AUTOCONTRACȚIA COMPOZITELOR PE BAZĂ DE CIMENT RANFORSATE CU NANOTUBURI DE CARBON LA PERIOADE SCURTE DE ÎNTĂRIRE
EARLY-AGE AUTOGENOUS SHRINKAGE OF HIGH PERFORMANCE CARBON NANOTUBES REINFORCED CEMENT-BASED COMPOSITES

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Mechanical performances of carbon nanotubes reinforced cement-based composites have been studied separately. The autogenous shrinkage of cement-based composites doped with multi-walled carbon nanotubes (MWNTs) were investigated with low MWNTs concentration of 0, 0.05%, 0.1% and 0.15% by weight(wt%) of cement in the early age in this paper. Ultrasonic processing and a commercially surfactant were utilized to achieve homogenous MWNTs suspensions. The addition of MWNTs decreased the autogenous shrinkage of cement composites compared to the reference sample. When the MWNTs dosage was 0.15 wt%, the autogenous shrinkage of specimen was the minimum, which was 28% lower than the reference sample. The water-cement ratio affects the early-age autogenous shrinkage more obviously. The results indicated that MWNTs can also have a beneficial effect on the early strain capacity, the early-age and long term durability of the cement-based composites.

Keywords: *Multi-walled carbon nanotubes; cement-based composites; durability; early-age autogenous shrinkage*

1. Introduction

As its low cost and high compressive strength, Portland cement has been used as the major construction material all over the world. However, these cement-based materials also exhibit extremely brittle failure, low tensile capacity and appear sensitive to early-age micro-cracking as a result of volumetric changes due to high autogenous shrinkage stresses. These characteristics of cement-based materials affect the long term durability of structures seriously. By improving the microstructure of cement-based materials, nano-materials have the great potential of enhancing the material mechanical properties and durability. Nanotechnology has made it possible to use carbon nanotubes and nanofibers as nano-reinforcement in cement-based composites [1-3].Since discovered in 1991 [4], multi-walled carbon nanotubes (MWNTs) are considered as one of the most beneficial material for nano-reinforcement [5,6]. The high physical strength, good chemical resistance and electrical properties make them as an attractive candidate for reinforcement of composite materials [7-10], including in concrete field. Especially, their higher aspect ratio is expected to effectively arrest the nano-cracks and demand significantly higher energy for crack propagation. Previous works on MWNTs reinforcing cement-based materials have focused on its mechanical and durability performance in the literature[11,12].

In this study, the 0, 0.05%, 0.1% and 0.15% weight fraction of MWNTs were incorporated to cement matrix. Autogenous shrinkage experiments in the early age (from the initial set ting to 7 days age) were conducted to determine the effect of the MWNTs on the early strain capacity of the cement composites. Field emission scanning electron microscopy (FESEM) was employed to study the morphology and the microstructure of the cement-based composites.

2. Experimental procedures

2.1. Materials

The cement used in this study was P.O 42.5R cement, which produced by Dalian Onoda Cement Co., Ltd., China, its chemical composition is shown in Tab.1 and Tab.2. Vapor grown MWNTs (length: μm; diameter: nm) were purchased from Shenzhen Nanotech Port Co., Ltd., China; their physical parameters are shown in Tab.3 and the microstructure of MWNTs is shown in Fig.1. The defoamer and the utilized surfactant were provided by SINOPHARM Chemical Reagent Co., Ltd., Shenyang, China; the polycarboxylate-based water-reducing agent (superplasticizer) was supplied by Dalian Mingyuanquan Group Science & Technology Development Co., Ltd., China. The fine aggregate used was China ISO Standard Sand with the

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Table 1

Chemical composition of P·O 42.5R cement

CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O_{eq}
61.13	21.45	5.24	2.89	2.50	2.08	0.77

Table 2

Physical properties of P·O 42.5R cement

Loss on ignition (%)	Specific surface area (m^2/kg)	Setting time (min)		Compressive strength (MPa)		Flexural strength (MPa)	
		Initial setting	Final setting	3d	28d	3d	28d
2.76	319	176	229	29.8	52.5	6.2	8.2

Table 3

Physical parameters of MWNTs

Length (μm)	Diameter (nm)	purity (%)	Special surface area (m^2/g)	density (g/cm3)
5~15	20~40	>97	90~120	1.6

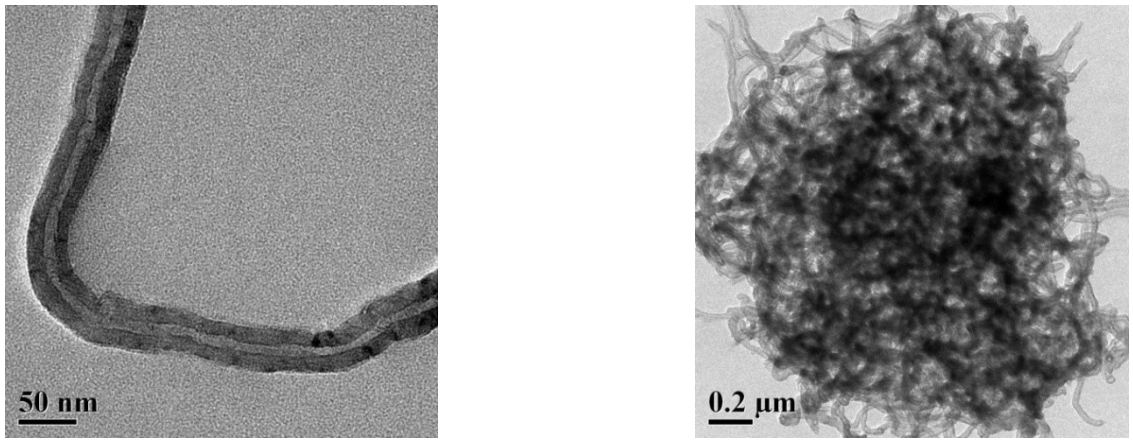
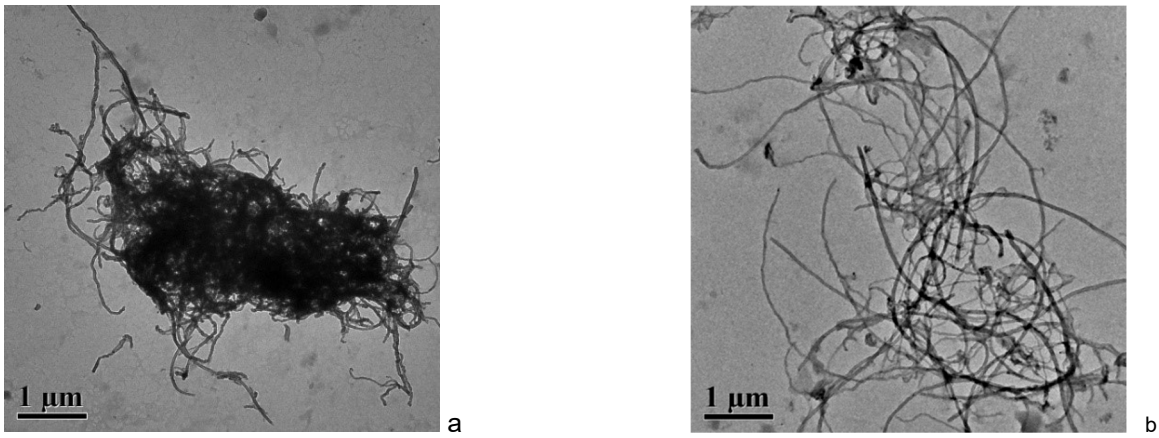


Fig.1 - The morphology of MWNTs



a b

Fig. 2 - TEM images of MWNTs in aqueous solution: (a) before dispersion; (b) dispersed by GA

execution criterion of GSB08–1337–2001 from Xiamen ISO Standard Sand Co., Ltd.

2.2 Preparation

According to the previous research, MWNTs were dispersed in aqueous solution using ultrasonic energy with the chosen surfactant (Gum Arabic, (GA)) and the optimum GA to MWNTs ratio of 6:1 by concentration was required to achieve homogenous distributed aqueous GA solution [1]. The homogenous MWNTs suspensions were gained after ultrasonic processing (DS-3510DT, Shanghai Sonxi Ultrasonics Instrument Co., Ltd., China, operating frequency 40 KHz, power 180W) for 30 minutes. Fig.2 shows TEM images of MWNTs in aqueous solution before and after the addition of GA dispersant.

The prepared homogenous MWNTs suspension, defoamer and superplasticizer were

Table 4

The mix proportion of cement/MWNTs composites

Sample	Water to cement ratio	Cement to sand ratio	Mix proportion (wt. %)			
			MWNTs	GA	TBP	Superplasticizer
P0	0.35	1:1.5	0	0	0.13	0.05
T1	0.35	1:1.5	0.05	0.3	0.13	0.05
T2	0.35	1:1.5	0.10	0.6	0.13	0.05
T3	0.35	1:1.5	0.15	0.9	0.13	0.05
W1	0.30	1:1.5	0.10	0.6	0.13	0.05
W2	0.35	1:1.5	0.10	0.6	0.13	0.05
W3	0.40	1:1.5	0.10	0.6	0.13	0.05

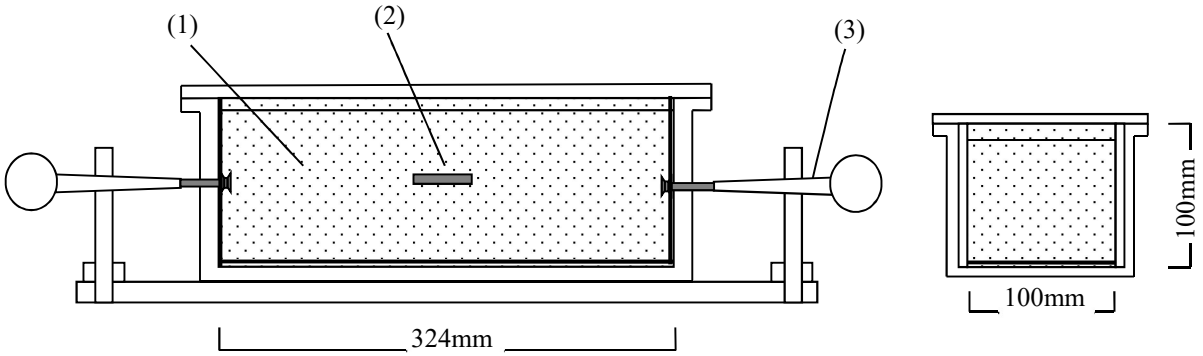


Fig.3 - The schematic diagram of autogenous shrinkage measuring device: (1) test mold; (2) temperature meter; (3) dial gauge stand.

mixed with cement and sand in a mixer for 6 minutes. After 6 minutes, the prepared mixture was poured into a stainless steel shaped mold. Then the mold was placed in a standard curing box, the temperature inside which was 20 ± 2 °C and the relative humidity was over 90%.The reference sample was labeled as P0. One group of samples were labeled as “T1”, “T2” and “T3”, respectively. Another group of samples were labeled as “W1”, “W2” and “W3”, respectively. The cement to sand ratio was 1:1.5 and the mix proportion of these samples is shown in Table 4.

2.3. Testing Procedures

2.3.1. Autogenous Shrinkage Testing

The autogenous shrinkage of cement composites was studied using a modified version of Chinese Standard GB/T50082-2009. Specimens were made for 100mm × 100mm × 324mm and sealed immediately after casting. Autogenous shrinkage of cement composites was tested with mold. The measuring device consisted of the following three parts: test mold, temperature meter and dial gauge stand. The insole lining of sealing mold is a layer of polytetrafluoroetylene. There are two PMMA pluggable plates inside of mold. One gasket was set between sealing cover and mold. On the ends of mold, there are two holes which measuring heads could be out. In the whole process of testing, the mold and dial gauge stand should be avoided from vibration. The schematic diagram of autogenous shrinkage measuring device is shown in Fig.3.

The autogenous shrinkage was calculated by this formula:

$$\varepsilon_t = \frac{(L_{10} - L_{1t}) + (L_{20} - L_{2t})}{L_0}$$

Where ε_t is the autogenous shrinkage at the time of ‘t’, L_{10} is the initial reading of dial gauge on the left (mm), L_{1t} is the reading of dial gauge on the left at the time of ‘t’ (mm), L_{20} is the initial reading of dial gauge on the right (mm), L_{2t} is the reading of dial gauge on the right at the time of ‘t’ (mm), and L_0 is the distance between two measuring heads(mm).

2.3.2 Microstructure

After mechanical properties test, the samples were crushed for the size about 5mm × 5mm × 1mm. An ultra-high resolution field emission scanning electron microscopy (FE SEM) (NOVA NanoSEM 450, FEI Co., Ltd., USA) and an energy-dispersive X-ray spectroscopy (EDS) (Oxford INCA-7260, FEI Co., Ltd., USA) were used to analyze the microstructure of the samples. Before the observation, the samples should be coated with a 20nm thick Au film to enhance surface conductivity.

3. Results and Discussion

3.1 Autogenous Shrinkage

Typically, changes in the nanostructure affect the transport properties (properties that are related with the movement of the water in the pores). Recently, it has been increasingly

recognized that high strength and high performance concrete is sensitive to the microcracking that occurs at early ages, as a result of the volumetric changes due to the development of high autogenous shrinkage stresses [14]. Fig.4 shows the autogenous shrinkage results of the reference sample and samples reinforced by MWNTs. Compared to the reference sample, the samples reinforced by MWNTs exhibited lower shrinkage. Furthermore, it is observed that the samples reinforced with higher amount of MWNTs demonstrated lower autogenous shrinkage. From setting time to one day, curve of autogenous shrinkage developed rapidly. When MWNTs dosage was 0.15 wt%, the autogenous shrinkage of specimen was the minimum, which was 28% lower than that of reference sample.

The shrinkage development is known to be proportional to the amount of the fine pores (pores with diameter < 20 nm) in the binder at early ages [15, 16].The reducing of autogenous shrinkage is attributed to the addition of MWNTs. Due to their small diameters MWNTs appear to reduce the amount of fine pores. This leads to the reduction of the capillary stresses, which result in lower autogenous strains. However, at the relative high concentration of MWNTs, MWNTs are easily agglomerated in the mixes and weak bond between agglomerated MWNTs and partial hydration products is formed. That's why there is little difference between curve T2 and curve T3.

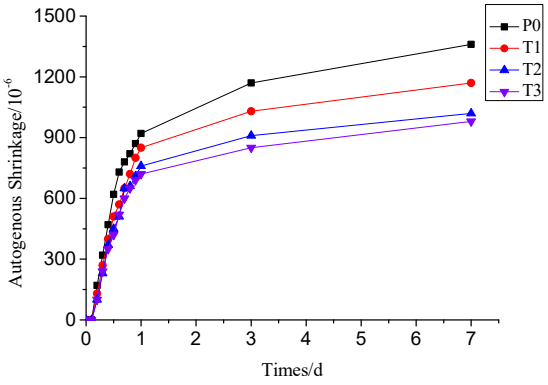


Fig. 4 - Autogenous shrinkage of reference cement mortar (w/c=0.35) and cement composites reinforced with MWNTs.

As it is shown in Fig.5, water-cement ratio affects early-age autogenous shrinkage more obviously. As the water-cement ratio increases, autogenous shrinkage presents decreasing trends. At one day age, the autogenous shrinkage of specimen W1 was about 50% larger than that of specimen W3. After three days curing age, the autogenous shrinkages developed slowly at almost the same rate. When water-cement ratio is small, the content of free water that contributes to cement hydration inside the specimen reduces, and the internal relative humidity decreases rapidly. At the same time, the pores become smaller and the critical radius (r_0) reduces, thus autogenous shrinkage value caused by drying is larger.

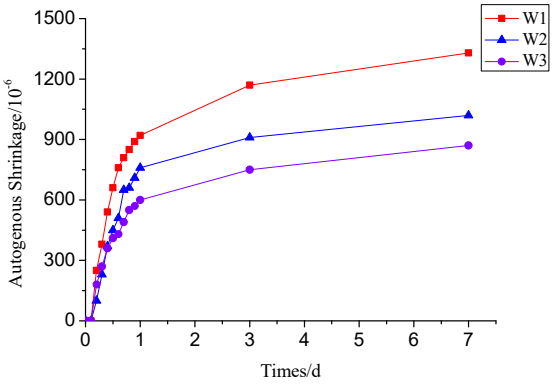


Fig.5 - Autogenous shrinkage of cement composites reinforced with 0.1 wt% MWNTs.

3.3 Microstrucutre analysis

Fig.6 shows the microstructure of the sample with 0.1 wt% MWNTs incorporation. The

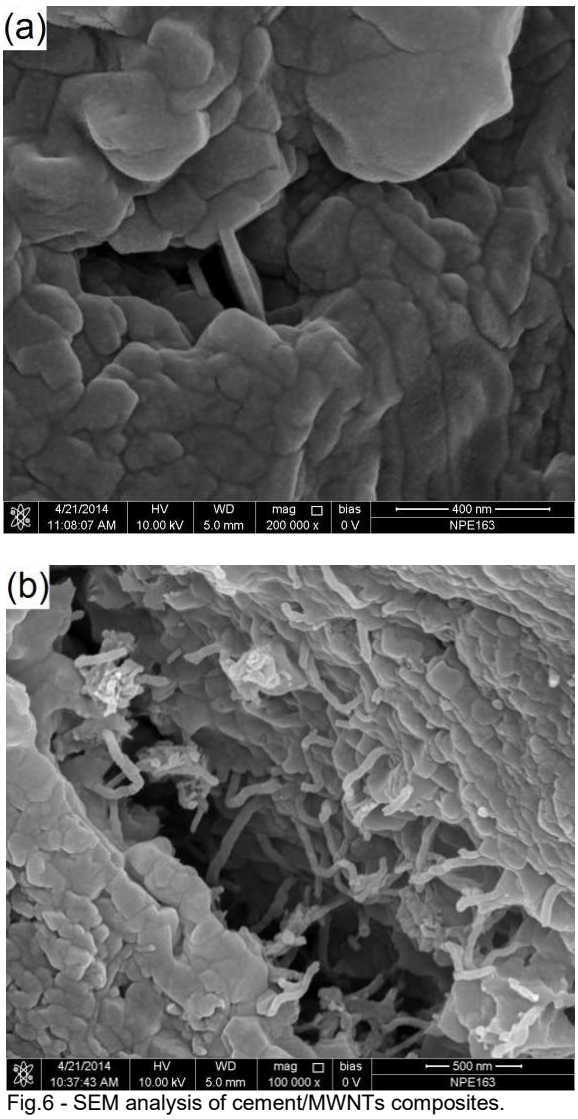


Fig.6 - SEM analysis of cement/MWNTs composites.

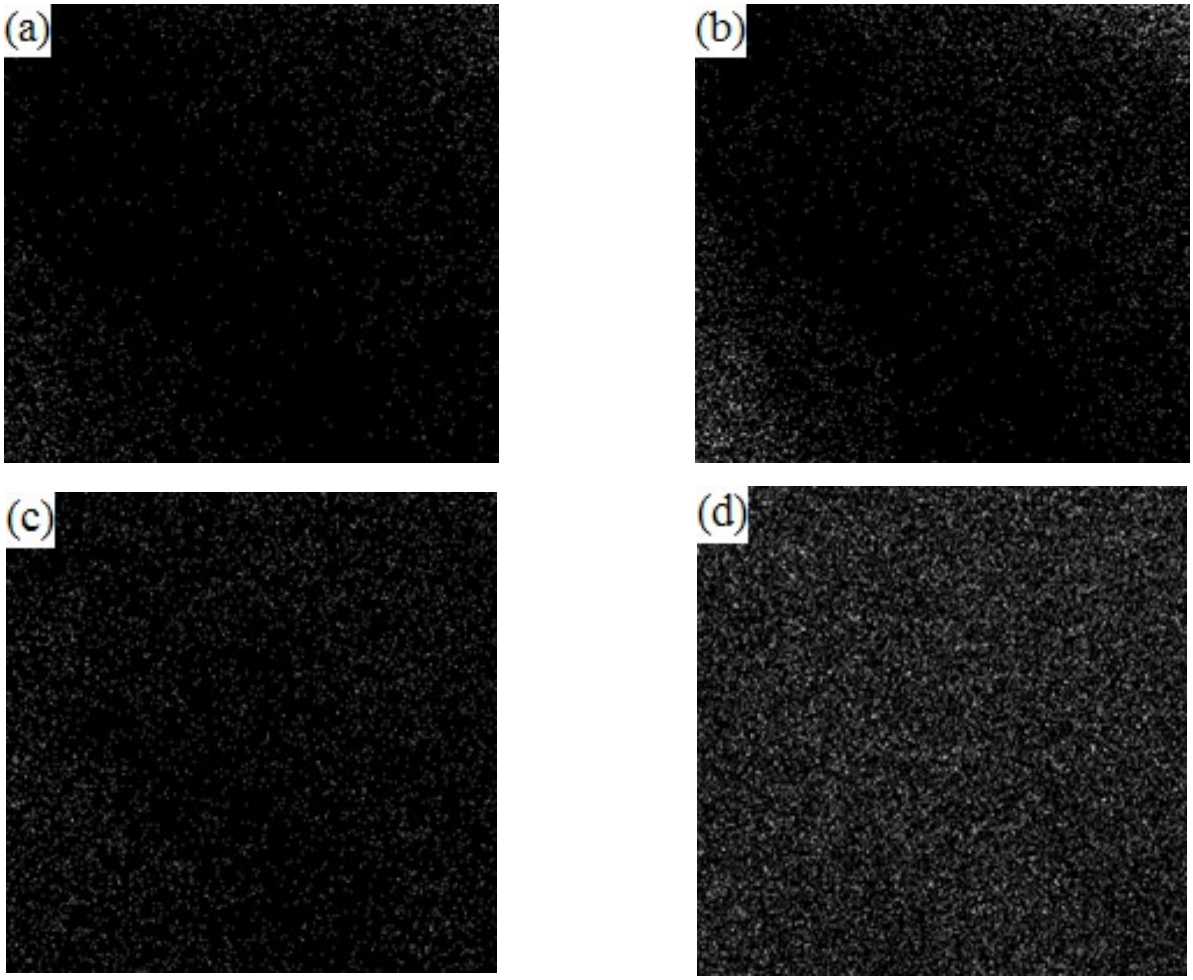


Fig.7 - EDS mapping of cement/MWNTs composites incorporating 0.1 wt% MWNTs at 28 days: (a) carbon; (b) oxygen; (c) silicon and (d) calcium

diameter of the observed MWNTs is about 15nm, which agreed with the manufacturer's report. The fracture surface of MWNTs-cement composites shows a uniform and compact structure and more gelatinous mass. Typical SEM analysis illustrates that the MWNTs act as bridges and networks across voids and cracks, and integrated with the cement hydration products closely so that harmful substances invasion are under effective control [17,18]. Meanwhile, the embedded MWNTs are wrapped a surface coating of hydration products, which indicates the high bonding strength is obtained between the MWNTs and the matrix.

3.4 EDS Analysis

Energy-dispersive X-ray spectroscopy (EDS) has been widely used to characterize the distribution of element in cement-based materials [19-21]. In this research, EDS technique, in combination with SEM, was employed to analyze the distribution of MWNTs in cement matrix. Fig.7 (a)~(d) shows the EDS mapping of MWNTs-cement composites incorporating 0.1 wt% MWNTs in Fig.6 (b), presented as different elements (carbon, oxygen, silicon and calcium). Carbon, the main constituent of MWNTs, is found to disperse between the hydration products of cement matrix in Fig.6 (b).

Additionally, EDS technique quantificationally confirmed the quantity of MWNTs in matrix. For the selected area in Fig.6 (b), the amount of carbon (by weight) is 4.38%. The detected amount of oxygen, sodium, aluminum, silicon, calcium, potassium and calcium, shown in Tab.6, are 20.14%, 0.58%, 0.90%, 2.11%, 1.30% and 70.59%, respectively. These given percentages indicate the composition of MWNTs and the hydration products in matrix.

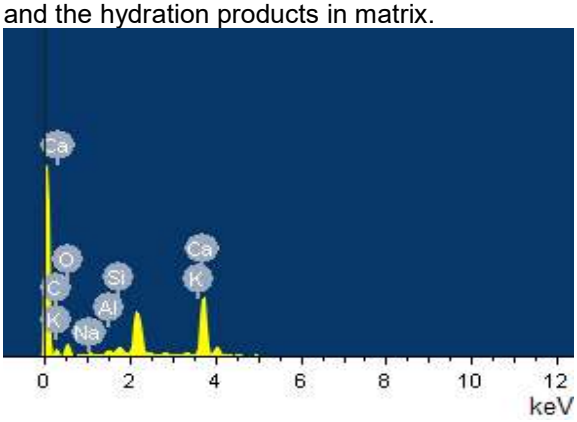


Fig.8 -EDS analysis of cement/MWNTs composites from Fig.6 (b).

Table 5

Elemental analysis of EDS mapping from Fig.6 (b)

Element	Weight (%)	Atomic (%)
C	4.38	10.26
O	20.14	35.45
Na	0.58	0.71
Al	0.90	0.94
Si	2.11	2.11
K	1.30	0.94
Ca	70.59	49.59
Total	100.00	

4. Conclusions

In this paper, the early-age autogenous shrinkage and microstructure of cement-based materials incorporating MWNTs with concentration of 0, 0.05%, 0.1% and 0.15% by weight of cement were investigated. Compared to the reference sample, the added MWNTs decrease the autogenous shrinkage of cement composites. When MWNTs dosage was 0.15 wt%, the autogenous shrinkage of specimen was the minimum, which was 28% lower than the reference sample. The water-cement ratio affects the early-age autogenous shrinkage more obviously. with the water-cement ratio increases, the autogenous shrinkage presents decreasing trends.

In addition, SEM micrographs show that the embedded MWNTs act as the bridges and networks across voids and cracks. Ultimately, the MWNTs have a beneficial effect on the early strain capacity of the cement composites, improving this way the early-age and long term durability of the cement composites

Further researches are necessary to obtain better homogeneity of MWNTs/cement composites and more characterizations are needed. Meanwhile, the mechanical, electrical and electromagnetic properties can be explored. We believe that our results, at least in the trend, are helpful for the research of MWNTs-cement composites.

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