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# Effect of graphite nanoplatelets and carbon nanofibers on rheology, hydration, shrinkage, mechanical properties, and microstructure of UHPC

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ABSTRACT

This study evaluates the effects of two types of graphite nanoplatelet (GNP-C and GNP-M) and one type of carbon nanofiber (CNF) on rheological properties, hydration kinetics, autogenous shrinkage, and pore structure of ultra-high-performance concrete (UHPC). The dispersion method was optimized to secure uniform dispersion of the nanomaterials in the UHPC. The plastic viscosity decreased with the nanomaterials content as the content was increased from 0 to 0.05%. As the nanomaterials content increased from 0 to 0.3%, the duration of induction period was extended by the addition of CNF, but shortened by use of GNP-C or GNP-M; cumulative hydration heat release was increased by introduction of nanomaterials; the autogenous shrinkage of UHPC with CNF, GNP-C, and GNP-M was increased by 30%, 20%, and 20%, respectively. The use of 0.3% CNFs reduced the total porosity of the UHPC by approximately 35%, indicating that the presence of CNFs refined the microstructure of UHPC.

## 1. Introduction

With appropriate combination of cement and supplementary cementitious materials, adequate sand gradation, low water-to-binder (w/b) ratio, fiber reinforcement, and high-range water reducer (HRWR), ultra-high-performance concrete (UHPC) can be produced to deliver high flowability, high mechanical properties, and excellent durability [1,2]. By incorporating 2% or more micro steel fibers as reinforcement, UHPC can exhibit strain hardening behavior and ductile failure modes in tension and in flexure [3–5]. However, the high amount of steel fibers significantly increases the initial cost and self-weight of UHPC [1,6,7]. In addition, although the steel fibers can be used to bridge cracks and increase the overall tensile properties, such as the tensile capacity and fracture energy, the steel fibers are ineffective in delaying the presence of microcracks. This is possibly due to the relatively large spacing and less interlocking between the steel fibers [8,9]. The presence of cracks makes concrete vulnerable to ingress of moisture and deleterious materials, thus resulting in accelerated deteriorations [10]. It was found that when the width of microcracks was < 50 μm, the chloride diffusion coefficient is significantly lower than that of cracks larger than 150 μm in a steel reinforced concrete composite [11]. Therefore, controlling the cracking resistance at microscale is critical for improving the durability of concrete structures.

To further enhance the cracking resistance and fracture toughness of cement-based materials, carbon nanofibers (CNFs) and graphite nanoplatelets (GNPs) have been utilized to provide microscale reinforcement [12–17]. Typically, the CNFs have a diameter of tens of nanometers and a length of tens to a few hundreds of micrometers; the GNPs have a diameter of tens of nanometers and a thickness of a few nanometers. Gao et al. [14] observed that the compressive strength of a cementitious composite made with 0.16% CNFs increased by 40% compared with that of plain cementitious composite without any CNF. With an addition of 0.13% of GNPs, Peyvandi et al. [15] obtained a 70% increase in the flexural strength of a cement paste with a w/b of 0.2. By adding 0.2% of CNFs, Tyson et al. [16] reported an increase in flexural strength of 80% and fracture toughness of 270% compared with the cementitious composite without any CNF. Huang [17] obtained an increase of 80% in flexural strength by using 0.2% GNPs in paste with a w/b of 0.6. Mechanical property improvement of these cement-based nanocomposites could be attributed to reduction in porosity and nucleation effect [17–20]. The nanoscale materials promote growth of hydration products, i.e. calcium-silicate-hydrate (C-S-H), on their surface [21,22]. In addition, the nanoscale spacing and high specific surface areas make large-aspect-ratio nanomaterials effective in suppressing inception and propagation of microcracks [23,24].

While the enhancement of mechanical properties by incorporating CNFs and GNPs was demonstrated in the above studies, the effect of their addition on other key properties of UHPC has not been fully investigated. The introduction of CNF or GNP may affect the compatibility between cementitious particles and chemical admixture [25],

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**Table 1**
Properties of the investigated nanomaterials.

| Fiber type | Specific gravity (g/cm$^3$) | Fiber length or platelet thickness (nm) | Diameter (nm) | Specific surface area (m$^2$/g) | Elastic modulus (GPa) | Tensile strength (GPa) | Carbon content (%) |
|---|---|---|---|---|---|---|---|
| CNF | 2.00 | (50–200) × 10$^3$ | 100 | 45 | 240 | 30 | > 95.0 |
| GNP-C | 1.95 | 2–10 | 25 | 300 | 1000 | 5 | > 99.5 |
| GNP-M | 1.95 | 2–10 | 30 | 150 | 1000 | 5 | > 99.5 |

thus influencing the rheological properties of UHPC. Due to the low w/b, typically < 0.25, UHPC can exhibit large early-age autogenous shrinkage, which can cause cracking [26,27]. Thus far, there is limited information on the effects of CNF and GNP on autogenous shrinkage, hydration kinetics, and the pore structure of UHPC. Such knowledge gap constrains the wider acceptance of nanomaterials in developing UHPC and drives the need of further research to advance the understanding.

Another constraint of using nanomaterials in UHPC is the lack of effective dispersion method. The effective and efficient use of nanomaterials depends on their dispersion condition. Given the very small size, agglomeration of nanomaterials becomes notable and can highly compromise their reinforcing performance [28,29]. Ultra-sonification has been used to undermine agglomeration and facilitate uniform dispersion of nanomaterials in aqueous media [30]. Surfactants have been used to convert hydrophobic surface into hydrophilic surface for better dispersion of nanomaterials [31].

Based on the above review, research on CNF and GNP have been focused on two main aspects: (1) how to render nanomaterials uniformly dispersed in cementitious matrix [30,31]; (2) whether the use of nanomaterials offers substantial improvement in performance of cementitious matrix and at what dosage of nanomaterials [17,18]. For the case of UHPC, the first aspect is reported in Section 2.2. For the second aspect, the incorporation of nanomaterials has been found able to increase the compressive, tensile, and flexural properties of UHPC [32]. As the content of CNFs or GNPs was increased from 0 to 0.30%, the compressive, tensile and flexural properties were all significantly increased; the bond strength and post-debonding performance of the interface between steel fiber and cementitious matrix were also improved [32].

The objective of this study is to evaluate the effects of two types of GNP and one type of CNF on rheological properties, hydration kinetics, autogenous shrinkage, and pore structure of UHPC. The mechanical properties of the investigated mixtures are also discussed. The content of the nanomaterials is increased from 0 to 0.3% by mass of binder. The higher dosages of nanomaterials were not investigated due to the high capital investment and difficulty in uniformly dispersing the nanomaterials. The study also seeks to compare the dispersion methods for the nanomaterials. The outcome of this research provides insight of CNF and GNPs used as a key component of UHPC.

## 2. Experimental program

### 2.1. Materials and mix design

A cost-effective UHPC [2] with w/b of 0.2 and sand-to-binder volume ratio of 1.0 was used. The binder was composed of ASTM Type III Portland cement, Class C fly ash, and silica fume with volume fractions at 55%, 40%, and 5%, respectively, of the total binder. The Blaine finenesses of the cement and the fly ash are 560 and 465 m$^2$/kg, respectively. Fine silica fume with particles smaller than 1 μm in diameter, mean diameter of 0.15 μm, the BET specific surface area of 18,200 m$^2$/kg, and a $SiO_2$ content of 95% was used.

A polycarboxylate-based high-range water reducer (HRWR) was incorporated to enhance the flowability [33]. The HRWR has a solid mass content of 23% and a specific gravity of 1.05. The sand was composed of 70% river sand (0–4.75 mm) and 30% masonry sand (0–2 mm), by mass. The fineness moduli of the river sand and masonry sand are 2.71 and 1.76, respectively. The water absorptions of the river and masonry sand are 0.14% and 0.06%, respectively. The specific gravities of the river sand and masonry sand are 2.64 and 2.63, respectively. Straight steel fibers measuring 0.2 mm in diameter and 13 mm in length were used at 0.5% by volume of UHPC. The fibers have a tensile strength and modulus of elasticity of 1.9 and 203 GPa, respectively.

The UHPC mixture without any nanomaterial was taken as the reference mixture and designated as “Ref”. The investigated contents of the nanomaterials were 0, 0.05%, 0.10%, 0.15%, 0.20%, and 0.30%, by mass of binder. The UHPC mixture without any nanomaterial was taken as the reference mixture (Ref). In total, 16 UHPC mixtures were investigated.

The dimensions and material properties of the three types of investigated nanomaterials are listed in Table 1. The CNF and GNPs were selected with considerations of the unit cost and mechanical properties. The GNP-C and GNP-M were produced by exfoliation of natural graphite.

### 2.2. Treatment of nanomaterials

In order to secure uniform dispersion of nanomaterials, four different treatment methods were used to prepare four UHPC mixtures with 0.3% CNFs, by mass, which are designated as T-0, T-1, T-2, and T-3 methods. For the T-0 system, the CNFs were directly added into the mixing water, without applying any other treatment. The liquid (CNF + water) was directly used in batching the UHPC mixture. For the T-1 system, the CNFs were added into the mixing water, the liquid (CNF + water) was stirred for 4 h (h) before batching the UHPC. For the T-2 system, the CNFs, HRWR, and polyacrylic acid were added into the mixing water with a mass ratio of 1:4:0.1 [24]. The liquid solution of CNF, HRWR, polyacrylic acid, and water was stirred for 4 h before batching. The polyacrylic acid is a high-molecular-weight polyelectrolyte that can be physically adsorbed on the surface of nanomaterials [24]. Finally, for the T-3 system, the nanomaterials, HRWR, and polyacrylic acid were added into the mixing water with a mass ratio of 1:4:0.1 in 600-ml water. The liquid solution of CNF, HRWR, polyacrylic acid, and water was stirred for 4 h. Then, sonification was applied to the liquid solution for 70 min (min) using a 500-W, cup-horn high-intensity ultrasonic processor [30]. At every 60 s (s), ultra-sonification was paused for 30 s to prevent overheating of the suspension.

Flexural tests were conducted to evaluate the flexural properties of the four UHPC mixtures. A higher flexural strength indicates a more uniform dispersion of the nanomaterials. The investigated UHPC mixtures contained 0.3% CNFs and 0.5% steel fibers, by mass of binder.

Table 2 shows the results of the flexural properties, which were tested in accordance with ASTM 1609 C [34]. It can be observed that the flexural strength increases due to the treatment of CNFs before batching. Compared with the T-0 system, the flexural strength and toughness (T150) of the T-3 system increase approximately by 65% and 200%, respectively. Proper treatment can significantly improve the uniformity of the nanomaterials dispersed in the UHPC matrix, thus increasing the flexural properties and other mechanical properties. Based on the test results, the treatment method corresponding to the T-