Research Article

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Humic acid assisted stabilization of dispersed single-walled carbon nanotubes in cementitious composites

https://doi.org/10.1515/ntrev-2019-0046
Received May 02, 2019; accepted Oct 03, 2019

Abstract: Significant research has been done in recent decades in the field of the dispersion of carbon nanotubes in aqueous solutions and the reinforcement of ordinary Portland cement (OPC). However, the cementitious mixture, as an alkaline environment, easily leads to the re-agglomeration of dispersed single-walled carbon nanotubes (SWCNTs) and influences their enhancing effects. Humic acid (HA) is a type of natural organic matter which can assist the stabilization of dispersed single-walled carbon nanotubes in cementitious composites. The present study characterizes the influence of HA in stabilizing the dispersion of SWCNTs by means of ultraviolet spectrophotometer tests. The fluidity of fresh cement slurry and mechanical performance of hardened OPC pastes were measured to better illustrate the dispersion of SWCNTs in real cement composites. The results not only reveal that the addition of an alkaline environment to the SWCNT suspensions results in a rapid decrease of the dispersion, but also suggest that the appropriate content of HA (0.12 wt.%) can play a significant role in stabilizing the dispersion of SWCNTs. When the mixed hybrid of SWCNTs and HA with a concentration of HA/c equal to 0.05 wt.% is used, the fluidity of the fresh cement slurry experiences a maximum decline and this mixture content of materials will dramatically increase the compressive and flexural strength by about 31% and 48%, which indicates that more SWCNTs are in a dispersed state under this concentration. SEM images further prove that a suitable HA/c can inhibit the expansion of cracks in the cementitious composites.

Keywords: Single-walled carbon nanotubes, humic acid, dispersed stabilization, cementitious

1 Introduction

Carbon nanotubes (CNTs), categorized as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), generally have low density [1, 2], high aspect ratio [3, 4], and superior mechanical properties [5–7]. By virtue of these superior properties, CNTs have found applications in reinforcing the strength and electrical properties [8] of different kinds of composites, including organic polymers [9, 11], ceramics [12], metal [13], biomaterials [14, 15] and cement-based composites [16, 17]. Research on cementitious composites containing CNTs shows that these kinds of materials can improve their properties through the crack-bridging effect, pulling-out behavior and nano-filling function [18–22].

Sadly, pristine CNTs attach to each other easily by van der Waal’s interaction due to the high aspect ratio [23, 24], and CNT bundles or agglomeration acting as defects in the cement pastes will cause a stress concentration and induce more cracks [25]. Therefore, the uniform dispersion of CNTs is the key when incorporating them into cement-based pastes, because only individually distributed CNTs are effective in terms of nano reinforcement [19, 25, 26]. According to previous studies [20, 27, 28], combining ultrasonication with the assistance of polycarboxylate superplasticizer (PC) is the most effective method to disperse CNTs during the preparation of suspensions. However, when well-dispersed CNTs are mixed into fresh cement slurry, more than 95% of the CNTs exist in the pore solution, which is full of various ions such as Na⁺, K⁺, Ca²⁺, SO₄²⁻ and OH⁻ [29, 30]. These ions will seriously influence the stabilization of the dispersed CNTs [29]. Before the hardening of the fresh pastes, the individual CNTs may attach to each other over a period of time and re-agglomerate together, because the chemical reaction be-

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tween the above-mentioned icons and CNTs reduces the steric repulsion [25]. Furthermore, due to the higher specific areas of SWCNTs compared with MWCNTs [2], the stabilization of the dispersed SWCNTs in a fresh cementitious environment is significant if they are to play their role in strength enhancement.

Natural organic matter (NOM) is ubiquitous [31], originating from the chemical or biological decomposition of animals and plants. The main components of NOM are humic acid, proteins [32], polysaccharides [33], and compatible acids [34]. Yang et al. [31, 35] found that NOM can adsorb on the surface of CNTs by electrostatic interaction, \(\pi-\pi\) interaction, hydrophobic interaction and hydrogen bonding, assisting the dispersion of CNTs in water. Humic acid (HA), one of the most commonly used NOM in biological fields [36], has been used to delay the re-agglomeration of CNTs in both neutral and alkaline environments [37, 38]. This is because the hydrophobic surface properties of the CNTs are associated with biological macromolecules [37]. Han et al. [39] have found that the addition of 1 and 5 mg L\(^{-1}\) HA can greatly increase the stabilization of the degree of dispersion of carbon black nanoparticles in an aquatic environment. Saleh et al. [37] proved that the mixed HA in solution significantly improved the colloidal stability of CNTs, reducing the aggregation rate by about 2 orders of magnitude. Yang et al. [38] further found that HA enhanced the dispersibility of nanobiochar in an alkaline aqueous medium. Due to the hydrophily [40], steric repulsion [41], and mobility properties [41], HA has a great potential to be used to stabilize the dispersion of CNTs in cementitious environments.

Therefore, the aim of the present study is to use HA to assist the stabilization of the dispersed SWCNTs in cementitious composites. The effect of the stability will be tested through three aspects, namely the suspensions, fresh cement slurry and the hardened OPC pastes. The degree of dispersion was measured using an ultraviolet-visible spectrophotometer (TU-1901). The fluidity of the fresh cementitious composites was tested by self-devised mini-slump. The compression and flexural strength of the hardened cement pastes were measured by an electronic testing machine (DNS100). A scanning electron microscope (SEM, HITACHI, SU8220) was used to characterize the role of the SWCNTs distribution in the hardened pastes.

2 Experimental process

2.1 Materials and instrumentation

Non-functionalized SWCNTs with a diameter of 1-2 nm and length about 5-30 \(\mu\)m were manufactured by Nanjing XF-NANO Materials Tech Co., Nanjing City, Jiangsu Province, China. The purity of the SWCNTs was greater than 60% and their specific areas were more than 407 m\(^2\)/g. The tap density and true density are 0.14 g/cm\(^3\) and 2.1 g/cm\(^3\), respectively. Polycarboxylate superplasticizer (PC), purchased from SUBO Co., was used to disperse the SWCNTs in this study. Humic acid (HA), supplied by Innochem Co., Beijing City, China, containing two kinds of functional groups, namely phenolic hydroxyl and hydroxy, was used to assist the dispersion in the cementitious composites environment. OPC, Type P.O. 42.5, was selected to prepare the ternary cement-based binders containing SWCNTs.

A horn sonicator, SONICS VCX 500W, with a cylindrical tip (13-mm diameter) was applied to disperse the SWCNTs in aqueous solutions. The degree of dispersion was measured using an ultraviolet-visible spectrophotometer (TU-1901). The fluidity of the fresh cementitious composites was tested by self-devised mini-slump. The compression and flexural strength of the hardened cement pastes were measured by an electronic testing machine (DNS100). A scanning electron microscope (SEM, HITACHI, SU8220) was used to characterize the role of the SWCNTs distribution in the hardened pastes.

2.2 Preparation of SWCNT suspensions containing HA

As presented in Figure 1a, SWCNT suspensions were prepared by mixing SWCNTs and PC powders with distilled water under ultrasonication treatment. The ultrasonication time and power were set as 15 min and 94 W. To prevent overheating of the suspensions influencing the physical properties of the SWCNTs, the SWCNT suspensions were placed in a water-ice bath environment during the whole ultrasonication process. The mass concentrations of SWCNTs and HA are exhibited in Table 1. According to previous research [42], the weight of PC powders was chosen as eight times that of the SWCNTs. Then the HA powders were added into the SWCNTs with a moderate and high rate of stirring for approximate 3 min, respectively. After that, four groups of HA-SWCNT (H/S) suspensions with different dosages of HA were prepared. For better analysis, suspensions without HA and no simulated cementitious pore
Humic acid assisted stabilization of dispersed single-walled carbon nanotubes in cementitious composites

Figure 1: Preparation of (a) SWCNT suspensions; (b) UV-vis tests of SWCNTs-based suspensions; (c) fluidity and mechanical properties tests of SWCNTs-based cement pastes

Table 1: Mass concentrations of SWCNTs, PC and HA in the HA/SWCNT suspensions and cementitious composites

| Mix  | S/s (wt.%) | P/s (wt.%) | HA/s (wt.%) | S/c (wt.%) | P/c (wt.%) | HA/c (wt.%) |
|------|------------|------------|-------------|------------|------------|-------------|
| Ref  | 0          | 0          | 0           | 0          | 0          | 0           |
| H/S-0| 0.08       | 0.64       | 0.12        | 0.032      | 0.256      | 0.05        |
| H/S-1| 0.25       |            | 0.50        |            |            |             |
| H/S-2| 0.50       |            |             |            |            |             |

Note: S/s, P/s and HA/s represent SWCNTs, PC and HA to suspensions weight percentage. S/c, P/c and HA/c represent MWCNTs and PC to cement weight percentage.
Table 2: Concentration of chemicals in simulated OPC pore solution

| Compounds | NaOH | KOH | CaSO₄·2H₂O | Ca(OH)$_2$ |
|-----------|------|-----|------------|------------|
| Concentration (g/L) | 8 | 22.4 | 27.6 | Saturated |

Figure 2: The zero-intercept linear relationship between absorbance and $C_m$ of SWCNTs in suspensions at $\lambda = 500$ nm

solution were also prepared to compare the reinforcing effects of HA.

It can be seen in Table 1 that the HA concentration was chosen as 0.00 wt.%, 0.12 wt.%, 0.25 wt.%, and 0.50 wt.%, relative to that of the SWCNT suspensions. The preparation process of SWCNT suspensions and the dissolving of the powders were carried out under laboratory conditions. In order to measure the stability of the SWCNT suspensions in the cementitious environment, a simulated OPC-like pore solution was prepared and mixed into the SWCNT suspensions, as shown in Figure 1b. The mixture content of chemicals [29, 30] in the simulated cementitious composites pore solution is exhibited in Table 2. According to previous studies [29, 30], the Na$^+$, K$^+$, Ca$^{2+}$, SO$_2^-$, and OH$^-$ ions are provided as the main composition of the OPC pore solution in the early-age matrix.

2.3 Samples preparation

The well-prepared H/S suspensions without OPC pore solutions were then mixed with cement powders with a water-to-cement ratio (w/c) equal to 0.4 [43]. That is to say, the cementitious composites contained 0.00 wt.%, 0.05 wt.%, 0.10 wt.%, and 0.20 wt.% of HA, respectively. After enough stirring and vibrating to ensure the mixing effects and removal of extra air bubbles, the fresh pastes were poured into two kinds of molds, of 50 mm × 100 mm and 40 mm × 160 mm, for the preparation of compression and flexure strength experiments, as presented in Figure 1c. After 24 h, the specimens were demolded and then cured in a saturated lime environment at a temperature of about 25°C for 28 days for aging before the mechanical tests.

2.4 Testing procedure

The time-dependent degree of dispersion of the H/S suspensions in alkaline environments and the reference suspensions were measured by UV-vis tests. The measurements of the absorbance (ABS) at a certain wavelength have a linear relationship with the degree of dispersion [44–46]. The H/S suspensions were diluted by a factor of 50 because the primary solutions exceeded the measuring range of the UV machine. Then the ABS was measured at a wavelength ($\lambda$) equal to 500 nm until 18 hours at intervals of 1 hour, because although the initial setting time of cementitious composites often ranges from 3 to 4 hours, the high w/c ratio and humid laboratory conditions prolonged the time until the OPC pastes hardened entirely. After the UV tests, the concentration of SWCNTs ($C_d$) can be calculated by Beer–Lambert’s law [44–46] as follows:

$$C_d = \frac{A}{\epsilon l}$$  \hspace{1cm} (1)

where $A$ is the average value of ABS, $\epsilon$ describes the extinction coefficient [44–46], and $l$, which equals 1 cm, is the optical path length of light through the SWCNTs suspensions.

First, 0.08 wt.% SWCNTs were mixed into aqueous solutions and ultrasonicated for 1 hour at 120 W to guarantee that the maximum ABS of the suspensions was achieved. Afterwards, the well-dispersed SWCNT suspensions were diluted with distilled water in eight gradients, as shown in Figure 2. According to Eq. (1), $\epsilon$ was determined by the zero-intercept linear fitting between the tested ABS and the theoretical maximum concentration ($C_m$) of SWCNT suspensions. As exhibited in Figure 2, the linear regression equation indicates that $\epsilon$ is 21.73 mL mg$^{-1}$ cm$^{-1}$ of SWCNTs, with the goodness of fit suggested by the correlation coefficient $R^2 = 99.8\%$. Based on this linear fitting, the degree of the dispersion of SWCNTs in the suspensions can be calculated.

The fluidity of the fresh SWCNT-based cement pastes and reference cement pastes was tested by a self-devised mini-slump cone. During the test process, the mini-cone was set aside on a level platform. The fresh OPC pastes were then poured into the cone with enough vibration to ensure compaction, and the excess paste was scraped off the top surface of the cone. It was important to ensure that
the cone was lifted up perpendicularly to ensure the minimal influence on the results. After 24 hours, the diameter of the spread hardened OPC pastes was scaled around the outline three times and the value can be deemed to describe the fluidity.

The flexural strength ($\sigma_t$) and compressive strength ($\sigma_c$) of the SWCNT-based cement pastes were tested using a universal loading machine, with the constant loading rates of 0.1 and 0.5 mm/min, respectively. At least three specimens were used in the mechanical tests for strength performance measurement.

3 Result and discussion

3.1 Effects of HA on the dispersed stabilization of SWCNTs in pore solution

The dispersion concentration ($C_d$) of single-walled carbon nanotubes is one of the most important factors affecting the enhancement efficiency of carbon nanomaterials. Previous studies [21] have reported that the reinforcing effect of carbon nanotubes is proportional to the content of well-dispersed materials in the cementitious composites. Therefore, improving the degree of the dispersion of SWCNTs is the key for the application. Sadly, due to the agglomeration of the SWCNTs, the dispersion concentration ($C_d$) in suspensions is not always equal to the maximum theoretical concentration ($C_m$) of the nanomaterials. That is to say, a higher ratio of $C_d/C_m$ in the figure means that more SWCNTs are in the dispersed state. In practical application, due to the difference of water-to-cement (W/C) ratios and humidity, particularly at high humidity such as underground grouting projects, the initial time of cement paste hardening requires about 18 hours [26, 29]. Figure 3a presents the results of the ratio of $C_d/C_m$ based on Eq. (1) changing with the time after ultrasonication, which reflects the degree of dispersion of the SWCNTs in the suspensions.

As shown in Figure 3a, the dispersibility of the aqueous solution of SWCNTs is relatively stable. After 18 hours, the ratio of $C_d/C_m$ in the suspensions only decreases by approximately 13%, while the ratios of the other four curves experience a dramatic decline in this time interval. This indicates that the cement-like alkaline environment in the simulated cement pores greatly reduces the dispersion of SWCNTs in the suspensions. Over time, more SWCNTs form agglomerations, and the ratio of $C_d/C_m$ drops steadily to below 20% after 18 hours. However, it can be seen that the suspensions containing 0.12 wt.% of HA are able to maintain a relatively high proportion of dispersed SWCNTs of more than 60% up to 6 hours.

At 3 hours, the proportion of SWCNTs dispersed in the suspensions containing 0.12 wt.% HA was about 78%, while the proportion of specimens without HA was only 63%, a decrease of 15%. The difference of these proportions reached a maximum value at 6 hours, when they were 64% and 42%, respectively. However, when the concentration of HA exceeds 0.12% by weight, the stabilizing effect on the dispersibility of the SWCNTs is lower. The reason for this phenomenon may be the fact that, at low concentration, humic acid adsorbs on the surface of SWCNTs, which significantly changes the surface properties of the materials in the suspensions, such as adding steric repulsion among SWCNTs to work against the van der Waals forces [23, 24] or increasing the zeta potential.
Table 3: Transition time in dispersion state

| HA concentration (wt.%) | Transition point (h) | Rate of decrease of $C_d/C_m$ (% per h) |
|------------------------|----------------------|--------------------------------------|
| 0.00                   | 2                    | 14.9                                 |
| 0.12                   | 8                    | 8.4                                  |
| 0.25                   | 5                    | 9.9                                  |
| 0.50                   | 3                    | 10.9                                 |

among the particles, which reduces agglomeration [41]. However, when the HA molecule is further absorbed, adjacent SWCNTs may join to form larger agglomerates [47, 48] since the HA has a medium molecular weight of about 308 g/mol and a rich functional group. The adjacency is not conducive to further dispersion of SWCNTs. Therefore, it can be concluded from the UV-vis test results that there is an optimum content of HA to assist in the dispersion of SWCNTs.

Figure 3b shows the transition point during the descent of $C_d/C_m$, which can be determined by the curve gradient [26, 29]. It can be seen that, before the transition point, the ratio of $C_d/C_m$ in the suspension changes relatively uniformly, and the $C_d/C_m$ reaches a maximum decline within one hour after the inflection point. The point at which the transition point appears on the curve indicates that at that time the re-agglomeration of dispersed SWCNTs is more likely to occur, which will be explained in Section 3.4. Table 3 lists the detailed measurements of the dispersion rate of the decrease of $C_d/C_m$ and the transition point for the four specimens (except for the aqueous solution of SWCNTs without a transition point). According to previous studies, the transition point and the maximum rate of decline are influenced by the concentration of HA, and the appropriate HA content will enhance the spatial repulsion resistance and the stabilization of the suspensions in the alkaline environment [49, 50]. In this research, it is found that the time of the transition point was obviously prolonged after the addition of HA, and especially when the concentration of HA equals 0.12 wt.% the transition point reached 8 hours. The cement slurry usually condenses at around 3 to 4 hours, thus maintaining the stability of the SWCNT suspensions under alkaline conditions for a short period of time (particularly before the transition point of the dispersed state), which is important for reinforcing the performance of SWCNTs-based cementitious composites.

3.2 Effects of HA on the fluidity of H/S-OPC fresh pastes

The fluidity of fresh cement pastes is another important measurement index and appropriate fluidity can slow the agglomeration of carbon nanotubes and increase their stability in cementitious composites [27]. The fluidity of the SWCNTs-based fresh cement slurries and the reference slurries was measured by mini-slump tests [27]. As shown in Figure 4, the diameter of the mini-slump spreads changes with the concentration of the HA mixture. When the HA/c increases from 0.00 wt.% to 0.20 wt.%, the fluidity of the cement slurry is continuously lowered, suggesting that as the slurry adsorbs the HA, the electrons on the surface of the cement powders will repel each other and then the steric hindrance will increase [25]. Finally, the kinetic performance deteriorates [26], thereby inhibiting the fluidity of the fresh cement slurry.

As presented in Figure 4, the addition of SWCNTs reduces the fluidity of the fresh cement slurry further. The fluidity of the cement containing SWCNTs is always lower than that of the comparative slurry in all specimens. The reason for this phenomenon may come from two aspects: the main factor is that SWCNTs can act as nucleation sites to accelerate the hydration reaction and thereby reduce the fluidity of the fresh cement slurry [20]; the second factor is that the dispersed SWCNTs absorb the polycarboxylate-based water-reducing agent molecules [27], leading to a decrease in these molecules in the slurry that interact with cement powders, which ultimately reduces the fluidity. Interestingly, as can be seen in Figure 3, the maximum reduction in the mini-slump diameter is a decrease from about 113 mm to 106 mm at the
HA/c equaling 0.05 wt.%, a reduction of 6.2%, which is obviously larger than that of other groups. The reason may be that more SWCNTs are in a dispersed state under this concentration, a finding that is consistent with the results of Section 3.1.

3.3 Effects of HA on the mechanical performance of H/S-OPC hardened pastes

Figure 5 shows the mean value and standard deviation of the compressive strength ($\sigma_c$) and flexural strength ($\sigma_f$) of the hardened cement pastes at 28 days of curing versus the different concentrations of HA. It can be seen from the red lines of the figure that the mechanical properties of the reference group are relatively stable. The fluctuation of the mechanical performance is always within 5%, indicating that the content of HA does not influence the cementitious composites without extra mixing of SWCNTs.

For the SWCNT-OPC pastes, the optimum enhancement of the mechanical performance is at the concentration of HA corresponding to about 0.05 wt.%. Compared with the reference hardened pastes, the specimens containing HA/c of 0.05 wt.% show the largest reinforcement, the $\sigma_c$ and $\sigma_f$ increasing by about 31% and 48%, respectively. However, the cementitious pastes with the mixture of SWCNTs were only enhanced by 18% and 24% when no HA was added. The results illustrate that when no HA is added, the SWCNTs in the cement pastes are easily re-agglomerated in an alkaline environment, thus forming a stress concentration during the test processes and finally resulting in a weakening effect. When the HA/c content reaches 0.20 wt.%, the reinforcing effect is also significantly lower than that of the optimum concentration. The findings of this test are in good agreement with the dispersion stability of SWCNTs (as shown in Figure 3): when no HA is mixed or when the concentration of HA is excessive, the degree of dispersion of SWCNTs in an alkaline environment will decrease in both cases. A suitable concentration of HA not only facilitates the dispersion of SWCNTs in cementitious pore solutions but also enhances the mechanical properties of the hardened pastes.

3.4 Distribution of SWCNTs in hardened cement matrixes

In order to characterize the roles of SWCNTs dispersed in the cementitious composites, the failure surface of the specimens was observed under SEM. As presented in Fig-
Figure 6a, when the composites do not contain HA, the SWCNTs are mostly agglomerated in individual pores, while in the other cracks and pores, few SWCNTs are visible. This observation is a good explanation of the agglomeration caused by the decrease in $C_d/C_m$ when there is no extra HA mixing, as presented in Section 3.1, and ultimately leads to the decrease in mechanical properties reported in Section 3.3.

Figure 6b presents the sample H/S-1; the agglomeration of SWCNTs in this specimen is significantly reduced and the dispersed carbon nanoparticles can be observed in most of the pores and cracks. In addition, compared with Figure 6a, more carbon nanotubes are sufficiently long to adhere on both sides of the cracks and pores, indicating that the SWCNTs with good dispersion can act as crack-bridging materials, with the effect of inhibiting crack propagation [20, 21], and finally improving the mechanical properties of the cementitious composites.

4 Conclusions

In this paper, the effect of HA in assisting the stabilization of dispersed SWCNTs in an alkaline environment and the fluidity, as well as the mechanical performance of the SWCNT-OPC pastes, were investigated. The main findings obtained are as follows:

1. It was found from UV-vis tests that the addition of an alkaline environment to the SWCNT suspensions would result in a rapid decrease of the dispersion of this kind of carbon nanomaterial, and the appropriate content of HA can play a significant role in stabilizing the dispersion of SWCNTs. When H/s equals 0.12 wt.%, the suspensions consistently maintain the highest $C_d/C_m$ ratio over time, and the increment in dispersibility is particularly pronounced between 3 and 9 hours.

2. As the HA/c rises from 0.00 wt.% to 0.20 wt.%, the fluidity of the fresh cement slurry continues to decline. The incorporation of SWCNTs further reduces the fluidity of the fresh pastes and the maximum degradation value occurs at the HA/c content equal to 0.05 wt.%, where the mini-slump diameter decreases by about 6.2%.

3. The mechanical properties of the hardened cement pastes confirm that the appropriate concentration of HA/c, about 0.05 wt.%, can effectively reflect the roles of SWCNTs and enhance the strength. The compressive strength and flexural strength increased by about 31% and 48%, respectively, at the most appropriate content.

4. The SEM images prove that a suitable concentration of HA can advance the dispersion of SWCNTs in cementitious pore solutions and act as crack-bridging materials, which have the effects of inhibiting crack propagation and enhancing the strength of cementitious composites.

Acknowledgement: This study was supported by the State Key Program of National Natural Science of China, (No.51734009), the National Key Basic Research and Development Program of China, (No. 2017 YFC0603001).

Conflict of Interests: The authors declare no conflict of interest regarding the publication of this paper.
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