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EXPERIMENTAL STUDY ON MECHANICAL PROPERTIES OF NANO-MODIFIED CEMENT PASTE

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The mechanical properties of cement paste modified by nano-TiO_2 (nT) and nano-SiO_2 (nS) were experimentally studied. The compressive strength increased first and then decreased with the increase of nanoparticle content. When nanoparticles were added into the cement paste as a filler to improve the microstructure, the two kinds of particles both could form a tighter mesh structure, which would enhance the density and strength of the structure. The elastic modulus increased rapidly with the increase of the nT content and reached a peak when the nanoparticle content is about 3%, which was about twice the elastic modulus of ordinary cement paste. The Scanning electron microscopy (SEM) observation results showed that the microstructure of cement was network connection and fiber tube. The hydration progress of ordinary cement slurry was insufficient, and many unreacted cement particles remained. With the addition of nanoparticles, the internal structure of the cement became denser, with fewer pore cracks, smaller pore diameters, more complex fiber tube arrangements, and significant anisotropy, thereby improving strength and mechanical properties.

Keywords: Nano-modified, mechanical properties, nano-TiO_2, nano-SiO_2, cement paste

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1. INTRODUCTION

Cement-based materials are the most widely used important building materials in the world. About 20 billion tons of concrete are produced every year [1]. With the continuous progress of human society and the continuous development of science and technology, the application of cement is becoming more and more extensive, and higher requirements are placed on its performance. High performance, special function cement-based materials preparation, and application are some of the most important research topics that have been discussed all over the world [2]. With the continuous advancement of nanotechnology, a lot of research has been carried out in the past decade to understand the impact of nanoparticles on cement properties [3-5]. The most commonly used nano-modified particles in cement products are SiO_2 [6-7], TiO_2 [8-9], Al_2O_3 [10] and $CaCO_3$ [11]. These studies have shown that the specific surface area of nanoparticles has a great influence on the mechanical properties, electrical resistivity, microstructure, and durability of cement-based composites. It is feasible to add nanoparticles to improve the mechanical properties of concrete [12-13]. Nanoparticles of silica (nS) can improve the compressive strength of cement mortar by more than 20%. The principle of performance improvement is not only due to the micro-aggregate filling of nanoparticles, but also the hydration of cement. Observation of the microstructure between cement mortar mixed with nanoparticles and ordinary cement mortar showed that nanoparticles filled the pores in the hydrate and reduced the $Ca(OH)_2$ compound [14-15]. Nanoparticles of titania (nT) particles have unique photocatalytic, excellent color effects, UV shielding, and other functions. It has broad application prospects in photocatalysts, cosmetics, anti-ultraviolet absorbers, functional ceramics, gas-sensitive sensing equipment, and environmental problem solving [16]. Studies showed that blending nT into cement-based materials can make cement have photocatalytic performance, and using this cement as pavement material can make it have the function of photocatalytic degradation of automobile exhaust [17-19]. Senff et al. [20] reported an experimental study on the effect of nS and nT on the rheological properties, using different test times and design of experiments (DOE) as the test method. The hydration temperature and compressive strength were also measured. The micro-mechanism for the mechanical properties enhancing has not been reported. It is greatly significant to study the mechanical properties of nT and nS cement-based materials in engineering

In this paper, silica nanoparticles and titanium dioxide nanoparticles were selected to mix cement pastes. The influence of nT and nS on the mechanical properties of cement pastes was studied by changing the incorporation ratio and content. The microscopic mechanism of improving the properties of cement pastes with nanomaterials was revealed through scanning electron microscopy method.

2. PREPARATION OF TEST

Portland cement, silica nanoparticles and titanium dioxide nanoparticles were provided by Jiaozuo City White Cement Company and Hangzhou Wanjing New Material Company, respectively. The particle sizes and specific surface area of nT and nS are about 15-30 nm, 30 nm, 50-90 m^2/g, and 220m^2/g, respectively. SN-5040 polycarboxylate sodium salt is adopted as a dispersant. In this study, the water/binder (w/b) ratio of the modified cement slurry was 0.5. In order to obtain a better dispersion effect, 1.5wt% dispersant was used. Specimens were prepared with 0-3wt% replacement of cement by nanoparticles. The preparation procedure of the specimen is as follows: The preparation procedure of the specimen is as follows: (a) Add 1.5wt% of dispersant to the appropriate amount of water and stir it evenly with a stirrer. (b) Add nanoparticles and stir well, then add enough cement to fully stir; c) Put the mixed mixture into a rectangular mold of 50mm × 50mm × 100mm; (d) Put the mold on the shaker Fully vibrate; (e) Peel and cure at room temperature.

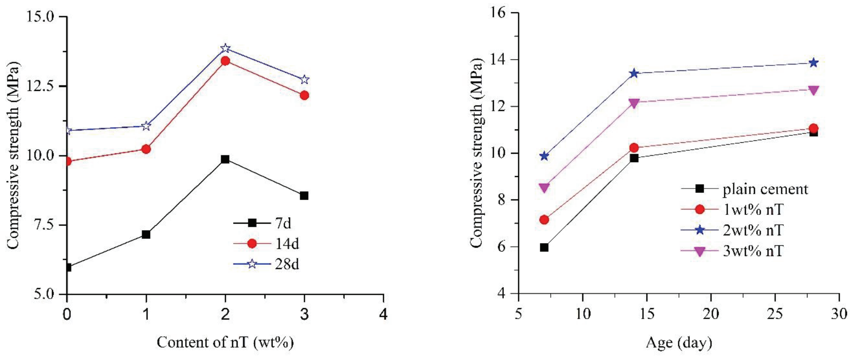
The uniaxial compressive strength, elastic modulus and Poisson's ratio of different cured ages were tested. Displacement control was performed at a loading rate of 5mm / min. The load-displacement curve and peak load were recorded during the test. The broken sections were collected and placed under a JSM-7500F field emission scanning electron microscope for microstructure testing. The specific ingredients of the mixture were listed in the Table. 1.

Table 1. Mix proportions of the cement pastes

No.	P1	T1	T2	T3	S1	S2	S3	TS1	TS2	TS3
nT (wt%)	0	1	2	3	0	0	0	2	2	2
nS (wt%)	0	0	0	0	1	2	3	1	2	3

3. TEST RESULT

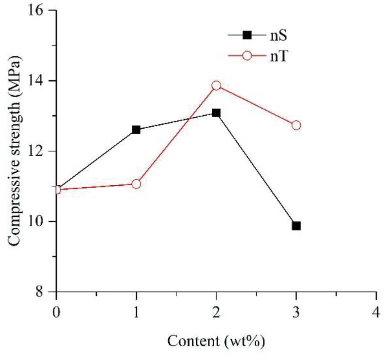
Strength is one of the most important mechanical properties of the cement paste. One of the main objectives of this study is to explore how the content of nanoparticles affects the strength properties of cement paste. Due to its good pozzolanic activity, nT can completely react with the components in cement. The pores of cement slurry are easily filled with nanoparticles, and this leads to an increase in strength. The experimental results show that the compressive strength of nT modified cement paste with different curing ages is improved compared with plain cement paste. Figure 1 shows the changing law of compressive strength of nT modified cement paste with different curing ages and different contents. It can be seen that as the nT content increases, the compressive strength of the cement paste first increases and then decreases. When the nT content is 2wt%, the average compressive strength reaches the maximum value. This may be due to the small size of the nanoparticles, which is likely to cause the nucleation of C-S-H, and the nucleation of nanomaterials will be more significant. However, the compressive strength of cement paste increases rapidly in the early stage and slowly increases in the late stage, which is completely consistent with the overall results. With nanoparticles as the core, cement hydration products are dispersed and wrapped in them, forming a denser network structure, which will accelerate hydration and improve the early performance of cement strength. Due to the small size of the nanoparticles, water consumption may tend to increase as the nanoparticle content increases, which will result in a decrease in strength. Therefore, without the use of a water-reducing admixture, when the positive effect of the nanocrystalline core is less than the negative effect of reducing water consumption, the strength will decrease. For this study, the crossover point occurs when the nT content is 2wt%, which is recommended as the optimal ratio.



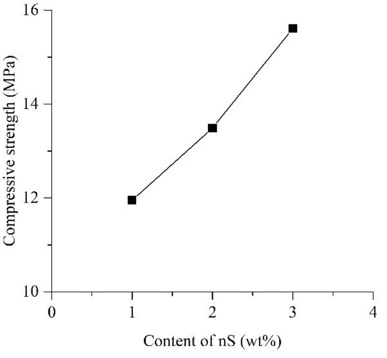
(a) The influence of addition (b) The influence of cure age

Fig. 1. Effect of nT on compressive strength of cement paste

Fig. 2a shows the effect law of single additive on the compressive strength of cement paste. It can be seen that the effect of the incorporation of the two kinds of nanoparticles on the compressive strength of cement is the same: the compressive strength of 28d increases first and then decreases as the content of nanoparticles increases. At the same time, the average strength reaches the maximum value when the incorporation amount is 2wt%. At the same content, the maximum strength of nT modified cement paste is greater than that of nS modified cement paste. When the content of nS exceeds 2wt%, the strength of nS modified cement paste suddenly decreases or even lower than that of plain cement paste. For single nano-particle modified cement paste, the recommended optimal ratio is 2wt%. To study the interaction between nS and nT and its effect on the compressive strength, 2wt% nT and 1-3wt% nS was blended with cement paste. The test result showed that the strength of cement paste increased with the increase of nS content (Fig.2b). It indicates that due to the complementary size, the simultaneous presence of nT and nS can effectively enhance the density of the structure. It means that the combination between nS and nT modified the characteristics of cement paste and assured additional performance compared to only single nano additive [21].



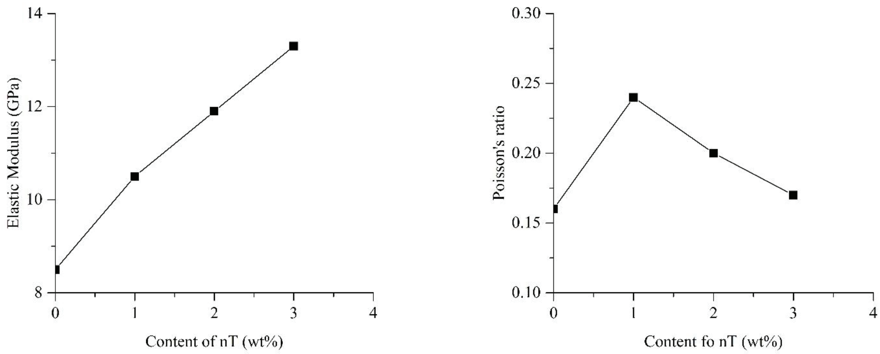
(a) Single nanoparticle



(b) 1-3wt% nS and 2wt%nT

Fig. 2. Effect of nS on Compressive Strength of Cement paste at age of 28d

Fig. 3 shows the influence of nT incorporation on the elastic modulus and Poisson's ratio. It can be seen that the content of nT has an important effect on the elastic modulus, but has a slight effect on the Poisson's ratio. The elastic modulus increases rapidly with increasing of nT content and the elastic modulus of the 3wt% nT modified cement paste is about twice that of plain cement paste. The Poisson's ratio first increases and then decreases with the increase of nT content. Compared with the influence on strength, it can be verified that the hydration of nanoparticles will induce a dense network structure. Dense microstructures mean less deformation occurs at higher loads which will be seen in the later SEM analysis parts.



(a) Elastic modulus (b) Poisson's ratio

Fig. 3. Effect of nT on Elastic Modulus and Poisson's ratio of Cement

4. DAMAGE MECHANISM ANALYSIS

The typical damage trajectories of different curing ages (7d, 14d, 28d) are shown in Fig. 4. When the load reached 90% of the peak value, horizontal tensile cracks initialed from the middle part of the specimens and then expanded rapidly through the whole specimens. The final destructive form of the specimen was dominated by transverse rupture.

(a) 7d (b) 14d (c) 28d

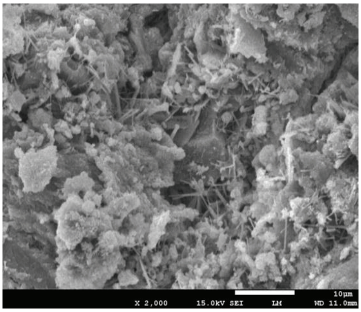
Fig. 4. Failure diagram of specimens

Scanning Electron Microscopic observation (SEM) by JSM-7500F field emission scanning electron microscope shows agglomeration of the grains and verified the silicon and titania content (Fig. 5 and Fig. 6). It can be seen from the images that the structures of the plain cement paste hydration reaction products are network connection and fiber tubular structure. These network structures are very loose with many large diameter pores. The microscopic internal structure of cement is one of the most important factors that determine the mechanical properties of cement. Compared with nanoparticle modified cement, the hydration reaction of the plain cement is not sufficient and there are still many large cement particles (Fig. 5a and Fig. 6a).

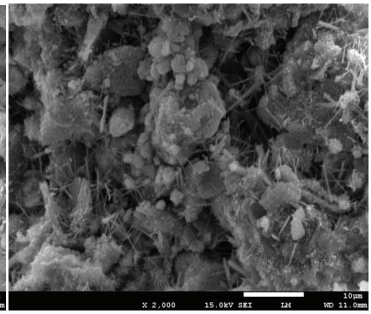
After comparing the SEM images of the plain cement paste and the 2wt% nT modified cement, it can be seen that the internal structure of cement becomes denser because of the filling effect of nanoparticles (Fig. 5b) and Fig. 6b). The number and diameter of pore cracks decrease with the decrease of the fibrous tubular structures. It indicates that after nT is incorporated into cement, due to its extremely small particle size and nucleation, the cement hydration reaction is more sufficient, and the internal pores and cracks are effectively filled. The internal structure of the cement paste becomes dense because of the connection of a large number of reticular structures and the obvious reduction of the large cement particles. Therefore, the interface strength of the cement paste is enhanced, and the mechanical properties such as the compressive strength of the cement are significantly improved.

It can be seen from the SEM micrograph of 2wt% nS modified cement that the internal structure of cement has also been re-arranged to become denser than that of plain cement. A reticular structure can be formed (Fig. 5c) and Fig. 6c). However, compared with 2wt% nT modified cement, the pores and the network structure of 2wt% nS modified cement are larger and looser. This is also consistent with the macroscopic intensity characterization. Under the same addition content, the strength of nT modified cement is stronger than that of nS modified cement.

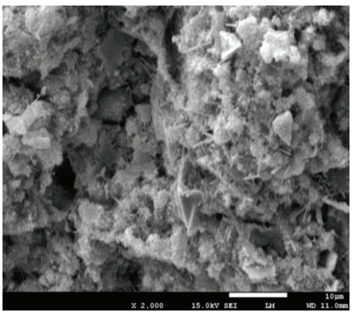
The SEM micrographs of 2wt% nT and 3wt% nS modified cement are shown in Fig. 5d and Fig. 6d. Compared with other specimens, the internal structure of this group is the most compact one than the other three groups. Different diameters of nT and nS particles can be complementarily filled into the micro-cracks and pores. Coupled with the reaction between the two particles, more dense and complex micro-mesh can be formed. Thus, the anisotropy of mechanical properties can be greatly enhanced and the strength in the macro scale can be increased correspondingly. The experimental results show that the compressive strength of 2wt% nT and 3wt% nS modified cement was much higher than that of other specimens.



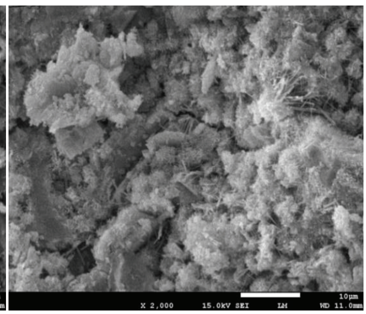
(a) plain cement paste



(b) single addition of 2wt% nT

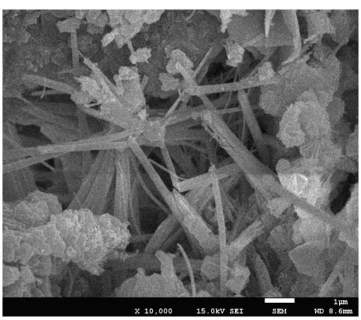


(c) Single addition of 2wt% Ns



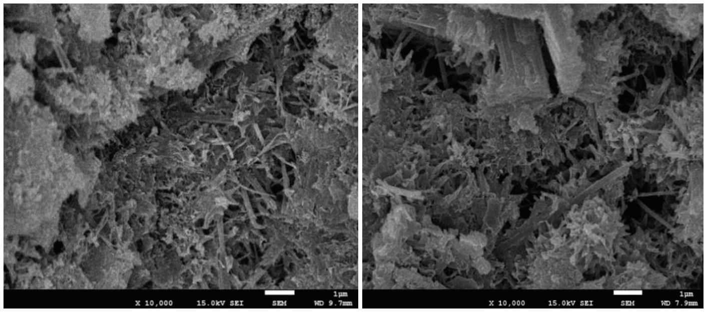
(d) 2wt% nT and 3wt% nS

Fig. 5 Micrographs of specimens (×2000)



(a) plain cement paste

(b) single addition of 2wt% nT



(c) Single addition of 2wt% nS (d) 2wt% nT and 3wt% nS

Fig. 6 The microstructure of specimens (×10000)

5. CONCLUSIONS

To reveal the mechanism of strength enhancement of nanoparticles modified cement paste, different admixture contents of single addition nT, single addition nS, and two-addition nanoparticles were added into the cement paste. The compressive strength of different ages, the Elastic Modulus, Poisson's ratio, and micrographs of fractured surfaces were determined. From the above discussion, some important conclusions can be drawn:

(1) The compressive strength of nT modified cement paste at different ages was both improved. The compressive strength of both nT modified cement paste and nS modified cement paste increases firstly and then decreases with the increase of nanoparticles content and the crossover point occurred at the nanoparticles content of 2wt% which was suggested as an optimal ratio for single addition.

(2) To study the interaction between nS and nT and their effect on the compressive strength, 2wt% nT and 1-3wt% nS was mixed with cement paste. The test result showed that the strength of cement paste increased with the increase of nS content. The simultaneous presence of nT and nS can effectively enhance the compactness of the structure because of the complementary dimensions.

(3) The incorporation of nanoparticles has a large effect on the Elastic Modulus and little effect on the Poisson's ratio. The Elastic Modulus increase rapidly with the increase of nT content.

(4) The Scanning electron microscopy (SEM) observation results showed that the cement microstructure was mesh connection and fiber tubular. The hydration progress of plain cement paste was not sufficient and many unreacted cement particles remained. After adding nanoparticles, the internal structure of the cement became more compact with fewer pore cracks, smaller pore

diameter, more complex fiber tube arrangement, and obvious anisotropy which resulted in enhanced strength and mechanical properties.

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LIST OF FIGURES AND TABLES:

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