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Study on the Mechanical Properties of CNTs/SiO_2 Composite Modified Cement based Composites

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Abstract

This paper studies the hybrid application of carbon nanotubes (CNTs) and nano-SiO_2 sol in cement-based composites. Using water-bath ultrasonic dispersion technology, CNTs/SiO_2 composite fillers were prepared to enhance cement composites. The results show that carbon nanotubes (CNTs) can be uniformly dispersed in cement-based composites with nano-SiO_2 sol as the dispersion medium. When the contents of SiO_2 sol and CNTs are 1.50wt.% and 0.15wt.% respectively, the mechanical properties of cement-based composites are improved most significantly.

Keywords

Carbon nanotubes (CNTs); SiO_2 sol; Fluidity; Setting time; Mechanical properties.

1. Introduction

Cement-based composites represented by concrete are one of the most widely used engineering materials in the construction field, featuring low cost, high strength, easy access to raw materials, and strong molding ability. Meanwhile, cement - based composites have a series of serious inherent drawbacks, such as easy cracking, low tensile strength, and significant brittleness, which greatly affect the safety and durability of the overall structure and make it difficult to meet the requirements of special engineering construction. Studies have found that adding nanomaterials such as carbon fiber materials [1], silica powder [2], and multi-walled carbon nanotubes[3] · to cement mortar can significantly improve the comprehensive properties of cement-based composites. Among them, carbon nanotubes have attracted much attention due to their excellent elastic modulus, tensile strength, corrosion resistance, and electrical conductivity. The unique mechanical properties of CNTs make them the most promising and competitive nano-reinforcing materials [4-7].

Due to their large specific surface area and high surface energy, carbon nanotubes are prone to agglomeration when added to cement mortar, thus reducing the performance of cement - based composites [8]. To address this issue, Xu et al. modified CNTs using surfactants and mechanical ball-milling methods and found that the dispersion effect of CNTs in water was significantly improved[9]. Fan et al. dispersed carbon nanotubes into styrene-acrylic emulsion by ultrasonic technology, and then mixed the uniformly dispersed CNTs/SAE emulsion into cement paste. It was found that the combined addition of CNTs/SAE significantly increased the strength of the cement paste [10]. Studies have found [11] that due to their low wettability and insufficient active groups, carbon nanotubes have a weak bonding ability with cement paste, resulting in an insignificant improvement in the mechanical properties of cement-based composites. Therefore, how to effectively disperse CNTs in the cement matrix, enhance the interfacial bonding strength between them, and give full play to their performance characteristics has become a key issue that current scholars urgently need to solve.

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Nano-silica particles have received increasing attention due to their application prospects in cement composites. Nano-SiO_2 is a kind of nanomaterial with a particle size between 1 and 100 nm, which is close to that of CNTs. The SiO_2 in the sol contains a large amount of water and hydroxyl groups(-OH), showing strong pozzolanic properties. When applied to cement-based materials, compared with SiO_2 powder, it has better dispersibility, which can promote the hydration product CH to bond to the surface of SiO_2 and generate a more abundant C-S-H gel, thus making the microstructure of cement-based materials denser. The process of cement hydration reaction after adding SiO_2 sol can be simply expressed in Figure 1. At the same time, the SiO_2 sol provides nucleation sites for the C-S-H gel, gradually expanding outward and developing into a structure similar to "grape clusters", significantly increasing the tensile stress inside the cement-based materials[12,13]. Therefore, SiO_2 sol can be used to strengthen the connection between CNTs and the cement matrix. However, current research on the synergistic enhancement of the properties of cement mortar by CNTs and SiO_2 sol is still insufficient.

In this paper, the water-bath ultrasonic method was used to uniformly disperse CNTs into the SiO_2 sol to prepare a CNTs/SiO_2 mixed dispersion, which was incorporated into cement mortar and relevant performance tests were carried out.

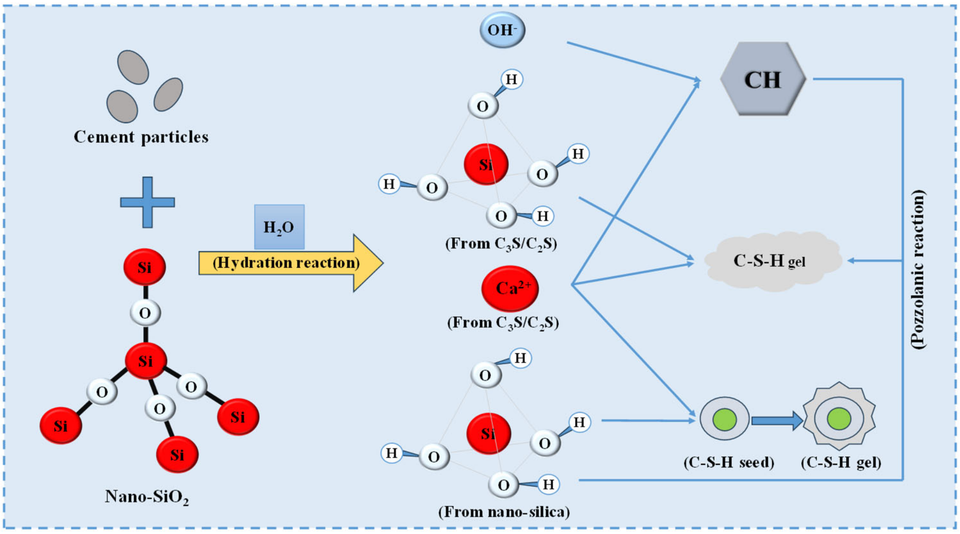

Figure 1. The process of cement hydration reaction

2. Experiments

2.1. Experimental Materials

Shanshui cement of P·O 42.5 grade and P·O 52.5 grade produced by a company in Shandong; Carbon nanotubes (TCNs), type TNMC5, produced by Chengdu Organic Chemistry Co., Ltd.; SiO_2 sol, type HS-3-25, produced by Zhejiang Yuda Chemical Co., Ltd.; Xiamen ISO standard sand; PC-303 powder polycarboxylic acid high-performance water reducer produced by Wuhan Huaxuan High-tech Co., Ltd.; The experimental water used is deionized water.

2.2. Experimental Design

The experimental groups are divided into the SiO_2 sol group and the SiO_2-CNTs mixed group; The water-cement ratio adopted in the experiment is 0.50. The dosages of SiO_2 sol in the sol group are 0%, 1.0%, 1.5%, 2%, 2.5%; The dosage of the water reducer is 0.2% of the cementitious materials. The proportion of cement mortar and SiO_2 sol is shown in Table 1.

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Table 1. The Mix Proportion of the SiO_2 Sol and Cement Mortar Group

Cement	Types	Cement/g	SiO_2 /ml	SiO_2 /g	Water/g	Sand/g
	A0	450	/	/	225	1350
	A1	450	18	1.0	207	1350
425#	A2	450	27	1.5	198	1350
	A3	450	36	2.0	189	1350
	A4	450	45	2.5	180	1350
	B0	450	/	/	225	1350
	B1	450	18	1.0	207	1350
525#	B2	450	27	1.5	198	1350
	B3	450	36	2.0	189	1350
	B4	450	45	2.5	180	1350

Through the subsequent analysis of the research results on the mechanical properties of the modified and strengthened cement mortar composites in the SiO_2 sol group, it was found that the SiO_2 sol with a dosage of 1.5wt.% is most beneficial to the strength increase of the cement mortar composites. Therefore, here we take the SiO_2 sol with a dosage of 1.5wt.% as the precursor, and incorporate CNTs at a proportion of 0.1wt.%, 0.15wt.%, 0.2wt.%, and 0.25wt.% of the cement mass, and further study the improvement results of the mechanical properties of the cement mortar composites by the doping of CNTs in the SiO_2 sol, which is named the SiO_2-CNTs mixed group. The mix proportion of the SiO_2-CNTs mixed solution and the cement mortar group is shown in Table 2.

Table 2. The Mix Proportion of the CNTs-SiO_2 Sol and Cement Mortar

Cement	Types	Cement/g	SiO_2 /g%	CNTs/g	Water/g	Sand/g
	SC-0	450		/	225	1350
	SC-1	450		0.10	207	1350
425#	SC-2	450	1.5	0.15	198	1350
	SC-3	450		0.20	189	1350
	SC-4	450		0.25	180	1350
	CS-0	450		/	225	1350
	CS-1	450		0.10	207	1350
525#	CS-2	450	1.5	0.15	198	1350
	CS-3	450		0.20	189	1350
	CS-4	450		0.25	180	1350

3. Specimen Preparation and Test Methods

3.1. Specimen Preparation

The water-bath ultrasonic method was adopted to uniformly disperse CNTs into the SiO_2 sol to prepare a CNTs/SiO_2 mixed dispersion, which was incorporated into the cement mortar and used to prepare the test specimens required for the experiment as required. The simple process of preparing the test samples is shown in Figure 2:

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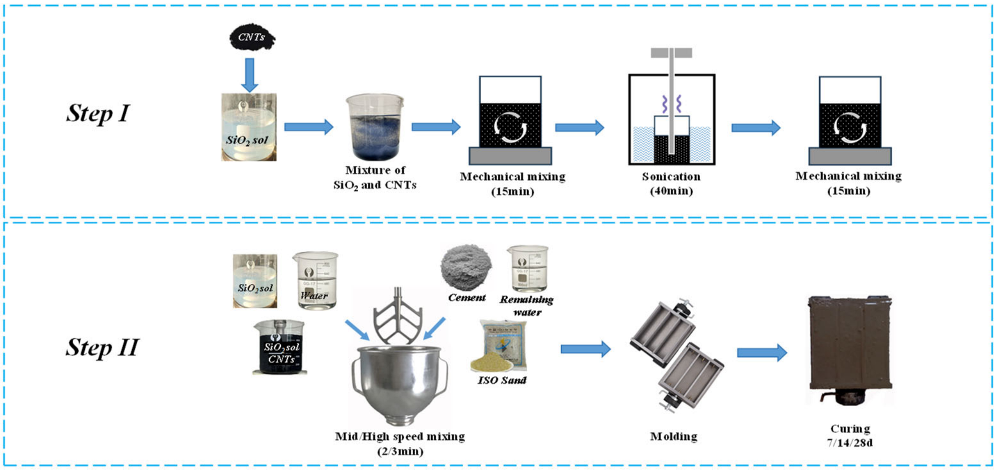

Figure 2. Simple Process of Preparing Test Samples

3.2. Performance Testing

According to relevant national standard specifications, the fluidity of the mortar was tested, and the initial setting time and final setting time were measured. After curing to the specified age, the mechanical strength of the cement mortar specimens was tested.

4. Results and Analysis

4.1. Fluidity and Setting Time

Table 3 shows the fluidity of the mortar with different proportions of SiO_2-CNTs.

Table 3. The Fluidity of the Mortar with Different Dosages of SiO_2-CNTs (mm)

SiO_2	CNTs/wt.%				
sol/%	0	0.10	0.15	0.20	0.25
0	207	190	192	195	196
1.0	180	183	188	181	186
1.5	179	171	180	177	168
2.0	145	147	148	140	145
2.5	126	121	117	125	122

The data in Table 3 shows that when the dosage of carbon nanotubes remains unchanged, with the increase of the dosage of silica sol, the fluidity of the mortar shows a downward trend. This is because the SiO_2 sol has a large specific surface area, and its nanoscale colloidal particles can disperse freely in the mortar. A large number of active groups react with Ca^{2+}, reducing the free water in the mortar system, thus weakening the interaction between cement particles, causing agglomeration inside the mortar, and leading to a decrease in the fluidity of the mortar. Some studies have pointed out that this may be caused by the high specific surface area and reactivity of nanoparticles [14-16]. When the dosage of SiO_2 sol remains unchanged, the change in the dosage of CNTs has little effect on the fluidity of the mortar.

As can be seen from Figure 3, the incorporation of SiO_2 sol can accelerate the hydration process and shorten the setting time of the cement-based composite material. Compared with the blank control group, with the increase of the dosage of SiO_2 sol, both the initial setting time and the final setting time are gradually shortened, and the fluidity of the mortar is also reduced. It is worth noting that the interval between the initial and final setting times is also shortened. The reduction of the setting time is due to the characteristics of the SiO_2 sol, which has rapid pozzolanic activity and a large specific surface area, and the rate of the pozzolanic reaction is proportional to the surface area available for the reaction [17]. Therefore, during the hydration reaction process, the amount of calcium and hydroxyl ions in the pore fluid environment will decrease rapidly, which also indicates that the SiO_2 sol has an accelerating effect on the end of the induction period of cement hydration [15].

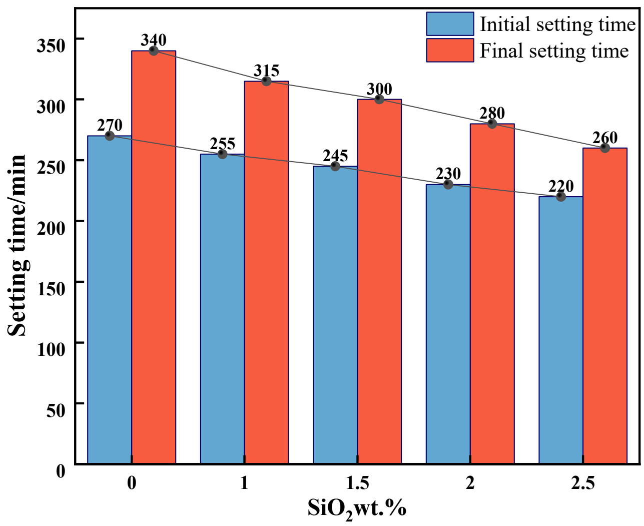

Figure 3. The Setting Time of Cement Mortar

4.2. Mechanical Properties

4.2.1. Flexural Strength

The flexural strengths of the cement mortar specimens in the SiO_2 sol group after curing for 7 days, 14 days, and 28 days are shown in Figure 4. It can be seen that adding SiO_2 sol to the two different types of cement mortars can improve the strength of the cement mortar specimens, and there is an appropriate dosage. Both groups reach the maximum flexural strength when the dosage of SiO_2 sol is 1.5wt.%.

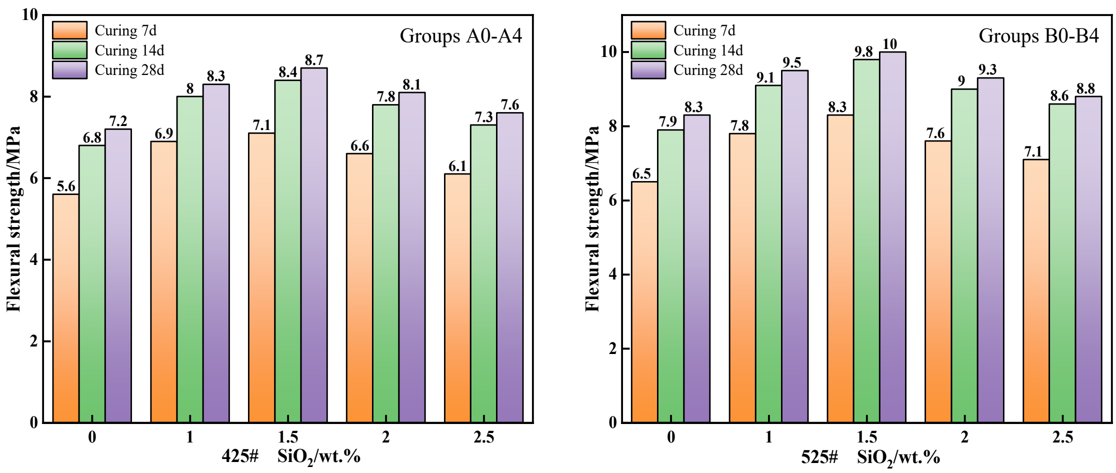

Figure 4. The Flexural Strength of Mortar Specimens at Different Ages

The flexural strengths of the cement mortar specimens in the SiO_2-CNTs mixed group after curing for 7 days, 14 days, and 28 days are shown in Figure 5. Compared with the SiO_2 sol group, the strength is further improved. Both groups reach the maximum flexural strength when the dosage of CNTs is 0.15wt.%.

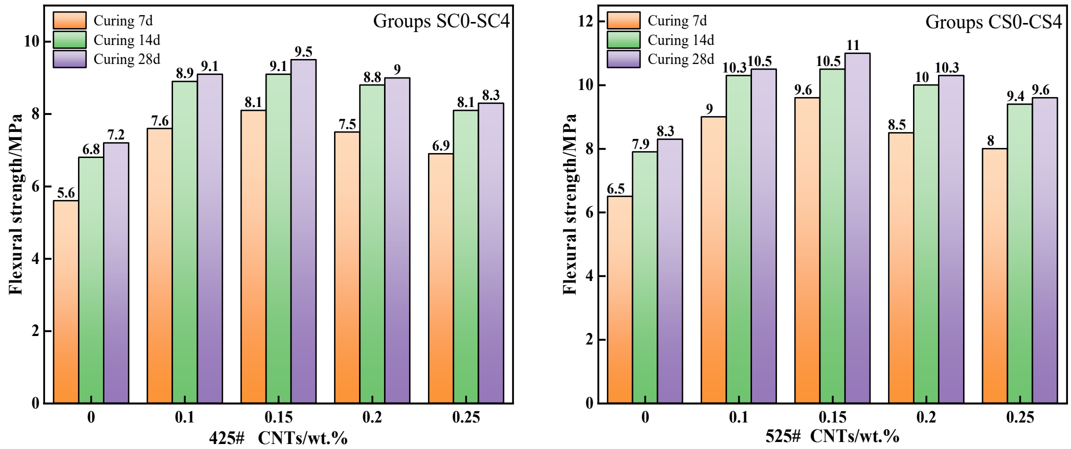

Figure 5. The flexural strength of mortar specimens at different ages

Compared with the blank control group and the group with only SiO_2 sol added, the further improvement of the flexural strength of the mortar specimens in the SiO_2-CNTs mixed group is because CNTs fill the voids in the mortar. They act as fibers at the interface between the cement paste and fine aggregates, bridging the micro-cracks between the structural components, and providing higher crack propagation resistance at the nanoscale. The nano-SiO_2 particles adsorbed on the surface of the carbon nanotubes further improve the microstructure of the interface between the carbon nanotubes and the cement matrix. As a result, it greatly increases the energy consumption required for crack propagation and enhances the flexibility of the mortar [12,18].

4.2.2. Compressive Strength

The compressive strengths of the cement mortar specimens in the SiO_2 sol group after curing for 7 days, 14 days, and 28 days are shown in Figure 6. It can be seen that adding SiO_2 sol to the two different types of cement mortars can also improve the compressive strength of the cement mortar specimens. Both groups also reach the maximum compressive strength when the dosage of SiO_2 sol is 1.5wt.%.

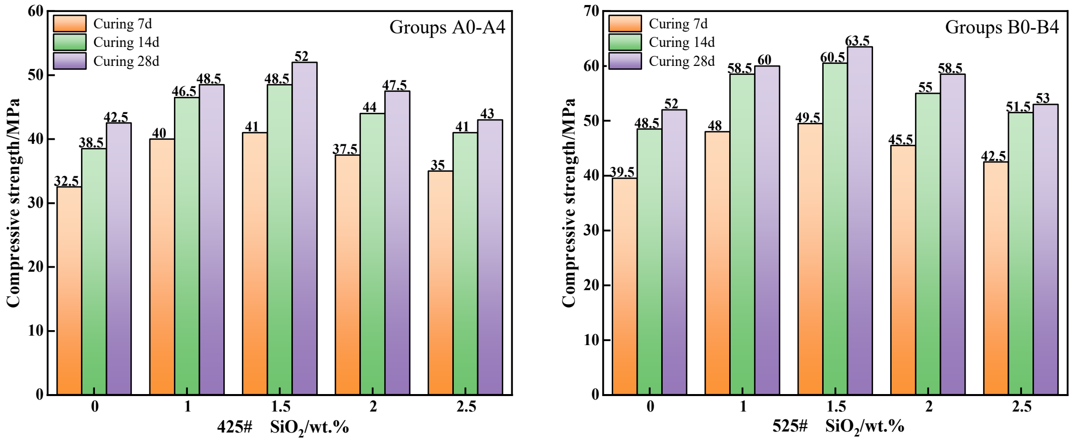

Figure 6. The Compressive Strength of Mortar Specimens at Different Ages

The compressive strengths of the cement mortar specimens in the SiO_2-CNTs mixed group after curing for 7 days, 14 days, and 28 days are shown in Figure 7. Similarly, it can be seen that adding the SiO_2-CNTs mixed solution to the two different types of cement mortars can further improve the compressive strength of the cement mortar specimens. Both groups reach the maximum compressive strength when the dosage of CNTs is 0.15wt.%.

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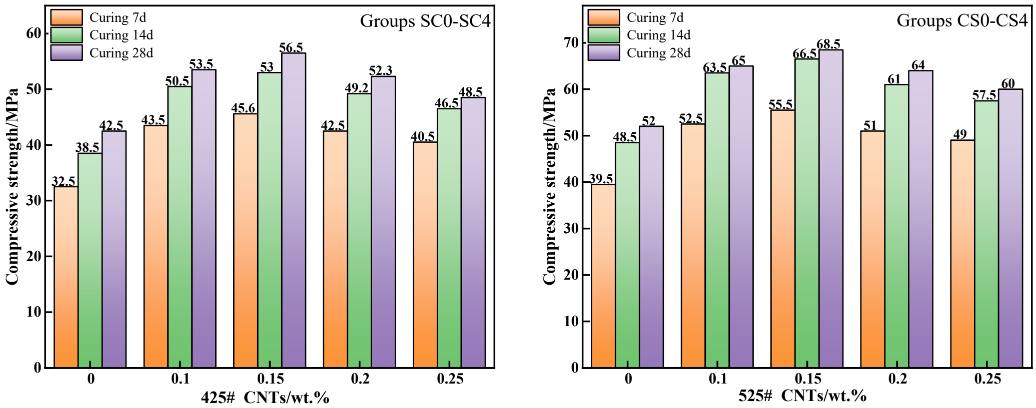

Figure 7. The Compressive Strength of Mortar Specimens at Different Ages

The above test results show that incorporating an appropriate amount of SiO_2 sol and CNTs into cement mortar can promote the improvement of the mechanical strength of the mortar. Calcium silicate hydrate (C-S-H) and crystalline calcium hydroxide (CH) are two important products of the cement hydration reaction. C-S-H gel is produced by the hydration of C_3S and C_2S, which can improve the mechanical properties and microstructure of cement-based composites. CH is another product of cement hydration, accounting for 20%-25% of the volume of hydration products. The location of CH is a relatively weak area, which will weaken the overall performance of cement composites. However, the C-S-H gel generated due to the high pozzolanic reactivity of the SiO_2 sol can reduce the content of CH, especially in the early stage of the cement hydration reaction, and the reduction efficiency is more obvious. The SiO_2 sol can also react with the available C-S-H gel to form C-S-H with a higher degree of polymerization [19-22].

5. Conclusion

(1) Using the water-bath ultrasonic method, CNTs can be uniformly dispersed in the SiO_2 sol, effectively reducing the degree of agglomeration in the CNTs cement-based composites and further enhancing the strength of the cement mortar.

(2) The pozzolanic activity of the SiO_2 sol can accelerate the hydration reaction rate of cement, reduce the fluidity of the cement mortar, shorten its initial setting time and final setting time, and reduce the time interval between the initial setting and the final setting.

(3) It is very important to determine the appropriate dosage of the mixture of nano-silica and carbon nanotubes to obtain the desired effect. When the dosages of SiO_2 sol and CNTs are 1.50wt.% and 0.15wt.% respectively, the mechanical properties of the cement-based composites are improved most significantly.

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