

Cement and Concrete Research 34 (2004) 435-438

A study on mechanical and pressure-sensitive properties of cement mortar with nanophase materials

Hui Li*, Hui-gang Xiao, Jin-ping Ou

School of Civil Engineering, Harbin Institute of Technology, PO Box 2546, 2nd Campus, Harbin 150090, China Received 2 May 2002; accepted 25 August 2003

Abstract

The mechanical properties and self-monitoring capability of cement mortar containing nano-SiO₂ or nano-Fe₂O₃ were experimentally studied and compared with that of plain cement paste. The results showed that the compressive and flexural strengths measured at the 28th day of cement mortar containing nano-SiO₂ or nano-Fe₂O₃ were both higher than that of plain cement mortar with the same water—binder ratio (w/b). Furthermore, the self-monitoring capability of cement mortar with nano-Fe₂O₃ is also presented in this paper. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Composite; Mortar; Electrical properties; Mechanical properties

1. Introduction

Health monitoring of structures by embedded or attached sensors has been gaining increasing interest and is more effective to guarantee structural safety in service. However, smart concrete, which can sense its own strain and damage, is more attractive due to its strong mechanical properties and self-monitoring characteristics. Smart concrete with short carbon fiber has been systematically developed [1,2]. The advantages of intrinsically smart concrete in contrast to smart sensing materials such as optical fibers, piezoelectric sensors, etc. are low cost, great durability, absence of mechanical property degradation due to the embedding of sensors, etc. [1].

In consideration of nanoparticles with many novel properties and significant improvement on some properties of materials mixed with nanoparticles such as nanophase ceramic, etc. [3,4], cement mortars mixed with nano-SiO $_2$ or nano-Fe $_2$ O $_3$ were proposed and fabricated, and their mechanical properties and self-sensing of strain were experimentally studied in this paper. The results indicated that cement mortar with nano-Fe $_2$ O $_3$ could sense its own compressive stress in the elastic and inelastic regimes because

E-mail address: lihui@hit.edu.cn (H. Li).

the volume electric resistance of cement mortar with nano- Fe_2O_3 could change with the applied loading. This property is valuable for structure health monitoring in real time. Furthermore, the compressive strength of cement mortar with nanoparticles was also simultaneously improved.

2. Experimental methods

2.1. Materials and specimens

Cement mortar is composed of small grains of hydrated calcium silicate gels and large crystals of hydrated products, with nanosized individual pores and capillary pores (structural defects) distributed among them. There should be room for nanoparticles to improve the properties of plain cement mortar. Fe₂O₃ nanoparticles in the amounts of 3%, 5% and 10% by weight of binder (the sum of cement and nanoparticles) were used, and the same amount for SiO₂ nanoparticles. Nano-SiO₂ was obtained from Zhoushan Mingri Nanophase Material Co. (Zhejiang, China); its properties are shown in Table 1. The mean grain diameter of the nano-Fe₂O₃ is 30 nm; nano-Fe₂O₃ was obtained from Fangyuan Nanophase Material Institute (Anhui, China).

The cement used was Portland cement (P.O32.5). NF water-reducing agent (a sulfonate surfactant, China) and UNF water-reducing agent (one kind of β -naphthalene sulfonic acid and formaldehyde condensates) were used to

^{*} Corresponding author. Tel.: +86-451-86282013; fax: +86-451-86282013.

Table 1 The properties of nano-SiO₂

Item	Diameter (nm)	Surface-volume ratio (m ² /g)	Density (g/cm ³)	Purity (%)
Target	15 ± 5	160 ± 20	< 0.15	>99.9

aid the nanoparticles' dispersion, with 0.25 wt.% nano-Fe₂O₃ and 0.5 wt.% nano-SiO₂, respectively (Table 2). The defoamer, tributyl phosphate (made in China), was used to decrease the amount of air bubbles. Fine aggregate (natural sand) only was used.

The water-binder (w/b) ratio was 0.5, and the binder content was taken as the sum of cement and nanoparticles. Ten compositions, as listed in Table 2, were studied. The compositions A-8 to A-10 were used to study the self-stress sensing properties. The amount of the cement was larger than the mixtures A-1-A-7 to obtain good sensing ability by increasing the absolute amount of the Fe_2O_3 nanoparticles and keeping the same ratio of the cement and nanoparticles.

2.2. Testing procedure

Defoamer and NF water-reducing agent (if applicable) were dissolved in water, and then the nanoparticles were added and stirred at high speed for 2 min. This mixture and the cement were mixed in a mortar mixer at a low speed for 1 min, then the mixture and sand were mixed in the same mixer at a low speed for 1.5 min. Finally, the mortar was poured into oiled molds to form cubes of size $40 \times 40 \times 40$ mm for all mix proportions, in which compositions A-1-A-7 were used for compressive testing and A-8-A-10 for self-monitoring testing, and prisms of size $40 \times 40 \times 160$ mm, in which compositions A-1-A-3, A5-A6 and A-8 were used for flexural testing. Note that flexural strength test was not conducted for mixtures A-4 and A-7 because it was found

Table 2
Mix proportions of the specimens

Mixture	W/b	Mix proportions (kg/m ³)						
no.		Water	Cement	Sand	Nano- SiO ₂	Nano- Fe ₂ O ₃	NF	Defoamer
A-1	0.5	230	460	1380	_	_	_	_
A-2	0.5	230	446.2	1380	_	13.8	3.5	0.5
A-3	0.5	230	437	1380	_	23	5.8	0.5
A-4	0.5	230	414	1380	_	46	11.5	0.5
A-5	0.5	230	446.2	1380	13.8	_	6.9	0.5
A-6	0.5	230	437	1380	23	_	11.2	0.5
A-7	0.5	230	414	1380	46	_	23	0.5
Mixture	W/b	Mix proportion (kg/m³)						
no.		Water	Cement	Sand	Nano- SiO ₂	Nano- Fe ₂ O ₃	UNF	Defoamer
A-8	0.5	255	510	1275	_	_	_	_
A-9	0.5	255	494.7	1275	_	15.3	3.8	0.5
A-10	0.5	255	484.5	1275	_	25.5	6.4	0.5

that nanoparticles were more difficult to uniformly disperse when the contents were large. After pouring, an external vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 24 h and then cured in air at room temperature for 7 and 28 days, respectively.

Compressive testing was performed on a side of each cubic specimen to obtain the compressive strength. Compressive testing under force control was performed using a hydraulic mechanical testing system (MTS) with 120-kN maximum loading capacity. Flexural testing was conducted in accordance with GB/T 17671-1999 (standard test method for strength of hydraulic cement mortar of China).

Another compressive testing to measure the electric resistance of the specimens was performed on a side of each cubic specimen. As an initial study, the scheme of monotonically static loading up to specimen failure was arranged. DC electric resistance measurement was made in the stress axis, using a two-probe method, in which aluminum foil bonded on the parallel opposite surface with conductive gel (a compound of black carbon and epoxy resin) served as electric contacts. A FLUKE 8842A multimeter was used to measure the volume resistance of these specimens.

3. Results and discussion

3.1. Compressive and flexural strengths

Table 3 shows the compressive strengths of all specimens. It can be seen that the compressive strengths of the specimens with mixtures A-2, A-3 and A-4 (cement mortar with nano-Fe₂O₃) at the 7th and 28th day were all higher than that of a plain cement mortar with the same w/b. As for the strength at the 28th day, the effectiveness of the nano-Fe₂O₃ in increasing strength increased in the order A-4 < A-3 < A-2 (with the decreases on the nano-Fe₂O₃ volume fraction). Furthermore, the strength enhancement for A-4 at the 7th day is evidently higher than that at the 28th day. These results indicated that the appropriate content of nano-Fe₂O₃ for reinforcing cement mortar purposes should be less

Table 3
Compressive strengths of specimens

Mixture no.	Compression at the 7th	ve strength day	Compressive strength at the 28th day		
	Target (MPa)	Enhanced extent (%)	Target (MPa)	Enhanced extent (%)	
A-1	17.6	0	28.9	0	
A-2	21.4	22.7	36.4	26.0	
A-3	20.6	16.7	33.1	14.5	
A-4	21.1	20.0	30.0	3.7	
A-5	18.6	5.7	32.9	13.8	
A-6	21.3	20.1	33.8	17.0	
A-7	21.3	20.1	36.4	26.0	

Table 4
Flexural strengths of specimens at the 28th day

Mixture no.	A-1	A-2	A-3	A-5	A-6
Flexural strength (MPa)	4.90	5.77	6.04	5.84	6.23
Enhanced extent (%)	0	17.76	23.26	19.18	27.14

than 10% (by weight of cement) under the present dispersion condition.

The compressive strengths of the specimens with mixtures A-5, A-6 and A-7 (cement mortar with nano-SiO₂) were all higher than that of plain cement mortar. The effectiveness of the nano-SiO₂ in increasing strength increased in the order A-5 < A-6 < A-7 (with the increases on the nano-SiO₂ volume fraction).

The origin of the ability to increase the compressive strength can be interpreted as follows. When a small amount of the nanoparticles is uniformly dispersed in the cement paste, the nanoparticles act as a nucleus to tightly bond with cement hydrate and further promote cement hydration due to their high activity, which is favorable for the strength of cement mortar. The second reason is that the nanoparticles among the hydrate products will prevent crystals from growing, such as Ca(OH)₂ and AFm, and such fine crystals are also favorable for the strength of cement paste [5,6]. The third reason is that the nanoparticles fill the cement pores, thus increasing the strength, as silica fume does. However, when the contents of nano-Fe₂O₃ are too large, nano-Fe₂O₃ cannot be well dispersed to form weak zones by the aggregating nano-Fe₂O₃ and the homogenous hydrate microstructure cannot be formed. Nano-SiO₂ can participate in the hydration process to generate C-S-H through reaction with Ca(OH)₂. The small amount of aggregating nano-SiO₂ is not a weak zone, so the strength of cement mortar increases with increasing content of nano-SiO2 even when the small amount of nano-SiO₂ is not well dispersed.

As shown in Table 4, the flexural strengths of specimens A-2, A-3, A-5 and A-6 were all higher than that of plain cement mortar, which indicated that nanoparticles were also efficient for improving the toughness of cement mortar.

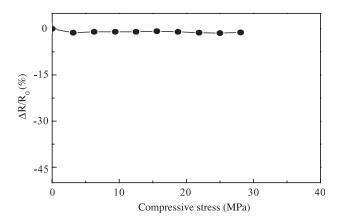


Fig. 1. Stress-sensing property of composition A-8.

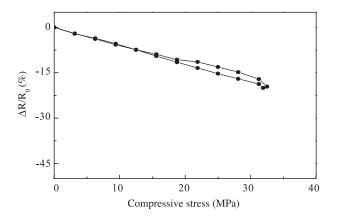


Fig. 2. Stress-sensing property of composition A-9.

3.2. Stress-sensing properties

The stress-sensing properties of A-8–A-10 compositions are also investigated in this study. The results show that their initial resistivities change slightly from 144×10^3 to 180×10^3 Ω cm, which indicate that nano-Fe₂O₃ particles do not decrease the resistivity of cement mortar. Such property is beneficial to the durability of reinforced concrete structures. Furthermore, the fractional change in resistance is the self-diagnostic criterion, not the resistivity itself.

Fig. 1 shows the fractional change of resistance $(\Delta R/R_0)$ along the stress direction versus stress with compressive loading of a plain cement mortar. It shows that the $\Delta R/R_0$ of the plain cement mortar slightly changed with different compressive loadings. The plain mortar is poor in monitoring its stress.

Figs. 2 and 3 also depict the variations of the resistance $\Delta R/R_0$ versus stress for A-9 and A-10 compositions with 3% and 5% nano-Fe₂O₃, respectively, in the monotonically compressive loading test (up to failure). The measured direction of the resistance is also along the stress direction. The figures show that the resistance $\Delta R/R_0$ linearly decreased with the increase of the compressive loading and the

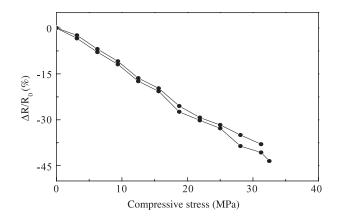


Fig. 3. Sress-sensing property of composition A-10.

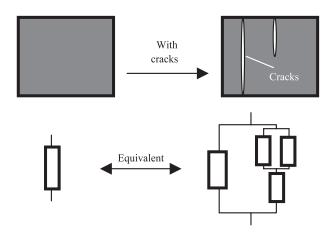


Fig. 4. Equivalent DC circuit model of the specimen with and without cracks.

resistance $\Delta R/R_0$ of specimen A-10 decreased more sharply than A-9. The results show that the more nano-Fe₂O₃ the mortar contained, the more sensitive the mortar is to monitor stress. Compared with that of the plain cement mortar, the volume resistance of cement with 3% and 5% nano-Fe₂O₃ decreases about 20% and 45%, respectively.

It is also shown from the figures that the fractional change of electric resistance gradually decreased even when the applied loading increased enough to expand the cracks of the specimens, which is different from that of the carbon fiber concrete. This is because the cracks of the specimens mainly grow along the compressive loading axis, and the transverse cracks perpendicular to the stress axis are very few. A simple equivalent DC circuit with a series-parallel array of electrical resistors, as depicted in Fig. 4, is used to model the electrical characteristics of the specimen with cracks parallel to the loading direction to analyze the influence on the fractional change of electric resistance due to cracks. Assuming the resistance of the specimen without cracks is R_0 , we can easily infer that the electric resistance of the specimen with parallel cracks is also R_0 , which shows that the longitudinal cracks of the specimen have no influence on the electric resistance.

Nano-Fe₂O₃ is a type of semiconducting material that absorbs energy, and the energy gap of nanoparticles is narrowed down when compressive force is applied to the mortar specimen, which makes the electrons of nanoparticles transit easily to enhance the electrical conductivity of nanoparticles. Another reason is that with the application of the compressive force, the nanoparticles are also compelled

to approach each other, which makes the tunneling current flows become more intense. Therefore, the electrical resistivity of the cement mortar decreases gradually [7].

4. Conclusions

The compressive and flexural strengths of cement mortar with nano-SiO₂ or nano-Fe₂O₃ were both higher than that of plain cement mortar with the same w/b, indicating that nanoparticles are valuable for reinforcing cement mortar.

Besides the enhancement on the strengths, the fractional change in resistance $\Delta R/R_0$ linearly decreases with increasing compressive loading and the change is more sharply with increasing the content of nano-Fe₂O₃, indicating that the cement mortar with nano-Fe₂O₃ is better in the ability to monitor stress itself and the self-diagnostic ability increases with increasing content of nano-Fe₂O₃ by mass of binder, so the cement mortar with nano-Fe₂O₃ is a smart structural material that can sense its own stress.

Acknowledgements

This study was financially supported by NSFC grant No. 50238040, and Ministry of Science and Technology grant No. 2002AA335010.

References

- M.Q. Sun, Q.P. Liu, Z.Q. Li, Y.Z. Hu, A study of piezoelectric properties of carbon fiber reinforced concrete and plain cement during dynamic loading, Cem. Concr. Res. 30 (2000) 1593–1595.
- [2] D.D.L. Chung, Cement reinforced with short carbon fibers: a multifunctional material, Composites. Part B 31 (2000) 511–526.
- [3] K.T. Lau, D. Hui, The revolutionary creation of new advanced materials—carbon nanotube composites, Composites. Part B 33 (2002) 263–277.
- [4] X.M. Yu, Y.L. He, Piezo-resistance effect of hydrogenated nano-crystalline silicon films with PECVD deposition method, Journal of Beijing University of Aeronautics and Astronautics 1 (1996) 84–87 (in Chinese).
- [5] Z.W. Wu, H.Z. Lian, High Performance Concrete, China Railway Press, Beijing, 1999 (in Chinese).
- [6] X. Wang, X.Y. Tan, Analysis on toughening mechanisms of ceramic nano-composites, J. Ceram. 2 (2000) 107–111 (in Chinese).
- [7] M. Hussain, Y.H. Chos, Fabrication process and electrical behavior of novel pressure-sensitive composites, Composites. Part A 32 (2001) 1696–1698.