Assessing the Dispersion Quality of Carbon Nanotubes Suspensions by Low Field Nuclear Magnetic Resonance

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Abstract. In this study, a novel method based on low field nuclear magnetic resonance measurements were used to characterize the dispersion quality of carbon nanotube suspensions. The liquid specific surface area, which calculated with the relaxation time, were used as an indicator of dispersion quality of the carbon nanotubes suspensions. The experimental results were compared with those measured by the conventional method methods, including Zeta potentiometer method and ultraviolet visible spectrophotometer method. The results show that low field nuclear magnetic resonance has the advantages in the characterizing the dispersion quality of high concentration carbon nanotube suspensions and tracking its re-agglomeration process non-destructively.

1. Introduction

Previous studies have shown [1-3] that carbon nanotubes (CNTs) are nanomaterials with low density, high strength, high hardness, high elastic modulus and excellent electrical properties. Carbon nanotubes, which are widely used as new nanomaterials, are widely used to reinforce matrix materials. And many scholars in the field of building materials have applied them to cement-based materials. Many studies have shown that [4-6], with the addition of carbon nanotubes, the flexural strength, compressive strength, freeze-thaw resistance, damping and microscopic properties of cement-based materials have improved. However, CNTs are hardly soluble in water and organic solvents. And it has a high van der Waals force and aspect ratio, so the phenomenon of intertwining and agglomeration between carbon nanotubes is very easy [7]. The uniform dispersion of CNTs is a prerequisite for the better use of CNTs.

Preparation of homogenous dispersed carbon nanotubes suspension is the premise of homogenous dispersion of carbon nanotubes in cement-based composites. It is critical to find a means to quickly and accurately assess the dispersion quality of carbon nanotubes. The Ultraviolet visible (UV -Vis) spectrophotometer method [8] and the Zeta potentiometer method [9] are currently used to characterize the dispersion effect of carbon nanotube suspensions. But both methods of characterization have limitations. The Zeta potentiometer method has requirements on the conductivity and potential of the dispersion itself, which greatly limits the scope of application. The UV-Vis spectrophotometer method needs to dilute the stock solution, which may destroy the original dispersion state of the carbon nanotubes in the stock solution. Due to the deficiencies of the above methods, it is necessary to find a method which can quickly and accurately determine the dispersion stability of carbon nanotubes in solution.
Baranowska-Korczyc et al. [10] observed that the improvement in dispersibility of PEG-MWNCTs / Fe was associated with an increase in the relaxation rate of water. Since CNTs have a strong influence on the molecular structure of water in solution, Davide Porrelli et al. [11] used low field nuclear magnetic resonance (LF-NMR) to characterize aqueous dispersions of different covalently functionalized multi-walled carbon nanotubes. It has been found that the transverse relaxation rate $r_2$ of water molecules can be used to assess the concentration and dispersion of CNTs. Studies have shown that the relaxation rate and transverse relaxation time measured by LF-NMR techniques can characterize the specific surface area of suspended particles [12]. The surface of the imaginary suspended particles is adsorbed with a layer of water molecules having a thickness of $L$, which is adsorbed water. The water molecules are free water outside the layer. According to the relaxation time of water molecules in two different states, the average relaxation rate ($R = \frac{1}{T_2}$) of the suspension can be obtained as:

$$R_2 = P_bR_{2b} + P_fR_{2f} = P_b(R_{2b} - R_{2f}) + R_{2f}$$

where $P_b$ is the ratio of the bound solvent; $R_{2b}$ is the relaxation rate of the bound solvent; $P_f$ is the ratio of the free solvent; and $R_{2f}$ is the relaxation rate of the solvent.

Therefore, the specific surface area of the suspended particles depends on the specific surface area of the surface adsorbed water thickness $L$. The relaxation time measured by LF-NMR technology is related to the specific surface area of the material [13]. Therefore, the specific surface area ($S_a$) of the suspended particles can be calculated using the transverse relaxation time ($T_2$) measured by LF-NMR. Its calculation equation (2) is:

$$S_a = \frac{R_2 - R_{2f}}{K_p \varphi}$$

Where $K_p$ is the specific surface area relative coefficient and $\varphi$ is the volume ratio of suspended particles to solvent.

These findings have focused our attention on whether the specific surface area of suspended particles measured by LF-NMR techniques can be used to characterize the dispersion stability of carbon nanotube suspensions.

This study used the specific surface area measured by LF-NMR to characterize the dispersion quality of carbon nanotube suspensions. Then, the dispersive quality of the carbon nanotube suspension was characterized by Zeta potential method and UV-Vis spectrophotometer to verify the accuracy of the LF-NMR test results. Then, the advantages and disadvantages of these characterization methods are summarized.

2. Experimental Materials and Methods

2.1. Materials

Carbon nanotubes are multi-walled carbon nanotubes and produced by the Chinese Academy of Sciences Chengdu Organic Chemistry Co., Ltd. by chemical vapor deposition (CVD). The basic parameters of multi-walled carbon nanotubes are shown in Table 1. The experimental water uses deionized water produced by Huanan High-Tech Water Treatment Equipment Co., Ltd. Surfactant (SAA): Polyvinylpyrrolidone (PVP), produced by Shanghai Jingchun Biochemical Technology Co., Ltd.; Arabic gum powder (GA), produced by Sinopharm Chemical Reagent Co., Ltd.

| Table 1. Basic parameters of carbon nanotubes |
|------------------------------------------------|
| Outer diameter (nm) | Inner Diameter (nm) | Length (μm) | Special Surface Area (m²/g) | Tap density (g/m³) | True density (g/m³) | Purity (%) | Electric Conductivity (S/cm) |
|---------------------|---------------------|-------------|-----------------------------|-------------------|---------------------|------------|-------------------------------|
| 20–30               | 5–10                | 10–30       | >110                        | 0.28              | ~2.1                | >98        | >100                          |
2.2. Preparation of Carbon Nanotube Solution

Three kinds of carbon nanotube suspensions were prepared in this experiment, named C1, C2, and C3. The preparation ratio is shown in Table 2. First, 0.6 g of each surfactant was added to a beaker containing 200 ml of deionized water, and stirred with a glass rod for 5 minutes. After the surfactant was completely dissolved, the carbon nanotubes were directly added, and a magnetic stirrer (model RH digital, Stirred by Ningbo Xinzhi Technology Co., Ltd.) at a rate of 600 rpm for 15 minutes. Finally, it was placed in an ultrasonic cell pulverizer (model JY92-IIN, produced by Ningbo Xinzhi Technology Co., Ltd.) with a power adjustment of 60%. The ultrasonic wave was treated for 3 seconds at intervals of 3 seconds for 30 minutes.

| Sample | CNTs(g) | GA(g) | PVP(g) | water(ml) | Sonication time(min) |
|--------|---------|-------|--------|-----------|----------------------|
| C1     | 0.2     | -     | -      | 200       | 30                   |
| C2     | 0.2     | 0.6   | -      | 200       | 30                   |
| C3     | 0.2     | -     | 0.6    | 200       | 30                   |

Note: GA: gum arabic powder; PVP: polyvinylpyrrolidone;
20 ml of the dispersed carbon nanotube suspension was poured into a 30 ml centrifuge tube. Then, the centrifuge tube was placed in a centrifuge (the centrifuge model was TG16-WS, produced by Xiangyi Centrifuge Instrument Co., Ltd.). It was centrifuged at 8000 rpm for 10 min, 30 min and 60 min, named C1-10, C1-30, C1-60, C2-10, C2-30, C2-60, C3-10, C3-30 and C3-60.

2.3. Characterization of Dispersion Quality of Carbon Nanotube Suspensions

The dispersion quality of the above carbon nanotube suspensions was characterized by using New Size's particle size specific surface area analyzer model PQ001. 1.5 ml of the dispersed carbon nanotube suspension was placed in a glass sample tube, and then the glass sample tube containing the sample was inserted into the instrument probe coil to start the test. The specific surface area (Sa) measurement of the suspended particles was carried out at 32 °C using a CPMG (Carr-Purcell-Meiboom-Gill) sequence.

The dispersed carbon nanotube suspensions C1, C2 and C3 were diluted 100-fold. Immediately measure a certain volume of suspension and characterize the dispersion quality of the carbon nanotube suspension by Zeta potential meter (Model Zetasizer Nano-ZS90, produced by Malvern Instruments, UK) and UV-vis spectrophotometer (Model Lambda 750 is produced by American PerkinElmer company).

3. Results and Discussion

3.1. Dispersion Quality of Carbon Nanotube Suspensions with Different Dispersants

Figure 1 shows the three dispersed carbon nanotube suspensions doped with different dispersants. Since the carbon nanotubes were well dispersed in the suspension just after sonication, and no precipitation occurred, the dispersion quality of the three sets of carbon nanotube suspensions could not be directly distinguished by the naked eye. Therefore, it is necessary to use a relatively sophisticated instrument to characterize its dispersion quality.

Figure 2 shows the dispersion quality of carbon nanotube suspensions doped with different dispersants was characterized by LF-NMR. The transverse relaxation time of the carbon nanotube suspension measured by LF-NMR. The relaxation time was calculated according to the equation (2) to obtain the liquid specific surface area of each suspension, and Figure 3 shows the results. The dispersed carbon nanotubes have a larger specific surface area than the carbon nanotubes which are agglomerated together. Therefore, the dispersion quality can be judged according to the specific surface area of the carbon nanotube suspension. According to this principle, it can be concluded from figure 3 that the dispersion quality of the three groups of dispersions is C2, C3, and C1 from high to low. That is, the carbon nanotube suspension with the addition of gum arabic powder has the best dispersibility, followed by the addition of polyvinylpyrrolidone. Carbon nanotube suspensions without the addition of a dispersant have the worst dispersibility.
UV-Vis spectrophotometer and Zeta potential meter are currently the most common methods for characterizing the dispersion quality of carbon nanotube suspensions. This study uses both characterization methods to verify the correctness of the LF-NMR method.

The Zeta potential value can reflect the structure and characteristics of the diffused electric double layer in the system. It is an important indicator of the electrokinetic properties of colloids. The higher the electron density of the surface of the nanoparticles, the greater the electrostatic force generated, the more effectively the agglomeration between the particles is prevented from dispersing well [14]. Figure 4 shows the results. The potentials measured by the carbon nanotube suspensions were all negative, the potential of C2 was the lowest, and the potential of C1 was the highest. It can be seen that the dispersion quality of each dispersion is C2, C3, and C1 from high to low. High concentrations
of carbon nanotube suspensions also need to be diluted to lower concentrations for testing. However, the dispersion state of the diluted carbon nanotube solution may change to affect the accuracy of the detection result.

![Figure 4. Zeta potentiometer test results.](image)

The UV-Vis spectrophotometer method determines the quality of the dispersion by the absorption of the specific peaks of ultraviolet light and visible light by the carbon nanotubes in the suspension, and the more the specific peak absorption amount, the better the dispersibility. According to the existing research, the absorption peak of carbon nanotubes is between 250 nm and 260 nm [15]. Due to the high concentration of the three samples, the dispersion quality of the three samples could not be distinguished directly by the UV-Vis spectrophotometer. So the three samples were diluted a hundred times. And figure 5 shows the analysis results of the UV-Vis spectrophotometer. Each suspension had the highest absorbance at a wavelength of 260 nm. The suspension containing the surfactant has a higher absorbance than the suspension without the surfactant, and the absorbance of the suspension C2 is the highest. Therefore, the degree of dispersion of the dispersion measured by UV-Vis spectrophotometer is C2, C3, and C1 in descending order.

![Figure 5. UV-Vis spectrophotometer test results.](image)
The test results of Zeta potentiometer and UV-Vis spectrophotometer are consistent with the results obtained by LF-NMR in this experiment, and the accuracy of the results of LF-NMR test is verified. However, the test principle of the Zeta potentiometer is to judge the dispersibility according to the conductivity of the solution. The solution added with the surfactant has a charge affecting the conductivity of the carbon nanotube solution, which leads us to misjudge the dispersion quality of the carbon nanotube solution. Therefore, the Zeta potentiometer is not suitable for the characterization of the dispersion quality of carbon nanotube suspensions with strongly charged surfactants. The UV-Vis spectrophotometer method is not affected by the conductivity of the solution. However, the concentration of the carbon nanotube suspension has an effect on the UV-Vis spectrophotometer. Therefore, two different concentrations of carbon nanotube suspensions need to be diluted to the same concentration to compare their dispersibility. Therefore, the use of UV-Vis spectrophotometer to measure the dispersion of carbon nanotube solution has certain limitations. The characterization method of LF-NMR used in this study is not affected by solution concentration and conductivity. It can take the solution directly for testing, which is convenient and quick, and the test time is short. In summary, the use of LF-NMR to characterize the dispersion quality of carbon nanotube suspensions is accurate and has few influencing factors, which is an accurate characterization method.

3.2. LF-NMR Characterization of Suspension Dispersion Quality with Increasing Centrifugation Time

The LF-NMR method is further applied to investigate the re-agglomeration process of three groups of carbon nanotube suspensions. C1, C2 and C3 were centrifuged for 0 min, 10 min, 30 min and 60 min, respectively, to accelerate the re-agglomeration process of the carbon nanotubes. The LF-NMR method was used to characterize the dispersion quality of the suspensions at different centrifugation times, and the dispersion quality of the suspension was observed with time. Figure 6 shows the suspension of carbon nanotubes at different centrifugation times. It can be clearly seen that the suspension of C1 group decreases with centrifugation time, as the carbon nanotubes precipitated. The re-agglomeration of C2 and C3 cannot be identified visually, which will be further investigated with LF-NMR and UV-Vis spectrophotometer.

![Figure 6. Comparison of dispersion quality of carbon nanotube suspensions under different centrifugation times.](image-url)

The solution needs to be diluted when characterizing the dispersion quality of the carbon nanotube suspension using an UV-Vis spectrophotometer and a Zeta potentiometer. However, the dilution process changes the precipitation state of the sample. The re-agglomeration process can only be tested by LF-NMR. Figure 7 shows the specific surface area of a carbon nanotube suspension at different centrifugation times as measured by nuclear magnetic resonance. Because of the severe sedimentation of C1, the specific surface area value is much smaller than C2 and C3. The agglomeration of carbon nanotubes increased under centrifugation, so the specific surface area of the three samples decreased with time. The specific surface area of C2 decreased more slowly than C3, indicating that the C2 reagglomeration degree is lower than C3. So the LF-NMR can be also used to determine the rate of re-agglomeration of the carbon nanotube suspension. And the results again
confirmed that C2 has the best dispersion quality, followed by C3 and finally C1. It further demonstrates the accuracy of characterizing the dispersion quality of carbon nanotube suspensions using LF-NMR.

![Figure 7. The specific surface area of the CNTs suspension as a function of centrifugation time.](image)

### 4. Conclusion

In this study, a novel method based on LF-NMR were used to characterize the dispersion quality of carbon nanotube suspensions. The following conclusions were obtained:

- LF-NMR can be used to characterize the dispersion quality of carbon nanotube suspensions, and the results are in agreement with the UV-Vis spectrophotometer and Zeta potential.
- The Zeta potentiometer is not suitable for the determination of carbon nanotube suspensions as its test results are greatly affected by the conductivity of the suspension. The UV-Vis spectrophotometer needs to dilute the solution when testing the high concentration of carbon nanotube suspension. Therefore, the LF-NMR method has obvious advantages for the characterization of the dispersion quality of the high-concentration carbon nanotube dispersion.
- As the LF-NMR method does not require dilution of the sample, it can be used to determine the rate of re-agglomeration of the carbon nanotube suspension.

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