Article

Strength Analysis of Cement Mortar with Carbon Nanotube Dispersion Based on Fractal Dimension of Pore Structure

Jinjun Guo 1, Yanling Yan 1,2, Juan Wang 1,3,* and Yaoqun Xu 1,2,*

1 Yellow River Laboratory, Zhengzhou University, Zhengzhou 450001, China
2 School of Water Conservancy Engineering, Zhengzhou University, Zhengzhou 450001, China
3 State Key Laboratory of Hydroscience and Engineering, Tsinghua University, Beijing 100084, China
* Correspondence: wangjuan@zzu.edu.cn (J.W.); yaoqunxu_zzu@163.com (Y.X.)

Abstract: Carbon nanotubes (CNTs) are considered among the ideal modifiers for cement-based materials. This is because CNTs can be used as a microfiber to compensate for the insufficient toughness of the cement matrix. However, the full dispersion of CNTs in cement paste is difficult to achieve, and the strength of cement material can be severely degraded by the high air-entaining property of CNT dispersion. To analyze the relationship between the gas entrainment by CNT dispersion and mortar strength, this study employed data obtained from strength and micropore structure tests of CNT dispersion-modified mortar. The fractal dimensions of the pore volume and pore surface, as well as the box-counting dimension of the pore structure, were determined according to the box-counting dimension method and Menger sponge model. The relationship between the fractal dimensions of the pore structure and mortar strength was investigated by gray correlation. The results showed that the complexity of the pore structure could be accurately reflected by fractal dimensions. The porosity values of mortar with 0.05% and 0.5% CNT content were 15.5% and 43.26%, respectively. Moreover, the gray correlation between the fractal dimension of the pore structure and strength of the CNT dispersion-modified mortar exceeded 0.95. This indicated that the pore volume distribution, roughness, and irregularity of the pore inner surface were the primary factors influencing the strength of CNT dispersion-modified mortar.

Keywords: carbon nanotubes; cement mortar; fractal dimension; pore structure; gray correlation analysis

1. Introduction

Cement-based materials are widely used in various engineering structures such as buildings, bridges, dams, and roads because of their excellent compressive properties and durability. However, cement-based materials have certain limitations, such as low tensile strength and insufficient toughness [1–4]. When engineering structures are exposed to the external environment and subjected to loading, pores and cracks are easily generated, severely degrading the normal service life of these structures. In view of its shortcomings, a large number of scholars have made some rich achievements in studying the methods of improving the strength and toughness of cement-based materials by changing water–cement ratio, cementitious materials, types and content of fibers, admixtures, etc. Rao and Chen et al. studied the effect of water–cement ratio on mortar and considered it an important parameter that affects the strength of mortar [5,6]. Pereira-De-Oliveira et al. studied the effects of different kinds of fibers such as polypropylene fiber, glass fiber, and polyethylene fiber on the strength of mortar, and thought that the effects of different fibers on the strength and durability of mortar were similar [7]. In engineering applications, fiber materials are often used to improve the properties of cement-based materials [8]. However, crack development can only be limited to a certain extent by steel fibers, acrylic textile fibers, polypropylene fibers, etc., and the generation of cracks cannot be fundamentally improved. Therefore, some scholars focus on microfiber materials, among which CNTs are the focus of research.
CNTs are a kind of nanofiber material with exceptional tensile properties and toughness, and their tensile strength is 100 times greater than that of steel. Moreover, as a microfiber, CNTs can not only inhibit the emergence and development of microcracks in cement-based materials, but also improve the mechanical properties and durability of cement-based materials. Some studies have shown that the shrinkage of hardened cement mortar can be inhibited by CNTs, and crack resistance can be significantly improved. When 0.1% CNTs are added to hardened cement mortar, the self-shrinkage inhibition rate can reach 40%, and the porosity and microcracks of cement paste are significantly reduced [9]. Xu and Rocha reported that the strength of mortar increased with the addition of CNTs; 0.1% CNTs could increase the flexural strength by 46%. The bridging and filling effects of CNTs have been observed by scanning electron microscopy (SEM) [10,11]. However, Liu and Huang reported that the mortar strength first increased and then decreased with CNT addition. In the study by Huang, the mortar strength increment reached 30% [12–14]. Thus it can be seen that the conclusions of different scholars are diametrically opposite. In order to explore this reason, many scholars have conducted in-depth studies on the microstructure of cement-based materials.

Some studies are exploring the reasons for the different CNT effects on mechanical properties and durability. Wang and Nochaiya analyzed the influence of CNTs on pore structure and found that CNTs could reduce mortar porosity [15,16]. Gdoutos reported that the macroscopic and nanoscale mechanical properties and nanostructure of mortar could be improved by the addition of CNTs. The matrix of mortar was strengthened by CNTs on a nanometer scale by increasing the C–S–H quantity and decreasing the porosity [17]. CNTs have high surface atomic ratio and surface energy; therefore, it is easy to agglomerate. The effect of CNTs on mortar is limited by agglomeration. The surfactant used to disperse CNTs has a great negative effect on cement-based materials. Therefore, some scholars think that CNTs as a dispersant increase the porosity. Reales et al. mixed a surfactant with CNT dispersion and found that the negative effect of the surfactant on the mortar matrix was greater than the positive effect of CNTs [18]. Hu et al. analyzed the effects of 0.05% and 0.5% CNT dispersions on the mechanical properties and microstructure of cement mortar. They found that the air introduced into the dispersant increased the porosity and affected the strength of the mortar [19]. Correlation analysis of the effect of CNT dispersion on strength of cement-based materials is rarely performed. Therefore, such study has significance for the utilization of CNT-reinforced cement-based materials.

The relationship between the macroscopic properties and microstructure of cement-based materials has been a key problem in the research on cement materials. Most studies explored the microstructure characteristics of cement-based composites through SEM, X-ray diffraction, nanoindentation, and other microanalysis technologies. A theoretical model that considers the relationship between microstructure changes and macro-performance evolution was subsequently established. Li et al. established the flexural strength curve of cement-based composites with porosity and capillary content; CNTs could optimize the pore structure and improve compactness [20]. Gao et al. derived the curves of flexural and compressive strengths, including porosity. Then, they analyzed the relationship between the CNT diameter and porosity [21], considering that the pore structure of mortar has an important influence on strength and durability. However, the pore structure characteristics of cement-based materials are intricate. Conventional parameters, such as porosity and pore size distribution, which can characterize the pore structure, cannot quantitatively describe the pore shape, specific surface area, diameter, and spatial distribution [22,23].

Because the traditional parameters cannot meet the needs of the test, some scholars combine cement-based materials with mathematics to seek new parameters to quantitatively evaluate the complex changes of pore structure. The fractal dimension has been a hot topic in recent years. Fractal theory provides a scientific method for examining the irregular and complex natural phenomena. As a basic mathematical concept and a measure of complex structures, the fractal dimension is mainly applied to quantitatively represent the intricacy of geometric forms and space filling ability. The emergence of fractal
theory has offered a new avenue for the exploration of complex and disordered phenomena in cement-based materials. Previous studies have shown that the fractal dimension can be effectively applied to study the pore structure (e.g., pore shape, specific surface area, diameter, and spatial distribution) of cement-based materials [24–28]. Some scholars have studied using different types of fractal dimensions to characterize pore structure, such as the fractal dimension of pore volume, fractal dimension of pore surface, and fractal dimension of porosity. Wang et al. introduced the principle, testing technology, and fractal dimension model of seven kinds of fractal dimensions commonly used in cement-based materials [29]. Qing et al. used the box-counting method to calculate the fractal dimension from the scanning electron microscope image [30]. Some scholars have established a correlation between macro-cement-based and micro-cement-based materials through the fractal dimension [31–33]. Jin studied the correlation between mortar strength and pore structure through experiments. The results indicated that the fractal theory was more accurate than conventional parameters in characterizing pore size distribution [34]. Han investigated the correlation between fractal characteristics and concrete strength, and subsequently formulated a mathematical model that considered fractal dimension and compressive strength [35].

The influence of pore structure change caused by CNT dispersion on the strength of cement-based materials is a key problem in the application of CNT-reinforced cement-based materials. To analyze the correlation between the pore characteristics and strength of CNT-modified cement-based materials, this study employed the box-counting dimension method and Menger sponge model. The fractal dimensions of pore volume and pore surface, as well as box-counting dimensions, of mortar modified by 0.05% and 0.5% CNT dispersions were determined. The correlation between the mechanical properties (including strength) and pore structure of CNT-modified cement-based materials was quantitatively analyzed.

2. Materials and Tests

2.1. Raw Materials

A dispersion of CNTs was prepared with nonionic surfactant (named TNWDIS, carbon nanotube water dispersant provided by Chengdu Organic Chemicals Co., Ltd. (Chengdu, China)) and multiwalled carbon nanotubes with diameters in the range 30–80 nm; the dispersion medium was deionized water. As a dispersant, the content of TNWDIS was 0.25 times the mass of CNTs. The CNT image shown in Figure 1a, captured using a transmission electron microscope (TEM), was provided by Chengdu Organic Chemical Co., Ltd.; it can be seen that the CNTs were rarely intertwined. Furthermore, the CNT diameter shown in the image is about 50 nm, which agrees with the size range of CNT diameter 30–80 nm. The 10% CNT content of the dispersion is the black liquid shown in Figure 1b. Cement P.I 42.5 (Chinese standard) was used; its fundamental properties are summarized in Table 1. Natural river sand with a fineness modulus of 2.94 was utilized. Superplasticizer was applied to modify the working properties of fresh cementitious composites.

<table>
<thead>
<tr>
<th>Chemical Compositions</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>Loss</th>
<th>Specific Gravity</th>
<th>Specific Surface (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>20.56</td>
<td>4.6</td>
<td>3.23</td>
<td>62.56</td>
<td>2.57</td>
<td>0.59</td>
<td>2.95</td>
<td>2.94</td>
<td>3.13</td>
<td>3530</td>
</tr>
</tbody>
</table>

Table 1. Properties of cement.
2.2. Preparation and Curing of Mortar

Cement mortar specimens containing CNTs at 0.05% and 0.5% of the cement mass were prepared. CNTs were mixed into mortar through a CNT dispersion, and the content of CNTs in the CNT dispersion was 10%. The dosage of the CNT dispersion in the two CNT mortar groups was 2.25 g and 22.5 g, respectively. Ordinary mortar specimens without CNTs were also prepared for comparison. The three groups of mortar specimens had the same water–cement ratio of 0.5, and the mass ratio of sand to cement was 3:1. The mortar specimens, 40 × 40 × 160 mm³ in size, were formed according to the preparation method specified in the Chinese national standard, GB/T 17671-2021. Mortar fluidity was tested before the specimens were formed. Each test group had four groups of mortar specimens, and each group was prepared using triple test molds. The test group number and the quantity of raw materials used in each group are summarized in Table 2.

Table 2. Mix proportions of mortar.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Sand (g)</th>
<th>Cement (g)</th>
<th>Water (g)</th>
<th>Admixture (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CNTs</td>
</tr>
<tr>
<td>C0</td>
<td>1350</td>
<td>450</td>
<td>225</td>
<td>0</td>
</tr>
<tr>
<td>C1</td>
<td>1350</td>
<td>450</td>
<td>223</td>
<td>2.25</td>
</tr>
<tr>
<td>C2</td>
<td>1350</td>
<td>450</td>
<td>205</td>
<td>22.5</td>
</tr>
</tbody>
</table>

The poured specimens were maintained in a standard curing box for 48 h. After removing the molds, the specimens were immersed and maintained in water and then placed in the standard curing room at 25 °C until the test age was reached. The four groups of specimens were cured for 3, 7, 14, and 28 days; they were removed from water upon reaching the curing age. The compressive and flexural strengths of the mortar specimens were tested, and pore structure analysis and SEM observation were performed.

2.3. Testing Procedures

2.3.1. Mortar Strength Test

Mortar strength testing includes checking the compressive and flexural strengths. First, all the 40 × 40 × 160 mm³ specimens were placed on the flexural loading frame. Three-point flexural loading was implemented at a loading rate of 0.06 mm/min along a span of 120 mm. After the mortar specimens failed by flexural loading, the damaged specimens were placed on a compressive loading fixture. A 40 × 40 mm² area in the middle of the damaged specimen was obtained for a compressive loading test with a compression loading rate of 0.12 mm/min. Twelve strength tests were conducted for the four experimental groups: three for each age group.

Figure 1. Images of CNTs: (a) TEM; (b) CNT dispersion.
2.3.2. Pore Structure Measurement

The pore structure of mortar cured for 28 days was measured using the linear traverse method (LTM). After completing the flexural strength test, a $20 \times 30 \times 30$ mm$^3$ slice was selected. The LTM was implemented according to the standard “Test code for hydraulic concrete” (SL352-2006). First, the slices were ground and buffed using a burnisher with a rotary speed of 50 rpm for 30 min. Then, the ground and polished surfaces were dried at 50 °C for 3 h. White barium sulfate powder was appropriately dusted on the measured surface of the slice, and the excess powder was removed after pressing. Lastly, the processed slice was placed in an automatic pore structure analyzer to determine its pore distribution and porosity.

2.3.3. SEM Test

The microstructure of mortar samples with different CNT contents was observed by SEM. After completing the flexural strength test, cubic particles, 1 cm on each side, were obtained from damaged specimens and immersed in alcohol to prevent hydration. Then, the samples were removed from ethanol and vacuum-dried at 50 °C. The distribution of CNTs in the mortar and the effect of CNTs on mortar porosity and hydration products were observed by SEM.

The experimental program, test method, and parameters set in the test of CNT mortar specimens are shown in Figure 2. The results of mortar fluidity, specimen weight, strength, and porosity fraction are provided in Table 3.

![Figure 2. General overview of experimental program.](image)

Table 3. Properties of mortar.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Mortar Fluidity (mm)</th>
<th>Unit Weight (kg·m$^{-3}$)</th>
<th>28 Day Compressive Strength (MPa)</th>
<th>28 Day Flexural Strength (MPa)</th>
<th>Porosity Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>160</td>
<td>2050</td>
<td>40.9</td>
<td>7.09</td>
<td>6.22</td>
</tr>
<tr>
<td>C1</td>
<td>165</td>
<td>1914</td>
<td>41.9</td>
<td>7.77</td>
<td>15.50</td>
</tr>
<tr>
<td>C2</td>
<td>180</td>
<td>1552</td>
<td>23.2</td>
<td>5.3</td>
<td>43.26</td>
</tr>
</tbody>
</table>

3. Methodology

Fractal theory has been introduced to describe the pore structure of mortar. On the basis of the fractal dimension of the pore structure, the correlation between the mortar strength and pore structure can be established. The Menger sponge model and box-counting method are the main models used to calculate the fractal dimensions of the pore structure. In this study, using the slices as samples, the fractal dimensions were calculated by employing the Menger sponge model [35,36] and the box-counting method [37–40].
3.1. Menger Sponge Model

The fractal dimensions of pore volume, $D_v$, and pore surface, $D_s$, of the mortar are calculated using Menger sponge model. The pore structure test classifies bubbles according to their chord lengths; hence, the number of bubbles and porosity can be determined. The fractal dimension can be calculated by combining the experimental data with the Menger sponge model. The construction process is shown in Figure 3, and the specific construction method is described below.

$$r_k = R/m^k, \quad (1)$$
$$N_k = N_1^k = \left(m^3 - n\right)^k. \quad (2)$$

In the above equations, $N_k$ and $k$ can be expressed as

$$N_k = \left(r_k/R\right)^{-D}, \quad (3)$$
$$k = \frac{\lg\left(R/r_k\right)}{\lg m}, \quad (4)$$

where $D = \lg \left(m^3 - n\right)/\lg m$ is the fractal dimension. The volume, $V_k$, of the leftover cube can be expressed as

$$V_k = r_k^3N_1^k = \frac{r_k^3}{R^{D-3}}. \quad (5)$$

The pore volume can be expressed as

$$V = R^3 - V_k. \quad (6)$$

Combining the Menger sponge model with the pore structure test, the necessary parameters to calculate the fractal dimension are provided by the pore structure test data. The pore volume, $V_\phi$, can be calculated on the basis of the volume and porosity of the sample. The pore diameter is $r_k$, and $R$ is the maximum pore diameter measured in the sample. Various parameters and methods of derivation are selected depending on the different interpretations of Menger sponge model. Accordingly, $V_\phi$, $V_s$, and $V_p$ (fractal dimension of porosity) are derived. In the process of calculating fractal dimension, the multifractal phenomenon may occur because of the complex pore structure. Multifractals are defined as follows: let $R^d$ be a d-dimensional space. $F$ is a d-dimensional subset of $R^d$ and a support of measure $\mu$. If, under a certain partition, the fractal set produced by
\( (F, \mu) \) is the union of several fractal subsets, and each fractal subset has different fractal dimension, \((F, \mu)\) is called multifractal.

**Figure 4.** Cross-section mortar diagram based on Menger’s sponge: (a) grayscale image of mortar section; (b–d) construction process.

### 3.2. Box-Counting Method

The basic mathematical expression of the box-counting method is as follows: let \( F \) be any nonempty bounded subset on \( \mathbb{R}^d \); \( \delta \) is the size of the box, and \( N(\delta) \) is the minimum number of boxes required to cover \( F \). If \( D \) exists when \( \delta \) approaches 0, the following formula applies:

\[
n(\delta) \propto \delta^{-D},
\]

where \( D \) is called the box-counting dimension of \( F \). A positive number, \( K \), is given by Equation (8).

\[
\lim_{\delta \to 0} \frac{n(\delta)}{\delta^d} = k.
\]

The box-counting dimension is expressed by Equation (9).

\[
D = \lim_{\delta \to 0} \frac{\log K - \log n(\delta)}{-\log \delta} = \lim_{\delta \to 0} \frac{\log n(\delta) - \log (1/\delta)}{-\log \delta}.
\]

The pore structure parameters measured by the pore structure analyzer include the number of bubbles in a certain range of the chord length. The bubbles in the mortar are assumed to be regular spheres. Combined with the definition of the box-counting dimension, \( n \) round boxes are used to cover the bubbles in the mortar. The size, \( \delta \), of each box corresponds to the diameter, \( d_i \) (\( i = 1, 2, \ldots, n \)), of bubbles. These boxes are used to cover bubbles with diameters \( \geq d_i \). The bubble diameters \( \geq d_i \) are converted into diameter \( d_i \) using the principle of equal area. The number of converted bubbles with diameter \( d_i \) is obtained. The sum of the numbers of converted bubbles and bubbles whose original diameter is \( d_i \) is recorded as \( N_{d_i} \). From the foregoing, a group of data \( ((d_1, N_{d1}), (d_2, N_{d2}), (d_3, N_{d3}), \ldots, (d_n, N_{dn})) \) composed of the diameters and numbers of bubbles can be obtained.

When the group of data are linearly regressed in double logarithmic coordinates, the slope of the regression line is the box-counting dimension \( (D_d) \). It can be simplified as shown in Equation (10).

\[
\log N_{d} = -D_d \log d + C
\]

### 4. Results

#### 4.1. Mortar Strength

The test results of the compressive and flexural strengths of three groups of mortar specimens, \( C_0, C_1, \) and \( C_2 \), at four ages (3, 7, 14, and 28 days) are shown in Figure 5a. Figure 5a shows the increase curves of the compressive strengths of \( C_0, C_1, \) and \( C_2 \) obtained by linear regression analysis. The relationship between the compressive strengths of \( C_0, C_1, \) and \( C_2 \) and age was logarithmic; the \( R^2 \) value of the linear regression exceeded 0.98. The slope can represent the increasing rate of compressive strength with age. The slopes of \( C_0, C_1, \) and \( C_2 \) were 16.753, 13.822, and 14.288, respectively, indicating that the increasing rate of the compressive strength of the mortar without CNTs exceeded that of the mortar with 0.05% and 0.5% CNT dispersions. However, the test results indicated that the compressive
strengths of the mortars with 0.05% and 0.5% CNT dispersions increased and decreased, respectively.

![Figure 5](image)

**Figure 5.** Cement mortar strength: (a) compressive strength and (b) flexural strength of C0, C1, and C2.

Figure 5b shows the increase curves of the flexural strengths of C0, C1, and C2 obtained by linear regression analysis. The relationship between the flexural strengths of C0, C1, and C2 and age was logarithmic. The $R^2$ value of the linear regression exceeded 0.97. The slopes of C0, C1, and C2 were 2.840, 2.241, and 3.842, respectively, indicating that the increase rate of the flexural strength of the mortar with 0.5% CNT dispersion was higher than those of the mortars with 0.05% CNT dispersion and without CNTs. However, the test results indicated that the flexural strengths of the mortars with 0.05% and 0.5% CNT dispersions increased and decreased, respectively.

4.2. Pore Structure

Figure 6a shows binary images of the pore distributions of samples C0, C1, and C2 (black for the mortar matrix and white for the pores). It can be intuitively indicated that the porosity of C1 and C2 was significantly higher than that of C0, and, as the amount of CNTs increased, the porosity increased. The porosity of hardened mortar varied with the pore radius, as shown in Figure 6b. The results show that the change trends of the porosity of the three groups of mortar specimens were fundamentally the same. Overall, the order of the porosity of mortar specimens was C2 > C1 > C0. In the pore radius range 1–30 μm, porosity increased with the pore size. The porosity fluctuated over a small range when the pore radius range was 30–350 μm. Lastly, the porosity fluctuated greatly and reached the peak when the pore radius range was 350–900 μm. The peak porosity values of the three groups of mortar specimens (C0, C1, and C2) were 2.1%, 4.4%, and 12.5%, respectively, and the overall porosity values were 6.22%, 15.50%, and 43.26%, respectively.

Apparently, CNT dispersion increased both the pore size and the porosity of mortars to different degrees. This was the reason for the reduction in the strength of the mortar with 0.5% CNT dispersion. This observation is consistent with the results of other studies. Surfactants and dispersants negatively affect the microstructure and mechanical properties of mortar [16,17]. In the experiment, the porosity of CNT-modified mortar increased significantly; the measured porosity of the mortar was 43.8%, and the compressive strength test shows that the strength of mortar was 23.2 MPa. The previous mortar model composed of pores and mortar matrix was used to quantitatively analyze the effect of CNTs dispersion on mortar. The relationship between the increase of porosity and the enhancement effect of CNTs on matrix was explored, and the enhancement range of mortar matrix by CNTs...
was calculated. The results show that the matrix strength of CNTs modified mortar was significantly improved; when the content of CNTs was 0.5%, matrix relative matrix strength increased by 71.18% [23].

![Figure 6](image_url)

**Figure 6.** Porosity distribution in the LTM test: (a) binary images of sample pore distributions; (b) pore size distributions.

4.3. **SEM Results**

Representative sample fragments for SEM are shown in Figure 7; it can be seen that the colors of C0, C1, and C2 deepened with the increase in CNT content. The microstructure of blank group C0 showed the presence of C–S–H in amorphous form, and tiny pores are distributed in the matrix of the mortar. In the microstructures of C1 with 0.05% CNT dispersion and C2 with 0.5% CNT dispersion, the CNTs in the cement hydration product were well dispersed. The CNT content of C2 was observed to significantly exceed that of C1. The structures of C1 and C2 were obviously looser than that of C0, with a large number of pores. The CNTs and the hydration products (C–S–H) of cement formed a meshwork microstructure. The meshwork microstructure composed of CNTs and hydration products of cement can be used as a strengthening structure to improve the mortar strength and toughness [19,41,42]. In this study, the compressive and flexural strengths of C1 were found to increase. However, the SEM images show that the pore size and number of C1 and C2 distinctly exceeded those of C0. The increase in porosity is disadvantageous to strength improvement; this is also the main reason for the reduction in the strength of C2. The main cause of this phenomenon is the strong air-entraining property of CNT dispersion. In this study, the influence of the change in pore structure on strength caused by CNT dispersion was analyzed according to fractal theory.
4.3. SEM Results

Representative sample fragments for SEM are shown in Figure 7; it can be seen that the colors of C0, C1, and C2 deepened with the increase in CNT content. The microstructure of blank group C0 showed the presence of C–S–H in amorphous form, and tiny pores are distributed in the matrix of the mortar. In the microstructures of C1 with 0.05% CNT dispersion and C2 with 0.5% CNT dispersion, the CNTs in the cement hydration product were well dispersed. The CNT content of C2 was observed to significantly exceed that of C1. The structures of C1 and C2 were obviously looser than that of C0, with a large number of pores. The CNTs and the hydration products (C–S–H) of cement formed a meshwork microstructure. The meshwork microstructure composed of CNTs and hydration products of cement can be used as a strengthening structure to improve the mortar strength and toughness [19, 41, 42]. In this study, the compressive and flexural strengths of C1 were found to increase. However, the SEM images show that the pore size and number of C1 and C2 distinctly exceeded those of C0. The increase in porosity is disadvantageous to strength improvement; this is also the main reason for the reduction in the strength of C2. The main cause of this phenomenon is the strong air-entraining property of CNT dispersion. In this study, the influence of the change in pore structure on strength caused by CNT dispersion was analyzed according to fractal theory.

4.4. Fractal Dimension of Pore Structure

The pore structure test results indicate that the porosity values of slices C0, C1, and C2 were 6.69%, 15.5%, and 43.26%, respectively. The porosity of C1 was twice as high as that of ordinary mortar, and the porosity of the mortar with 0.5% CNT dispersion was six times greater than that of ordinary mortar. However, the change in the porosity value does not accurately and quantitatively represent the intricacy of the pore structure. To examine the change in the pore structure of mortar, the fractal dimension was applied to characterize the intricacy of the pore structure. The calculation results are presented below.

4.4.1. Fractal Dimension of Pore Volume

Equation (11) can be derived from Menger sponge model:

\[ V_k \propto r_k^{3-D}. \]  \hspace{1cm} (11)

The calculation formula for the fractal dimension of pore volume, \( D_v \), can be derived by taking the logarithm of Equation (11):

\[ \lg V_k = (3 - D_v) \lg r_k, \]  \hspace{1cm} (12)

where \( V_k \) is the solid volume, and \( r_k \) is the pore diameter. The solid volume and corresponding pore diameter are calculated according to the measurement data of the pore structure. Then, the logarithm is obtained to draw the curve; \( D_v \) is given by the curve gradient.

Figure 8 shows the logarithmic curves of the solid volume and pore diameters of C0, C1, and C2. The diagram shows that the solid volume increased with the pore size; however, the growth trends of the three curves differed. The increase in C0 was the smallest, and that in C2 was the largest, indicating that the CNT content affected the pore volume of mortar. As the CNT content increased, the pore volume also increased. Moreover, the change trend was more significant.

The overall changes in the three logarithmic curves were similar. Figure 8 indicates that the growth rate of the solid volume in the early stage of the logarithmic curve was relatively low. Then, it gradually increased with the pore diameter. Evidently, the growth rate of solid the volume varied. Hence, one linear regression fitting was insufficient to describe the overall trend in the change of the logarithmic curve and the complex change process of the pore structure; multistage linear fitting was required. The logarithmic curve can be divided into two parts according to the change in the slope of the curve. This reflects the multifractal characteristics of the mortar’s pore structure that were mainly due to the irregularity of the pore distribution and variety of pore shapes.
To describe these characteristics clearly, the three logarithmic curves were divided into two parts: region I (bubble chord length: <100 μm) and region II (bubble chord length: >100 μm). Then, the fractal dimensions of these two regions were calculated. The calculation results show that the fractal dimensions of the two regions differed. Although the fractal dimension of region I was between 2 and 3, and the $R^2$ value of the linear regression was less than 0.8. This indicates that, although the pore structure with the bubble chord length of <100 μm had fractal characteristics, the complexity of the structure could not be accurately reflected. The fractal dimension of region II was between 2 and 3, and $R^2$ was greater than 0.98. This indicates that the fractal characteristics of the mortar’s pore structure with the bubble chord length of >100 μm were significant. The pore distribution and intricacy of the pore structure were quantitatively and accurately reflected by the fractal dimension.

Therefore, the fractal dimension of the pore volume of region II could be applied as a parameter to characterize the complex process of the variation in the mortar pore structure with the CNT content quantitatively.
4.4.2. Fractal Dimension of Pore Surface

Equations (13) and (14) can be derived from Menger sponge model:

\[
\frac{dV_k}{dr_k} \propto (rk)^{2-D},
\]

(13)

\[
V_\psi = V - V_K
\]

(14)

The fractal dimension of the pore surface, \(D_s\), can be obtained by taking the logarithm of Equation (13):

\[
\lg \left( -\frac{dV_\psi}{dr_k} \right) \propto (2 - D_s) \lg r_k,
\]

(15)

where \(r_k\) is the pore diameter, and \(V_\psi\) is the accumulative pore volume (diameter \(\geq r_k\)). The parameters required for the calculations can be obtained by testing the pore structure and then obtaining the logarithm to draw the curve. The gradient of the curve yields \(D_s\); \(D_s = 2\) denotes that the pore structure has a completely smooth plane. When \(D_s\) approaches 3, the pore structure becomes coarser and more intricate; hence, \(D_s\) must satisfy \(2 < D_s < 3\).

Figure 9 shows the logarithmic curve of \(-dV_\psi/dr_k\) and the pore diameters of C0, C1, and C2. Note that \(-dV_\psi/dr_k\) decreased as the pore diameter increased. The decreasing trends of the three curves varied; this was opposite to the change process of the logarithmic curve in the volume fractal dimension. Similarly, the decrement in \(-dV_\psi/dr_k\) of C0 was the smallest, and that in C2 was the largest. This indicates that the CNT content affected the mortar’s pore surface. The range of change in the pore surface increased with the amount of CNTs; moreover, the change trend was more significant.

The change processes of the logarithmic curves of C0, C1, and C2 were similar. Figure 9 indicates that the decrease rate of \(-dV_\psi/dr_k\) in the early stage of the logarithmic curve was relatively low and gradually rose with the pore diameter. The slope of the curve evidently varied. Thus, one linear regression fitting was insufficient to describe the overall change trend of the logarithmic curve and the complex change process of the pore structure; multistage linear fitting was necessary. This also reflects the multifractal features of the mortar’s pore structure.

The curve could be divided into three parts according to the change in the slope of the logarithmic curve: region I (bubble chord length: <100 µm), region II (100 µm < bubble chord length < 500 µm), and region III (bubble chord length: >500 µm). The pore surface fractal dimensions of regions I, II, and III were calculated as described above; the results are shown in Figure 9. The calculation results indicate that the fractal dimensions of the three regions considerably varied, indicating that the roughness and irregularity of the inner surface of pores with different chord lengths considerably differed. The fractal dimensions of region I (2.0196, 2.039, and 2.0168) were between 2 and 3, and the \(R^2\) value of the linear regression was less than 0.9. This shows that, although the pore structure of the mortar with a chord length of <100 µm had fractal characteristics, these could not exactly represent the complexity of the structure. The fractal dimensions of region III (4.291, 3.9395, and 3.8424) exceeded 3, which is nonphysical from the point of view of surface geometry [35,43]. The fractal dimensions of region II were 2.1773, 2.3521, and 2.1412, and \(R^2\) exceeded 0.94. This indicates that the fractal characteristics of the pore structure of the mortar with a bubble chord length between 100 and 500 µm were remarkable. The roughness and irregularity of the pore internal surface were quantitatively and accurately reflected by fractal dimensions.

Therefore, \(D_s\) of region II could be applied as a parameter to characterize the complex process of the variation in the mortar’s pore structure with the CNT content quantitatively.
Figure 9. Logarithmic curves and calculation results of fractal dimensions of pore surfaces of C0, C1, and C2; (a) Logarithmic curves of C0, C1, and C2; (b) C0; (c) C1; (d) C2.

4.4.3. Box-Counting Dimension

According to the box-counting method, the bubbles with a diameter > d_i were converted into those with a diameter of d_i using the principle of equal area. The distribution of the total number of bubbles is shown in Figure 9a. The figure shows that the difference in the number of bubbles of C0, C1, and C2 decreased with the increase in pore size. When the bubble chord length was 10–100 μm, the number of bubbles rapidly changed.

The logarithmic curves of the pore diameter and bubble number are shown in Figure 10b. Figure 10 indicates that the change processes of the logarithmic curves of C0, C1, and C2 were similar, and the total number of bubbles decreased with the increase in pore diameter. Moreover, the logarithmic curve of the bubbles was virtually linear. The pore structure had no multifractal characteristics; hence, it could be fitted by linear regression. The R^2 value of the linear regression exceeded 0.95, indicating that the bubble distribution of the mortar had significant fractal characteristics. The box-counting dimension, D_f, can be obtained using Equation (10). The fractal dimensions of C0, C1, and C2 were 2.2479, 2.3572, and 2.3237, respectively.
1.0 1.5 2.0 2.5 3.0 3.5 4.0
-1
0
1
2
3
4
5
6
7
8
 C0 without CNTs
 C1 with 0.05% CNTs
 C2 with 0.5% CNTs
 ... 10.0552
R2 = 0.9784
D = 2.3237
y = −2.3572x + 9.4920
R2 = 0.9582
D = 2.3572
y=−2.2479x+8.8317
R2=0.9771
D=2.2479

101 102 103
0
5,000,000
10,000,000
15,000,000
20,000,000
Total number of bubbles
Chord length of bubble (μm)
 C0 without CNTs
 C1 with 0.05% CNTs
 C1 with 0.5% CNTs

Therefore, the complexity of the pore structure was quantitatively and accurately reflected by the box-counting dimension. The box-counting dimension could be applied as a parameter to characterize the complex process of the variation in the pore structure of the mortar with the CNT content quantitatively.

5. Gray Relational Analysis

The mechanical properties of mortar are determined according to its internal microstructure, and the pore structure is a significant part of the microstructure. Many parameters, which reflect the internal defects of mortar from different aspects and affect the mortar strength to a certain extent, can characterize the pore structure. However, each parameter can only reflect the change in the pore structure of mortar in a particular aspect; it is not the only factor influencing the mortar’s mechanical properties. Accordingly, to analyze the influence of various parameters on the mechanical properties of mortar, the introduction of gray relational analysis (GRA) is necessary [31,44–46].

To study the superficial and deep-seated relationship among the various factors in the system, the GRA uses the indeterminate system with small samples and inferior data as the study object. The main factors among the influencing factors are identified to comprehend the main characteristics of the system. In this study, the main parameters characterizing the pore structure of mortar include $D_{v}$, $D_{s}$, $D_{d}$, and porosity; however, the amount of test data of each parameter is low. Therefore, GRA was used to study the effect of various parameters on mortar strength. The specific calculation method of the GRA is described below.

The data series of $D_{v}$, $D_{s}$, $D_{d}$, and porosity of mortar are defined as a comparison series expressed in $X_{i}(k)$. The data series of mortar strength with different CNT contents are defined as a reference series expressed in $Y(k)$. Considering the variation in the size and dimension of each series, the test data were normalized using Equations (16) and (17).

$$X'_{i}(k) = X_{i}(k) / X(1).$$  \hspace{1cm} (16)

$$Y'(k) = Y(k) / Y(1).$$  \hspace{1cm} (17)

The absolute value of the difference between the reference series and comparison series is calculated and expressed as $\Delta_{i}(k)$ at point $k$:

$$\Delta_{i}(k) = |Y'(k) - X'_{i}(k)|.$$  \hspace{1cm} (18)
The gray coefficient is calculated using Equation (19).

\[ r_i(k) = \frac{\Delta_{\text{min}} + \zeta \cdot \Delta_{\text{min}}}{\Delta_i(k) + \zeta \cdot \Delta_{\text{min}}}, \]

where \( \Delta_{\text{min}} = \min \Delta_i(k), \Delta_{\text{max}} = \max \Delta_i(k), \) and \( \zeta = 0.5. \) The gray grade is calculated using Equation (20).

\[ r_i = \frac{1}{n} \sum_{i=1}^{n} r_i(k), \]

where the gray grade is between 0 and 1, representing the numerical measure of the correlation between the reference series and comparison series. The gray grade approaches 1 if the degree of coincidence of the two sequences is high.

5.1. Strength Correlation Analysis with Multifractal Dimensions

The resulting fractal dimensions show that the pore volume and pore surface had multifractal dimension characteristics, indicating that pore structures of different size grades had different self-similarity in volume and surface characteristics. With the increase in pore diameter, \( D_v \) and \( D_o \) increased, and the corresponding pore structure became more complex. In this study, the gray grades between the double fractal dimensions of pore volume and strength, and those between the triple fractal dimensions of pore surface and strength are calculated.

The correlation analysis results between the multifractal dimensions of pore volume and strength are shown in Figure 11. For the compressive strength, the gray grade of regions I and II was approximately 0.74. For the flexural strength, the gray grades of regions I and II were 0.64 and 0.63, respectively. The correlation results were fundamentally the same. The outcomes indicate that \( D_v \) and mortar strength had a close correlation, and the correlation between and compressive strength was higher than that between \( D_v \) and flexural strength.

![Figure 11. Correlation between strength and multifractal dimension of pore volume.](image)

The GRA result between the multifractal dimensions of pore surface and strength is shown in Figure 12. Distinct variations can be observed. For the compressive strength, the gray correlation coefficients of the three regions (0.75, 0.71, and 0.63) decreased with the
increase in pore size. For the flexural strength, the gray correlation coefficients of the three regions were 0.64, 0.75, and 0.58, respectively. The range of the chord length in regions I and II was 1–500 μm, indicating that the correlation between $D_s$ and strength was high when the pore size range was small.

![Figure 12](image_url)

**Figure 12.** Correlation between strength and multifractal dimension of pore surface.

The change in pore size resulted in pore volume and pore surface with multifractal dimensions, showing that the pore structure had different complexities under different pore size grades. In this study, the fractal characteristics of harmful pores [47,48] (pore size: 1–1000 μm) were mainly characterized. For the CNT-modified mortar, the strong air-entraining property of the dispersant in CNT dispersion was the main reason for the change in pore structure. The correlation analysis of the multifractal characteristics of the pore structure of mortar revealed the correlations between $D_v$ and strength and between $D_a$, and strength under different pore size grades. The connections between the $D_v$ values of the two regions and strength were basically the same. The connections between $D_s$ of region I and compressive strength and between $D_s$ of region II and flexural strength were the largest. According to the analysis results of the multifractal dimensions and other characteristic parameters (such as porosity), the gray correlation between strength and multiple parameters was calculated.

### 5.2. GRA of Strength with Pore Structural Features

The pore structure complexity can be accurately reflected by $D_v$, $D_a$, and $D_d$. They can be applied as parameters to characterize the complex process of the variation in the pore structure with the CNT content quantitatively. However, some fractal dimensions only represent certain sides of the pore structure. Mortar has different pore structures under different mix ratios, curing conditions, and working environments; hence, selecting a reasonable fractal dimension is critical to show the change in pore structure. Many studies [49–53] have demonstrated that porosity, which is a traditional parameter, is also a critical element influencing the mechanical properties of mortar. Therefore, mortar porosity was also included in the analysis.

The correlations between mortar strength and $D_v$, between mortar strength and $D_a$, between mortar strength and $D_d$, and between mortar strength and porosity were calculated and evaluated using GRA. The GRA calculation results of the compressive strength and parameters indicate that the correlation between compressive strength and $P$ (porosity)
was 0.676, but the correlations between compressive strength and $D_v$, between compressive strength and $D_s$, and between compressive strength and $D_d$ were 0.955, 0.953, and 0.952, respectively, which are higher than that between compressive strength and $P$. The order was $D_v > D_s > D_d > P$. The results indicate that porosity was not the central factor influencing the compressive strength of mortar. Moreover, the fractal dimension was the main parameter of the pore structure affecting the change in mortar strength, in which the relevance between $D_v$ and compressive strength was the strongest.

The GRA calculation results of flexural strength and parameters also indicate the high correlations between flexural strength and $D_v$, between flexural strength and $D_s$, and between flexural strength and $D_d$, and the gray correlation degrees were 0.962, 0.973, and 0.964, respectively. The order was $D_s > D_d > D_v > P$ (0.678). The results indicate that porosity was not the main factor influencing the flexural strength of mortar. Furthermore, fractal dimension was the main parameter of pore structure affecting the change in mortar strength, in which the relevance between $D_s$ and flexural strength was the strongest.

The above calculation and analysis show that the strongest correlations were between $D_v$ and compressive strength and between $D_s$ and flexural strength. Therefore, the pore volume distribution was the main factor influencing the compressive strength of mortar, and the roughness and irregularity of the pore internal surface were the main factors influencing the flexural strength of mortar.

6. Conclusions

The effect of CNT content on the macroscopic properties and microstructure of mortar was studied in terms of strength and pore structure using SEM. The compressive and flexural strength test results showed that a 0.05% CNT content could improve the mortar strength, whereas a 0.5% CNT content had an adverse effect. To explore the primary cause of the change in strength, a pore structure test was implemented on the mortar, and fractal theory was introduced to analyze the quantitative relationship between the pore structure and mortar strength. The conclusions of the study are as follows.

(1) The experimental results show that the strength of mortar was improved by adding 0.05% CNT, while a negative impact occurred with the addition content of CNTs up to 0.5%. The total porosity of mortar containing 0.05–0.5% CNTs was increased by 15–43% compared to that of the reference normal mortar.

(2) The fractal dimensions of pore volume and pore surface, as well as the box-counting dimensions of mortar, were calculated using fractal theory. The pore volume and pore surface were found to have multifractal dimensions. The addition of CNTs changed the pore morphology characteristics of mortar and increased the pore volume and pore surface. The complexity of the pore structure distribution varied according to the pore size. The fractal dimension could accurately reflect the complexity of the pore structure and be used as a parameter to characterize the complex process of the variation in the pore structure with mortar CNT content quantitatively.

(3) The gray correlation coefficient between the fractal dimensions of the pore structure and mortar strength exceeded 0.95. The strongest correlations were between the fractal dimensions of the pore volume and compressive strength and between the fractal dimensions of the pore surface and flexural strength. The fractal dimensions revealed the complexity, roughness, and irregularity of the pore structure. Compared with porosity, the fractal dimension was more suitable for establishing the relationship between mortar strength and pore structure.

(4) There is no doubt that both the strength of the cement matrix and the porosity of the mortar increase with the addition of CNTs. However, the mortar strength is irregular under the combined effect of the microfiber reinforcement and mortar compactness. The strength decrease of the mortar with 0.5% CNTs was mainly due to the sharp increase in porosity, which may have been caused by the use of dispersant. Therefore, it is necessary to study the application method of CNTs to take advantage of the excellent improvement capability of CNTs toward cement matrix strength.
Author Contributions: Conceptualization, J.G. and J.W.; methodology, X.Y. and Y.Y.; validation, J.W., X.Y., and Y.Y.; data curation, Y.Y.; writing—original draft preparation, X.Y. and Y.Y.; writing—review and editing, Y.Y.; visualization, J.W.; supervision, J.W.; project administration, Y.X.; funding acquisition, J.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was primarily supported by the National Natural Science Foundation of China (Grants U2040224 and 52179145), the Scientific and Technological Research Project in Henan Province (Grant No. 222300420081), the Program for Science and Technology Innovation Talents in Universities of Henan Province (21HASTIT013), and the Open Research Fund Program of State key Laboratory of Hydroscience and Engineering (sklhse-2022-c-01).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References


