Influence of chemical admixtures on the dispersion of carbon nanotubes in water and cement pastes

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Abstract. The influence of ultrasonic and three types of chemical surfactants (including cationic surfactants: CTAB, anionic surfactants: SDS, and nonionic surfactants: TX-405) on the dispersion of CNTs was investigated. The techniques include UV-Vis-NIR spectrophotometer, laser particle size analyser and scanning electrical microscope (SEM). The results show that: 1) Ultrasonic leads to a dispersive effect on CNTs in water, and the optimal ultrasonic time is 120 s; 2) Three types of surfactants have positive effects on the dispersion of CNTs in water, among which cationic surfactant (CATB) leads to the best dispersibility; 3) CNTs with more carboxyl groups show better dispersion in water indicated from UV-vis-NIR spectra and particle size measurement; 4) The optimum concentration of surfactants is 5:1 (the mass ratio of dispersant to CNTs); 5) Three types of surfactants can improve the dispersion of CNTs in cement pastes indicated from SEM images at the optimum dosage.

Keywords: Carbon nanotubes, dispersion, surfactants, cement-based materials

1. Introduction
The application of carbon nanotubes (CNTs) has generated tremendous interests due to their excellent physical and chemical properties [1]. Nowadays, CNTs are considered an attractive candidate for cement reinforcement [2]. The Young’s modulus and tensile strength of CNTs are tens and hundreds of times that of the strongest steel respectively [3,4].

Over the last few decades, extensive research endeavors have been made to development of composites cementitious materials with CNTs [5-8]. Researchers have carried out in studying the effects of CNTs (0.02% to 2.0% by weight of cement) on mechanical properties of various cementitious systems incorporated with CNTs, and found that the addition of CNTs can increase strength and toughness of cementitious materials [7,9-11]. However, it is noticeable that the reported investigations focused on the reinforced cement based materials with CNTs are always divergent and conflicting, which is related to the dispersion of CNTs within the cement paste matrix [12,13]. CNTs have tendency to aggregate and form bundle structures due to the extremely strong Van der Waals forces, thus making it difficult to disperse and separate CNTs [14]. Poor dispersion of CNTs results in the formation of many microcracks in the composites matrix and limits the efficiency of the CNTs in the cement based materials [15].

Ultrasonic technology is one effectively mechanical method to disperse the CNTs. However, the mechanically dispersion method through ultrasound have potential to damage the structure of CNTs. [16] Therefore, it is necessary to determine the optimal ultrasound time. Chemical methods include pre-treatment of the surface of CNTs chemically by using covalent or non-covalent modification
approaches. A mixture of H₂SO₄ and HNO₃ was commonly used to modify the CNTs to form carboxyl functional groups in their structure, thus leading to steric repulsion between CNTs [5]. The non-covalent modification approaches include employing cationic, anionic and neutral surfactants to improve the dispersibility of CNTs [17-19]. A lot of researching studies indicated that some chemical surfactants such as CATB (1-hexadecylpyridine bromide); SDS (sodium dodecyl sulfate); and TX-405 (Triton X-405) were effectively in dispersibility of CNTs [18,20,21]. Results from dispersing CNTs with non-covalent modification approaches also suggest the concentration of surfactants have significance influence the dispersibility of CNTs in water [19]. However, there is limited literature focused on the effect of surfactants on the dispersion of carboxylic CNTs.

In this study, the influences of ultrasound time, surfactant type and concentration of chemical surfactants (cationic, anionic and nonionic surfactants) on the dispersion of CNTs in water were systematically investigated.

2. Experimental methods

2.1. Raw materials

Multi Walled Carbon Nanotubes (MWCNTs) with COOH functional groups, provided by Beijing DK nano S&T Ltd, were used. The MWCNTs have outside diameter from 8 nm to 30 nm, inside diameter from 3 nm to 10 nm and length ranging from 10 μm to 30 μm, according to the manufacturer, as presented in table 1. Chemical surfactants include CATB (1-hexadecylpyridine bromide; cationic surfactants); SDS (sodium dodecyl sulfate; anionic surfactants); and TX-405 (Triton X-405; nonionic surfactants) were supplied by J&K Scientific Ltd. Deionized water was used for all experiments.

![Chemical structure of surfactants used in this study.](image)

Table 1. Physical properties of MWCNTs.

| Type   | Inside diameter | Outside diameter | Length | Density   | Thermal conductivity | Special surface area | Carboxyl content |
|--------|-----------------|------------------|--------|-----------|----------------------|----------------------|-----------------|
| CNT-1  | 3~10 nm         | 8~30 nm          | 10~50 μm | 2.1 g/cm³ | >100 s/cm            | >110 cm²/g          | 1.23%           |
| CNT-2  | 3~10 nm         | 8~30 nm          | 10~50 μm | 2.1 g/cm³ | >100 s/cm            | >110 cm²/g          | 2.00%           |

2.2. CNTs suspensions preparation and characterization

For preparation of MWCNT dispersions, three surfactants and a sonicator were used. In a typical procedure, suspensions were prepared by mixing the MWCNTs in a concentration of 16 mg/ml in an aqueous solution with or without different amounts of surfactant and the resulting dispersions were sonicated at room temperature. Constant energy was applied to the samples using a 300 W cup-horn...
high intensity ultrasonic processor with a 6 mm cylindrical tip and temperature controller. Throughout sonication the beaker with the suspended MWCNTs was cooled in a water bath.

Table 2. Chemical composition and mineralogical composition of cement (wt/%).

| Chemical composition | Mineralogical composition |
|----------------------|---------------------------|
| CaO  | SiO₂ | SO₃ | MgO | Al₂O₃ | Fe₂O₃ | C₃S | C₂S | C₃A | C₄AF |
| 61.91 | 22.10 | 2.87 | 2.66 | 4.04 | 3.38 | 57.34 | 18.9 | 6.47 | 11.25 |

2.2.1. Determination of ultrasounds time. The carbon nanotubes (MWCNT-1) were dispersed in a concentration of 0.16 g/ml in an aqueous solution, and the ultrasounds time was set at 60s, 120s and 180s. At first, the amount of CNT-1 was added into a 150 ml breaker with water previously prepared. Then, the suspension in the beaker (water + CNT-1) was subjected to ultrasounds for different time. The last stage corresponds to the assessment of the dispersion of the suspension through conductivity test and zeta potential analysis to determination of ultrasounds time (t). Before measurements, each sample was diluted by distilled water to the concentration of one-twentieth of its initial concentration.

2.2.2. Effect of surfactant type and concentration on dispersion of CNTs suspensions. The content of MWCNTs was kept constant in an aqueous solution at an amount of 0.16 g/ml, and the surfactant to carbon nanotubes weight ratio is 3:1, 4:1 and 5:1 respectively. The solutions were subjected to ultrasounds for a regular time (t) to make MWCNTs suspensions.

The dispersion of CNTs suspensions was evaluated by UV-vis-NIR spectrophotometer (U-4100, Hitachi, Japan), with a wavelength range from 230 nm to 800 nm. Before measurements, each sample was diluted by distilled water to the concentration of one-twentieth of its initial concentration. The corresponding surfactant aqueous solution was used as the blank.

2.2.3. Effect of carboxyl content of CNTs on dispersion of CNTs suspensions. At the presence of cationic surfactants (1-hexadecylpyridine bromide), CNT suspensions prepared from CNTs with different carboxyl content were characterized by UV-vis-NIR spectrophotometer and particle size distribution.

3. Results and discussion

3.1. Effect of ultrasounds time on dispersion of CNTs

Conductivity test and zeta potential are significant parameters determining the dispersion and stability of nanoparticles in solution. In order to better understand the effect of different ultrasounds time on dispersion of MWCNTs, conductivity test and zeta potential analysis of MWCNTs suspensions were performed.

Table 3. Conductivity and zeta potential of MWCNTs suspensions measured for three times.

| Ultrasounds time | Conductivity (μS/cm) | Zeta potential (mV) |
|------------------|----------------------|---------------------|
| 0s               | 0.0034               | -10.4               |
| 60s              | 0.0243               | -20.3               |
| 120s             | 0.0303               | -19.3               |
| 180s             | 0.0246               | -18.3               |

The results presented in table 3 show that ultrasounds time have effects on dispersion and stability of MWCNTs in water. It is evident that MWCNTs suspensions sonicated for different time show better Conductivity than that without ultrasounds treatment, among which suspension sonicated for
120 s shows the best Conductivity. This indicated that ultrasounds treatment can effectively disperse the MWCNTs in water. From the results obtained by zeta potential analysis, it can be found that CNT-2 are negative charged as the presence of functional groups (-COOH). In addition, ultrasounds treatment leads to a positive effect on stability of CNTs suspensions, indicated by increased zeta potential value. According to literature [22], the higher the zeta potential is, the more probable the preservation of suspensions stability. Different ultrasounds time (60s~180s) have no obviously effect on stability of CNTs suspensions. Therefore, the optimal ultrasounds time (t) was 120s and performed in the following experiments.

3.2. Effect of surfactant type and concentration on dispersion of MWCNTs

![Figure 2. UV-vis-NIR absorption spectra of MWCNT dispersed in CATB surfactant solutions: (a) CNT-1 and (b) CNT-2](image)

![Figure 3. UV-vis-NIR absorption spectra of MWCNTs dispersed in SDS surfactant solutions: (a) CNT-1 and (b) CNT-2](image)

![Figure 4. UV-vis-NIR absorption spectra of CNT dispersed in TX-405 surfactant solutions: (a) CNT-1 and (b) CNT-2](image)
The effect of surfactant type and concentration on dispersion of MWCNTs suspensions has been investigated by the UV-vis-NIR spectroscopy. Figure 2-4 show the UV-vis-NIR absorption spectra of dispersions in which MWCNTs were dispersed in CTAB, SDS and TX-405 solutions, respectively. The absorbance of all solutions show a maximum between 240 nm and 280 nm which agree with the report from literature [23], and the intensity of absorbance is related to the concentration of CNTs in suspensions according to the Lambert-Beer’ law. From figure 4(a) and 4(b), it can be seen that the maximum intensity in the absorbance curves increases continuously with increasing the concentration of CATB, indicating CATB leads a dispersion effect on MWCNTs. In addition, similar results obtained from MWCNTs prepared from the same surfactant for CNT-1 and CNT-2. However, the absorbance intensity beyond 280nm did not increase when more CATB was added in suspensions. For SDS and TX-405 samples, the absorbance intensity and peak values increase with increasing concentration of surfactants. Therefore, it is obviously that the three surfactants at high concentration have positive dispersion effect on MWCNTs in water. Among different surfactants samples at dosage of 1:5 (mass ratio of CNTs to surfactant), MWCNTs suspensions prepared by CATB have the highest absorbance value, which indicated that CATB (cationic surfactants) has a better ability to disperse CNTs.

The measurement of the mean particle size of MWCNTs is important to explain the effect of three surfactants on the dispersion of MWCNTs particles in aqueous suspensions. The mean cluster size of MWCNTs suspension with CTAB, SDS or TX-405 is depicted in figure 5(a-c). From the data, it can be found that the cluster size of MWCNTs is distributed between 240 nm and 300 nm, which indicated that MWCNTs still formed agglomerations even in surfactant suspensions. However, it is obvious that the mean particle size decreases with increasing the concentration of surfactants.

![Figure 5](image.png)

**Figure 5.** Mean particle size of MWCNT agglomerates in suspensions prepared from (a) CTAB; (b) SDS and (c) TX-405.

3.3. The effect of carboxyl content of MWCNTs on dispersion of suspensions

The maximum absorbance values and the mean particle size are two important parameters to understand the dispersion of MWCNTs with different carboxyl content in aqueous solutions. Table 4 and table 5 depict the variation of the maximum absorbance values and the mean particle sizes of two
types of MWCNT with the different type and concentration of surfactants. When MWCNTs were added into suspensions with the same type and concentration of surfactant, the maximum absorbance values of CNT-2 suspensions are larger than that of CNT-1 suspensions, and the mean particle sizes of CNT-2 become smaller. Therefore, it is obvious that the dispersing ability of CNT-2 with more carboxyl content is better than that of CNT-1 at the same type and concentration of surfactant.

**Table 4** The maximum absorbance values of CNTs suspensions with different surfactants.

| Type  | CTAB 1:3 | CTAB 1:4 | CTAB 1:5 | SDS 1:3 | SDS 1:4 | SDS 1:5 | TX-405 1:3 | TX-405 1:4 | TX-405 1:5 |
|-------|----------|----------|----------|---------|---------|---------|------------|------------|------------|
| CNT-1 | 1.802    | 2.539    | 2.788    | 1.005   | 1.035   | 1.196   | 1.007      | 1.031      | 1.083      |
| CNT-2 | 2.346    | 2.700    | 3.150    | 1.136   | 1.186   | 1.237   | 1.031      | 1.155      | 1.202      |

**Table 5.** Mean particle size of CNTs in the suspensions prepared from different surfactants.

| Type  | CTAB 1:3 | CTAB 1:4 | CTAB 1:5 | SDS 1:3 | SDS 1:4 | SDS 1:5 | TX-405 1:3 | TX-405 1:4 | TX-405 1:5 |
|-------|----------|----------|----------|---------|---------|---------|------------|------------|------------|
| CNT-1 | 264.5    | 245.1    | 238.7    | 267.5   | 253.1   | 239.1   | 285.5      | 279.8      | 254.0      |
| CNT-2 | 257.4    | 235.2    | 225.0    | 255.6   | 243.0   | 240.7   | 260.9      | 255.8      | 240.0      |

3.4. Dispersion of MWCNTs in cement pastes

![Figure 6. Effect of different types of surfactants on the dispersion of CNTs in hardened cement pastes curing for 7 days: (a) no surfactant; (b) CTAB; (c) SDS; and (d) TX-405.](image)
microstructures of cement pastes prepared from CNT-2 suspensions within the following mixtures: (a) no surfactant; (b) cationic surfactant: CTAB; (c) anionic surfactant: SDS and (d) nonionic surfactant: TX-405. It can be observed that in case of surfactant, CNTs seem well dispersed in cement pastes and only individual MWCNTs can be identified on the fracture surface. In contrast, MWCNTs in cement paste without any surfactant were hardly to find out in the micrographs, which may result from the aggregation of CNTs to form bundle structures and totally coated by hydration products.

4. Conclusions
This paper reports the research results of the dispersion of two types MWCNTs with different carboxyl in the aqueous solutions prepared from three different surfactants including CATB, SDS and TX-405. The following conclusions can be drawn:
(1) Ultrasonic leads a dispersive effect on CNTs in water and the best ultrasonic time is 120 s;
(2) Three types of surfactants have positive effect on the dispersion of MWCNTs in water, among which cationic surfactant (CATB) leads to the best dispersability;
(3) MWCNTs with more carboxyl groups show better dispersion in water indicated from UV-vis-NIR spectra and particle size measurement;
(4) The optimum concentration of surfactants is 5:1 (the mass ratio of dispersant to MWCNTs) among the three concentrations;
(5) Three types of surfactants can improve the dispersion of MWCNTs in cement pastes indicated from SEM images at the optimum dosage.

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