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Mechanical Properties and Microstructure of Sulfur Aluminate Cement Composites Reinforced by Multi-walled Carbon Nanotubes

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Abstract: The effect of multi-walled carbon nanotubes (MWCNTs) on the mechanical properties and microstructure of sulfur aluminate cement (SAC) composites was investigated. The dispersed MWCNTs were added into SAC in various weight contents.The results of mechanical properties of the MWCNTs/SAC composites indicated that the addition of 0.08 wt% MWCNTs can improve the SAC compressive strength, flexural strength, and bend-press ratio by 15.54%, 52.38%, and 31.30% at maximum , respectively. The degree of SAC hydration and porosity and pore size distribution of the matrix were measured by X-ray diffraction (XRD), thermal analysis (TG/DTG), and mercury intrusion porosimetry (MIP). Results show that the addition of MWCNTs in SAC composites can promote the hydration of SAC and the formation of C-S-H gel, reduce the porosity and refine the pore size distribution of the matrix. The microstructure was characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). It is found that the MWCNTs have been dispersed homogeneously between the hydration products of SAC paste and act as bridges and networks between cracks and voids, which prevents the development of the cracks and transfers the load.

Key words: multi-wall carbon nanotubes(MWCNTs); sulfur aluminate cement (SAC); mechanical properties; microstructure

1 Introduction

Sulfur aluminate cement (SAC) is a kind of special cement with the unique properties such as early strength, fast hardening, low energy consumption and easy grinding. It is also well known as an eco-friendly construction material with only half of the carbon dioxide emission compared with conventional Portland cement. However, due to the characteristics of weak toughness and low tensile strength, this material can be vulnerable and easy to break, which may lead to short service life and impact construction safety. Therefore, it is crucial to enhance the toughness of SAC materials for better application in construction industry.

Multi-wall carbon nanotubes (MWCNTs) belong to the family of Fullerenes,which is composed of hollow cylindrical carbon nesting. In 1991, Iijima observed MWNTs composed of multiple concentric graphene cylinders with high resolution TEM for the first time[1]. Two years later, Iijima *et al* prepared successfully single carbon nanotubes (SWCNTs), which consisted of only one graphene sheet rolled into a cylinder[2]. Compared with SWCNTs, MWCNTs are comparatively cheaper and easier to produce, and they also have a higher dispersibility, giving them several advantages from an industrial viewpoint and thus making them more suitable for mixing with cement-based materials[3]. Carbon nanotubes (CNTs) have a lot of excellent properties[4-8]. For example, Treacy[9,10] and Yu[11] have reported that the Young's modulus of CNTs can reach 5 TPa with a density of around 2.0 g/cm^3. Additionally, Artukovic[12] and Cattanach[13] have shown that CNTs can be highly conductive, and compatible with flexible substrates. Because of their significant mechanical properties, MWCNTs have been used in ordinary portland cement in order to reinforce the cement composites[14-16]. Previous researchers[17] found that the 7-day compressive strengths of cement paste increased by 22% incorporating 0.1 wt% MWCNT.

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Parveen *et al*[18] investigated the effect of functionalized SWCNTs on the mechanical properties of cement composites and found that 0.1 wt% SWCNTs improved the flexural modulus of cement mortar by 72% and flexural and compressive strengths by 7% and 19% after 28 days curing.CampilloI *et al* analyzed the influence of CNTs on the compressive strength of cement based composites and found that the cement paste with MWCNTs showed a higher compressive strength than the one containing SWCNTs[19]. The dispersion and bonding strength with matrix of CNTs are the key to improve the mechanical properties of CNTs reinforced cement paste. On the one hand, SWCNTs are very difficult to disperse because they are easier to aggregate to form bundles or "ropes" than MWCNTs[3]. On the other hand, compared with SWCNTs, MWCNTs have many defects which can increase the interaction points with matrix and avoid sliding[19]. Based on the cost and dispersibility and interaction with matrix of CNTs, MWCNTs are often chosen to improve the mechanical properties of composites.

However, few studies have been made to use MWCNTs to enhance the mechanical properties of SAC composites. In this paper, we investigated the effect of MWCNTs on the mechanical properties and microstructure of SAC composites. Firstly, MWCNTs were dispersed in aqueous solution using gum arabic powder as the dispersing agent. And then, the MWCNTs suspensions were mixed into SAC paste with several different concentrations. The mechanical properties of MWCNTs/SAC composite were measured at 28 days of aging. In addition, the X-ray diffraction (XRD) and thermal analysis (TG/DTG) were used to explore the effect of MWCNTs on the degree of SAC hydration. The pore size distribution and microstructure of MWCNTs/SAC composite were studied using mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

2 Experimental

2.1 Materials

The MWCNTs with 5-15 μm in length and 20-40 nm in diameter were provided by Shenzhen NANO-Technology Co.Ltd.(see Table 1). The microstructure of MWCNTs is shown in Fig.1. The cement used in the experiments was SAC 42.5R cement (Sulfur aluminate cement). X-ray fluorescence spectrometer (XRF) was used to analyze its chemical composition. The result is shown in Table 2. The dispersant used to disperse MWCNTs was gum arabic (GA, AR), purchased from Sinopharm Chemical ReagentCo., Ltd., China.

Table1 Physical parameters of MWCNTs

Products	Outer diameter/nm	Length/μm	Purity/%	Ash/wt%	Special surface area /($m^2 \cdot g^{-1}$)
L-MWNTs	20-40	5-15	> 97	< 3	90-120

Table2 Chemical composition of SAC 42.5R cement/%

CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	TiO_2
44.09	13.45	20.38	2.38	14.82	2.34	1.33

2.2 Preparation

GA was used as the dispersant in the experiments. The ratio between GA dispersant and carbon nanotubes was set to be 6:1. The mixture of MWCNTs and GA solution was sonicated for 20 min[20].

Multi-walled carbon nanotubes/sulfur aluminate cement composites (abbreviated as MWCNTs/SAC composites) used in this work were prepared by adding different amounts of MWCNTs to sulfur aluminate cement, as 0 wt%(J30-0), 0.05 wt% (J30-5), 0.08 wt% (J30-8), 0.1 wt% (J30-10), 0.12 wt% (J30-12),and 0.15 wt% (J30-15). The cement pastes were cast into 40 mm×40 mm×160 mm size molds for further flexural and compressive strength tests. The water-cement ratio of the paste was 0.30. All specimens were demolded after 24 hours and then cured in water at room temperature for 28 days.

2.3 Testing procedures

After cured for 28 days, a series of tests were carried out based on standard GB/T 17671-1999. The flexural strength test was performed using the three point bending method with a WDW-50 electronic universal testing machine (span=100 mm,loading rate=0.20 mm/min). After the flexural strength test, a WAW-300 electro-hydraulic servo universal testing machine was used

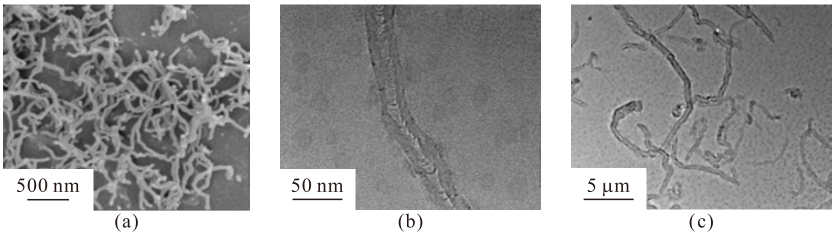

Fig.1 The microstructures of MWCNTs: (a) SEM image; (b, c) TEM images of MWCNTs

for compressive strength measurements. The hydration products of MWCNTs/SAC composites were analyzed by X-ray diffraction (XRD, D8 Advance, Bruker AXS Co., Karlsruhe, Germany).TG/DTG analysis was conducted by using a thermal analyser (TG/DSC, Mettler Toledo Stare, Mettler Toledo Co. Zurich, Switzerland). An AUTOPORE IV 9500 series MIP produced by MIC (Micromertics) was used for measuring the porosity and pore size distribution of the composites. The morphology and microstructure of MWCNTs/SAC composites were investigated using FESEM (NOVA NANOSEM450, FEI Co., USA) and EDS (Oxford INCA-7260, FEI Co., USA).

3 Results and discussion

3.1 Mechanical properties

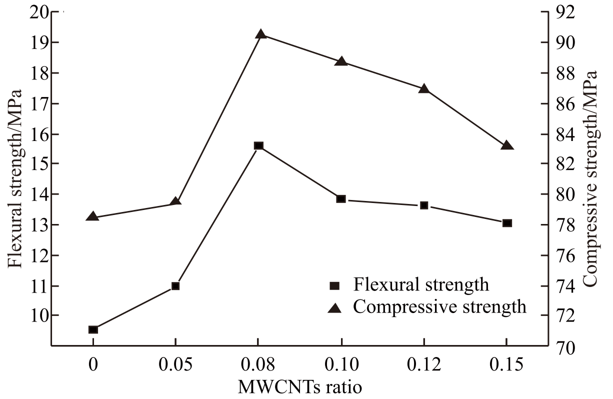

Fig.2 Flexural and compressive strength of MWCNTs/SAC with different MWCNTs (28 d)

Table 3 and Fig.2 present the results of both the flexural and compressive strength of MWCNTs/SAC samples after 28 days curing. It can be found that the flexural strength and compressive strength of the SAC paste increase and then decrease as the content of MWCNTs increases from 0 to 0.15 wt%, and reach the highest value at the same time as shown in Fig.2. The flexural strength reaches the highest value of 16.0 MPa at 0.08wt% of MWCNTs, which is 52.38% higher than that of the pristine cement sample. In addition, as shown in Table 3, adding the MWCNTs can enhance the compressive strength of SAC paste by 15.54% with 0.08 wt% of MWCNTs.

It is known that the bend-press ratio of the material can reflect the toughness of the material, *i e*, bigger bend-press ratio results in higher material toughness. Table 3 shows that with increasing content of MWCNTs, the bend-press ratio of the SAC paste shows similar trend as the flexural strength, reaching 31.34% increase in total with only 0.08 wt% MWCNTs addition.

3.2 XRD analysis

The effect of MWCNTs on the products of SAC hydration can be estimated using X-ray diffraction patterns. The XRD patterns of samples J30-0 and J30-8 are shown in Fig.3. Compared with sample J30-0, no new diffraction peak can be found in sample J30-8, suggesting that the addition of MWCNTs cannot change the type and structure of the final hydration products of SAC.

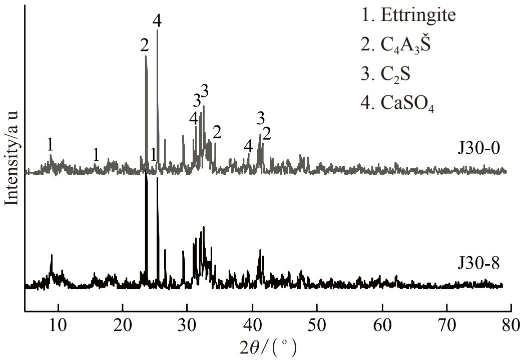

Fig.3 XRD analysis of samples J30-0 and J30-8

Additionally, the degree of SAC hydration can be characterized by monitoring the formation of hydration products and the consumption of SAC raw constituents qualitatively. The diffraction peak of ettringite in sample J30-8 is stronger than that in sample J30-0, indicating that the addition of MWCNTs can make ettringite crystallize better. Meanwhile, the intensity of unhydrated anhydrous calcium sulphoaluminate ($C_4A_3\check{S}$),

Table 3 Mechanical strength of the MWCNTs/SAC composites with different MWCNTs (28 d)

Sample	MWCNTs ratio / wt%	Flexural strength of 28 d/MPa	Compressive strength of 28 d/MPa	Flexural strength improvement/%	Compressive strength improvement /%	Bend-press ratio
J30-0	0	10.5	78.5	-	-	0.134
J30-5	0.05	11.8	79.5	12.38	1.27	0.148
J30-8	0.08	16.0	90.7	52.38	15.54	0.176
J30-10	0.1	14.4	88.7	37.14	12.99	0.162
J30-12	0.12	14.2	86.9	35.24	10.70	0.163
J30-15	0.15	13.7	83.2	30.50	5.99	0.165

dicalcium silicate (C_2S) and $CaSO_4$ is much weaker than that in sample J30-0, which indicates the higher hydration degree of sample J30-8. The XRD analysis results demonstrate that the MWCNTs can accelerate the hydration of SAC paste.

3.3 Thermal (TG/DTG) analysis

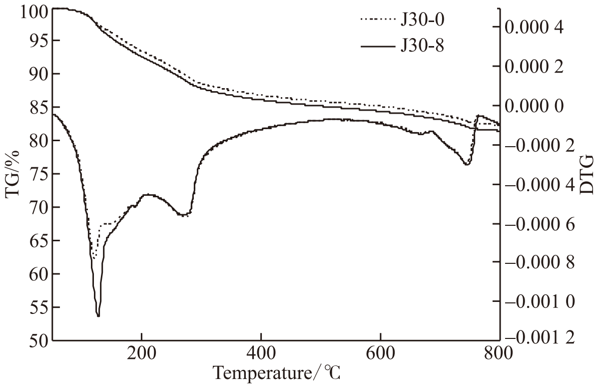

Fig.4 Thermal analysis (TG/DTG) of samples J30-0 and J30-8

TG/DTG is another method to investigate the hydration degree of SAC paste as a supplement to XRD analysis which cannot measure amorphous material. The TG/DTG curves of the two samples J30-0 and J30-8 are presented in Fig.4. The curves of the two samples have a similar trend, demonstrating that the MWCNTs don't induce the formation of any other phrase in accord with the result of XRD analysis. In Fig.4, there are three main losses in the DTG curve, corresponding to the dehydration of hydrated C-S-H gel (100-120 ℃) and AH_3 gel (290-300 ℃) and the decomposition of calcium carbonate (790-800 ℃) respectively. Compared with sample J30-0, the mass loss of the main hydration products of SAC in sample J30-8 is higher in Fig.4, especially the mass loss of C-S-H gel, which indicates that the content of hydration products is higher than that of sample J30-0. Thus, TG/DTG further demonstrates that the addition of MWCNTs can promote the hydration of SAC paste and be conducive to the formation of C-S-H.

3.4 Porosity and pore size distribution

The results of MIP analysis are shown in Table 4. The results show that the total intrusion volume of SAC paste is decreased and then increased with increasing MWCNTs percentage from 0% to 0.15 wt% by weight of SAC . Compared to other samples, the total intrusion volume of sample J30-8 is around 0.0604 mL/g, exhibiting the lowest total intrusion volume. Meanwhile, the total intrusion volumes of other samples are 0.081 4, 0.061 8, and 0.067 8 mL/g, respectively. In addition, the results indicate that all MWCNTs/SAC samples show lower porosity, and less total pore area and average pore diameter with respect to the reference sample (J30-0) in Table 4. With the addition of MWCNTs, the large pores in SAC paste have been filled. Fig.5 shows the relationship in logarithmic scale between the differential intrusion and different pore size diameter of the MWCNTs/SAC composites. The differential intrusion with pore size diameter of the MWCNTs/SAC moves to the right and the peak reduces, suggesting that the porosity and pore size of MWCNTs/SAC composite can be reduced with the addition of MWCNTs.

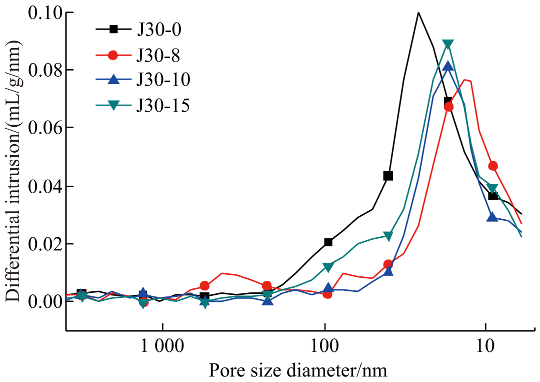

Fig.5 MIP analysis of pore size of MWCNTs/SAC composite

It is known that a lot of pores and voids can affect negatively the mechanical properties of cement material, because of its porous characteristics. From MIP analysis, it can be found that the MWCNTs can reduce the porosity and fine pore sizes of SAC matrix. Therefore, the mechanical properties of MWCNTs / SAC composite are enhanced because of the lower porosity and finer pore structure of the matrix.

3.5 Morphology

The morphology of MWCNTs/SAC composite

Table 4 MIP analysis of the prepared cement/CNFs composites

Sample	Total intrusion volume/(mL/g)	Total pore area/ (m^2/g)	Median pore diameter volume/nm	Median pore diameter area/nm	Average pore diameter/nm	Porosity/%
J30-0	0.0814	12.76	31.5	15.4	25.5	15.95
J30-8	0.0604	10.27	24.5	14.1	23.1	12.22
J30-10	0.0618	11.49	24.8	14.3	23.3	12.58
J30-15	0.0674	11.63	25.3	14.4	23.6	13.39

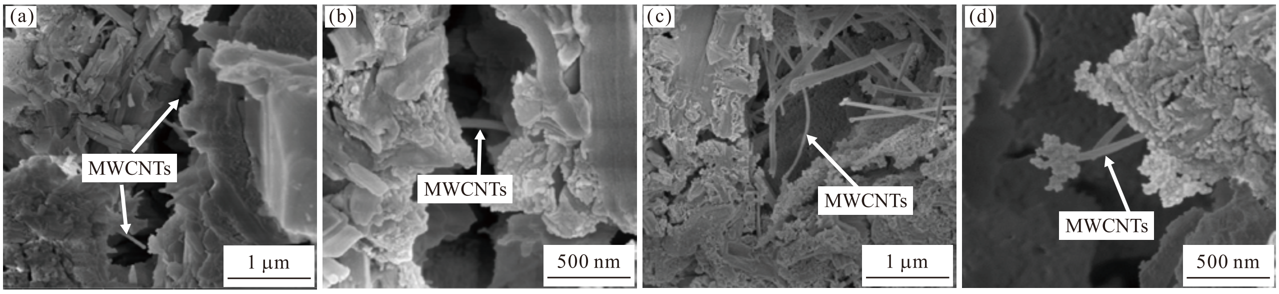

Fig.6 FE-SEM images of sample J30-8 after 28 days curing: (a) and (b) Crack bridging of MWCNTs; (c) Intertwine between MWCNTs and ettringite; (d) Pull-out of MWCNTs

Table 5 Elemental analysis of EDS

Element	C	O	Al	Si	Ca	S	Mg	Fe	K
Content/wt%	11.66	46.65	6.66	4.04	27.34	2.45	0.62	1.19	0.39
Content/at%	19.30	56.73	4.91	2.86	13.56	1.52	0.50	0.42	0.48

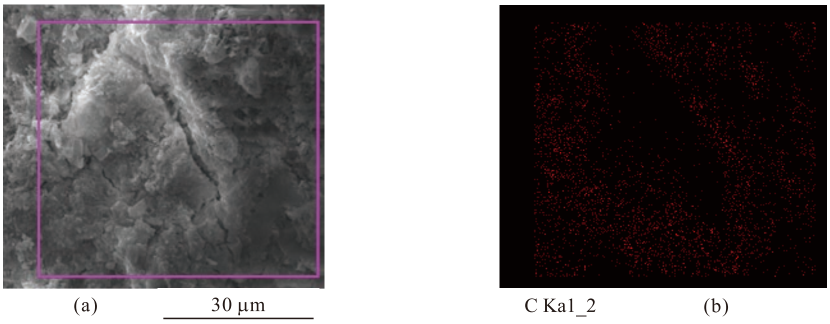

Fig.7 EDS mapping of sample J30-8 after 28 days curing: (a) SEM micrograph; (b) carbon

is shown in Fig.6. It can be found that the MWCNTs bridge between micro cracks in the composites, preventing the formation of more gaps within the material in Fig.6(a) and Fig.6(b). Fig.6(c) indicates that many MWCNTs are intertwined with the needle ettringite and form a network structure to improve the internal structure of hardened paste. As shown in Fig.6(d), the treated MWCNTs are pulled out from matrix, and a side of MWCNTs is wrapped tightly by the hydration products, which indicates that the bonding strength between the tubes and SAC cement matrix is high. The behaviors of MWCNTs in SAC matrix ensure good load-transfer efficiency from the SAC paste to MWCNTs, when the MWCNTs/SAC composite undergoes external load. As a result, the mechanical properties of MWCNTs/SAC composite could be improved significantly.

3.6 EDS analysis

EDS micro measurement technology has been widely used in the cement based materials. EDS technique can prove the existence of MWCNTs and confirm the amount of all elements in SAC paste, as shown in Table 5. For the area covered, the amount of carbon in the SAC composite with 0.08 wt% MWCNTs was 11.66% (proportion by weight). Additionally, oxygen, aluminum, silicon, calcium, sulfur and magnesium were 46.65%, 6.66%, 4.04%, 27.34%, 2.45% and 0.62%, respectively, which present the main composition of the hydration products of SAC paste. Further, Fig.7 is the EDS mapping of sample J30-8, which shows the distribution of carbon in the hydration products of SAC paste. Carbon, the main constituent of MWCNTs, is dispersed homogeneously on the surface of the hydration products of SAC as shown in Fig.7(b). Thus, the results can demonstrate that the MWCNTs have been dispersed homogeneously between the hydration products of SAC paste.

4 Conclusions

In this study, a series of concentrations of MWCNTs (0.05 wt%, 0.08 wt%, 0.1 wt%, 0.12 wt% and 0.15 wt%, respectively) were incorporated into SAC paste. The mechanical properties and microstructure of MWCNTs/SAC composite were investigated. Compared to the reference sample, the compressive strength, flexural strength and bend-press ratio of SAC paste reinforced with 0.08 wt% MWCNTs result in the greatest increase by 15.54%, 52.38% and 31.3%, respectively. XRD analysis and TG/DTG analysis show that the MWCNTs can accelerate the degree of SAC hydration and promote ettringite crystallization and the formation of C-S-H gel. Furthermore, the MWCNTs/SAC composite has a lower porosity and finer pore size distribution than those of the reference sample. The microstructure of the MWCNTs/SAC composite shows that the MWCNTs play a bridging role in SAC matrix, which transfers effectively load in case of tense. Meanwhile, there exist the MWCNTs pulled out from the matrix without rupture failure, indicating a higher bonding strength between MWCNTs and SAC matrix.

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