INFLUENCE OF THE DISPERSION DEGREE OF CARBON NANOFIBERS ON THE MECHANICAL PROPERTIES OF CEMENT-BASED MATERIALS

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To study the effects of different types of dispersions on the dispersion of carbon nanofibers (CNFs) and the mechanical properties of cement-based materials, polyvinylpyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB), and sodium dodecylbenzene sulfonate (SDBS) as dispersants were used to disperse carbon nanofibers (CNFs) in cement-based materials and the influence on the mechanical properties was studied. The dispersion degree of CNFs in the prepared dispersion was characterized by the UV-Vis absorption test and Tyndall light test. The mechanical properties of CNFs reinforced cement-based composites were tested. The results show the best dispersion effect when PVP is used as a dispersant. The flexural and compressive strength of the specimen are the largest when PVP is used alone. When the content of CNFs is 0.3%, the flexural and compressive strength of the sampler each the maximum, indicating that the addition of CNFs can effectively reduce the deterioration of pore structure to make its internal system more stable and denser.

Keywords: Carbon nanofiber, Dispersant, Cement-based materials, Mechanical property

1. Introduction

Cement-based materials are one of the most widely used materials in buildings. Butthey have the disadvantages of high brittleness, low toughness, and easy cracking, which affect the service life of facilities at home and abroad [1-3]. The methods of strengthening and toughening concrete and prolonging the service life of concrete mainly rely on active mineral powder and fiber. In recent years, the nanomaterials have been increasingly widely used in cement-based materials [4-7].

Relevant research shows that nanomaterials such as nano SiO_2, nano metal oxide, and carbon nanotubes are used in the construction field as new admixtures better than traditional fine powder and ultra-fine powder, breaking the limitations of conventional cement-based materials [8-10]. The family of carbon-based nanomaterials, such as carbon nanotubes, nano carbon black, nanocarbon fibers, graphene, and its derivatives, has attracted extensive attention because of their

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excellent mechanical and electrical properties [11-13]. The published literature reflects the fact that the integration of carbon nanomaterials in cement-based materials regulates the hydration process of cement and improves the microstructure of cement stone and strengthens the properties of composites. And functional cement-based materials can also be prepared. For example, mortar mixed with carbon nanotubes can shield electromagnetic waves, cement composites combined with graphene have thermoelectric properties, and cement-based materials combined with carbon black have pressure sensitivity [14, 15].

Carbon nanomaterials have been used to improve the mechanical properties, frost resistance, corrosion resistance, and carbonation resistance of cement-based materials at home and abroad, and fruitful results have emerged. The effective dispersion method of carbon nanomaterials is discussed and the mechanical properties of carbon nanofiber-reinforced cement-based materials are explored in this paper.

2. Experimental

2.1 Raw Materials and Main Instruments

The cement is P O 42.5 ordinary Portland cement produced by Tangshan Jidong Cement Co, Ltd. Its main chemical composition and physical properties are shown in Tab. 1. Carbon nanofibers are produced by Henan Keliwei Nano Carbon Material Co, Ltd., and their physical properties are shown in Tab. 2. Standard sand is produced by Xiamen Aisou StandardSand Co. Ltd. Polycarboxylic acid superplasticizer (PCs, water reduction rate of 20%), defoamer (tributyl phosphate TBP), and surfactants (polyvinylpyrrolidone PVP, cetyltrimethylammonium bromide CTAB, sodium dodecylbenzene sulfonate SDBS) are all commercially available products.

The instruments used in this study are listed below: TH-800BQ CNC ultrasonic cleaning machine (Jining Tianhua Ultrasonic Electronic Instrument Co. Ltd.), PerkinElmer Lambda 950 ultraviolet, visible spectrophotometer, Hitachi SU8220 field emission scanning electron microscope, Bruker D8-ADVANCE X-ray diffraction analyzer, JJ-5 cement mortar mixer (Wuxi Jianyi Instrument Machinery Co. Ltd.),DKZ-5000 electric bending tester (Wuxi Jianyi Instrument Machinery Co. Ltd.),NYL-300A pressure testing machine (Wuxi Jianyi Instrument Machinery Co. Ltd.).

Table 1

Chemical composition and physical properties of cement

Chemical composition of cement (%)						Fineness (%)	Loss on ignition (%)	Specific surface area (m^2/kg)
Cao	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO			
62.21	21.55	7.82	4.51	2.11	1.8	0.3	3.89	364

Table 2

Technical parameters of CNFs

Mean diameter/nm	Length /μm	Resistivity /(mΩ·cm)	Specific surface area/(m^2/g)	Bulk density/(g/cm^3)	Graphitization degree/%
150±50	6±2	<8	13~20	0.07±0.03	>70

2.2 Experiment Method

2.2.1 CNFs Characterization

The CNFs were characterized by SEM and XRD using Hitachi SU8220 field emission scanning electron microscope and Bruker D8-ADVANCE X-ray diffraction analyzer.

2.2.2 Spectrophotometric Test

This experiment is divided into three control groups for comparative investigation. The suspensions were all prepared by ultrasonic treatment, and the dispersants PVP, CTAB, and SDBS were designed with 0.4g/L aqueous solutions. These samples will be added 20% CNFs of the dispersant solution mass and perform the ultrasonic treatment (ultrasonic dispersion time 30min, power 400W, temperature 40°C), then uniform CNFs suspension was obtained.

The three dispersions are removed, and the light absorption of the three solutions is tested in the wavelength range of 190~690nm by Lambda 950 UV-Vis spectrophotometer. The Lambert Beer law has been used (Eq.1):

$$A = \log\frac{1}{T} = \log\left(\frac{I_r}{I_s}\right) = ecl \tag{1}$$

where: *A*-absorbance; *T*-light transmittance; *e*-absorption coefficient; *c*-solution concentration; *l*-optical path length.

It can be seen from this equation that the absorbance *A* of CNFs suspension is directly proportional to the suspension concentration c and the optical path length *l*. The greater is the absorbance of CNFs, the greater the suspension concentration, the more CNFs dispersed.

2.2.3 Tyndall Light Test

This experiment is divided into three control groups for comparative investigation. The suspensions were all prepared by ultrasonic treatment, and the dispersants PVP, CTAB, and SDBS were designed with 0.6g/L aqueous solutions. These samples will be added 20% CNFs of the dispersant solution mass and perform the ultrasonic treatment (ultrasonic dispersion time 30min, power 400W, temperature 40°C), then uniform CNFs will be obtained. Later, the dispersion was left standing for 1 day (1 d) and observed whether the CNFs agglomerate and whether the distribution has apparent stratification by light.

2.2.4 Basic Mechanics Test

The mechanical properties of dispersant/CNFs cement mortar mainly consider the compressive and flexural strength. Then, the water-cement ratio was set as 0.40; the sand-to-cement ratio was 3.0, and the CNFs content was varied to 0 wt%, 0.10wt%, 0.20wt%, 0.30wt% and 0.40wt%. Concentration of the water-reducing agent (polycarboxylic acid) was 0.2 wt%, and the defoaming agent (TBP) was 0.15 wt%. All CNFs cement mortar composite materials with mix ratios were considered the mechanical properties of 3d, 7d, and 28d at different ages. Preparation process: First, 60% of the water used in each group of samples is used to dissolve the dispersant. The weighed CNFs were added to the dispersant solution and subjected to ultrasonic treatment with an ultrasonic instrument for 30 min. We poured the uniformly dispersed CNFs suspension into the mixing pot of the cement mortar mixer and added 0.15wt% defoamer to eliminate the bubbles generated by the CNFs suspension during ultrasonication. The weighed cement was poured into the mixing pot and low speed stirred for 1min, then fine sand was added at a constant speed and continued to stir for 1 min, the remaining 40% water was added and stirred at high speed for 2 min. The stirring was stopped, and the hybrid CNFs cement mortar composite was taken out for a series of work such as molding. Tab. 3 shows the design coordination ratio of CNFs cement mortar composite materials. Cement mortar mixing, forming, curing, and mechanical performance testing shall refer to "Cement Mortar Strength Inspection Method (ISO Method)" (GB/T 17671-2021).

Table 3

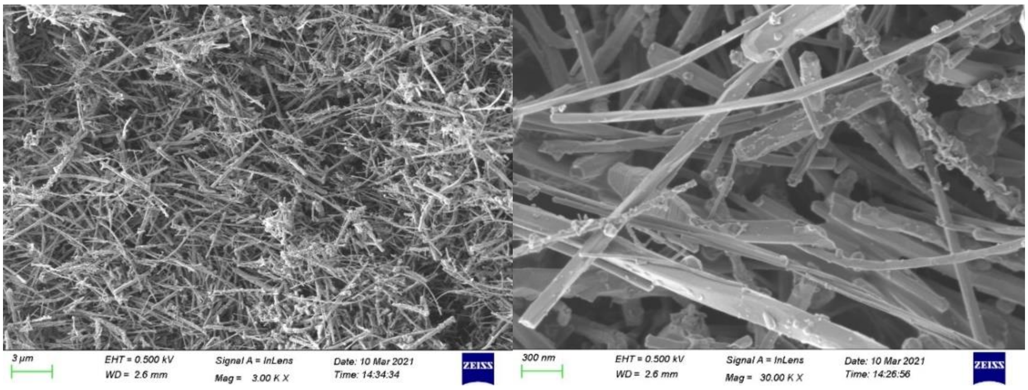
Mixing ratio of cement mortar with different content of carbon nanofiber

Numbering	Water-cement ratio (w/s)	Sand-cement ratio (s/c)	Mix design (wt%)					
			CNFs	PVP	CTAB	SDBS	Defoamer	Water reducing agent
1	0.40	3.0	0	0	—	—	0.15	0.2
2	0.40	3.0	0.1	0.2	—	—	0.15	0.2
3	0.40	3.0	0.2	0.4	—	—	0.15	0.2
4	0.40	3.0	0.3	0.6	0.6	0.6	0.15	0.2
5	0.40	3.0	0.4	0.8	—	—	0.15	0.2

3. Results and Discussion

3.1 Microscopic Characterization of CNFs

Fig. 1 is a scanning electron microscope picture of CNFs. It can be seen from Fig. 1 that CNFs have a columnar morphology, smooth surface, no apparent agglomeration, good dispersion, and are not easy to entangle. The diameter is mainly concentrated at about 150nm, there is no evident bead string structure, and the whole is distributed in a disordered network with a high aspect ratio. The fiber length is about 6μm, and the structural integrity is good.



(a) (b)

Fig. 1 CNFs SEM image (a: magnification 3.0×10^3; b: magnification 3.0×10^4)

Perform XRD testing on CNFs, and the results are shown in Fig. 2. After analysis, it can be found that CNFs are mainly composed of carbon, and the characteristic peaks of carbon are distributed at 26°, 42° and 52° in 2θ. Compared with the standard PDF card, it can be seen that the three diffraction peaks of CNFs are consistent with the characteristic peaks of carbon, and the intensity of the diffraction peak at 26° of 2θ also indicates that the purity of the CNFs used is higher.

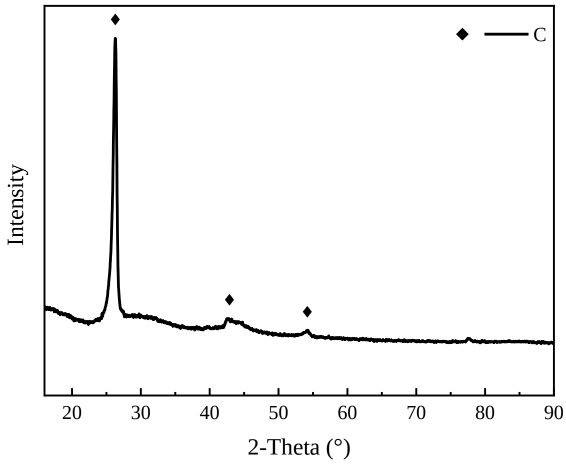


Fig. 2 XRD analysis chart of CNFs

3.2 Analysis of UV-Vis Absorbance Results

UV-Vis absorption can quantitatively characterize the change of the absorbance of CNFs suspension with time after adding dispersant to illustrate the evolution of the concentration of carbon nanofibers in the rest with the amount of dispersant added, and then describe the dispersion performance of the carbon nanofiber suspension. According to Lambert-Beer law, within a specific concentration range, the greater the absorbance, the greater the concentration of the CNFs rest, and the more CNFs will be dispersed. A UV-Vis spectrophotometer was used to test the CNFs dispersion suspensions under different dispersants. The test results are shown in Fig. 3.

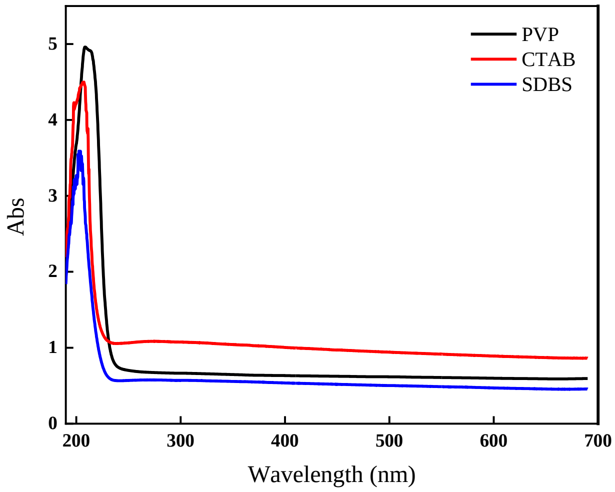


Fig. 3. The CNFs dispersion absorption spectra of three dispersants

Since PVP is a polymer with a flexible chain structure, the methylene group in its design is a non-polar group with lipophilicity. The intramolecular lactam is a solid polar group and has a hydrophilic effect. Among them, the oxygen atom tends to provide electrons to the pyrrolidone ring so that the oxygen is positively charged, making the whole molecule appear weakly cationic. The ring has a higher electron density. This structure allows PVP to exhibit surface activity and has a solid ability to form hydrogen bonds and form complexes. PVP has excellent solubility and has adhesion, thickening, suspension, dispersion, solubilization, and complexing. It also has various excellent properties such as combination and film formation. It can be seen from Fig. 3 that three dispersants are used to disperse CNFs, and the CNFs suspension has strong absorption in the range of 190~240 nm. In the visible light region, for the three types of CNFs dispersions, CTAB has the highest absorbance when used as a dispersant. However, since CTAB hurts cement-based materials when PVP is used as a dispersant, CNFs have the best dispersion effect in solution. When SDBS is used as a dispersant, the absorbance of the dispersion is the smallest, which indicates that the dispersion effect of CNFs in the answer is the worst

3.3 Analysis of the Results of the Tyndall Illumination Test

To characterize the stability of CNFs suspension, suspensions prepared by three different types of dispersants were used for static observation. Fig. 4 shows the stratification of the CNFs break after the three groups of dispersions are ultrasonically dispersed and allowed to stand for 1 d. It can be seen from Fig. 4

that a large amount of precipitation has occurred in the dispersion liquid mixed with SDBS when it is allowed to stand for 1 d. The PVP dispersion and CTAB dispersion have no obvious bubbles, there is only a little precipitation after standing for 1d, and the blackness of the suspension is relatively large. Therefore, according to the principle of the Tyndall phenomenon, SDBS suspension has the worst stability and is easy to precipitate. The PVP suspension has no apparent stratification, the dispersion is relatively uniform, and there are no air bubbles.

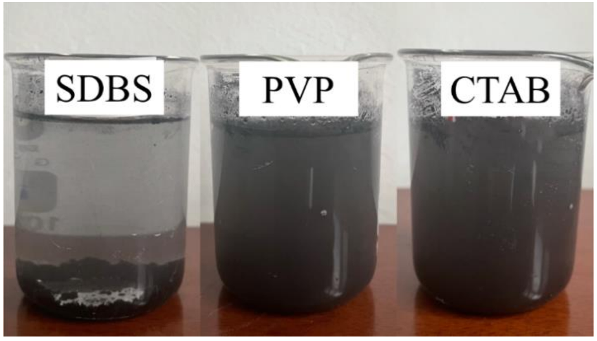
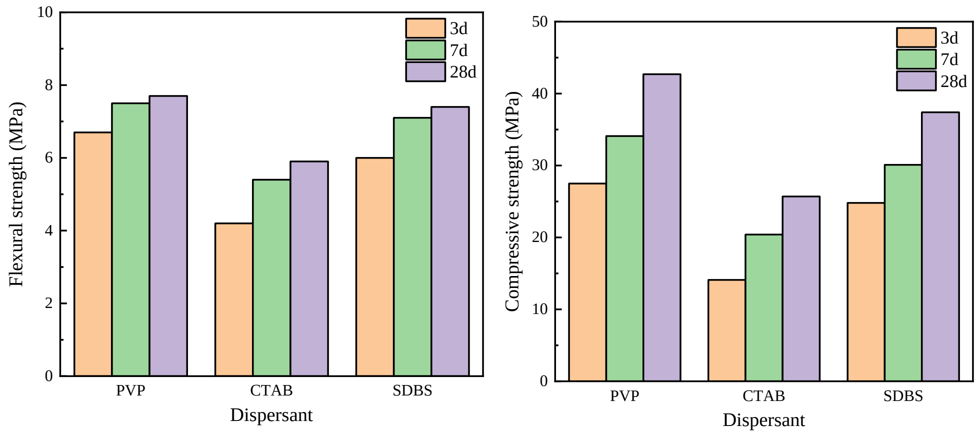


Fig. 4. The stratification of CNFs dispersions prepared by different dispersants in 1d

3.4 Analysis of Mechanical Test Results

3.4.1 Effects of Different Types of Dispersions on The Strength of Cement Mortar

A comparison of the flexural and compressive strengths of cement-based composites prepared with different dispersants under the same CNFs content ratio, and a study of the influence of dispersant types on the mechanical properties of specimens were carried out. Fig. 5 shows the flexural and compressive strengths of test pieces after 3 d, 7 d, and 28 d were prepared with different dispersants. It can be seen from Fig. 5 that under the same CNFs content ratio, the flexural and compressive strengths of the specimens are the largest when PVP is used alone as the dispersant, indicating that PVP has the best dispersing effect on CNFs. The main reason is that the use of PVP as a dispersant can improve the workability of cement-based composites. At the same time, it can maintain a uniform dispersion of CNFs in the distribution and cement mortar environment so that CNFs can be evenly interspersed in the hydration product. Between the interfaces, the pores are filled to form a dense structure, thereby increasing the strength of the cement-based material. It is observed that when CTAB and SDBS are used as dispersants, the flexural and compressive strengths of the specimens are very small. The reason is that when CTAB and SDBS dispersants are used, a large amount of them will be produced during the preparation of the dispersion and the mixing of cement mortar. Air bubbles result in more pores inside the cement test block, which significantly reduces the compactness of cement-based materials, resulting in a significant drop in the bending resistance and compressive strength of the test piece [16]. The above analysis shows that PVP has a good dispersing effect on CNFs, thus exerting a good influence of CNFs on cement-based materials.



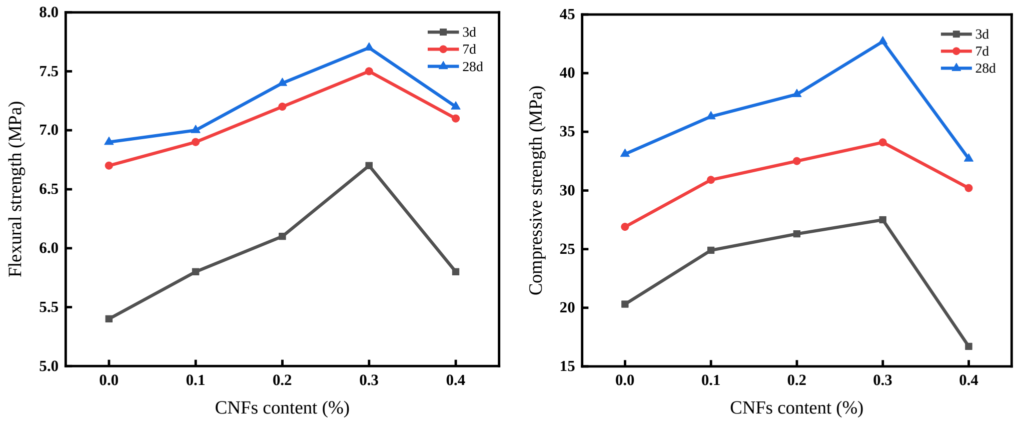
(a) Flexural strength (b) Compressive strength

Fig. 5 Test results of cement mortar strength under different dispersants

3.4.2 Effect of PVP/CNFs on mechanical properties of cement mortar

The PVP/CNFs suspension was prepared, and the influence of the content of CNFs on the flexural, compressive strength of standard cement mortar test blocks of different ages was studied. The test results are shown in Fig. 6. It can be seen from Fig. 6 that the PVP/CNFs suspension has a specific effect on the strength of cement test blocks of different ages. With the increase of the content of CNFs, the flexural and compressive strengths of the cement paste specimens at different ages all show a trend of first increasing and then decreasing. When the content of CNFs is 0.3%, the flexural and compressive strengths of the specimens have reached the highest value.

After adding 0.1% CNFs, the flexural and compressive strength of the specimens were improved. At the content of 0.3% CNFs, the flexural strength of the models at 3d, 7d, and 28d were 6.8MPa, 7.6MPa, and 7.8MPa, respectively, which increased by nearly 28.3%, 15.2%, and 12.8% compared with the blank specimens (5.3MPa, 6.6MPa, and 6.8MPa). At the content of 0.3% CNFs, the 3d, 7d, and 28d compressive strengths of the models were 27.7MPa, 34.4MPa, and 42.5MPa, respectively, which increased by nearly 37.8%, 29.8%, and 29.2% respectively compared with the blank specimens (20.1MPa, 26.5MPa, and 32.9MPa). Therefore, CNFs significantly influence the early flexural and compressive strength of cement mortar and better affect the compressive strength of cement paste specimens at different ages.



(a) Flexural strength (b) Compressive strength

Fig. 6 Test results of cement mortar strength under different CNFs content

4. Conclusion

1) Through the ultraviolet-visible absorbance test and the Tyndall light test, it can be seen that the dispersing effects of PVP, CTAB, SDBS, three kinds of dispersants on CNFs are significantly different. PVP has the best dispersion effect when used as a dispersant compared with the other two dispersants. The PVP suspension has no apparent stratification, and the dispersion is more uniform than other suspensions without bubbles.
2) According to the study of the influence of dispersant types on the mechanical properties of specimens, when CTAB and SDBS are used as dispersants under the same CNFs content ratio, the flexural and compressive strengths of models are very small. When PVP alone is used as a dispersant, the flexural and compressive strengths are the largest, therefore PVP has the best dispersing effect on CNFs.
3) With the increase of the content of CNFs, the flexural and compressive properties of cement mortar specimens increase first and then decrease. When the content of CNFs is 0.3%, the flexural and compressive strength of cement mortar specimens reaches the highest value. Compared with the control group, the 3 d, 7 d, and 28 d flexural strength of cement mortar specimens with CNFs content of 0.3% increased by 24.0%, 12.0%, and 11.6%, respectively, and the compressive strength increased by nearly 37.8%, 29.8%, and 29.2% respectively.

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