes powder; b) Nylon 66 pellets*

2.2 Samples preparation

In this study, the SWCNTs-N66 NFs were fabricated by electrospinning process. The SWCNTs-N66 polymer solution was prepared with the solvent: precursor proportion of 9:1 by mass. In this case, the solvent was obtained by two steps: 1) merging formic acid and chloroform with the volume proportion of 4:1 (formic acid: chloroform, respectively); 2) dispersing the SWCNTs in the solvent under the ultra-sonication process.

For obtaining the composite binders containing cement powder and hybrid nanofibers, the as-spun nanofibers were combined directly into cement by an improved collector as presented in the previous study [24] (**Fig. 2**).

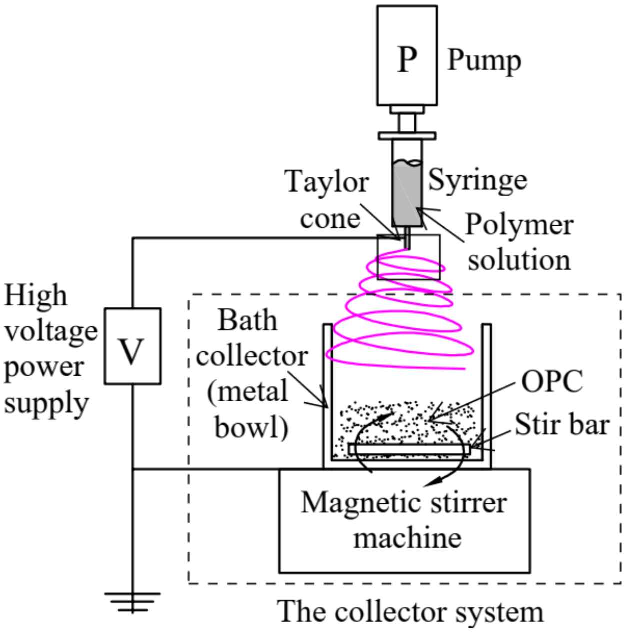


Figure 2. *Schematic of electrospinning system with the improved collector*

Table 2: Mixture designs of samples (by % mass)

Samples	Binder (B)			Water/Binder (w/b)
	OPC	N66	SWCNTs	
Control paste	100	0	0	0.5
SWCNTs-N66 MCP	99.5	0.485	0.015	0.5

“MCP” stands for “modified cement paste”

In order to investigate the influence of nanofibers on the mechanical strength of hardened cement paste, the tensile and compressive strength tests were conducted. In that manner, the hardened cement paste samples were prepared with the constant w/b of 0.5 according to ASTM C305-14 [26], using the cement blended nanofibers as prepared above. The mixture designs of all hardened cement paste samples were shown in **Table 2**. All samples were tested after 28 days of curing and the samples dimension can be specified in ASTM C307-03(2012) and ASTM C109/C109M-16a [27, 28].

3. EXPERIMENTS

Tensile strength tests were conducted by means of the 5kN-capacity mortar tensile strength test apparatus under the ASTM [27], while the compressive strength tests were carried out by means of the hydraulic universal testing machine with a loading capacity of 1000 kN, according to the ASTM [28]. Moreover, a set of three briquette samples and three cubic samples of each mixture after 28 days of curing in water were prepared for the test. In order to investigate the morphological properties of nanofibers as well as the behavior of the pastes containing nanofibers, SEM analyses were done under the accelerating voltage of 3 to 5 kV and the working distance of 7.1 to 7.9 mm. In addition, for higher definition observation, a 5Å-platinum layer was sputter-coated onto the samples. In order to demonstrate the existence of CNTs in N66 NFs, the field emission transmission electron microscope (FE-TEM) analyses were done with an acceleration voltage of 300 kV.

4. RESULTS AND DISCUSSION

4.1 Mechanical characteristics

The mechanical characteristics of hardened cement pastes that modified by nanofibers compared to the hardened plain cement paste were shown in **Fig. 3, Fig. 4** and **Fig. 5**. The results were summarized in **Table 3**. From an overall perspective, it was evident that the mechanical strengths of hardened cement pastes containing the hybrid nanofibers increased after 28 days of curing. As shown in **Fig. 3**, a significant increase in the tensile strength of the modified pastes was observed up to 43% compared to that of the control pastes. These observations were effective and comparative to the results from former studies of CNTs applications to cement. For instance, by comparing the results reported by Rocha et al. [10] based on directly tensile strength tests, the tensile strength of hardened cement paste increased by 40 % and 45 % when adding the content of Multi-walled Carbon nanotubes (MWCNTs) of 0.05 % and 0.1 % respectively. The present result showed the increase up to 43 % when reinforcing hardened cement paste by hybrid nanofibers with the content of 0.015 %. In addition, **Fig. 4** and **Fig. 5** showed the results of compressive strength tests, the compressive strength of the hardened cement pastes modified by nanofibers increased slightly approximate 10 %. From the typical compressive stress-strain curves in **Fig. 5** and the results in **Table 3**, there was a significant increase in the toughness characteristic of blended cement, approximately 30 % when modifying the hardened cement pastes by SWCNTs-N66 NFs.

Above all, the observations showed that there was a better performance in the tensile strength rather than the compressive strength when introducing Nylon 66 nanofibers as well as the hybrid nanofibers containing Nylon 66 and Carbon nanotubes into the hardened cement pastes. This observation signified the feasibility of this approach in enhancing the mechanical strengths of hardened cement paste using nanofibers reinforced by Carbon nanotubes.

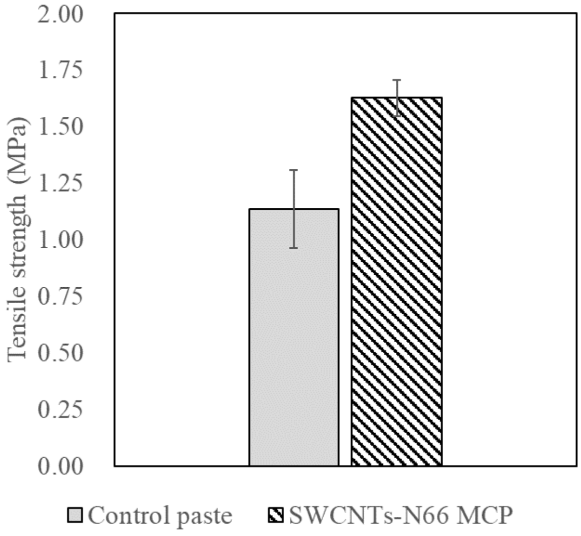


Figure 3. *Tensile strength results.*

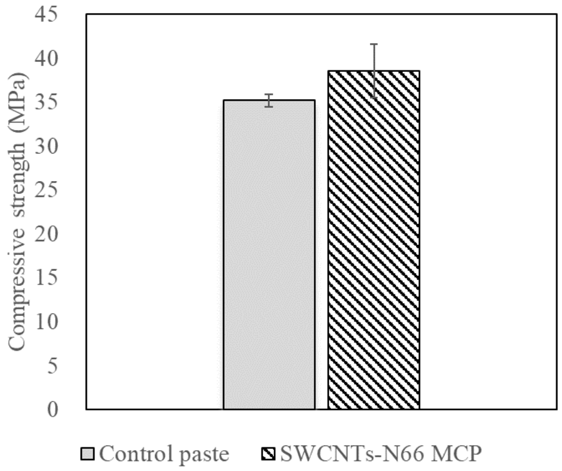


Figure 4. *Compressive strength results.*

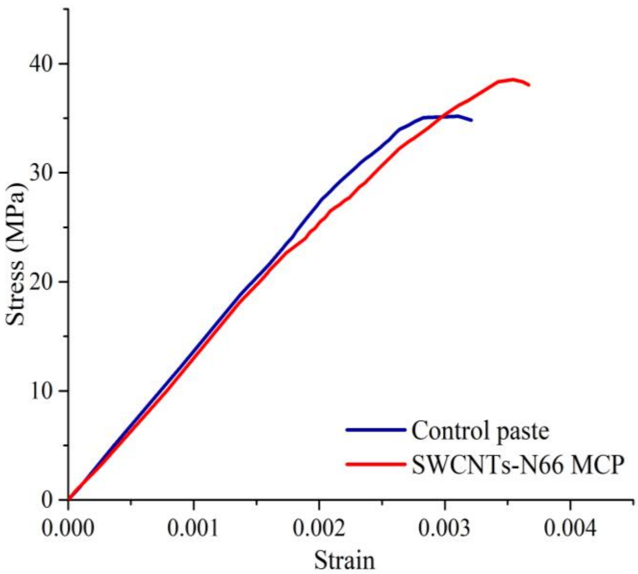


Figure 5. *Stress-strain curves.*

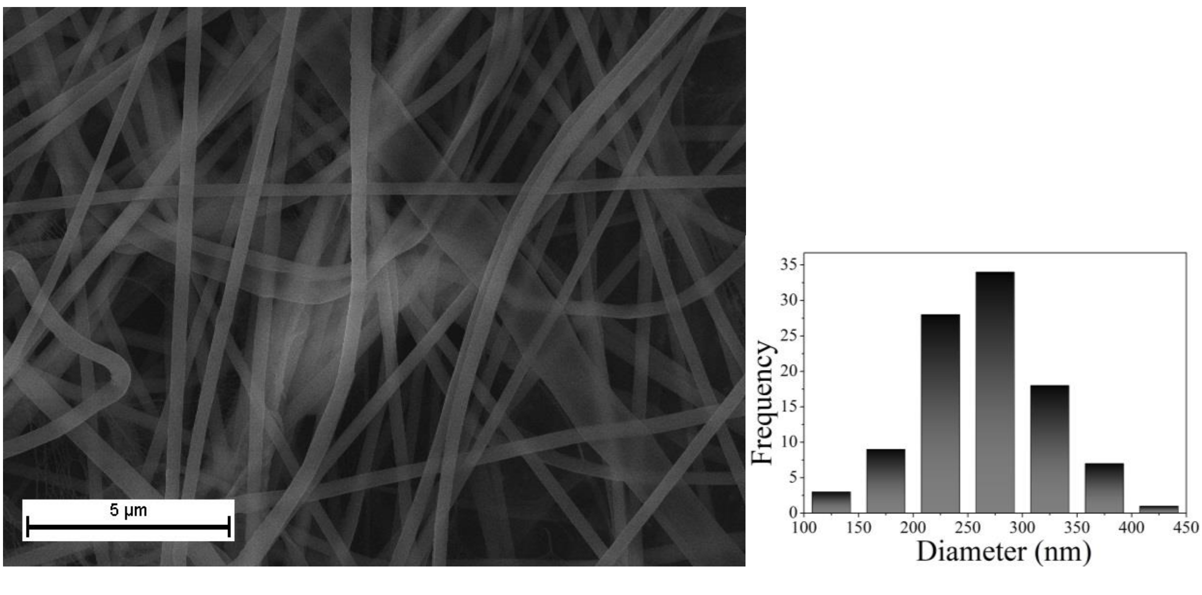
Table 3: Mechanical strength results after 28 days.

	Tensile strength (MPa)	Compressive strength (MPa)	Toughness(J/m^3)
Control paste	1.14 (0.172)	35.17 (0.725)	62031 (5049.7)
SWCNTs-N66 MCP	1.63 (0.080)	38.54 (3.077)	80882 (7196.5)

The values in parentheses are standard deviation

4.2 Morphological characteristics of Nanofibers

Fig. 6a showed the morphological characteristics of SWCNTs-N66 NFs. From an overall perspective, all nanofibers appeared as meshwork, with messing and disorientation shape. The smooth, glossy surface and almost uniform diameter along the axis of nanofibers can be observed in the SEM images of hybrid nanofibers. There were thin membranes and beads formed and connected between nanofibers with sparsely level. In general, the mean diameter of SWCNTs-N66 NFs was 264 nm (See **Fig. 6b**). It is worth adding that the hybrid structure of nanofibers containing Nylon 66 and CNTs can be shown in **Fig. 7** by FE-TEM analysis. As shown in **Fig 7**, there were many SWCNTs with diameter around 1 nm~2 nm gathered as bundle along the axis of the Nylon 66 nanofiber with diameter around 200 nm. These results are in agreement with the TEM result found in [29] and [30]. The existence of the CNTs, which higher tensile strength [12-14], enhanced the strength of hybrid nanofibers.



(a) (b)

Figure 6. *a) Morphological characteristics of the hybrid nanofibers; b) nanofiber diameter distribution.*

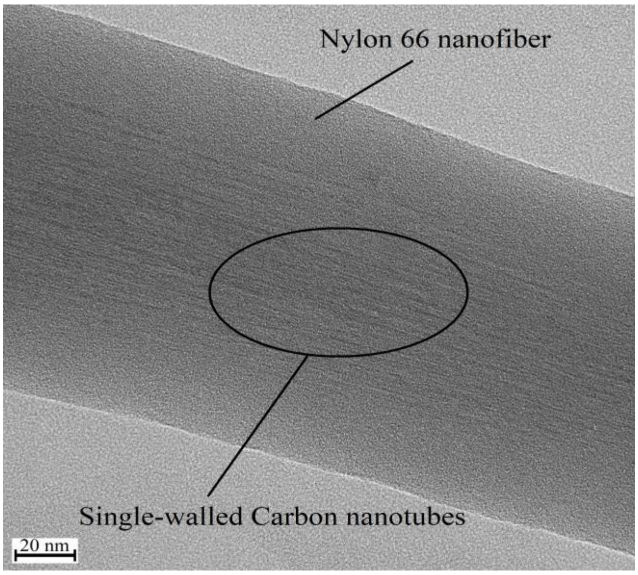


Figure 7. *FE-TEM images of the hybrid nanofibers.*

4.3 Microstructural characteristics of hardened cement paste

The SEM observations from the fractured surface of the tensile samples were shown in **Fig. 8**. As shown in **Fig.8**, there were numerous of nanofibers with the diameter over 200 nm grown in the cement matrix. As can be seen in the cement matrix, the calcium hydroxide (CH) appeared as large prismatic crystals and the fibrous morphology were calcium silicate hydrates (CSH). The diameter of these CSH varied around 50 nm [31]. Therefore, it is easy to distinguish between CSH and hybrid nanofibers in the microstructure of hardened cement paste. From the SEM images as shown in **Fig. 8**, these nanofibers acted as bridging agent among the hydration products. In addition, the surfaces of nanofibers were deformed by cement hydration products overlay. These phenomena made the surface of nanofibers become lumpy compared to the pristine morphology as shown in **Fig. 6**. From this result, the interaction between the hybrid nanofibers and cement hydration products were verified. Hence, in the microstructure of cement pastes, the added hybrid nanofibers with the deformed surface have shown the well-effect in linking among hydration products [9]. As a consequence, the higher tensile strengths were formed.

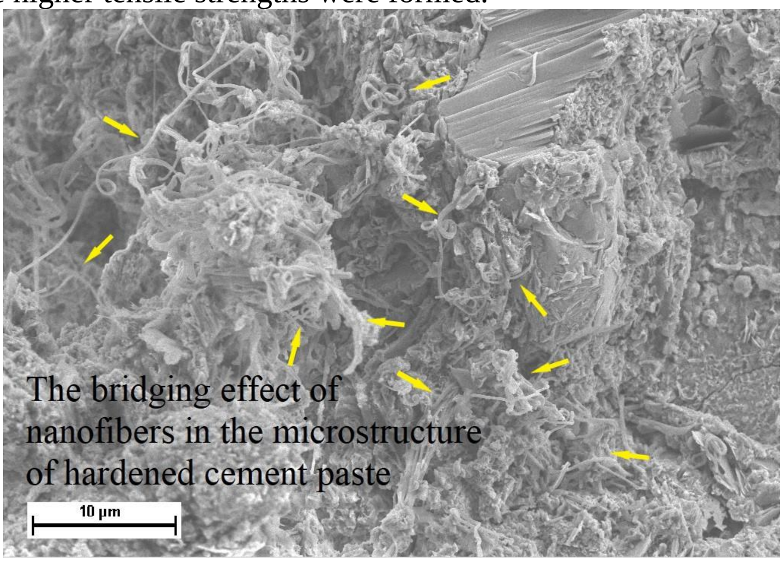


Figure 8. *Microstructure of the hardened cement paste containing the hybrid nanofibers.*

5. CONCLUSIONS

In this study, the effect of the hybrid nanofibers containing Nylon 66 and Single-walled carbon nanotubes on the mechanical strength and microstructure of hardened cement pastes have been estimated. The following conclusions can be drawn from the results of the present study:

- SWCNTs were dispersed in Nylon 66 nanofibers to fabricate the hybrid nanofibers by electrospinning process.
- There was a significant increase in tensile strength (43 %) and in toughness (30 %), respectively when introducing the hybrid nanofibers containing Nylon 66 and SWCNTs into the cement pastes with the content of 0.015%.
- The increase in mechanical strength can be explained by the bridging effect and the well-linking of nanofibers with cement hydration products (CSH, CH) in the microstructure of hardened cement pastes.

Above all, the hybrid nanofibers containing Nylon 66 and Single-walled carbon nanotubes can be a promising candidate for reinforcing cementitious materials.

ACKNOWLEDGMENT

The authors would like to acknowledge the National Research Foundation (NRF) Grant funded by the Korean government (No.2017R1A2B4010594).

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