Effect of Carbon Nanofibers on Strength and Pore Structural Characteristics of Concrete

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Abstract. In order to investigate the influence of carbon nanofibers (CNFs) on the strength and internal pore structural characteristics of concrete, the carbon nanofibers reinforced concrete (CNFC) specimens with the content of 0%, 0.1%, 0.2%, 0.3% and 0.5% were prepared. The characteristics of the internal pore structure of specimens in each group were analyzed by the method of mercury intrusion porosimetry (MIP). The results show that the appropriate amount of CNFs has a significant enhancement effect on the strength of concrete, but the excessive amount of CNFs (0.5%) will weaken the performance of concrete; CNFs can effectively reduce the total pore volume and average pore size of concrete, and the internal pore structure of concrete can be improved reasonably.

1. Introduction
As a traditional building material, concrete is still playing a leading role in the field of building materials due to its stable mechanical properties, good durability and excellent plasticity. However, with the continuous development of society, the continuous renewal of building styles, the gradual complexity of structural forms and the diversity of service environment, the traditional concrete materials cannot meet the diversity requirements of modern buildings, especially the strength of concrete structure needs to be greatly improved, which leads to the research in the field of concrete strength has always become the top priority of the concrete materials, and various theories and test methods of enhance concrete strength are constantly updated. Among all kinds of methods to enhance the performance of concrete, the additional reinforcement material is undoubtedly the most widely used and effective, and among these reinforcement materials, fiber material has become a hotspot of many scholars [1-5].

Carbon nanofibers (CNFs) is a new type of discontinuous nanometer graphite fibers [6-10], which are formed by the decomposition of gaseous hydrocarbons and with a length of about 0.5-100 μm and a diameter of about 50-100 nm. CNFs has the characteristics of small scale (aspect ratio up to 500), low density (about 2.10 g/cm), high strength (tensile strength is about 7 GPa) and high modulus (about 400 GPA). What’s more, its good toughness (fracture strain is about 50%), excellent conductivity
(resistivity is about 55 Ω·cm), and thermal conductivity (about 1950 w/(MK)) make it have the inherent properties of common carbon fiber and various effects of nano materials, so CNFs is a multifunctional material with excellent performance. While due to its immature production process and relatively high cost, the research on CNFs in China is not in-depth, and there are few reports on its application [11, 12]. At present, the research on CNFs mainly focuses on the basic properties, such as dispersion [13, 14], strength [15], electric heating [16] and so on, and there are few researches on the action law and principle of CNFs on the mesoscopic and micro level of concrete. In this paper, CNFs reinforced concrete (CNFC) specimens with the CNFs content of 0%, 0.1%, 0.2%, 0.3% and 0.5% were prepared to study the effect of CNFs on the macro strength and micro porosity of concrete.

2. Experiment

2.1. Specimens preparation

The materials for specimens preparation include: Ordinary Portland cement with the strength grade of 42.5R, crushed limestone, clean medium sand, tap water, FDN superplasticizer, tributyl phosphate defoamer, CNFs. The main performance indexes of CNFs are listed in table 1.

| Purity /% | Filament diameter /nm | Aspect ratio | Thermal conductivity /W·(m·℃)⁻¹ | Resistivity /Ω·cm | thermal expansion coefficient /℃⁻¹ | Specific surface area /m²·g⁻¹ | Density /g·cm⁻³ |
|-----------|----------------------|--------------|---------------------------------|------------------|-----------------------------------|-------------------------------|----------------|
| 99.9      | 100~200              | 70           | 2000                            | <0.012           | 1                                 | 300                           | 0.18           |

The mix proportion of concrete is shown in table 2, where PC is the reference specimens without CNFs, CNFC01, CNFC02, CNFC03 and CNFC05 are the reinforced concrete specimens with CNFs volume content of 0.1%, 0.2%, 0.3% and 0.5% respectively.

| Specimens number | Cement | Water | Medium sand | Crushed limestone | Superplasticizer | Defoamer | CNFs |
|------------------|--------|-------|-------------|-------------------|-----------------|----------|------|
| PC               | 495    | 180   | 672         | 1008              | 0               | 0        | 0    |
| CNFC01           | 495    | 180   | 672         | 1008              | 5.0             | 0.30     | 0.18 |
| CNFC02           | 495    | 180   | 672         | 1008              | 7.5             | 0.45     | 0.36 |
| CNFC03           | 495    | 180   | 672         | 1008              | 10.0            | 0.60     | 0.54 |
| CNFC05           | 495    | 180   | 672         | 1008              | 15.0            | 0.90     | 0.90 |

2.2. Compressive strength test

The compressive strength test were carried out in accordance with the relevant test provisions of Standard for test method of mechanical properties on ordinary concrete (GB/T 50080-2016) [17], and the corresponding test pieces were prepared. The device used for the test is hydraulically driven test system, as shown in figure 1.

2.3. Analysis of pore structure characteristics

The research of pore structure characteristics is carried out by mercury intrusion porosimetry (MIP). The test device is an automatic mercury porosimeter of PoreMaster33 which produced by Quantachrome, as shown in figure 2. This device is equipped with two low-pressure analysis stations, which can analyze one high-pressure specimen and two low-pressure specimens, it has the function of automatically vacuumize and accurately fill the specimen tube with mercury, and the safe measurement range of pore size is 6.4 nm~650 μm. During the test, the specimens were placed in the low-pressure and high-pressure analysis station respectively for the pore measurement. The mercury saturation angle was set at 140° and the pressure range was 20~30000 psi.
3. Experiment results

3.1. Compressive strength
Figure 3 is the failure test of the specimen under the static load, and figure 4 shows the relationship between the CNFs content and static compressive strength and compressive strain respectively. Here, the compressive strain refers to the corresponding strain value when the specimen reaches the maximum compressive strength (the peak point of the stress-strain curve).

It can be seen from figure 4 that, the effect of CNFs on the compressive strength and compressive strain of concrete is basically the same, both show the trend of strengthen first and then weaken; the optimal content of CNFs to improve the strength of concrete is 0.3%, and the strength increased by 4.22 MPa, the increase was 9.15%, the compressive strain reached its maximum at the same time, which was 9.75% higher than that of the PC group. However, when the content of CNFs increased to 0.5%, the strength and strain of concrete decreased by 0.95% and 1.69% respectively.

3.2. Pore structure characteristics
The pore characteristic parameters of specimens in each group are listed in table 3. The most probable aperture in the table is the pore size that corresponding to the peak value of the differential curve of pore size distribution. The median aperture is the pore size when pressed into half of the mercury solution. The average aperture is defined as the ratio of the total pore volume to the average pore surface area. Figure 5 shows the distribution differential curve of specimens in each group.
Table 3. Pore characteristic parameters of each group

| Specimens number | Most probable aperture /nm | Median aperture /nm | Total pore volume/mL·g⁻¹ | Average aperture /nm | Percentage of pore volume/% |
|------------------|-----------------------------|---------------------|---------------------------|----------------------|-----------------------------|
|                  |                             |                     |                           |                      | <10 nm | 10~100 nm | 100~1000 nm | >1000 nm |
| PC               | 9463                        | 309.10              | 0.0445                    | 111.58               | 4.27  | 33.93     | 22.25       | 39.55     |
| CNFC01           | 33.02                       | 87.66               | 0.0403                    | 72.18                | 4.08  | 47.70     | 15.26       | 32.96     |
| CNFC02           | 13.92                       | 31.87               | 0.0384                    | 54.76                | 12.23 | 52.13     | 10.62       | 25.02     |
| CNFC03           | 36.92                       | 55.91               | 0.0372                    | 45.90                | 4.29  | 59.68     | 14.52       | 21.51     |
| CNFC05           | 53.19                       | 91.15               | 0.0395                    | 83.21                | 2.12  | 48.68     | 18.78       | 30.42     |

Figure 5. Differential curve of pore size distribution of each group (a) Group PC (b) Group CNFC01 (c) Group CNFC02 (d) Group CNFC03 (e) Group CNFC05

In this paper, according to the pore distribution characteristics which measured based on the MIP, the classification method of reference [18] was introduced to divide the pores into gel pore (<10 nm),
transition pore (10~100 nm), capillary pore (100~1000 nm) and macropore (>1000 nm). The percentage distribution and the content of the four types of pore in specimens of each group are plotted in figure 6 and figure 7 respectively.

![Figure 6. Pore percentage distribution](image1)

![Figure 7. Pore content](image2)

As shown in figure 6 and figure 7, with the increase of CNFs content, the contents of macropores and capillary pores in concrete decreased significantly, and the proportion of gel pores and transition pores increased accordingly.

4. Mechanism analysis
On the one hand, the addition of CNFs has a remarkable effect on the improvement of pore content in concrete, which shows that the content of macropores decreases sharply, and although the content of pore with small size increases slightly, the total internal pore volume decreases obviously, which indicating that the compactness of the material has been effectively improved. The main reason for this phenomenon is that the diameter of CNFs is only 150~200 nm, for the dry shrinkage cracks produced by concrete molding, the incorporation of CNFs can result in a good filling effect, and for the relatively few pores with small size that produced by evaporation and consumption of water, parts of CNFs can be dispersed in these pores, which can further reduce the pore content in concrete. Therefore, the addition of CNFs can effectively reduce the pore content and improve the compactness, thus the strength has been significantly enhanced.

On the other hand, the addition of CNFs can improve the internal pore structure of concrete, which is manifested in the decrease of the proportion of macropores and the increase of micropores, thus the internal pore structure of concrete has been effectively refined. The main reason for this phenomenon is that, for the pores with a size greater than 100 nm, appropriate CNFs can effectively fill them, thus these pores are significantly decreased. While for the pores with a size less than 100 nm, due to the addition of fibers, there will be a small amount of pores on the contact interface between CNFs and concrete matrix, and generally, these pores are micropores with a size less than 100 nm, so the content of these pores will be increased to some extent.

5. Conclusions
In this paper, five groups of carbon nanofibers reinforced concrete specimens were prepared, and the improvement of concrete strength by CNFs was discussed, and the pore structure characteristics of specimens in each group were further studied by MIP method. The main conclusions are as follows:

1) The appropriate amount of CNFs can significantly enhance the strength of concrete, but the excessive amount (0.5%) will has a certain weakening effect on its performance.

2) The optimum content of CNFs to increase the compressive strength and compressive strain of concrete are both 0.3%, the strength increased by 4.22 MPa, the increase is 9.15%, and the compressive strain reached its maximum at the same time, which was 9.75% higher than that of the PC group.
The addition of CNFs can effectively reduce the total pore volume and average pore size of concrete, and the content of macropores can be greatly reduced, while the content of micropores will increase slightly.

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