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Effect of Graphene Nanotube on the Ultra High-Performance Fiber-Reinforced Concrete (UHPFRC) Under High Elevated Temperature

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ABSTRACT

Ultra High-Performance Fiber-Reinforced Concrete (UHPFRC) is a revolutionary material with an ultra-dense matrix reinforced by adding fine particles and reinforcing fibres. This innovative approach addresses the shortcomings of conventional concrete and gives UHPFRC exceptional compressive and tensile strength. The rise of nanotechnology and nanomaterials has promoted the development of various advanced materials. Graphene nanotubes (GNTs) as nanoscale additives can further enhance the performance of UHPFRC. This paper added 0.2%, 0.4% and 0.6% graphene nanotubes to UHPFRC. Upon completing 7 and 28 days of curing, the sample's strength under compression was measured at room temperature (25℃) and high temperatures of 200℃ and 400℃. The objective is to test the performance of UHPFRC under high elevated temperatures. It can be concluded that the temperature ranges from 25℃ to 200℃; the higher the graphene content, the higher its compressive strength. When the specimen is exposed to 200℃ - 400℃, the enhancing impact of graphene on the compressive performance of cement mortar is reduced. A noticeable phenomenon is that the graphene's strengthening impact on the cement binder demonstrates a trend of first inreasing and then decreasing with the increase in temperature.

Keywords: High temperature; UHPFRC; graphene nanotube

INTRODUCTION

In recent years, building fire accidents have happened frequently all over the world, and terrorist organisations burn and explode different buildings, resulting in endless damage to human society. As a result, studying the high-temperature tolerance of various construction materials is extremely important. Concrete fire resistance has a direct impact on building safety. As we all know, traditional concrete has low thermal conductivity and does not burn when heated, so it can be used as a good insulation material to protect steel bars from heat. Thus, developing concrete compositions that perform well in high temperatures and fire conditions is necessary.

Ultra-high-performance fibre-reinforced concrete composites (UHPFRC) is an innovative material designed to compensate for the shortcomings of existing concrete with a micro-fine, fibre-strong, intensive substrate. UHPFRC, despite its exceptional strength and durability, its performance at high temperatures is still a central issue that needs to be thoroughly investigated (Martens et al. 2018).

Recently, interest in graphene as an additive in concrete formulations has increased geometrically due to its outstanding properties. Graphene is a one-atom-thick layer of carbon atoms arranged in a hexagonal lattice with outstanding thermal and mechanical advantages and electrical conductivity. Due to these properties, graphene is an interesting candidate for improving the performance of construction materials.

Graphene nanotubes (GNTs) substantially affect the mechanical characteristics of cube boron nitrides (CBNs), which mainly depend on the length, content, surface groups, and dispersion effect of GNTs. Table 1 summarises the improvement effects of different dispersion methods and different contents of GNTs on the mechanical properties of CBNs. Nowadays, many researchers mainly choose Paste as the object of strengthening and toughening.

The utilization of mortar and concrete materials as subjects of research is comparatively infrequent which are mainly affected by two factors: on the one hand, the content and scale of graphene nanotubes are small, and they are more easily dispersed into a single paste matrix under high-speed stirring; subsequently, the matrix of the mortar can be fairly solid., and the internal defects are much less than those of mortar and concrete materials, which is beneficial to study the strengthening and toughening effect of graphene nanotubes. It can also be seen from Table 1 that the reinforcement effect of graphene in cement paste is better than that of mortar and concrete matrix.

As indicated in the experimental results presented in Table 1, which have been obtained from previous studies, the experiments after adding graphene may enhance the mechanical characteristics of cement-based composites. The mechanical properties of cement composites can be improved by incorporating graphene.

TABLE 1. Improvement of graphene to mechanical

Matrix	Graphene Content	w/c	Dispersion Method	Improve Mechanical Properties	Ref.
Paste	0.05 wt%	0.35	Dispersant	3% - 8% Compressive strength; 15% - 24% Flexural strength.	(Wang, B. et al. 2016)
Paste	0.025 wt%	0.4	Superplasticizer, Defoamer, Ultrasonication Dispersant, Superplasticizer.	14.9% Compressive strength, 23.6% Flexural strength, and 15.2% Tensile strength.	(Liu, J., et al. 2019)
Paste	0.06 wt%	0.3	Ultrasonication Dispersant; Defoamer.	11.2% Compressive strength and 20% Flexural strength.	(Wang, B. et al. 2019)
Paste	0.05 wt%	0.3	Ultrasonication Dispersant, Superplasticizer, Defoamer, Ultrasonication.	27.4% Compressive strength and 25.2% Flexural strength.	(Wang, B. et al. 2018)
Paste	0.06 wt%	0.3	Dispersant, Superplasticizer, Defoamer, Ultrasonication	11% Compressive strength and 27.8% Flexural strength.	(Baomin W. et al. 2019)
Mortar	0.02 wt%	N/A	Ultrasonication	25.4% Compressive strength and 20.3% Flexural strength.	(Ebrahim, A. et al. 2023)
Mortar	0.05 wt%	N/A	Dispersant, Superplasticizer, Ultrasonication	8.3% Compressive strength and 15.6% Flexural strength.	(Tao, J., et al. 2019)
Mortar	5 vol.%	0.6	Superplasticizer, Ultrasonication	1.5 - Fold hardness	(Cui, X., et al. 2017)
Concrete	0.05 wt%	0.43	Ultrasonication	113% Compressive strength and 36% Flexural strength.	(Jyothimol, P et al. 2020)
Concrete	0.16 wt%	0.48	Mechanical stirring, Ultrasonication	13.9% Compressive strength	(Matalkah, F et al. 2020)
Concrete	0.03 wt%	0.4	Mechanical stirring, Ultrasonication	23% Compressive strength and 29% Flexural strength.	(Mohsen, M.O et al. 2020)
UHPC	0.30 wt%	0.2	Dispersant, HRER, Ultrasonication	187% Energy absorption capacity and 45% Tensile strength.	(Meng, et al. 2018)

\The particular interest in graphene nanotubes from their unique tube structure, which provides improved mechanical properties and a way to reinforce concrete on a nanoscale. The cylindrical geometry (Figure 1) enhances dispersion within the concrete substrate and contributes to effective heat dissipation (Wang et al. 2020). Graphene nanotubes with these two functions are promising additives for solving high-temperature exposure problems in UHPFRC.

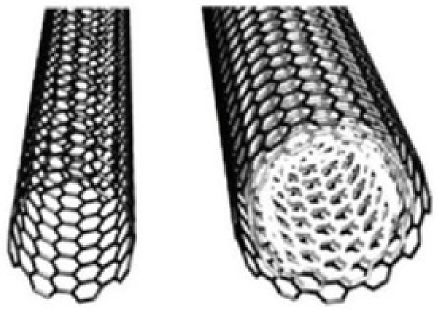

FIGURE 1. Structural model of GNTs.

METHODOLOGY

EXPERIMENT DESIGN AND PROCEDURE

This study aimed to assess the impact of graphene nanotubes on the characteristics of UHPFRC at various temperature conditions through detailed experimental methods. We will prepare multiple concrete specimens and add different proportions of graphene nanotubes to them to explore their specific effects on the performance of UHPFRC.

Multiple experiments with different weight/percentage ratios of GNTs were performed using GNTs with different doping ratios (0.2%, 0.4%, 0.6%). Prepare a cube mould of 50mm x 50mm x 50mm. After a curing period of 7 and 28 days, the compressive strength of the specimen was tested at room temperature (25°C) and high temperature (200°C, 400°C).

MATERIALS

Materials used for the UHPFRC preparation include graphene, cement, slice fume, sand, pp-fiber water, and superplasticiser. The graphene used for this experiment is GNTs (Figure 2). The properties of graphene nanotubes are shown in Table 2

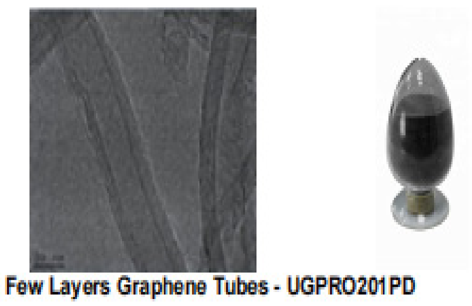

FIGURE 2. Participant's posture.

TABLE 2. Properties of GNTs

Properties	Typical Value
Available Diameters	8~16nm
Available Lengths	2 ~16um
Purity	>97%
Amorphous Carbon	<2%
Ash	<0.12 wt%
Specific Surface Area	230 -300m^2/g
pH	7-8
Resistivity	90-100 mΩ.cm
Layer	8-10

CONCRETE MIX DESIGN

The incorporation of the new material necessitated the consideration of novel mix designs. This experiment evaluates the impact of varying replacement percentages on the mix design by substituting cement with GNTs at proportions of 0.2%, 0.4%, and 0.6%.(TABLE 3) The experiment includes a control mix without graphene nanotubes to serve as a baseline for comparison. For clarity in this research, each mixture is assigned a specific code name, as detailed in TABLE 1 of the concrete mix design. The key properties of compressive strength are important for evaluating the effects of GNTs on improving the performance of UHPFRC.

TABLE 3. Materials proportions of the mix design

Specimen	M2	M4	M6
Cement (kg/m^3)	916	916	916
Silica Fume (kg/m^3)	183.2	183.2	183.2
Graphene Tubes (kg/m^3)	1.832	3.664	5.496
Graphene Tubes(%)	0.2	0.4	0.6
Water (kg/m^3)	229	229	229
Sand (kg/m^3)	916	916	916
SP 1% (kg/m^3)	9.16	9.16	9.16
Retarder 0.5% (kg/m^3)	4.58	4.58	4.58
PP fibre (kg/m^3)	1.832	1.832	1.832

EXPERIMENT EQUIPMENT

The compressive resistance of UHPFRC specimens was tested at different temperatures. The room temperture was 25°C and high temperature was 200°C, and 400°C, respectively. The whole heating process is carried out using the ISO834 fire curve. The heating test was carried out by an electric furnace(FIGURE 3) with 3 concrete cubes, and the heating rate was 9°C/min. After heating the sample at the target temperature for two hours, the heating is stopped, and the sample is cooled to room temperature.

ASTMC109-109M conducted the tests. The cube size was 50 mm ´ 50 mm ´ 50 mm, and there were three cubes per set of tests. According to the standard, the cube sample is prepared and placed on the compressor. Following that, apply an uninterrupted force of (1000 N/s) to the sample until it fails and record the results . Using the measured failure load, the compressive strength (CS) samples in MPa were determined using the following equation.

$$CS = {}^{P}/_{A} \tag{1}$$

A represents the area of the UHPFRC cube (in mm^2), and P represents the vertical load (in N).

FIGURE 3. Electric furnace.

RESULTS AND DISCUSSION

The primary parts of the UHPFRC composition are cement and silica fume. The material's particle size distribution was studied and tested with a laser diffraction particle size analyser. Figure 4 shows the results, including the overall volume as an amount for every particle size level is shown in Figure 5.

Concerning the findings above, we can say that the particle size of cement and silica fume in UHPFRC materials is relatively fine, mostly distributed between 0.84 and 60.82um, and silica fume has finer particles than cement. Among them, the particle size distribution range of cement is 0.84-11.64µm (when the particle size proportion exceeds 2%), the particle size distribution range of silica fume is 5.24-60.82µm (when the particle size proportion exceeds 2%), and the median particle size of silica fume is 2.49µm and 12.42 µm, respectively.At the micro-nano scale, the main solid phase of cured UHPFRC consists of C-S-H aggregates. The use of GNTs has two major effects on the microstructure of cement hydration products: first, the filling effect of pores at the nano-scale, preventing the formation and development of cracks at the micro-nano-scale; second, nanomaterials with a certain reactivity can promote the cement hydration reaction.

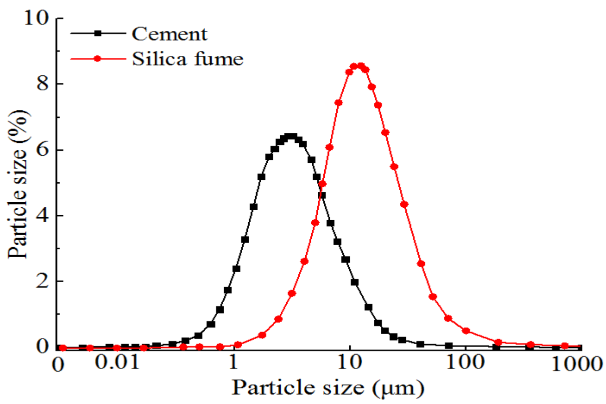

FIGURE 4. Particle size distribution.

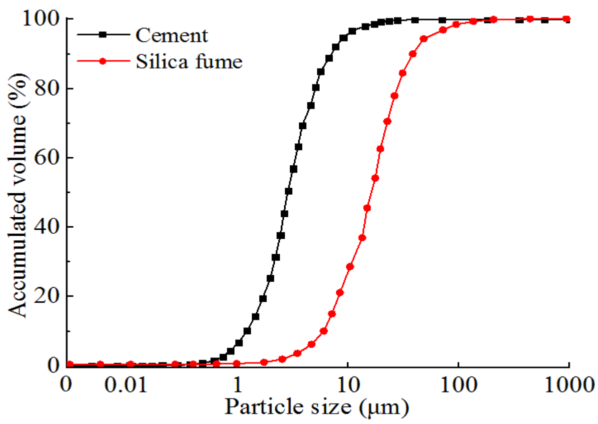

FIGURE 5. Accumulated particle volume

Figures 6 and 7 show specimens' experimental compressive strength results with different graphene nanotubes (GNTs) contents in UHPFRC concrete materials after curing for 7 days and 28 days under different temperature conditions, respectively. Each UHPFRC material includes a specified quantity of silica fume, and GNTs are used to precisely measure each parameter's role in the concrete mortar strength. Figure 6 displays the compressive strength test results for the samples after 7 days of curing, while Figure 7 shows the results after 28 days.

It can be seen from Figure 6 that under the condition of 25°C, when the content of GNTs rose from 0.2% to 0.6%, and the specimens' median compressive strength went from 92.67 MPa to 108.67 MPa. As the curing temperature rose to 200°C, the specimens' median compressive strength increased to 101.68 MPa when the content of GNTs was 0.2%. Under these conditions, when the content of GNTs increased from 0.4% to 0.6%, the average compressive strength of the specimens increased from 111 MPa to 112.67 MPa. From this result, it can be seen that under the condition of 200°C, although the increase in graphene nanotubes (GNTs) content can still improve the strength of the specimen, its growth rate is already very weak. When the curing temperature increased to 400°C, the compressive strength of the specimen decreased to 75.33MPa - 98MPa (the content of GNTs was 0.2% - 0.6%). Compared with the curing conditions at 25°C, the average compressive strength of the specimen decreased by 9.82% to 18.71%, respectively. Compared with the curing conditions at 200°C, the average compressive strength of the specimen decreased by 13.02% - 25.90%, respectively.

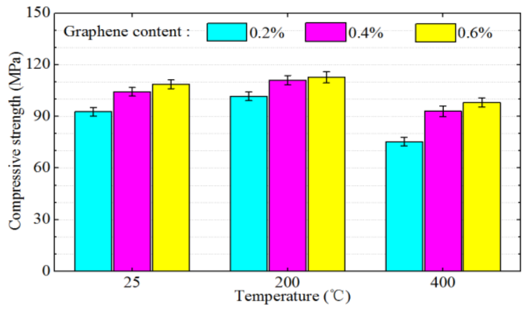

FIGURE 6. Compressive strength under different conditions after 7 days of curing

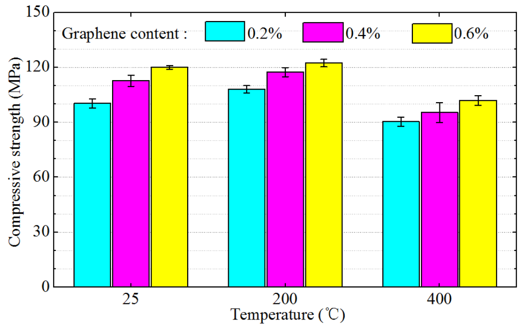

FIGURE 7. Compressive strength under different conditions after 28 days of curing

Figure 7 demonstrates that at 25°C and 0.2% GNTs concentration, the sample had an average compressive strength of 98.01 MPa, 5.75% greater than the 7-day curing strength. As the GNTs content grew from 0.4% to 0.6%, the median compressive strength of the specimens also increased by 7.35% to 11.34% compared to the 7-day curing strength. When the curing temperature rose to 200°C, the average compressive strength of the specimen reached its maximum value of 120.10 MPa when the content of GNTs increased to 0.4%. Afterwards, as the content of GNTs continued to increase, the specimens' average compressive strength also remained unchanged. However, when the curing temperature increased from 200°C to 400°C, the average compressive strength of the specimens also decreased by 15.45% -20.83% (the content of graphene nanotubes was 0.2% - 0.6%).

Based on the above analysis results, it can be concluded that an appropriate amount of GNTs can improve the compressive strength of cement mortar at room temperature and effectively alleviate the strength loss of cement mortar at high temperatures. As the temperature increases, the trend of compressive strength change for each specimen is roughly the same. When the curing temperature of the specimen is less than 200°C, the compressive strength of the specimen increases with the gradual increase of GNTs content (from 0.2% to 0.6%). At the same time, under the condition of 200°C, When GNTs concentration surpasses 0.4%, successive increases in content have a relatively small influence on the compressive strength. As the curing temperature reaches 200°C, the sample's average compressive strength steadily decreases. The specimens' compressive strength decreased at 400°C curing conditions decreased by 13.02% -25.90% (curing for 7 days) and 15.45%-20.83% (curing for 28 days) with different GNTs contents compared to 200°C. This is attributable to at temperatures of 200°C and 400°C, the thin mesopores transform into coarse mesopores due to the deformation of the graphene nanotubes. Due to the presence of the large pore volume exaggeration and thermal damage, the graphene nanotubes gradually lose control of the nanoscale damage, and the enhancement efficiency of the graphene tube-enhanced reinforced samples shows a downward trend.Therefore, a significant observable result is that the strengthening effect of graphene on the cement matrix shows a trend of increasing and decreasing.

CONCLUSION

This paper mainly explores the influence of GNTs and different temperature conditions on the mechanical properties of UHPFRC and studies the compressive strength, particle size distribution range of each component, and hardened cement-based products at high temperatures. The results are as follows:

1. Including GNTs can significantly increase the high-temperature performance of cement-based materials, with the strengthening effect occurring in two different phases.
2. Under other unchanged conditions, the change in graphene content significantly impacts the mechanical properties of UHPFRC materials. Within a certain range, as the amount of graphene added increases, the compressive strength of UHPFRC materials will also increase.
3. Despite the mechanical characteristics of UHPFRC materials, which include compressive strength, they improve drastically with more GNTs content. Nevertheless, the effect of temperature variations on the mechanical properties of UHPFRC materials may not be overlooked. Increased GNTs content in UHPFRC material within 200°C improves compressive strength and mechanical characteristics. But when the temperature exceeds 200°C and gradually increases to 400°C, the contribution of temperature increase to the improvement of mechanical properties of UHPFRC materials quickly weakens. At the same time, it suppresses the contribution of increasing GNTs contents to improving the mechanical properties of UHPFRC materials.

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DECLARATION OF COMPETING INTEREST

None.

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