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Cement & Concrete Composites 29 (2007) 377–382
Cement & Concrete Composites
www.elsevier.com/locate/cemconcomp

Pressure-sensitive properties and microstructure of carbon nanotube reinforced cement composites

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Received 26 December 2005; received in revised form 5 December 2006; accepted 20 December 2006
Available online 19 January 2007

Abstract

Carbon nanotubes (CNTs) treated by using a mixed solution of H_2SO_4 and HNO_3 were uniformly dispersed into cement paste by means of ultrasonic energy. Electrical resistivity and pressure-sensitive properties under cyclic compressive loading of this composite were analyzed and compared to that of untreated-CNT reinforced cement paste. Results show that the addition of treated or untreated CNTs to cement paste leads to a notable decrease in volume electrical resistivity and a distinct enhancement in compressive sensitivity. The microstructures of these cement composites were analyzed by using scanning electron microscope. The microscopic observation reveals that both treated and untreated CNTs were dispersed homogenously in the cement matrix. For untreated CNT-reinforced cement composites, the CNTs with glossy surface were zigzag and cling to cement matrix; the bridging of cracks and a well three-dimensional meshwork were also observed. For treated-CNT reinforced cement composites, the surface of CNTs was covered by C–S–H, which leads to a higher mechanical strength. The contact points of the treated-CNTs in composites were much fewer than that of the untreated-CNTs in cement matrix composites, which leads to a higher compressive sensitive properties and a lower electrical conductivity.

Keywords: Carbon nanotube; Electric resistivity; Microstructure

1. Introduction

Carbon nanotubes (CNTs), being the strongest known fiber and possessing exceptional electrical and thermal conductivity, are a promising candidate for the next generation high performance structural and multi-functional composite materials [1–4]. Much research efforts have concentrated on nanotube-reinforced polymer composites [5,6]. However, there could be some profound application of this new material in construction areas, which also deserves sufficient scientific investigation. Carbon nanotubes treated using a H_2SO_4 and HNO_3 mixture solution have been added to cement mortars. Preliminary research indicated that the treated carbon nanotubes could act as bridges across cracks and voids to form reinforcing mechanism and arrest cracking in cement matrix. It improves the flexural strength, compressive strength, and failure strain of cement matrix composites [7]. The electrical resistance and pressure-sensitive properties for cement paste incorporating treated or untreated CNTs are reported here. The microstructures of these composites were also studied by using scanning electron microscope (SEM).

2. Experimental

2.1. Materials

The cementitious material used in the test was ordinary Portland cement. Its chemical composition and physical properties are shown in Table 1. The multi-wall CNTs provided by Shenzhen NANO Tech. Port. Co. Ltd. (China)

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doi:10.1016/j.cemconcomp.2006.12.011

Table 1
Chemical and physical properties of cement

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI	Specific surface, Blaine ($m^2\ kg^{-1}$)	Compressive strength, 28-day (MPa)
20.6	4.0	3.1	62.8	2.6	3.1	1.8	392	56.7

with average diameters about 10–30 nm were used as reinforcing and sensing materials. They were fabricated by using catalytic pyrolysis of hydrocarbon. Their properties are given in Table 2, and their morphology and microstructure are shown in Fig. 1. To identify the effect of structure of CNTs on electrical properties, some CNTs were acid-treated [7]. Nano-SiO_x was obtained from Zhoushan Mingri Nanophase Material Co. (Zhejiang, China); its properties are shown in Table 3.

2.2. Sample preparation

Cement paste containing untreated CNTs (PCNT), and cement paste containing treated CNTs (SPCNT) were prepared for electrical resistance and pressure-sensitive properties testing. The water/cement ratio of these cement pastes was 0.40, carbon nanotubes were added in the amount of 0.5% by weight of cement.

Table 2
Properties of carbon nanotubes (CNTs)

External diameter	10–30 nm
Length	0.5–500 μm
Ash	0.2%
Purity	95
Special surface area	40–300 m^2/g
Amorphous carbon	3%
Electric conductivity	10^2–10^{-4} s/cm

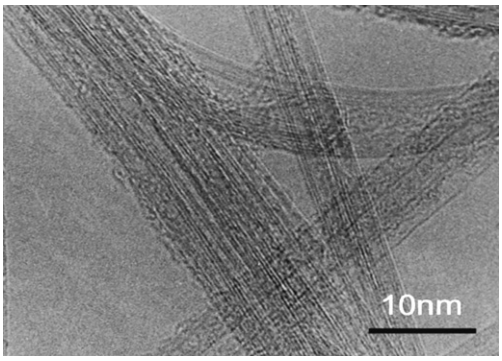


Fig. 1. TEM micrograph of multi-walled carbon nanotubes.

Table 3
Properties of nano-SiO_x

Diameter	15 ± 5 nm
Density	$<0.15\ g/cm^3$
Purity	95
Special surface area	$160 \pm 20\ m^2/g$

A rotary mixer with a flat beater was used for mixing. CNTs were firstly mixed with water and sonicated with a KQ 218 ultrasonic generator to make a uniformly dispersed suspension. Next, CNT-water solution, cement and water-reducing agent were mixed in the mixer for 3 min. Then, a defoamer in the amount of 0.13 vol% was used. The mixture was mixed for another 5 min.

After pouring the mixes into oiled molds ($40 \times 40 \times 160$ mm), an electric vibrator was used to ensure good compaction. The specimens were then surface-smoothed, and covered with wet clothes. All specimens were demolded 1day after casting. Thereafter, they were cured in water at a constant room temperature (30 °C). All specimens were dried in a vacuum drier at 50 ± 2 °C for 24 h before testing.

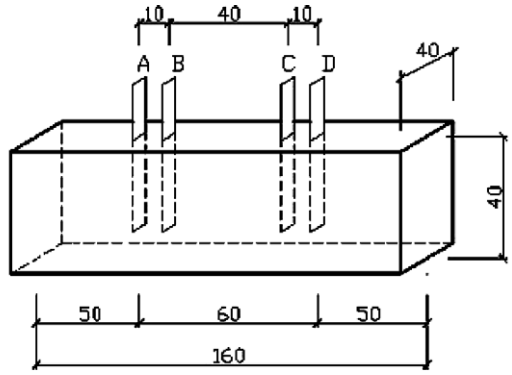
Noticing that needle-like ettringites formed during the hydration of cement may interfere the microscopic observation, and Nano-SiO_x can participate in the hydration process to generate C–S–H through reaction with $Ca(OH)_2$ [8,9], both nano-SiO_x/treated-CNTs/$Ca(OH)_2$ and nano-SiO_x/untreated-CNTs/$Ca(OH)_2$ composites were prepared for better microstructure observation.

The nano-SiO_x/treated-CNTs/$Ca(OH)_2$ composite was prepared as follow. First a saturated $Ca(OH)_2$ solution was prepared, then nano-SiO_x was mixed in $Ca(OH)_2$ solution and dispersed by using a KQ 218 ultrasonic generator, after 2 min the CNTs were added and sonification was continued for another 5 min. To ensure a good dispersion, the water/cement ratio of these pastes was chosen to be 1.0, CNTs were added in the amount of 0.1% by weight of nano-SiO_x. Next, the well dispersed solution was poured into a glass beaker and dried in a vacuum drier at 25 ± 2 °C up to 24 h, and then the sample was kept in a hermetic glass bottle.

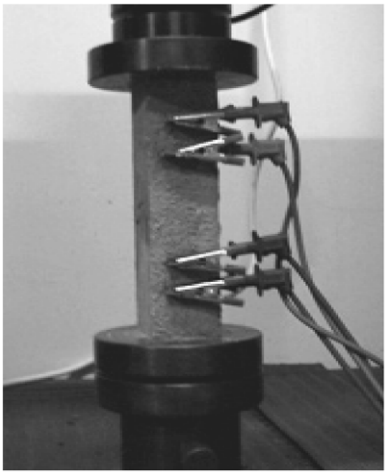
In order to reveal the aggregation structure and the surface characteristic of the untreated CNTs, the Nano-SiO_x/untreated-CNTs/$Ca(OH)_2$ composite was prepared as follow. First a saturated $Ca(OH)_2$ solution was prepared, and nano-SiO_x was added into $Ca(OH)_2$ solution and mixed by hand for 2 min, then the CNTs were added and mixed was continued for another 5 min. The water/cement ratio of these pastes was 0.45, carbon nanotubes were added in the amount of 0.5% by weight of nano-SiO_x. Next, the mixture was poured into a glass bearer and dried in a vacuum drier at 25 ± 2 °C, and then the sample was also kept in a hermetic glass bottle.

2.3. Testing procedures

Electrical resistance measurements were made at a four-probe method after 28 days curing [11]. In this method,



(a) Sample configuration for electrical resistance measurement



(b) Schematic diagram for pressure-sensitive properties testing

Fig. 2. Sample configuration and schematic diagram of pressure-sensitive properties testing. All dimensions are in mm. A, B, C and D are the four electrical probes.

four electrical contacts were applied by embedding four pieces of copper flake along the length of the specimen (Fig. 2a), such that the outer contacts (for passing current) were about 60 mm apart and the inner contacts (for measuring the voltage in relation to resistance determination) were about 40 mm apart. At least six specimens of each composite were tested. The electrical resistance testing apparatus used was 34401 A Digit multimeter. Electrical resistivity was obtained from the measured electrical volume resistance. The relationship between electrical volume resistivity ρ_V and volume resistance R_V is as follows:

$$\rho_V = \left(\frac{A}{L}\right) \times R_V$$

Here A is the cross-sectional area of the contact area between copper flake and nanocomposites, L is the inner electrical contacts length.

Pressure-sensitive properties test was carried out as follow (Fig. 2b). A compressive load was applied by using a hydraulic mechanical testing system (MTS) with a 100-kN maximum loading capacity, the displacement rate was 0.50 mm/min, and the maximum application compressive loading was 15 KN. All of the measurements were automatically recorded through a data logger.

The microstructures of the different composites were observed using a Philip XL 30 scanning electron microscope at an accelerating voltage of 25 kV. The sample was coated with a thin layer of gold before observation.

3. Results and discussion

3.1. Morphology

A typical TEM micrograph shown in Fig. 1 reveals that the CNTs powder contains carbon nanotubes with diameters from 10 to 30 nm. Fig. 3 is the typical SEM image of PCNT, it can be seen that the untreated-CNTs were embedded in cement matrix and four features can be noted. First, untreated-CNTs dispersed uniformly in the composite and there is no obvious aggregation of untreated-CNTs. Second, the untreated-CNTs contact each other to form a well three-dimensional meshwork. Third the effect of bridging up cracks provided by untreated-CNTs can be observed. Fourth, untreated-CNTs with glossy surface were curved and clung to cement matrix, which is different from that of the carbon fibers [10].

Fig. 4 is a typical SEM image of SPCNT. It can be observed that the treated-CNTs were also dispersed uniformly in the composite and there is no obvious aggregation of CNTs. By comparing Figs. 4 with 3, it can be

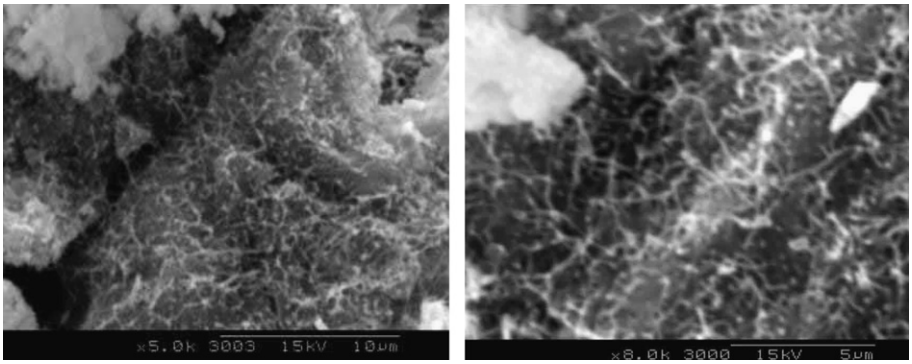


Fig. 3. Typical SEM image of untreated-CNTs reinforced cement matrix composites.

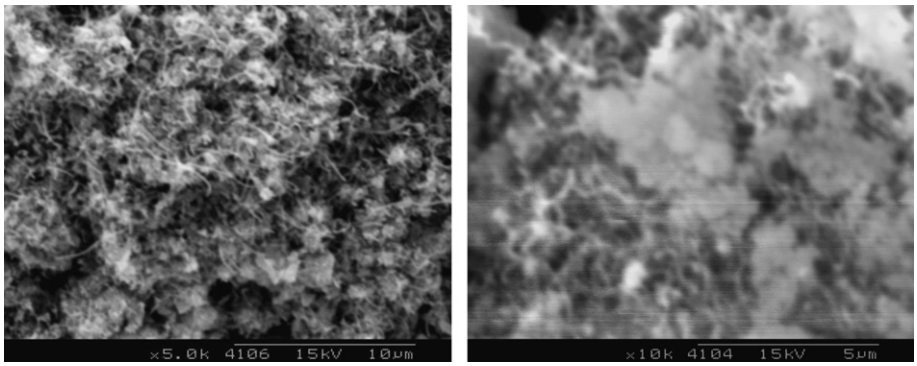


Fig. 4. Typical SEM image of treated-CNTs-reinforced cement matrix composites.

seen that the contact points of the treated-CNTs in SPCNT were much fewer than those of the untreated-CNTs in PCNT, no three-dimensional meshwork can be observed. The microscopic observation also reveals that the surface of treated-CNTs was covered by C–S–H, which is corresponding with the former research results of Li [7].

Fig. 5a and b are the typical SEM images of nano-SiO_x/treated-CNTs/$Ca(OH)_2$ composites. The low-magnification image (Fig. 5a) reveals that the treated-CNTs with length less than 100 μm were dispersed uniformly in this paste. The high-magnification image (Fig. 5b) reveals that the treated CNTs were covered by hydrated products; the diameter of the tube (larger than 5 μm) in the composite was about 100 times broader than that of pure CNTs (10–30 nm). Fig. 5c and d are the typical SEM images of nano-SiO_x/untreated-CNTs/$Ca(OH)_2$ composites; obvious aggregations of the untreated-CNTs in this sample can be observed; and the surface of the untreated-CNTs was glossy.

3.2. Mechanical properties

Table 4 shows both the compressive strengths and the flexural strength of PCNT and SPCNT after 28 days curing. This clearly shows that the compressive strengths of SPCNT are about 2.7 MPa higher than that of PCNT. It is also seen that the flexural strengths of cement-based composites increase due to the addition of treated carbon nanotubes. SPCNT has a higher flexural strength, about 0.4 MPa higher than PCNT.

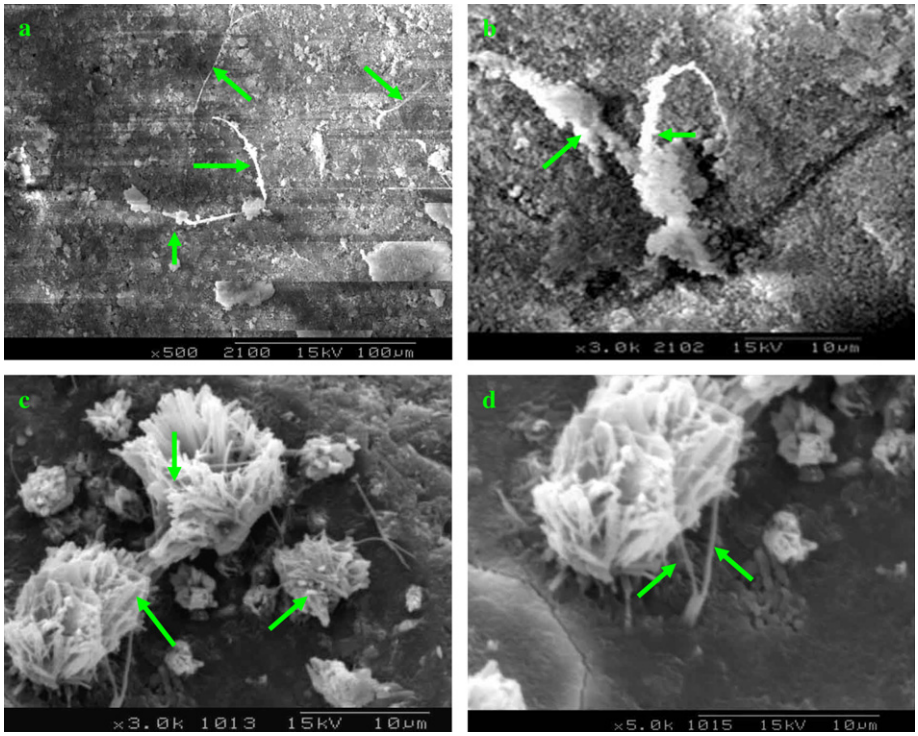


Fig. 5. Typical SEM image of treated CNTs/nano-SiO_x/$Ca(OH)_2$ composites: (a and b) for nano-SiO_x/treated-CNTs/$Ca(OH)_2$ composites; (c and d) for nano-SiO_x/untreated-CNTs/$Ca(OH)_2$ composites: (a) low-magnification image; (b) close-up of treated-CNTs indicated by arrows; (c) aggregation of CNTs indicated by arrows; (d) close-up of untreated-CNTs indicated by arrows.

Table 4
Strengths of different cement pastes after 28 days curing

Mix	Compressive strength (MPa)	Flexural strength (MPa)
PCNT	69.41 ± 3.3%	9.56 ± 3.6%
SPCNT	72.13 ± 4.2%	9.97 ± 2.7%

3.3. Electrical properties

According to Cao et al. [11], the time for the completion of depolarization was around 1000 s, and the time for polarization saturation was about 100 s for cement composites. In order to eliminate the effect of electric polarization and depolarization of cement-based materials on compressive sensitivity testing results, the measured resistance value at 1000 s was chosen as the initial resistance for each specimen. The resistance measurement was performed continuously more than 1500 s. The average resistance value from 1000 to 1500 s was determined as the electrical resistance for each specimen. The average value of six specimens is used as an index of the electrical resistance for one mix. As shown in Fig. 6, the volume electrical resistance of PCNT and SPCNT were about 130 and 149 ohm cm, respectively. The higher volume electrical resistance of SPCNT than those of PCNT may be due to: (1) the contact points of the treated-CNTs in SPCNT were fewer than those of untreated-CNTs in PCNT because the treated CNTs were covered by C–S–H. As demonstrated by SEM (Fig. 3) a well three-dimensional meshwork was formed in PCNT, whereas the treated-CNTs were covered by C–S–H, no meshwork could be observed in SPCNT. (2) The electrical conductivity and field emission of CNTs may decrease due to treatment. Recently it was reported that oxidative treatment by concentrated aqueous acids led to opening of the capped ends, and the opened CNTs were far less efficient emitters than closed CNTs due to the change in the work function that arose from the state of the tip [12]. For the same electric field and same space, the treated CNTs, therefore, produce a lower current density than that of the untreated CNTs. These results indicate that electrical conductivity of CNT-reinforced cement composites is dependent on the structural form of CNTs such as walls and caps structures, density as well as the contact points of CNTs.

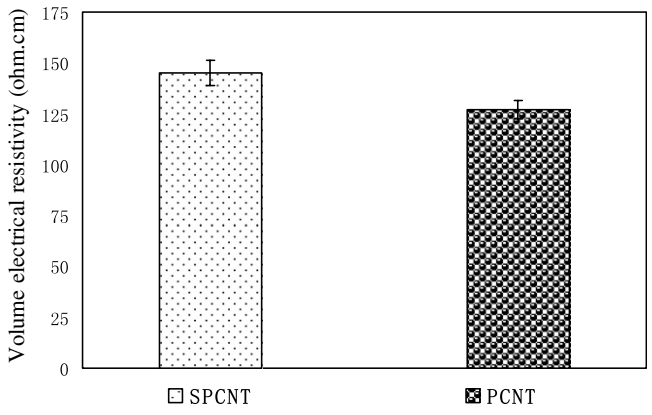


Fig. 6. Volume electrical resistivity of different mixes after 28 days curing.

3.4. Pressure-sensitive properties

Fig. 7 depicts the variations features of the resistivity of SPCNT and PCNT compositions under repeated compressive loading, respectively. The measured direction of the resistance is along the stress direction. The figure shows that the electrical resistances for SPCNT and PCNT remarkably changed under repeated compressive loading. The high sensitivity for PCNT and SPCNT is due to: (1) the electric conductivity of CNTs varies with stress (According to Tombler [13], the resistance of carbon nanotubes will increase 100 times when strain changes from 0.0% to 3.2% under tensile loading); (2) the number of contact points of CNTs increase with the increase of loading, and the more the contact points are the lower electric resistivity will be; (3) the effect of field emission on electric resistivity varies with stress. CNTs have a strong field emission property under electric field [14–17]. The shorter is the space among CNTs, the higher the field emission current density of the composites will be. With the application of the compressive force, the nanotubes are compelled to approach each other, which makes the field emission current flows become more intense.

Fig. 7 also shows that the relationship of resistivity along stress for PCNT was 10%, and the fractional change of resistivity of SPCNT was about 14%. As shown in Fig. 3, a three-dimensional meshwork was formed for PCNT leading to that the number of contact points of CNTs had relatively fewer changes with the variation of compressive load. Whereas, CNTs of SPCNT were covered by C–S–H, and no meshwork was formed (Fig. 4). This kind of microstructure leads to that both the contact points and the distances among tubes noticeably vary with the variation of applied compressive force. As a result the compressive sensitivity of SPCNT is higher than that of

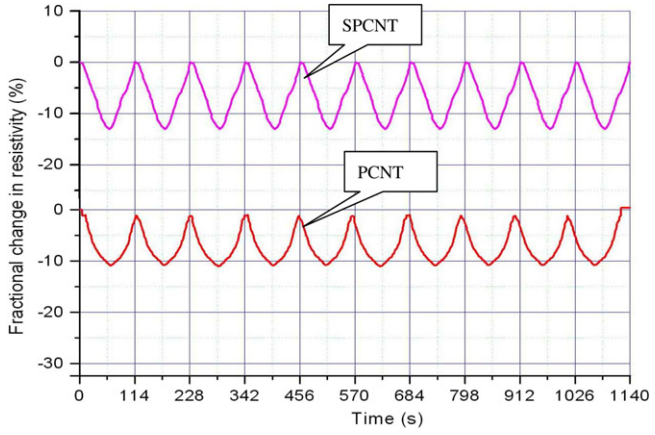


Fig. 7. The fractional change in resistivity vs. time under cyclic compressive loading (0–15 KN).

PCNT, though the latter has a higher electric conductivity. Evidence indicates that the deformation of CNT-modified cement composites can be detected without using traditional instruments.

4. Conclusions

The electrical resistivity, pressure-sensitive properties, mechanical properties as well as microstructure of the cement composites containing carbon nanotubes have been investigated through the experimental research. Both untreated-CNTs and treated-CNTs by using a H_2SO_4 and HNO_3 mixture solution can greatly decrease the electrical resistivity and improve pressure-sensitive properties for cement composites. The treated-CNTs have a stronger effect on enhancing pressure-sensitive properties, whereas the untreated-CNTs have more forceful effect on reducing electrical resistivity. The forceful effect on reducing electrical resistivity for the untreated-CNTs is mainly due to the formation of a well meshwork, as demonstrated by SEM. Microscopic observation reveals that the treated-CNTs were covered by C–S–H, and no meshwork was formed. This microscopic characteristic leads to that the contact points and distance among tubes mightily changes with the variation of compressive force. As a result the pressure-sensitive property of SPCNT is more intensive than that of PCNT. The mechanical properties of these composites were investigated and compared to control Portland cement matrix composite and the widely used carbon fiber-reinforced cement matrix composites. It is found that carbon nanotube-reinforced cement matrix composite shows a strong reinforced effect on flexural strength, compressive strength as well as failure strain.

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