

Article



Research on the Mechanical Performance of Carbon Nanofiber Reinforced Concrete under Impact Load Based on Fractal Theory

Wei Xia^{1,*}, Jinyu Xu^{1,2} and Liangxue Nie¹

- ¹ School of Aeronautical Engineering, Air Force Engineering University, Xi'an 710038, China; xujinyuafeua@163.com (J.X.); nieliangxueafeu@163.com (L.N.)
- ² College of Mechanics and Civil Architecture, Northwest Polytechnic University, Xi'an 710072, China
 - Correspondence: xiaweiafeu@163.com; Tel.: +86-18729263358

Abstract: The research is focused on the dynamic compressive strength, impact toughness and the distribution law of fragmentation size for the plain concrete and the carbon nanofiber reinforced concrete with four fiber volume contents (0.1%, 0.2%, 0.3% and 0.5%) under impact load by using the Φ 100 mm split-Hopkinson pressure bar. Based on the fractal theory and considering the micropore structure characteristics of the specimen, the impact of the strain rate and the dosage of carbon nanofibers on the dynamic mechanical performance of concrete is analyzed. According to the results, both the dynamic compressive strength and the impact toughness increase continuously with the improvement of the strain rate level at the same dosage of fiber, showing strong strain rate strengthening effect; at the same strain rate level, the impact toughness increases gradually with the increase in the fiber dosage, while the dynamic compressive strength tends to increase at first and then decrease; the distribution of the fragmentation size of concrete is a fractal in statistical sense, in general, the higher the strain rate level, the higher the number of fragments, the lower the size, and the larger the fractal dimension; the optimal dosage of carbon nanofibers to improve the dynamic compressive strength of concrete is 0.3%, and the pore structure characteristics of carbon nanofiber reinforced concrete exhibit obvious fractal features.

Keywords: carbon nanofiber reinforced concrete; impact load; dynamic compressive strength; pore structure characteristics; fractal dimension

1. Introduction

After its continuous development for almost two centuries, concrete has become one of the most widely used materials for the construction in the fields of both civil infrastructure and military defensive projects. In recent years, sudden explosion accidents due to terrorist attacks, local wars or negligence during industrial production and daily life have happened repeatedly, putting many concrete structures under the threat of extreme external loads, including impact and explosion [1–5]. In order to promote the performance of concrete in terms of explosion and penetration resistance, and improve its mechanical properties under impact stress, various fiber-modified forms of concrete have been developed to meet the requirements [6–9].

As a kind of new multifunctional material with excellent performance, carbon nanofibers (CNFs) [10–12] are characterized by small self-dimension, large specific surface area, and strong cohesiveness within the concrete matrix compared with carbon fiber, steel fiber, etc. CNFs are a kind of discontinuous nanoscale graphite fibers, which have excellent characteristics of both carbon fibers and nanomaterials. CNFs enjoy wide application prospects in the field of the modification design of composite materials, specifically, they are able to provide excellent performance in terms of tensile-resistance, crack-resistance, electric conduction and fatigue-resistance to the concrete when being mixed into concrete. However, most of the research on carbon nanofiber reinforced concrete (CNFC) focuses on certain basic physical and mechanical performances [13–17]; in the meantime, the research



Citation: Xia, W.; Xu, J.; Nie, L. Research on the Mechanical Performance of Carbon Nanofiber Reinforced Concrete under Impact Load Based on Fractal Theory. *Crystals* 2021, *11*, 387. https:// doi.org/10.3390/cryst11040387

Academic Editor: Adam Stolarski

Received: 23 March 2021 Accepted: 6 April 2021 Published: 7 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). on the characteristics of strength and energy, as well as the damage mode and distribution law of the fragments during impact breaking, is relatively rare. The essence of the failure of the concrete due to the impact load is the process that the internal damage cracks of the concrete are continuously expanded, extended and connected under the driving of energy, thereby resulting in material instability and failure [18-20]. The number and the size distribution of the broken fragments are exactly the macroscopic representation of this process. The particle size distribution and the pore structure characteristics inside the matrix of the destroyed products of the concrete under impact load show certain selfsimilarity and fractal characteristics [21]. Fractal theory can be used to describe fractal irregular features effectively. Fractal theory was founded by Mandelbrot in the 1970s. Its research object is the disordered but self-similar system widely existing in nature. At present, as a new method and concept, fractal theory has developed rapidly in many fields such as physics, biology, materials science, etc. Through the research on the changes of the strength, energy absorption and the breakup characteristics of the modified concrete under different dosages of CNFs and loading rates, the comprehensive analysis and assessment of the damage degradation degree, the energy consumption evolution mechanism and the ability to resist impact load can be implemented. Therefore, more in-depth research on the dynamic compression mechanical properties of CNFC is necessary, so as to understand their dynamic response law under impact load, thus ensuring the safety of the engineering structures in practice.

In view of this, the Φ 100 mm split-Hopkinson pressure bar (SHPB) is used as the test device for the impact compression test on the plain concrete (PC) and the modified concrete with four volume dosages of carbon nanofiber, thereby carrying out screening statistics against the fragments of the impact failure and exploring the effects of the impact velocity of the bullet (strain rate) and fiber dosage on the dynamic compressive strength, impact toughness, failure mode and fractal dimension of the fragments. In the meantime, taking into consideration the mercury intrusion test, the analysis of microscopic mechanism for the pore structure characteristics of the specimen is implemented based on the fractal theory, so as to provide better guidance to the engineering practice.

2. Materials and Methods

2.1. Raw Materials and Specimen Preparation

The following raw materials are utilized, including the cement of P·O 42.5R of brand Qinling with the initial setting time of 2 h, and the final setting time of 5 h; the coarse aggregate of limestone gravel, with the particle size ranging from 5~10 mm (accounting for 15%), and 10~20 mm (accounting for 85%); fine aggregate of medium sand which is used after washing and drying, with the apparent density of about 2630 kg/m³; clean tap water; water reducing agent of FDN high-efficiency water reducing agent with water reducing rate of 20%; as well as the fiber material of CNFs from Beijing Deke Daojin Science and Technology Co., Ltd., with its physical performance index shown in Table 1. Table 2 shows the mix proportion of the plain concrete with the strength grade of C40 and carbon nanofiber reinforced concrete, in which PC represents the plain concrete, CNFC01, CNFC02, CNFC03, and CNFC05 refer to the volume dosages of carbon nanofiber of 0.1%, 0.2%, 0.3% and 0.5%, respectively. The pouring of concrete specimens was based on the "method of sand and rubbles enveloped with cement". CNFs are prepared into dispersion solution and then uniformly mixed into the concrete mixture [22]. The test results of four-probe method show that the resistance of the sample is obviously reduced and the conductive effect is excellent. From this, it can be judged that CNFs achieves the purpose of dispersion. The preparation process of CNFC group mixture is shown in Figure 1. Sand and gravel are added to the mixer in turn, and part of the mixed liquid is added while stirring, and then cement was added, stirring for 120 s. After that, the remaining mixed liquid is added and stirred for 120 s to prepare the concrete mixture. The mixture is stirred evenly, and then put into the cylinder for die test and molding. The mold is removed after standing indoors for 24 h, and moved into the curing room for standard curing. After 28 days, the mixture is

taken out for polishing, thereby obtaining the short cylinder specimen with the geometric size of Φ 98 mm \times 48 mm for the impact compression test (as shown in Figure 2).

Table 1. Main physical performance index of CNTs.

Purity/	Diameter/	Resistivity/	Thermal Expansion	Specific Surface	Density/
%	nm	Ω∙cm	Coefficient/°C ⁻¹	Area/m ² ·g ^{−1}	g·cm ^{−3}
99.9	100~200	< 0.012	1	300	0.18

Table 2. Mix proportions of concrete (kg/m^3) .

Specimen No.	Cement	Coarse Aggregate	Fine Aggregate ¹	Water	Defoaming Agent ²	Water Reducing Agent	CNTs
PC	495	1008	672	180	0	0	0
CNFC01	495	1008	672	180	0.30	5.0	0.18
CNFC02	495	1008	672	180	0.45	7.5	0.36
CNFC03	495	1008	672	180	0.60	10.0	0.54
CNFC05	495	1008	672	180	0.90	15.0	0.90

¹ River sand of 2.8 fineness modulus. ² Aqueous defoamer of tributyl phosphate.



Figure 1. The preparation process of carbon nanofiber reinforced concrete (CNFC) group mixture.



Figure 2. The processed cylinder specimens.

2.2. Test Equipment and Method

The Φ 100 mm SHPB test device is used for the impact compression test (as shown in Figure 3). Figure 4 shows the propagation process of the stress wave in the test. A pneumatic gun is used in this device to drive the bullet, and makes it collide with the incident rod in a high-speed coaxial manner, thereby producing the incident wave $\varepsilon_I(t)$. The specimen placed between the incident bar and the transmission bar generates high-speed deformation under the loading of the incident wave. In the meantime, it transmits the reflected wave $\varepsilon_R(t)$ and the transmitted wave $\varepsilon_T(t)$ to the incident bar and the transmission bar, respectively. These required waveform information is measured and recorded by the high dynamic strain indicator, waveform memory, etc., and then the data are processed with the "three-wave method" (as shown in Formula (1)) [23,24], thereby obtaining the relevant parameters reflecting the dynamic compression mechanical properties of the specimen. The impact velocity of the bullet is jointly decided by the air pressure and its action distance applied. During the test, the action distance of air pressure is kept fixed, and the bullet velocity is controlled by the adjustment of the pressure of the input air. In the meantime, the impact velocity of bullet is also affected by the test environment, in this case, although the input pressure and its action distance can be kept constant each time, the bullet velocity may be different. The strain rate can also be deemed as the reflection of bullet impact velocity, and there is an approximate linear correlation between them [25,26]. The typical strain rate time history curve of the concrete specimen under dynamic compression is shown in Figure 5, where Point A refers to the inflection point of the rising section of the curve, and Point *B* represents the inflection point of the corresponding falling section. The average strain rate of the middle platform section is selected as the representative value of the strain rate of the specimen under the current impact velocity of bullet [27,28]. A total of five strain rate levels are set for the test, and the corresponding input pressures are 0.3 MPa, 0.35 MPa, 0.4 MPa, 0.45 MPa and 0.5 MPa, respectively. H62 circular brass sheet with the thickness of 1 mm is selected to shape the initial stress wave, and the typical waveforms of the shaped incident wave, transmission wave and reflection wave are shown in Figure 6. To ensure the effectiveness and reliability of the test results, the test should be repeated at least three times under each input pressure, then the average value of the obtained test data should be calculated and taken as the representative value of the test data under this working condition.

$$\begin{cases} \varepsilon_s(t) = \frac{C_e}{L} \int_0^\tau \left[\varepsilon_I(t) - \varepsilon_R(t) - \varepsilon_T(t) \right] dt \\ \dot{\varepsilon}_s(t) = \frac{C_e}{L} \left[\varepsilon_I(t) - \varepsilon_R(t) - \varepsilon_T(t) \right] \\ \sigma_s(t) = \frac{E_e A_e}{2A_s} \left[\varepsilon_I(t) + \varepsilon_R(t) + \varepsilon_T(t) \right] \end{cases}$$
(1)

where C_e , E_e and A_e refer to the wave velocity, elastic modulus and cross-sectional area of the compression bar; $\varepsilon_s(t)$, $\dot{\varepsilon}_s(t)$, $\sigma_s(t)$, A_s and L represent the strain, strain rate, stress, end area and length of the specimen, respectively; and τ denotes the propagation time of stress wave in the bar.



Figure 3. Φ 100 mm SHPB test system.



Figure 4. Schematic diagram of stress wave propagation.



Figure 5. Typical time history curve of strain rate.



Figure 6. Typical waveform diagram after shaping.

The screening test adopts the bushing screen with the screen size of 50 mm, 40 mm, 31.5 mm, 26.5 mm, 20 mm, 16 mm, 10 mm, 5 mm, and 2.36 mm, respectively. In the meantime, the mass of fragments retained on each screen is measured by the electronic balance. Mercury intrusion porosimetry (MIP) is used to study the structural characteristics of the microscopic pore of concrete [29]. The experimental equipment refers to PoreMaster33 automatic mercury intrusion instrument produced by Quantachrome Instruments from the United States of America. The fragments of the specimen with appropriate size after impact compression test are selected as the sample for analysis. Remove the residues and dust on the surface of the sample before placing them in a constant-temperature drying box for complete dehydration, and then carry out the determination.

3. Mechanical Properties of Dynamic Compression

3.1. Dynamic Compressive Strength

The dynamic compressive strength ($f_{c,d}$) represents the peak stress in the stress–strain curve of the specimen, indicating the strength characteristics of the concrete under impact load. Figure 7 illustrates the variation law of dynamic compressive strength of concrete specimen under different strain rates. It can be seen from the analysis that: (1) with the increase in strain rate level, the dynamic compressive strength of both PC group and CNFC group increases continuously, showing a significant strain rate strengthening effect. (2) It can be seen from the change in the dynamic compressive strength with the strain rate that there is an approximate linear correlation between them. When carrying out linear fitting, it is found from Formula (2) that the fitting effect of them is relatively good. (3) In general, compared with PC, the addition of appropriate amount of CNFs can significantly improve the dynamic compressive strength of concrete. At the same strain rate level, the dynamic compressive strength increases first and then decreases with the increase in the addition amount of fiber. When the addition amount of fiber content reaches 0.3%, the improvement effect is the best; in contrast, when the addition amount of fiber content is 0.5%, the improvement effect is relatively small. This may be due to the excessive addition of fiber, i.e., 0.5%, which means that CNFs cannot be evenly dispersed in the concrete matrix, resulting in the phenomenon of "agglomeration". The excessive CNFs intensify the internal defects of concrete matrix structure, resulting in stress concentration in local areas under impact load, which is not conducive to further improving the concrete strength characteristics.



Figure 7. Dynamic compressive strength of concrete under different strain rates.

3.2. Impact Toughness

The impact failure process of concrete is bound to be accompanied by the changes in energy, especially under the impact load; the transformation and dissipation of energy are extremely fast and active. The impact toughness (*IT*) can be used to characterize the entire stress–strain development process of the specimen under impact load until the energy for the failure of the specimen is absorbed. The physical meaning of impact toughness refers to the area surrounded by stress–strain curve and transverse axis [28], expressed as follows:

$$IT = \int_0^{\varepsilon_u} f d\varepsilon \tag{3}$$

where *f* refers to the dynamic stress–strain curve of the specimen; and ε_u represents the dynamic ultimate strain of the curve.

The variation relationship between the impact toughness and the strain rate of each group of specimen is shown in Figure 8. The analysis shows that: (1) the impact toughness is also highly sensitive to the strain rate, specifically, the impact toughness increases gradually with the increase in the strain rate level. (2) At a relatively low strain rate level, when the volume dosage of CNFs reaches 0.2%, the improvement effect on the impact toughness of concrete is weaker than that of 0.3%; in contrast, the improvement effect is opposite at high strain rate level. (3) It can be seen from the change in the impact toughness with the strain rate that there is an approximate linear correlation between them. Formula (4) shows the result of linear fitting between them, and it is found that the fitting effect is good. (4) Compared with PC, the addition of CNFs can improve the impact toughness of concrete to a certain extent. In general, with the increase in the dosage of CNFs, the impact toughness of concrete at the same strain rate level is increased to certain degree. The possible reason for the results of this experiment may lie in the fact that the impact toughness is jointly decided by the dynamic compressive strength and

the corresponding impact compression deformation. After the addition of CNFs, both the strength and deformation of concrete will receive certain enhancement, and the combined effect of the two leads to the improvement of the impact toughness of concrete under all dosages of fiber.



Figure 8. Impact toughness of concrete under different strain rates.

3.3. Mechanism Analysis

Both the dynamic compressive strength and the impact toughness of PC and CNFC increase with the increase in impact velocity of bullet, showing strong strengthening effect of strain rate, besides, both the dynamic compressive strength and impact toughness of CNFC are higher than their counterparts of PC. It can be seen from the microscopic mechanism of concrete failure that the initiation and propagation of internal microcracks are the main causes of the failure of the specimen. The greater the impact velocity of bullet, the greater the deformation rate of the specimen, the more the number of cracks generated, and the more energy absorbed. Under high-speed impact load, the action time of bullet on the specimen is rather short, and the material deformation buffering is small. Therefore, most of the energy accumulation of the specimen is achieved by increasing the stress instead of the strain, leading to the increase in the dynamic compressive strength of the material with the increase in the loading rate. In addition, as per the microstructure test results of CNFC impact fracture specimen, the matrix compactness has been significantly improved (the specific mechanism is shown in Section 5.2), and the failure of specimen is mainly due to the pull-out or fracture of the fiber (as shown in Figure 9a). The reason is that, for CNFC, CNFs can play a role of crack resistance and bridging adsorption [30]. The deformation released after the initiation of microcracks can first result in fiber debonding, rather than supporting the propagation of microcracks, thereby delaying the fracture process, and enhancing the toughness of concrete specimen. However, excessive addition of CNFs may result in "agglomeration" (as shown in Figure 9b), and CNFs may be intertwined to form new weak areas within the concrete matrix, which is not conducive to further improve the concrete strength.



Figure 9. Microstructure and morphology of CNFC (**a**) CNFs pull-out and fracture; (**b**) CNFs aggregation and winding.

4. Fractal Characteristics of Impact Fragmentation Size

4.1. Impact Failure Mode and Fragmentation Size Distribution

The instability and failure of concrete under the impact load refer to the process of continuous inoculation, development and aggregation of internal microdamage cracks under external load, which eventually leads to macroscopic breaking. Besides, different impact velocities and fiber dosages will inevitably result in the change in the breaking morphology. Figure 10 shows the typical failure modes of the specimen under different strain rate levels. Due to the space limitation of this paper, only PC group and CNFC02 group are used as the representative specimens for analysis. The comparative analysis shows that the failure modes of the specimen can be basically classified into four types, i.e., edge failure, core-retaining failure, fragment failure and crushing failure. With the increase in strain rate level, the number of broken concrete fragments increases, the size decreases and tends to be uniform, and the degree of fragmentation increases continuously. In addition, at the same strain rate level, the particle size of the PC group specimen after failure is smaller, while the breaking morphology of the concrete specimen modified by CNFs is greatly improved, and the particle size of the fragment is relatively large, indicating that the addition of CNFs has a significant improvement effect on the impact resistance of concrete.



Figure 10. Typical failure mode of concrete under different strain rates (a) PC; (b) CNFC02.

To further describe the distribution law and the dimensional characteristics of concrete fragmentation size, the mass screening statistics of the specimen fragments under the

impact load is carried out [21,31]. Additionally, based on the statistical theory, the average size d_{ave} of the fragments of the specimen is calculated, namely:

$$d_{ave} = \sum d_i \eta_i / \sum \eta_i \tag{5}$$

where d_i refers to the average particle size of the remaining fragments on each sieve screen, taking the average pore diameter of the primary sieve and the upper sieve; η_i represents the percentage of the mass of the retained fragments in the total mass of each sieve.

The variation law between d_{ave} and strain rate is shown in Figure 11. According to the analysis, both of them meet the requirements of relationship distribution of y = A-Bln (x + C). We carried out the nonlinear fitting based on the strain rate as the transverse axis, and d_{ave} as the longitudinal axis, with the fitting results shown in Formula (6). It was found that d_{ave} of each group of specimens decrease with the increase in strain rate level. At low strain rate level, d_{ave} decreased sharply, while at high strain rate level, d_{ave} decreased slightly. The reason is that the size of the fragments changes greatly when the mode of the specimen evolves from the "edge failure" to the "core-retaining failure", while the size change in the fragments is relatively small when the mode of the specimen evolves from the mode of the fragment failure", and the size change in the fragment failure" to the "crushing failure". Therefore, under the condition of high strain rate, even if the strain rate level increases greatly, the change amplitude of impact crushing degree of concrete is still relatively moderate.

$$\begin{cases} PC: & d_{ave} = 26.2690 - 3.5176 \ln(\dot{\epsilon} - 51.4599) & (R^2 = 0.9990) \\ CNFC01: & d_{ave} = 51.9066 - 10.6044 \ln(\dot{\epsilon} - 61.4724) & (R^2 = 0.9612) \\ CNFC02: & d_{ave} = 90.3682 - 20.7881 \ln(\dot{\epsilon} - 53.3802) & (R^2 = 0.9295) & (6) \\ CNFC03: & d_{ave} = 156.8900 - 35.8741 \ln(\dot{\epsilon} - 49.0569) & (R^2 = 0.9249) \\ CNFC05: & d_{ave} = 20.5064 - 1.4370 \ln(\dot{\epsilon} - 50.8900) & (R^2 = 0.9996) \end{cases}$$



Figure 11. Relationship between *d*_{ave} and strain rate.

4.2. Fractal Dimension

When the concrete specimen is broken under impact load, the particle size distribution of the fragments is in accordance with the distribution law of Gate-Gaudin-Schuhmann [21,32]. The distribution equation based on mass-frequency is:

$$y = \frac{M(r)}{M_T} = \left(\frac{r}{r_m}\right)^q \tag{7}$$

where *r* refers to the particle size of the fragments of the broken specimen; r_m represents the maximum particle size of fragments; M(r) denotes the sum of mass of all fragments whose particle size is less than r; M_T is the total mass of fragments when the specimen is broken; q refers to the fragment mass distribution parameter, taking the slope of $lg[M(r)/M_T]$ -lgr linear fitting curve.

According to the definition of fractal dimension, that is, $N = r^{-Db}$ (*N* refers to the number of fragments with particle size greater than *r*, and *D*_b represents the fractal dimen-

sion of fragments); in the meantime, considering the relationship between the increment of fragment number and the increment of fragment mass, that is, $dM \propto r^3 dN$, the fractal dimension D_b of fragments can be calculated with the mass-particle size method, namely:

$$D_b = 3 - q \tag{8}$$

According to the above analysis, the slope of the linear fitting curve between $lg[M(r)/M_T]$ and lgr is $3-D_b$. Taking lgr as the abscissa and $lg[M(r)/M_T]$ as the ordinate, the scatter diagram of the two is drawn, and the linear fitting is carried out, as shown in Figure 12.



Figure 12. $lg[M(r)/M_T]$ -lg*r* linear fitting curve (**a**) PC; (**b**) CNFC02.

The data points in Figure 12 show good linear correlation in the double logarithmic coordinate system, indicating that the distribution of concrete fragments after impact failure has fractal characteristics. This is because the microscopic cracks and pores in the concrete show self-similarity at different scales; besides, the breaking process and the shape of fragments are the direct results of crack propagation, thereby resulting in the power-law distribution of fragments, which is a fractal in the statistical sense. D_h describes the distribution characteristics of the concrete fragment size after breaking. The larger D_b is, the smaller the average particle size of the concrete fragments is, and the higher the degree of crushing of the specimen is. According to the analysis, the strain rate has a significant influence on the crushing morphology of the concrete under impact load. The relationship between the strain rate and D_h is shown in Figure 13. It is found that there is no strict positive correlation between the strain rate and D_b in this test. However, on the whole, the higher the strain rate level, the larger the value of D_b . The test results can reflect the distribution characteristics of the particle size of the broken specimen to a certain extent. Moreover, in this paper, the same series of screening apertures (the same size) are used under different working conditions; therefore, the fractal dimension values obtained are comparable.



Figure 13. Relationship between D_h and strain rate.

5. Fractal Characteristics of Microscopic Pore Structure

During the hardening and forming of concrete, due to its own drying shrinkage, external curing conditions, internal hydration reaction and other factors, a certain number of initial defects, such as pores and cracks, will be generated in the matrix. The damage of concrete is caused by the gradual development and evolution of these initial defects, and the gradual intensification of new damages. Therefore, it can be concluded that the microscopic pore structure characteristics, such as pore size distribution composition, porosity characteristics in concrete, determine its macroscopic mechanical properties.

5.1. Fractal Model Based on Thermodynamic Relationship

The pore structure parameters of each group of concrete samples are shown in Table 3. Figure 14 shows the differential curve of pore size distribution of PC group and CNFC02 group samples. The pore distribution characteristics measured by mercury intrusion method can be used to divide the pore into gel pores (<10 nm), transition pores (10~100 nm), fine pores (100~1000 nm) and large pores (>1000 nm). The pore volume distribution of the four types of pores and their percentage distribution of total pores in the samples of each group are shown in Figures 15 and 16, respectively. The analysis shows that with the increase in CNFs addition, the content of large pores and transition pores in the concrete decreases significantly, while the proportion of gel pores and transition pores increases to a certain extent.

Table 3. Pore characteristic parameters of each group of samples.

Sample No.	Most Probable Pore Size ¹ /nm	Medium Pore Diameter ² /nm	Total Pore Volume/mL·g ⁻¹	Average Pore Size ³ /nm	Pore Proportion/%			
					<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

¹ The aperture corresponding to the peak value on the differential distribution curve of aperture. ² The corresponding pore size when half of the mercury is injected. ³ Ratio of total pore volume to pore surface area.



Figure 14. Differential curves of typical pore size distribution of samples.



Figure 15. Proportion of various pores.



Figure 16. Pore volume distribution.

Under the vacuum state, mercury is pressed into the pores of concrete samples. According to thermodynamic theory, the work done by external force on mercury is equal to the increase in surface energy pressed into mercury [33], that is:

$$\int_0^V p \mathrm{d}V = -\int_0^S \sigma \cos\theta \mathrm{d}S \tag{9}$$

where *p* refers to the external pressure on mercury; σ represents the surface tension pressed into mercury; *V* denotes the volume pressed into mercury; *S* is the pore surface area of the sample; and θ refers to the mercury infiltration angle.

According to dimensional analysis, the pore surface area S of the tested sample can be expressed by the amount of mercury intake V and the pore size r. In the mercury-intake stage, Formula (9) can be obtained after discretization:

$$\sum_{i=1}^{n} \overline{p}_i \Delta V_i = C r_n^2 \left(V_n^{1/3} / r_n \right)^{D_p}$$
(10)

where *n* refers to the interval number of pressure applied throughout the mercury-intake stage; \overline{p} and ΔV_i represent the average pressure and mercury intake corresponding to the *i*th mercury intake, respectively; r_n and V_n denote the corresponding pore size and cumulative mercury intake at the *n*th mercury intake, respectively; D_p is the fractal dimension of pore surface area based on thermodynamic relationship.

Let $W_n = \sum_{i=1}^n \overline{p}_i \Delta V_i$, $Q_n = V_n^{1/3}/r_n$, and substitute it into Formula (10), and take the logarithm:

$$\ln\left(W_n/r_n^2\right) = D_p \ln Q_n + \ln C \tag{11}$$

5.2. Fractal Characteristics of Pore Structure

The fractal dimension is the characterization of the randomness and irregularity of the internal pores in the concrete, reflecting the distribution characteristics of the internal pores of concrete. The larger the fractal dimension, the more complex the pore structure inside the concrete, that is, the higher the distribution characteristics of pores and the complexity of their composition, specifically, the higher the content of large-aperture pores, the lower the content of small-aperture pores. According to Formula (11) and considering the mercury intrusion test results, the ln (W_n/r_n^2) and ln Q_n values of each group of samples are obtained, and the linear fitting of the two is performed. The x and y in the fitting equation shown in Figure 17 represent $\ln Q_n$ and $\ln (W_n/r_n^2)$, respectively. The corresponding fitting correlation coefficients R^2 are all above 0.998; therefore, the slope after curve fitting of each group could be used as the fractal dimension D_{v} of the pore surface area of this group of specimens. The relationship between the samples of each group D_p and CNFs dosage is shown in Figure 18. The analysis shows that the relationship between CNFs dosage and D_p is opposite to the strength characteristics of the concrete, that is, with the increase in CNFs dosage, D_p decreases first and then increases, and reaches the minimum at the dosage of 0.3%, which also proves the improvement law of CNFs on the internal pore structure of the concrete.



Figure 17. $\ln(W_n/r_n^2)$ - $\ln Q_n$ linear fitting curve.



Figure 18. The relationship between D_p and CNFs dosage.

In summary, the internal pore structure characteristics of CNFC show significant fractal characteristics. The addition of CNFs into concrete can mitigate the defects, such as filling the micro voids in concrete, etc., thus improving the original pore structure of the concrete, and effectively promoting its dynamic mechanical properties. On the one hand, the addition of CNFs has a significant improvement effect on the internal pore content of concrete, which is manifested by a sharp decrease in the pore content of large aperture. Although the pore content of small aperture increases slightly, the total pore content in the matrix decreases significantly, indicating that the compactness of the material has been effectively improved. The diameter of single filament of CNFs is only 100~200 nm, and the addition of CNFs can have a good filling effect on the dry shrinkage cracks produced by concrete molding. For the micropores generated after evaporation and consumption of water, the content of such pores is generally small, and the pore size is small. However, CNFs can be dispersed within such pores, thus further reducing the content of such pores. Therefore, CNFs can effectively reduce the pore content in concrete, and thus improve the compactness of the concrete. On the other hand, the addition of CNFs can improve the internal pore structure of concrete, reducing the proportion of large-aperture pores and increasing the proportion of small-aperture pores, indicating that the internal pore structure of concrete is effectively refined. For the pores with pore size greater than 100 nm, the addition of an appropriate amount of CNFs can effectively fill them, resulting in significantly decrease in such pores. At the same time, due to the addition of CNFs, a small amount of pores will be generated on the contact interface between CNFs and concrete matrix. Such pores are generally micropores with pore size less than 100 nm, therefore, to a certain extent, the content of such pores will increase.

6. Conclusions

The impact compression tests of PC and CNFC were carried out using Φ 100 mm SHPB test device. The dynamic compressive strength, impact toughness and fragmentation

size distribution law of PC and CNFC were analyzed, respectively. Considering the macroscopic failure mode and microscopic pore structure characteristics of the specimens, the change mechanism of the dynamic compressive mechanical properties of the concrete was explained based on fractal theory. The main conclusions are as follows:

(1) Both the dynamic compressive strength and the impact toughness of PC and CNFC increase continuously with the increase in strain rate level at the same dosage of CNFs, showing a strong strengthening effect of the strain rate—besides, both the dynamic compressive strength and impact toughness of CNFC are higher than their counterparts of PC.

(2) At the same strain rate level, the impact toughness of both PC and CNFC gradually increases with the increase in CNFs dosage, while the dynamic compressive strength first increases and then decreases with the increase in CNFs dosage.

(3) The fragmentation size distribution of PC and CNFC after impact failure shows self-similarity, which is a fractal in a statistical sense. In general, the higher the strain rate level, the larger the number of fragments, the smaller the size, and the larger the fractal dimension of particle size.

(4) CNFs can improve the internal pore structure of concrete, play the role of crack resistance, and effectively enhance the macroscopic dynamic mechanical properties of concrete. The optimal dosage of CNFs to improve the dynamic compressive strength of concrete is 0.3%, and the microscopic pore structure characteristics of CNFC show significant fractal features.

Author Contributions: Conceptualization, W.X. and J.X.; methodology, W.X.; software, L.N.; validation, J.X.; formal analysis, W.X.; investigation, J.X.; resources, W.X. and J.X.; data curation, W.X.; writing—original draft preparation, W.X.; writing—review and editing, L.N.; visualization, J.X. and L.N.; project administration, J.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 51208507 and 51378497.

Institutional Review Board Statement: The study did not involve humans or animals.

Informed Consent Statement: The study did not involve humans.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments: The authors express their thanks to all members of the laboratory team for their help with the technical support.

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

References

- 1. Torok, R. The 9/11 commission report and the reframing of the 'war on terror' as a new type of warfare. *J. Polic. Intell. Count. Terror.* **2011**, *6*, 137–150. [CrossRef]
- 2. Bamonte, P.; Gambarova, P.G. A study on the mechanical properties of self-compacting concrete at high temperature and after cooling. *Mater. Struct. Constr.* **2012**, *45*, 1375–1387. [CrossRef]
- 3. Akca, A.H.; Özyurt, N. Effects of re-curing on residual mechanical properties of concrete after high temperature exposure. *Constr. Build. Mater.* **2018**, *159*, 540–552. [CrossRef]
- 4. Yongliang, L.; Xiangming, K.; Yanrong, Z.; Peiyu, Y. Static and Dynamic Mechanical Properties of Cement-Asphalt Compsites. *J. Mater. Civ. Eng.* **2013**, *25*, 1489–1497. [CrossRef]
- 5. Ossa, A.; Gaxiola, A. Effect of water on the triaxial behavior under dynamic loading of asphalt concrete used in impervious barriers. *Constr. Build. Mater.* **2019**, *208*, 333–342. [CrossRef]
- Sun, X.; Zhao, K.; Li, Y.; Huang, R.; Ye, Z.; Zhang, Y.; Ma, J. A study of strain-rate effect and fiber reinforcement effect on dynamic behavior of steel fiber-reinforced concrete. *Constr. Build. Mater.* 2018, 158, 657–669. [CrossRef]
- 7. Afroughsabet, V.; Biolzi, L.; Ozbakkaloglu, T. High-Performance Fiber-Reinforced Concrete: A Review. J. Mater. Sci. 2016, 51, 6517–6551. [CrossRef]
- 8. Hassan, M.; Wille, K. Comparative experimental investigations on the compressive impact behavior of fiber-reinforced ultra high-performance concretes using split Hopkinson pressure bar. *Constr. Build. Mater.* **2018**, *191*, 398–410. [CrossRef]

- Daghash, S.M.; Soliman, E.M.; Kandil, U.F.; Reda Taha, M.M. Improving Impact Resistance of Polymer Concrete Using CNTs. Int. J. Concr. Struct. Mater. 2016, 10, 539–553. [CrossRef]
- 10. Li, W.; Li, M.; Adair, K.R.; Sun, X.; Yu, Y. Carbon nanofiber-based nanostructures for lithium-ion and sodium-ion batteries. J. Mater. Chem. A 2017, 5, 13882–13906. [CrossRef]
- 11. Gao, Y.; Zhu, X.; Corr, D.J.; Konsta-Gdoutos, M.S.; Shah, S.P. Characterization of the interfacial transition zone of CNF-Reinforced cementitious composites. *Cem. Concr. Compos.* **2019**, *99*, 130–139. [CrossRef]
- 12. Galao, O.; Baeza, F.J.; Zornoza, E.; Garcés, P. Strain and damage sensing properties on multifunctional cement composites with CNF admixture. *Cem. Concr. Compos.* **2014**, *46*, 90–98. [CrossRef]
- Gao, D.; Sturm, M.; Mo, Y.L. Erratum: Electrical resistance of carbon-nanofiber concrete. *Smart Mater. Struct.* 2009, 18, 095039. [CrossRef]
- 14. Konsta-Gdoutos, M.S.; Aza, C.A. Self sensing carbon nanotube (CNT) and nanofiber (CNF) cementitious composites for real time damage assessment in smart structures. *Cem. Concr. Compos.* **2014**, *53*, 162–169. [CrossRef]
- 15. Meng, W.; Khayat, K.H. Effect of graphite nanoplatelets and carbon nanofibers on rheology, hydration, shrinkage, mechanical properties, and microstructure of UHPC. *Cem. Concr. Res.* **2018**, *105*, 64–71. [CrossRef]
- 16. Sanchez, F.; Ince, C. Microstructure and macroscopic properties of hybrid carbon nanofiber/silica fume cement composites. *Compos. Sci. Technol.* **2009**, *69*, 1310–1318. [CrossRef]
- 17. Wang, B.M.; Zhang, Y. Synthesis and properties of carbon nanofibers filled cement-based composites combined with new surfactant methylcellulose. *Mater. Express* 2014, *4*, 177–182. [CrossRef]
- 18. Cao, S.; Hou, X.; Rong, Q.; Zheng, W.; Abid, M.; Li, G. Effect of specimen size on dynamic compressive properties of fiber-reinforced reactive powder concrete at high strain rates. *Constr. Build. Mater.* **2019**, *194*, 71–82. [CrossRef]
- 19. Ren, W.; Xu, J.; Su, H. Dynamic compressive behavior of basalt fiber reinforced concrete after exposure to elevated temperatures. *Fire Mater.* **2016**, *40*, 738–755. [CrossRef]
- 20. Cao, S.; Hou, X.; Rong, Q. Dynamic compressive properties of reactive powder concrete at high temperature: A review. *Cem. Concr. Compos.* **2020**, *110*, 103568. [CrossRef]
- 21. Ren, W.; Xu, J. Fractal Characteristics of Concrete Fragmentation under Impact Loading. J. Mater. Civ. Eng. 2017, 29, 04016244. [CrossRef]
- 22. Gay, C.; Sanchez, F. Performance of carbon nanofiber-cement composites with a high-range water reducer. *Transp. Res. Rec.* 2010, 109–113. [CrossRef]
- 23. Bagher Shemirani, A.; Naghdabadi, R.; Ashrafi, M.J. Experimental and numerical study on choosing proper pulse shapers for testing concrete specimens by split Hopkinson pressure bar apparatus. *Constr. Build. Mater.* **2016**, *125*, 326–336. [CrossRef]
- 24. Nie, L.; Xu, J.; Bai, E. Dynamic stress-strain relationship of concrete subjected to chloride and sulfate attack. *Constr. Build. Mater.* **2018**, *165*, 232–240. [CrossRef]
- 25. Lv, T.H.; Chen, X.W.; Chen, G. Analysis on the waveform features of the split Hopkinson pressure bar tests of plain concrete specimen. *Int. J. Impact Eng.* 2017, 103, 107–123. [CrossRef]
- Hassan, M.; Wille, K. Experimental impact analysis on ultra-high performance concrete (UHPC) for achieving stress equilibrium (SE) and constant strain rate (CSR) in Split Hopkinson pressure bar (SHPB) using pulse shaping technique. *Constr. Build. Mater.* 2017, 144, 747–757. [CrossRef]
- 27. Hao, Y.; Hao, H. Dynamic compressive behaviour of spiral steel fibre reinforced concrete in split Hopkinson pressure bar tests. *Constr. Build. Mater.* **2013**, *48*, 521–532. [CrossRef]
- 28. Hou, X.; Cao, S.; Zheng, W.; Rong, Q.; Li, G. Experimental study on dynamic compressive properties of fiber-reinforced reactive powder concrete at high strain rates. *Eng. Struct.* **2018**, *169*, 119–130. [CrossRef]
- 29. Zhang, B.; Liu, W.; Liu, X. Scale-dependent nature of the surface fractal dimension for bi- and multi-disperse porous solids by mercury porosimetry. *Appl. Surf. Sci.* 2006, 253, 1349–1355. [CrossRef]
- 30. Wang, B.M.; Zhang, Y.; Liu, S. Influence of carbon nanofibers on the mechanical performance and microstructure of cement-based materials. *Nanosci. Nanotechnol. Lett.* **2013**, *5*, 1112–1118. [CrossRef]
- 31. Xie, H.; Zhou, H.W. Application of fractal theory to top-coal caving. Chaos Solitons Fractals. 2008, 36, 797-807. [CrossRef]
- 32. Rieu, M.; Sposito, G. Fractal Fragmentation, Soil Porosity, and Soil Water Properties: I. Theory. *Soil Sci. Soc. Am. J.* **1991**, *55*, 1231–1238. [CrossRef]
- Wang, F.; Li, S. Determination of the Surface Fractal Dimension for Porous Media by Capillary Condensation. Ind. Eng. Chem. Res. 1997, 36, 1598–1602. [CrossRef]