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Research Article

Experimental Analysis of Mechanical Properties and Durability of Cement-Based Composite with Carbon Nanotube

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In order to study the mechanical properties and durability of cement-based composite with carbon nanotube, the test and analysis experiments are designed. Raw materials and related pharmaceutical instruments are prepared, to obtain cement-based composite with carbon nanotube samples by catalytic pyrolysis according to different proportions. The prepared sample is taken as the experimental object, and different bearing capacities are applied on different positions of the sample, to observe the change of the sample, and then, the experimental results of the mechanical properties of composite materials are obtained. The durability test results are obtained by combining the impermeability and frost resistance of the test object. The average compressive strength is 84.09 MPa, the average flexural strength is 16.9 MPa, and the crack resistance index is 22.5. In addition, the structure and diffusion coefficient of the sample also change in different degrees after the solution immersion and freeze-thaw treatment. Through longitudinal comparison, the more the carbon nanotubes are added into cement-based composite, the better its mechanical properties and durability are.

1. Introduction

Carbon nanotubes are one-dimensional quantum materials with special structure. When various nanoparticles are incorporated into the matrix, nanocomposites are created that outperform conventional materials in terms of performance. The major cause for the nanocomposites' enhanced features and qualities is the nanoparticles' modest loading into the base matrix, since nanoparticles have a superior dispersion in the parent matrix. [1–3]. Carbon nanotubes are mainly composed of hexagonal carbon atoms, which form several to dozens of concentric tubes. The distance between layers is about 0.34 nm, and the diameter is generally 2–20 nm. According to the different orientation of the carbon hexagon along the axial direction, it can be divided into three types: zigzag, armchair, and spiral. Among them, helical CNTs have chirality, while zigzag and armchair CNTs have no chirality. As one-dimensional nanomaterials, carbon nanotubes are light in weight, perfectly connected in hexagonal structure, and have many unusual mechanical, electrical, and chemical properties. In recent years, with the in-depth study of carbon nanotubes and nanomaterials, their broad application prospects are also constantly emerging [4, 5]. Carbon nanotubes can be regarded as curled graphene sheets. Therefore, according to the number of graphene sheets, they can be divided into single-walled carbon nanotubes and MWCNTs. According to the conductive properties of carbon nanotubes, they can be divided into metal type carbon nanotubes and semiconductor type carbon nanotubes. According to whether there are tube wall defects, they can be divided into perfect carbon nanotubes and defective carbon nanotubes. According to the shape, it can be divided into straight tube type, carbon nanotube bundle, *Y* type, snake type, and so on. As a raw material, carbon nanotubes are widely used in many fields because of their excellent mechanical, electrical, heat transfer, and optical properties.

Cement-based composite is a kind of composite material based on Portland cement, which is composed of alkali resistant glass fiber, general synthetic fiber, various ceramic fiber, carbon and aramid fiber, metal wire, natural plant fiber and mineral fiber as reinforcement, adding fillers, chemical additives, and water through composite process. It is better than ordinary concrete. Taking the short cut alkali resistant glass fiber composite with content of about 3%–10% as an example, its density is 1600–2500 kg/m^3, impact strength is 8.0–24.5 $N\cdot mm/mm^2$, compression strength is 48–83 MPa, and thermal expansion coefficient is (11–16) × 10-6k-1 [6]. The properties vary with the raw materials, ratio, process, and curing conditions used. Cement-based composite materials are basically used to manufacture building components, such as interior and exterior wall panels and ceilings. In 1994, foreign researchers used chemical cutting method to introduce active functional groups to the surface of carbon nanotubes, at the same time, combined with ultrasonic treatment method to get well dispersed carbon nanotubes aqueous solution, and studied the mechanism of different types of anionic surfactants on the dispersion of carbon nanotubes, to obtain cement-based composite with carbon nanotubes.

Gillani et al. [7] found that the uniform dispersion of the multiwall carbon nanotubes (MWCNTs) in the composite matrix holds the key for the mechanical properties of the resulting composite. Foldyna et al. [8] proposed a novel technique of CNTs dispersing using acoustic generator of pulsating jets. Saralch et al. [9] have found that the dispersion of nanoclay in the polypropylene matrix plays a significant role in the preparation of nanocomposites. Their study of stress-strain behaviour during the tensile testing of nanocomposite along with critical examining using field emission scanning electron microscope (FESEM) of the fracture surface has evolved that part per hundred of resin (phr) value around five provides maximum strength.

Carbon nanotube composites have been studied at home and abroad. However, unlike other matrix materials, there are few reports on cement-based composite with carbon nanotubes. In recent years, some scholars have made a preliminary exploration on the mechanical and electrical properties of cement-based composite with carbon nanotubes. Foreign researchers have studied the mechanical properties of cement-based composites with nanocarbon fiber. In order to improve the dispersibility of carbon nanofibers in cement matrix, dispersant and ultrasonic are used to make treatment First, the dispersed carbon nanofiber aqueous solution is prepared. The best dispersing suspension can be obtained when the ratio of dispersant and carbon nanofiber is the same. In the cement-based composite materials, the analysis shows that the nanocarbon fiber controls the growth of nanoscale microcracks, while the bending strength, elastic modulus, and hardness of the composite materials are greatly enhanced. In recent two years, Harbin University of Technology, Tongji University, Dalian University of Technology, and other universities have begun to explore the carbon nanotube reinforced cement-based materials and made some basic breakthroughs. Through uniaxial compression test and fatigue crack test, the basic mechanical properties of ordinary concrete and self-compacting concrete mixed with three types of nanocarbon fiber are tested, and the optimum mixing amount is discussed. It is found that nanocarbon fiber with proper mixing amount and good dispersion can improve the compressive strength and splitting tensile strength of concrete and has a good reinforcement effect on concrete materials.

Carbon nanotubes have excellent physical and chemical properties and have a very wide application prospect in cement-based composite materials. However, at present, researchers all over the world are faced with the following common problems: the large-scale preparation of carbon nanotubes is still a bottleneck, which greatly limits the application of development and research of carbon nanotubes; the mechanical properties of carbon nanotubes and its reinforcement mechanism are not clear; the durability of cement-based composite materials is almost not studied. To solve these common problems, we need to strengthen the cooperation between material researchers and experts and scholars in the field of chemistry. On the one hand, we need to break through the key technology, further research and develop new technology with low cost and suitable for large-scale production of carbon nanotubes, and continue to study its mechanical properties. On the other hand, through modeling and simulation to strengthen the research of growth phenomenon and mechanism, the experimental analysis results on the durability of composite materials are obtained, so as to truly realize its application in the field of cement concrete.

2. Preparation of Cement-Based Composite with Carbon Nanotube

Based on the analysis of the research situation of cement-based composite with carbon nanotube at home and abroad, the research content of this experiment is proposed, which mainly includes four aspects: the first is to study the preparation results and characterization of carbon nanotube by different types of water reducing agents; the second is to study the macro-mechanical properties of modified cement-based materials with carbon nanotube and the mechanism of carbon nanotube reinforced cement; the third is to study the method and technology of carbon fiber orientation arrangement in cement and the mechanical properties of cement-based materials modified by carbon fiber orientation arrangement; the fourth is to study the durability of the cement-based composite with carbon nanotube [10]. Therefore, first, the mechanical properties and durability of cement-based composite with carbon nanotube are prepared as the research samples.

2.1. Preparation of Raw Materials. The composition of raw materials is closely related to their macroproperties. The properties and types of raw materials have a crucial influence on the experimental results. Therefore, the selection and application of raw materials should meet the requirements of the experiment, which is the key link to ensure the smooth progress of the experiment. The raw materials used in this preparation will be introduced in detail in the following content.

2.1.1. Carbon Nanotubes. The carbon nanotubes used in the experiment include common multiwall carbon nanotubes (IMC6) and common carboxyl MWCNTs (IMC6—CH), which are produced by Beijing Boyu Hi-Tech New Material Technology Co., Ltd. [11]. IMC6—CH is a modified carboxylated derivative of IMC6 treated by chemical oxidation in liquid phase. The surface of IMC6 is inert and lack of active functional groups. There are a large number of COOH functional groups on the surface of IMC6—CH, which makes it easier for the MWCNTs with carboxyl group to bond with cement matrix and bridging agent. The physical parameters of MWCNTs are shown in Table 1.

It can be seen from Table 1 that the size of carbon nanotubes is very small, the length diameter ratio is large, the purity is high, and the specific surface is large.

2.1.2. Dispersant. Arabic gum is selected as the water dispersing agent of carbon nanotubes. Arabic gum can improve the hydrophilicity and dispersibility of MWCNTs by its long chain coating. Polyvinyl alcohol has good chemical cross-linking with cement matrix, and the hydroxyl group in polyvinyl alcohol may be connected with carboxyl group. Polyacrylamide is used to improve mortar performance with other fibers at the same time and shows good compatibility with fibers, so polyvinyl alcohol and polyacrylamide are selected as two bridging agents. The defoamer is tributyl phosphate.

2.1.3. Cement. As the most important cementitious material in construction engineering, the physical and chemical properties of cement have a great influence on the properties of cement products. The cement used is the benchmark cement produced by the Institute of Cement Science and New Building Materials Science of China Academy of Building Materials Science according to the National Standard of the People's Republic of China GB 8076-2008. Its chemical composition is shown in Table 2.

In addition, the physical parameters of P-O42.5 cement need to be analyzed, and the analysis results are shown in Table 3.

2.1.4. Water Reducing Agent. Water reducing agent is the key to improve the working performance of carbon fiber composite cement slurry. The water reducing agent molecules adsorb on the particles of cementitious materials in the fresh cement slurry to play a repulsive role and release water and form a layer of solvated film to play a lubricating role, so as to play a water reducing effect in the mixture [12, 13]. The water reducer used is the Bsaf powder water reducer MELFLUX® 2651F, which is a modified polycarboxylic ether made by spray drying process. The bulk density parameter of the water reducer is 30–60/100 cm^3, the drying loss is 2%, the pH value is 6.5–8.5, and the addition amount is 0.05%–1.5%.

2.2. Connection of the Preparation Instrument. Corresponding instruments are prepared according to the preparation method of cement-based composite with carbon nanotube, including QM - 3SP2 planetary ball mill, cement mortar mixer, cement mortar test body forming vibrating platform, $40\,mm \times 40\,mm \times 160\,mm$ cement mortar test mold, analytical balance, weighing paper, and so on [14], in addition, the type of ultrasonic instrument produced by Shanghai Shenganalytical Ultrasonic Instrument Co., Ltd., the type of microcomputer controlled full-automatic pressure testing machine produced by Shanghai Hualong Testing Instrument Co., Ltd., the type of microcomputer controlled electronic universal testing machine produced by Jinan Sida Testing Technology Co., Ltd., and the type of electrohydraulic servouniversal testing machine produced by the American System Company. The prepared preparation instruments are connected according to the preparation principle, and the resulting preparation experimental device is shown in Figure 1.

2.3. Smoke and Dust Emission Real-Time Monitoring Subsystem. According to the mechanical properties of the amount of carbon nanotubes to lead sulphate cement paste, the mechanical properties change of lead sulphate cement pastes with different water cement ratio and same amount of carbon nanotubes, and the effect of age on the mechanical properties of cement, based on the reference mix proportion of high-performance cement-based composite materials, the preparation mix proportion of cement-based composite materials with carbon nanotube as shown in Table 4 is designed.

2.4. Execution of Preparation Process. As one of the most potential materials in nanomaterials, the preparation of carbon nanotubes has been widely concerned. At present, the preparation methods of carbon nanotubes mainly include arc discharge method, laser evaporation method, and catalytic pyrolysis method, among which catalytic pyrolysis method is widely used in the preparation of carbon nanotubes due to its advantages of easy control of reaction process, strong applicability, simple preparation method, and high product purity [15]. The raw materials are added into the experimental device according to the designed mix proportion, and then, magnetic stirring and ultrasonic treatment are carried out. Then, the samples of cement-based composite with carbon nanotube are obtained by catalytic pyrolysis. The process of catalytic pyrolysis is as follows: dissolve a certain amount of analytical pure $Co(NO_3)_2$ in deionized water, add a certain amount of silica gel with a certain size, stir it evenly, and then, stand it; take the precipitate and put it into a porcelain boat, put it in a quartz tube, and get the nanometal particles attached to the silica gel through drying, burning, and high-purity hydrogen

Table 1: Physical parameters of MWCNTs.

Type	IMC6—CH	MWCNTs-OH
Diameter (nm)	20–40	>50
Length (μ m)	10–30	10–20
-Oh/-CH content (wt%)	0.71	0.71
Purity (wt%)	>95	>95
Bulk density (g/cm^3)	0.18	0.18
Specific surface (m^2/g)	>80	>60

Table 2: Chemical composition of reference cement.

P-O42.5 cement		Fly ash	
Chemical composition	Content	Chemical composition	Content
SiO2	20.93	SiO2	58.31
Al2O3	4.89	Al2O3	29.63
Fe2O3	2.89	Fe2O3	3.65
CaO	60.42	CaO	1.80
MgO	3.56	MgO	0.43
K2O	0.56	K2O	0.11
SO3	2.27	SO3	0.67
Loss	3.60	f-CaO	0.93
—	—	Cl-	0.011
—	—	Loss	4.53

Table 3: Physical parameters of P-O42.5 cement.

Parameter		Parameter value
Specific surface area (m^2·kg^{-1})		330
Loss on ignition (%)		3.65
Setting time (min)	Initial coagulation	197
	Final coagulation	263
Flexural strength (MPa)	3D	6.2
	28d	8.5
Compressive strength (MPa)	3D	29.8
	28d	52.5

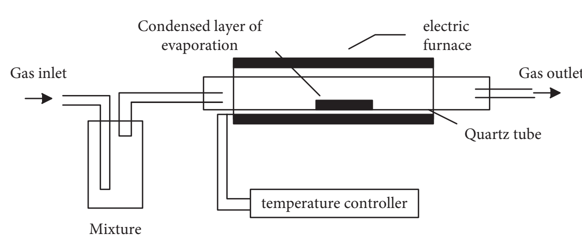

Figure 1: Preparation of experimental device.

reduction. This is the catalyst for thermal cracking of hydrocarbons [16]. The expression of the reaction process is shown as follows:

$$Co\left(NO_3\right)_2 \xrightarrow{\Delta} CoO + NO_2 + O_2 \quad (1)$$

At the same time, the following reaction occurs:

$$Co\left(NO_3\right)_2 + H_2 \xrightarrow{\Delta} Co + H_2O \quad (2)$$

The reaction process of pyrolysis of hydrocarbons is to mix C_2H_2 with a certain proportion of nitrogen as a compressed gas to pass through a quartz tube, which has been drained of oxygen. At high temperature, C_2H_2 decomposes carbon and grows carbon nanotubes under the catalysis of metal particles. The reaction is as follows:

$$C_2H_2 \xrightarrow{\Delta} C + H_2 \quad (3)$$

After the experiment, the sediment in the porcelain boat is taken for analysis, and the preparation results are shown in Figure 2.

2.5. Specimen Forming. The suspended carbon nanotubes are added to the cement-based material to form composite test

Table 4: Mix proportion of cement-based composite with carbon nanotube.

Sample no.	R-0	S-5	S-8	S-10	S-20	S-30	D-10
Water cement ratio	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Cement content	0	0.05	0.08	0.10	0.15	0.20	0.30
Types of carbon nanotubes	IMC6	IMC6	IMC6	IMC6	IMC6-CH	IMC6-CH	IMC6-CH
Content of carbon nanotubes	0.04	0.08	0.12	0.16	0.20	0.04	0.08
Deionized water (g)	236	236	236	236	236	236	236
Cement (g)	629	629	629	629	629	629	629
Dispersant (g)	0	0.2	0.32	0.40	0.58	0.80	0.80
Water reducing agent (g)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Fly ash (g)	157	157	157	157	157	157	157
Sand (g)	1218	1218	1218	1218	1218	1218	1218
PVP content	0	0.015	0.024	0.030	0.045	0.060	0.090
PMA content	0	0.015	0.024	0.030	0.045	0.060	0.090

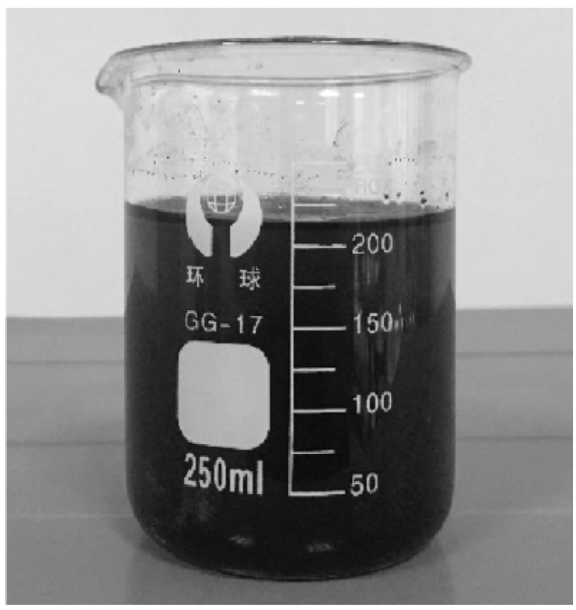

Figure 2: Configured carbon nanotube suspension.

pieces. The size of composite test pieces is 40 mm × 40 mm × 160 mm. The relationship between the modulus of carbon nanotubes and its diameter and length is obtained. The modulus of carbon nanotubes increases with the increase of diameter but finally tends to converge. The modulus of carbon nanotubes decreases with the increase of length and also tends to converge [17]. In this way, there are certain requirements on the length and diameter of the molecular structure mechanics model in terms of the size. The carbon nanotubes with the diameter of about and over the length are taken for analysis. Carbon nanotubes (10, 10) are selected for analysis, and the outer diameter and thickness structure of the specimen cost are shown in Figure 3.

3. Mechanical Properties of Cement-Based Composite with Carbon Nanotube

According to GB/t17617-1999 Test Method for Strength of Cement Mortar, DKZ - 5000 type bending strength tester is used to test the impact of MWCNTs on the bending strength of cement-based composite, and WHY type microcomputer controlled automatic press is used to test the impact of MWCNTs on the compressive strength of cement-based composite [18].The fracture morphology of cement-based composite with MWCNTs is characterized by means of SU-70 SEM, and the interaction mechanism between carbon nanotubes and cement is explored. Combined with the results of mechanical analysis of cement-based composite materials with carbon nanotube, specific tests are carried out for different mechanical properties, and corresponding mechanical properties experimental results are obtained.

3.1. Theoretical Analysis of Mechanical Properties. In the mechanical property test of carbon fiber cement nanocomposites, WDW-50 microcomputer controlled electronic universal testing machine is used to carry out three-point bending test, with a span of 100 mm, uniformly loaded at a rate of 0.20 mm/min until breaking. The compressive strength is tested by the WHY-300 microcomputer controlled automatic

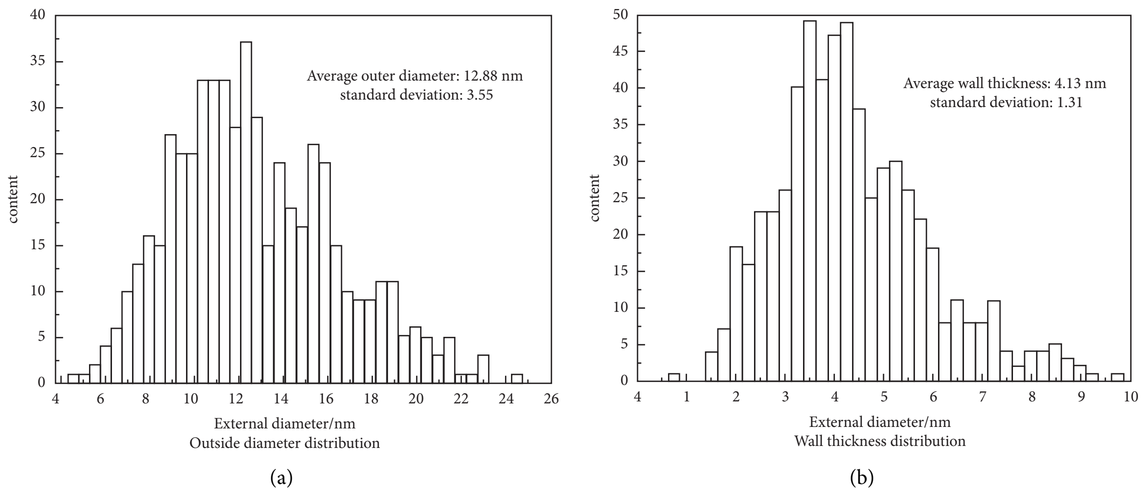

Figure 3: Outer diameter and thickness distribution of MWCNTs.

pressure testing machine and is loaded at the rate of 2400 N/s until the specimen is damaged [19]. WDW-50 microcomputer controlled electronic universal testing machine is used to test the tensile strength of fatigue crack, and the loading rate is 0.20 mm/min. The bending properties of the specimens are tested by MTS318 universal electrohydraulic servotesting machine at the loading rate of 0.10 mm/min. Finally, the mechanical properties of cement-based composite with carbon nanotube are obtained by synthesizing several mechanical properties.

Assuming that the diameter and length of the cement-based composite with carbon nanotube are D and L, the mechanical properties of the cylindrical solid can be determined by making its strain energy equal to the strain energy of the molecular structure mechanical model. The cement-based composite samples with carbon nanotubes are transversely isotropic materials, so they should have five elastic constants. In this way, combined with the intuitive geometric characteristics of molecular mechanics test and molecular structure mechanics, it can be based on the fact that carbon nanotubes are transversely isotropic, that is to say, they are symmetrical with respect to the cross-section, so that the equivalent continuum is also transversely isotropic [20]. According to the theory of composite mechanics, there is a stress-strain relationship. First, according to the generalized Hooke's law, the stress-strain relationship of different linear elastomers can be expressed as follows:

$$\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\end{bmatrix} = \begin{bmatrix}C_{11} & C_{12} & C_{13} & C_{14} & C_{15}\\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25}\\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35}\\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45}\\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55}\end{bmatrix}\begin{bmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\\ \varepsilon_5\end{bmatrix}. \tag{4}$$

In (4), C_{ij} is the stiffness coefficient, ε_i is the elastic strain coefficient, and σ_i is the stress coefficient. Through the transformation of matrix in (4), five independent stress moduli C_{11}, C_{12}, C_{23}, C_{22}, and C_{44} are obtained. The stress moduli obtained are the macroscopic constants of equivalent continuum model corresponding to cement-based composite with carbon nanotube [21]. The elastic stiffness coefficient of cement-based composite with carbon nanotube is defined as C_{11}, C_{12}, C_{23}, C_{22}, and C_{44}, the transverse shear modulus is G_{23}, the transverse bulk modulus is K_{23}, the axial shear modulus is G_{13}, and the axial style modulus is E_1. Then, the stress elastic stiffness coefficient of cement-based composite with carbon nanotube can be expressed as follows:

$$\begin{cases} G_{23} = \dfrac{C_{22} - C_{23}}{2} \\ G_{13} = C_{44} \\ K_{23} = \dfrac{C_{22} + C_{23}}{2} \\ E_1 = C_{11} - \dfrac{2C_{12}^2}{C_{22} + C_{23}} \end{cases} \tag{5}$$

From the previously mentioned description and the theory, it can be seen that the stress-strain relationship of the continuum can be obtained only by determining the elastic constant through the test method.

3.2. Setting of Mechanical Property Test Index. Under the support of the previously mentioned mechanical property theory of cement-based composite with carbon nanotube, the test index of mechanical property is set up. The flexural strength index of cement-based composite with carbon nanotube is calculated as follows:

$$R_f = \frac{3F_{\max} \cdot L}{2b^3}. \tag{6}$$

In (6), the parameter R_f is the flexural strength, $F_{\max}$ represents the load force when the cement-based composite with carbon nanotube specimen breaks, and L and b

represent the side length of the span and the direct contact surface of the experimental specimen, respectively [22]. Similarly, the calculation formula of compressive strength index in mechanical properties can be obtained as follows:

$$R_c = \frac{F_c}{A_y}, \tag{7}$$

where R_c is the compressive strength, F_c is the maximum load force when the specimen is damaged, and A_y is the area of the compression surface. In addition, the calculation formula of splitting tensile strength index is as follows:

$$R_t = \frac{2F_{\max}}{\pi A_p}, \tag{8}$$

where R_t and A_p, respectively, represent the splitting tensile strength and splitting surface area of the test piece [23]. The final mechanical property test index is the bending toughness index of cement-based composite with carbon nanotube. The corresponding fracture energy formula is as follows:

$$G_F = \frac{mg\delta_0 + W_0}{th} = \frac{mg\delta_0 + \int_0^{\delta_0} P(\delta)d\delta}{th}. \tag{9}$$

In (9), G_F is the fracture energy of the prepared specimen, W_0 is the area enclosed under the load deflection curve, m and g represent the mass and acceleration of gravity of the prepared specimen, δ_0 represents the displacement after the final fracture of the cement-based composite with carbon nanotube specimen, $P(\delta)$ represents the load deflection curve, and t and h are the height and thickness of the specimen respectively.

3.3. Mechanical Property Test and Result Analysis. The prepared cement-based composite with carbon nanotube samples are divided into several groups on average and are put into different experimental environments to test different mechanical properties.

3.3.1. Flexural Strength Test. Under the same water cement ratio, the flexural strength of different carbon nanotubes on the carbon nanotubes cement-based composite specimens is tested. The prepared specimens are placed in a horizontal position, the force application equipment is used to apply on both ends of the specimens, respectively, the force application value is recorded, and the surface change of the composite is observed [24]. When 0 N, 50 N, 100 N, and 200 N are applied, the change of composite is shown in Figure 4.

The loading force applied on the cement-based composite with carbon nanotube and the state of the experimental material are integrated. All the data are substituted into (6), and the flexural strength test results are obtained.

The results in Table 5 shows that the flexural strength of cement-based composite with carbon nanotube is 6.9 MPa at 1d, 14.1 MPa and 16.8 MPa at 3d and 28d, and 16.9 MPa at 56d, respectively [25].

3.3.2. Compressive Strength Test. When any of the six compressive strengths exceeds the average value, the average value shall be taken as the compressive strength result after it is eliminated. The compressive strength test process is shown in Figure 5.

Through the recording and calculation of compressive loading data, the experimental results of compressive strength of composite materials are shown in Table 6.

According to Table 6, at the same water-to-cement ratio, the addition of cement-based composite with carbon nanotube does not significantly improve the compressive strength of the cement pack. Under four different water cement ratios, the compressive strength of cement-based composite with carbon nanotube is close to that of blank sample or partially enhances its compressive strength [26]. The average compressive strength of cement-based composite with carbon nanotube is 84.09 MPa.

3.3.3. Test of Crack Resistance Index. Table 7 shows the test results of crack resistance index of cement-based composite with different carbon nanotubes.

In Table 7, l_i and d are the length and thickness of cement-based composite with carbon nanotube specimens, respectively. Finally, the crack resistance index test result of the composite is 22.5.

4. Durability Experiment of Cement-Based Composite with Carbon Nanotube

The durability of cement-based composites with carbon nanotube is the ability of materials to resist the long-term damage caused by both their own and natural environment. That is to ensure its durability. The better the durability is, the longer the service life of the material is. Taking the composite as the research object, the durability experiments of the composite are carried out from two aspects of impermeability and frost resistance.

Permeability refers to the transport and movement process of solution in some media under pressure gradient. For concrete, its permeability generally refers to whether the air, water, and salt ions in the water solution in the external environment are easy to invade into the internal characteristics of concrete and is expressed by permeability coefficient. The durability of cement-based materials has a direct impact on the safety and service time of the building structure, and the impermeability is one of its most important durability. The impermeability of cement-based materials is also related to the durability of other aspects, such as the penetration of water, air, and chloride ions into the reinforced concrete; the penetration of sulphate into the concrete is also due to the penetration of water and chloride ions into the concrete, the freeze-thaw damage, alkali aggregate reaction, and so on, which are closely related to the permeability. If the permeability of cement-based materials is good, all kinds of aggressive ions, water, and air are not easy to enter into the concrete, thus ensuring the durability of the concrete structure. The samples are saturated in saturated solution of Korean chloride for one hour and then soaked for 24 hours. Before the installation of the test piece, the ultrasonic bath shall be conducted for three minutes to ensure that the surface of the test piece is clean, free of oil, dust, and water drops. After fixing

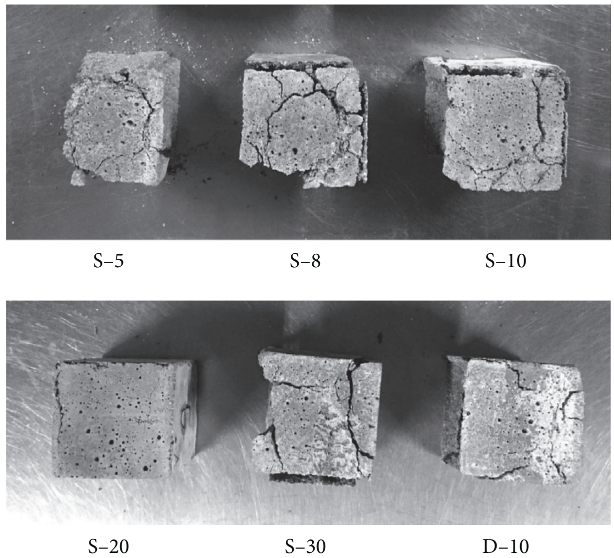

Figure 4: Cross-section picture of composite sample after bending test.

Table 5: Flexural strength of cement-based composite with carbon nanotube.

Sample	1D	3D	28d	56d
R-0	6.3 MPa	10.2 MPa	13.4 MPa	13.9 MPa
S-5	6.5 MPa	16.1 MPa	18.4 MPa	18.6 MPa
S-8	7.7 MPa	18.6 MPa	21.3 MPa	23.2 MPa
S-10	7.9 MPa	16.9 MPa	20.9 MPa	20.1 MPa
S-20	7.8 MPa	15.3 MPa	17.8 MPa	18.4 MPa
S-30	6.8 MPa	12.6 MPa	15.5 MPa	11.1 MPa
D-10	5.3 MPa	9.5 MPa	10.5 MPa	13.1 MPa

the test piece with a clamp, about 300 ml, 0.3 mol/l NaOH solution (or KOH solution) is injected into the cylinder of the test piece on the anode surface, and about 12 L sodium chloride solution with a mass concentration of 10% is put into the test container on the cathode surface. The test host is connected for power on test. According to the initial temperature, the instrument will automatically determine the test time, and the test data will be automatically recorded and saved. The permeability resistance of the cement-based composite with carbon nanotube is determined by observing the microstructure of the composite. The microstructure observation results of the composite at different soaking stages are shown in Figure 6. It is found that the reuniting of carbon nanotubes takes place, and then, the bridging was also observed. The scanning electron microcopy (SEM) image for sample A3 shows that the bridged tubes have growth/deposition of hydration products on them.

According to the statistics and comparison of relevant data, the chloride diffusion coefficient of cement-based composite with different carbon nanotube content at the age of 28 days is obtained, as shown in Figure 7.

The frost resistance refers to the property that the material resists multiple “freeze-thaw cycles” without fatigue, breakage, or damage. The test shall be conducted according to the relevant requirements of the quick-freezing method in the specification. Four days before the start of the freeze-thaw test, the carbon nanotube sample shall be taken out of the standard curing box for visual inspection, and then, it shall be immersed in an aqueous solution of $20 \pm 2^{\circ}C$, and the water level shall be more than 20 mm above the top surface of the sample outer surface. After four days, the sample is taken out from the water and the surface water is dried, to start the quality test and dynamic elastic modulus test of the sample after the sample label. Each group of samples is put into the sample box, and then, the sample box is put into the sample frame in the freeze-thaw box. During the test, it needs to ensure that the height of the water surface in the box is 5 mm higher than the top surface of the sample. The freeze-thaw solution is added into the freeze-thaw box until the liquid level of the freeze-thaw solution exceeds the liquid level in the box. In the center of the freeze-thaw box, a sample box with a temperature measuring sample is placed, and a temperature measuring sensor is inserted into the freeze-thaw liquid around. After multiple freeze-thaw treatments, the surface changes of cement-based composite with carbon nanotube are shown in Figure 8.

In Figure 8, the images 1–4 show the surface morphology of the test piece as the number of freeze-thaw cycles increases gradually. The pore quantification results of cement-based composite materials with different carbon nanotubes after freeze-thaw cycles are shown in Figure 9.

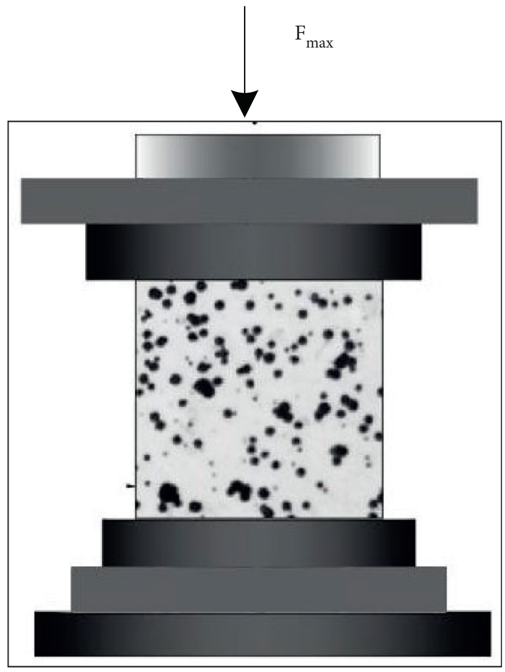

Figure 5: Diagram of compression loading.

Table 6: Compressive strength of cement-based composite with carbon nanotube.

Sample	Water-to-cement ratio (w/C)	Content of carbon nanotubes	Compressive strength (MPa)		
	0.25	0	77.6	84.8	89.9
S-5	0.25	0.05	76.8	87.4	91.0
S-8	0.25	0.075	76.6	85.8	88.8
S-10	0.25	0.1	77.9	85.2	91.5
S-20	0.25	0.125	78.1	85.1	90.2
S-30	0.25	0.15	79.0	76.2	91.8

Table 7: Crack resistance of cement-based composite with carbon nanotube.

Sample	/mm	d (mm)	A_p	$A_p * l_i$ (mm)	R_t
S-5	20	0.40	0.25	5	
S-8	10	0.35	0.25	2.5	
S-10	10	0.27	0.25	2.5	22.5
S-20	30	0.25	0.25	7.5	
S-30	20	0.33	0.25	5	

From Figure 9, it can be seen that the cement-based composite with high content of carbon nanotubes has smaller pores and fewer pores, which proves that the composite with high content of carbon nanotubes has higher frost resistance. Based on the test results of the frost resistance and permeability resistance of the cement-based composite with carbon nanotubes, it can be concluded that the more the carbon nanotubes are added into the cement-based composite, the better the durability of the corresponding material is.

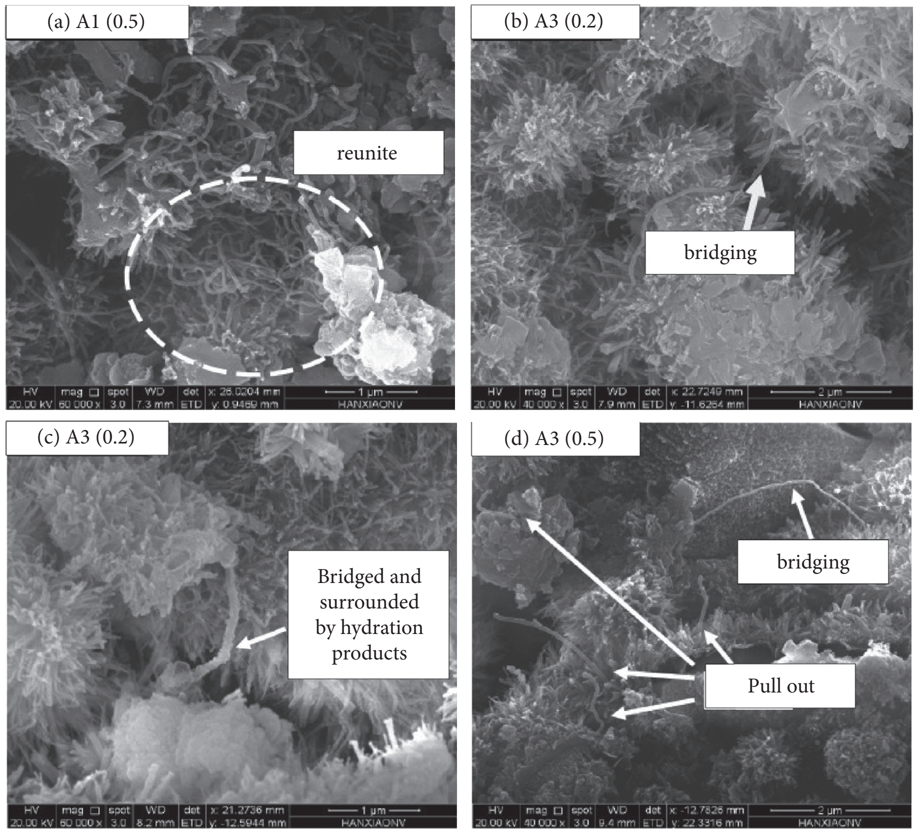

Figure 6: SEM of cement-based composite with carbon nanotube.

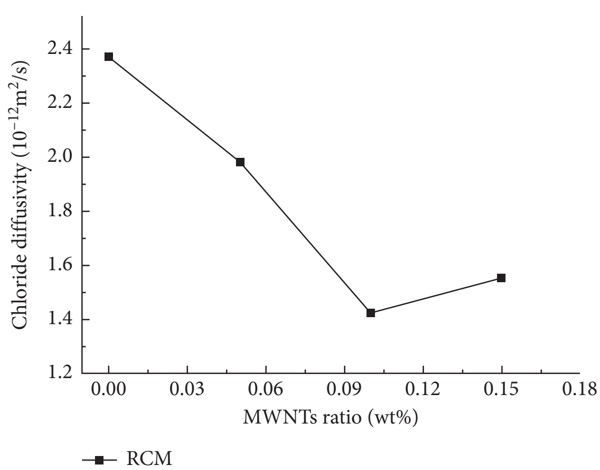

Figure 7: Chloride diffusion coefficient of cement-based composite with different carbon nanotubes content.

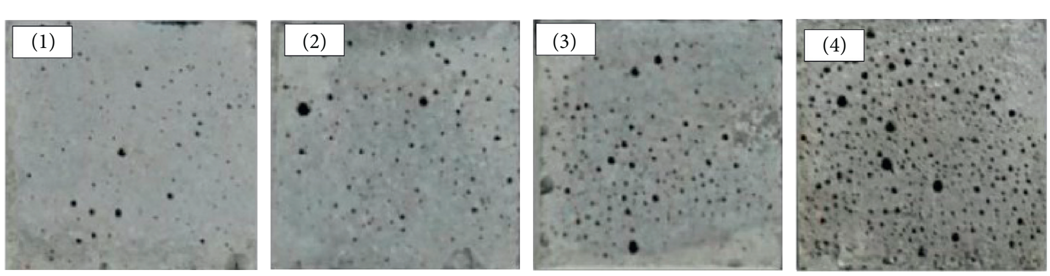

Figure 8: Test piece of cement-based composite with carbon nanotube after freeze-thaw cycle.

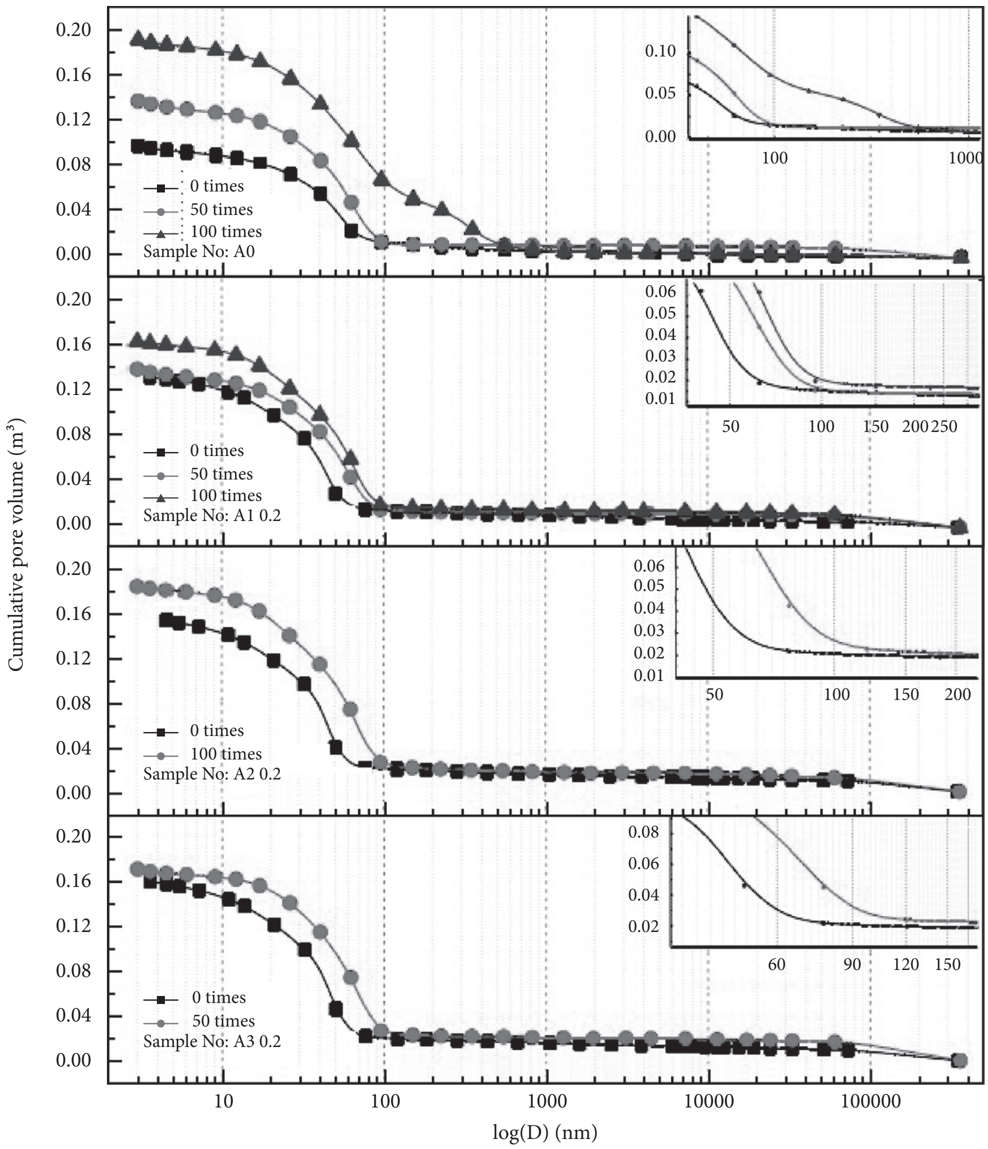

Figure 9: Pore volume and pore diameter curve under freeze-thaw cycle.

5. Conclusion

At present, the research of carbon nanotubes has become a global hotspot and has been applied in the fields of field emission, nanoelectronic devices, nanomachinery, composite materials, and so on. With the increasingly mature technology of preparation and synthesis and purification of carbon nanotubes, low-cost mass production of carbon nanotubes has become possible. However, the current high-tech concrete is still brittle, in terms of compressive strength. At present, the high-tech concrete has been very strong, comparable to the metal materials, but the tensile strength is far from the metal materials, so the key to study the high-tech concrete is to toughen, and the emergence of carbon nanotubes provides the possibility to solve this problem. Therefore, it has become an urgent task to explore and study the application of carbon nanotubes in cement concrete. It was found by the present study that the average compressive strength of cement-based composite with carbon nanotube is 84.09 MPa. Flexural strength of cement-based composite with carbon nanotube is 6.9 MPa at 1d, 14.1 MPa and 16.8 MPa at 3d and 28d, and 16.9 MPa at 56d, respectively. Once the production, preparation, and application of carbon nanotubes make an important breakthrough, it will certainly drive the development of the whole nanotechnology. At the same time, it will also drive the rise of a series of related high-tech industries, lead to a new technological revolution, and bring great benefits to the whole society.

Data Availability

The data used in this article are available upon request.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

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