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CHARACTERIZATION OF ULTRA-HIGH-PERFORMANCE CEMENTITIOUS COMPOSITE INCORPORATING CARBON NANOTUBES

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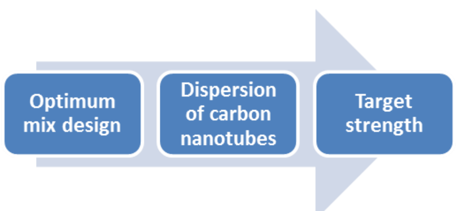
Graphical abstract



Abstract

Ultra-High-Performance Concrete (UHPC) is a type of concrete with unique mechanical and durability characteristics, developed to meet the global demand for extreme construction. Typically, UHPC is produced using customized mix design and subjected to special curing condition. Concrete is a brittle material in nature, where UHPC has its drawbacks in terms of lower tensile strength ratio and brittleness. Carbon nanotube (CNT) is a potential candidate to act as nano-reinforcement in UHPC matrix, to create a denser and a more ductile Ultra-High-Performance Cementitious Composite (UHPCC) system. The consistent dispersion of CNT in the cementititious matrix is a challenge due to their high aspect ratio and its agglomerating behavior. This paper presents on the fundamental UHPCC mix design which optimizes on its packing density with fewer constituent materials. The mechanical strength and microstructure characteristics of three types of UHPCC developed with CNT, which were produced with different dispersion methods are reported. It was found that stable CNT dispersion enhanced the microstructure characteristics of the UHPCC matrix, and achieved higher flexural strength (more than 60% higher) and marginally higher compressive strength, compared to control specimens without CNT.

Keywords: Carbon nanotubes (CNT), Ultra-High-Performance Cementitious Composites (UHPCC), Nano-engineered, Microstructure, Mechanical Properties

Abstrak

Konkrit Berprestasi Ultra Tinggi (UHPC) adalah sejenis konkrit yang yang memiliki kecirian mekanikal dan ketahanlasakan yang unik, di mana is dibangunkan untuk memenuhi permintaan sejagat untuk pembinaan ekstrem. UHPC selalunya dihasilkan dengan menggunakan kaedah reka bentuk bancuhan yang khusus dan dikenakan kaedah pengawetan khas. Konkrit secara semulajadinya adalah bahan yang rapuh, di mana UHPC mempunyai kelemahan dari segi nisbah kekuatan tegangan yang lebih rendah dan kerapuhan. Tiub-nano karbon (CNT) adalah satu bahan yang berpotensi untuk digunakan sebagai tetulang-nano dalam matrik UHPC, untuk menghasilkan sistem Komposit Bersimen Berprestasi Ultra Tinggi (UHPCC) yang lebih padat dan mulur. Penyebaran CNT yang konsisten dalam matrik bahan berasaskan simen adalah satu cabaran disebabkan oleh nisbah bidangnya yang tinggi dan kelakuan penggumpalannya. Kertas kerja ini membentangkan asas kaedah reka bentuk bancuhan UHPCC yang mengoptimumkan ketumpatan pengisipaduannya dengan bilangan bahan konstituen yang lebih rendah. Ciri-ciri mekanikal dan struktur-mikro tiga jenis UHPCC yang telah dibangunkan dengan CNT yang telah dihasilkan dengan kaedah penyebarannya yang berbeza telah dilaporkan. Didapati bahawa penyebaran CNT yang stabil meningkatkan kecirian struktur-mikro matrik UHPCC, dan mencapai kekuatan tegangan yang lebih tinggi (melebihi 60% lebih tinggi) dan kekuatan mampatan yang sedikit lebih tinggi, berbanding spesimen kawalan tanpa CNT.

Kata kunci: Tiub-nano karbon (CNT), Komposit Bersimen Berprestasi Ultra Tinggi (UHPCC), Kejuruteraan-nano, Struktur-mikro, Kecirian mekanikal

1.0 INTRODUCTION

Ultra-High-Performance Concrete (UHPC) is a type of special concrete developed to realize the need for impressive megastructures and extreme construction. UHPC usually exhibits ultra-high-strength properties with characteristic compressive strength of 150 MPa or higher, at 28 days [1] and is typically produced using low water-to-cement ratio with high volume of cement or supplementary cementitious materials, various grading and types of fine aggregates, fiber reinforcements and chemical admixtures. The UHPC system eliminates all the coarser materials used in typical normal-strength concrete. Instead, its matrix is packed with micro-scaled materials such as silica fume and ultra-fine sand. Due to the brittle nature of concrete, high volume of metallic fiber reinforcing system is important to provide the required ductility and delaying crack propagation [1, 2]. The use of micro-scaled fiber system has been commercialized by Bouygues and Aalborg Portland for construction applications since mid-2000s [3]. Ductal is the most common UHPC product with applications in bridges, water dam and special constructions, with unique compressive strength of above 180 MPa under steam curing at 90°C. Further, it consists of 8 different constituents in its mix design [4].

Carbon nanotube (CNT) was introduced by Iijima in 1991. CNT is the strongest material which provides both diameter and length in the nano-scale range [5]. Its discovery has provided researchers in concrete technology with the means to further enhance and utilize the advantage of nanotechnology in high-performance concrete. The nano-particles of CNT enhances the microstructure of UHPC by filing-up all voids at nano-scale and making the matrix denser. However, researchers have reported that the contribution of CNT have shown inconsistent and sometimes contradictory results on concrete properties, on the compressive strength in particular.

Although CNT comes with superior properties, its dispersion technique is the key that determines its contribution on the concrete's performance [6]. Ultrasonication technique is the most effective method to disperse CNT in colloidal form. However, CNT can also agglomerate to form bigger particles, thus contributing to a lower concrete strength. The ultrasonication method can be improved by incorporating a surfactant during the dispersion process [7], where this technique shows positive improvement due to the acceleration of nano particles with a higher early strength and micro-structure reinforced with CNT in the matrix [6, 8]. However, researchers have proven that a low amount of CNT will result in better dispersion without any agglomeration. Different percentage of multi-walled CNT have been prepared, where the amount of 0.5% wt. of CNT resulted in the desired compressive strength and splitting tensile strength, with an enhancement of 15% and 36%, respectively [9, 10].

This article explores the use of locally available materials and CNT in the synthesis of ultra-high-performance cementitious composites (UHPCC). This study was initiated to develop UHPCC with a compressive strength of 150 MPa and higher, under normal curing conditions and with a "simpler" mix design. The contribution of the CNT on the strength characteristics of UHPCC is also discussed.

2.0 METHODOLOGY

2.1 Materials and Mix Design

The first step in the experimental work is to analyze the compatibility of cement from various sources, namely Cement-A, Cement-B and Cement-C used in this study. There are a total of 3 different mixes with locally sourced ordinary Portland Type I cement with control water/cement (w/c) ratio of 0.28. The subsequent step was to identify the most suitable cement for three different w/c ratio, i.e. 0.28, 0.25 and 0.20, in order to obtain the optimum mix for the UHPCC. The lowest w/c ratio mix was selected to investigate the effect of CNT on the properties of UHPCC. Two different types of CNT, namely CNT-A and CNT-B were prepared by using different dispersion techniques. Two mixes were prepared using CNT-A with and without the use of surfactant with ultrasonification dispersion method. Meanwhile, another mix was prepared using CNT-B without surfactant under ultrasonification dispersion method. The details of the mix proportions are presented in the Table 1.

Table 1 UHPCC mix proportions

% by weight	UHPCC Cement-A	UHPCC Cement-B	UHPCC Cement-C	UHPCC-0.25	UHPCC-0.20	UHPCC CNT-A	UHPCC CNT-B
Cement	1	1	1	1	1	1	1
Graded Sand	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Water	0.28	0.28	0.28	0.25	0.20	0.20	0.20
Superplastizer	0.008	0.008	0.008	0.009	0.01	0.01	0.01
CNT	–	–	–	–	–	0.00066	0.00066

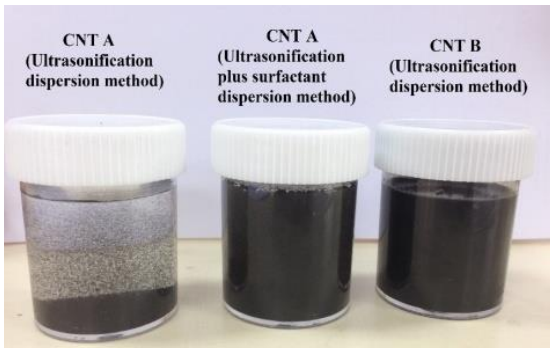


Figure 1 Types of CNT suspensions produced

The constituent materials used in producing the mix proportions designed in this study were ordinary Portland Type I cement, graded sand, superplastizer, and two types of CNT suspensions. CNT-A was produced through the chemical vapor deposition (CVD) method while CNT-B was produced using the plasma method. The CNT were dispersed using the methods described earlier to produce two variations of UHPCC incorporating CNT-A and one type of UHPCC with CNT-B. Figure 1 shows the types of CNT that were produced with different dispersion method in this study.

The particle size analysis of the cement and graded sand was performed using the Malvern Master Sizer 2000 Laser granulometry analyzer. Meanwhile, the chemical composition of the cement was determined using the XRD technique and are as summarized in Table 2. Scanning Electron Microscope (SEM) was used to study the microstructural characteristics of the UHPCC matrix produced in this study.

Table 2 Chemical composition of cement

Composition	Cement-A CEM I 42.5 N (%)	Cement-B CEM I 42.5N (%)	Cement-C CEM I 42.5 N (%)
C_3S	75.3	79.9	72.3
C_2S	6.8	5.8	6.5
C_3A	5.6	2.9	7.9
C_4AF	7.8	6.9	8.8
Gypsum	4.5	4.5	4.5
$C_3S + C_2S$	82.1	85.7	78.8

2.2 Specimen Preparation and Testing

The principle of optimized blending of cement and graded sand to produce a good concrete mix were adopted by designing the mix based on the Fuller-Thompson curve [11]:

$$P(D)=(d/D)^q \quad (1)$$

where P is the fraction passing the sieve with opening D, d is the particle size and D is maximum particle size of the mix. The parameter q has a value between 0 and 1. The theoretical equation by Fuller is obtained when $q = 0.5$, whereas the modified version by Andreasen and Andersen can be obtained when $q = 0.37$ [11].

In this analysis, cement and graded sand were sieved and passed through mesh No. 50 (approximately 0.3 mm). The optimized grading curve of cement and graded sand was calculated to obtain best grading to the modified Andreasen's curve as presented in Figure 2. Optimum grading contributed to a denser matrix of the mix.

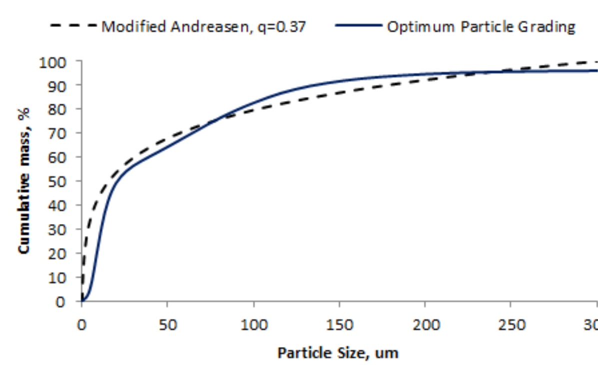


Figure 2 Optimum particle packing grading

To produce the UHPCC mixes, cement and graded sand were blended in the Hobart N50 planetary mixer for 3 minutes. Water and superplasticizer were added and mixed for 5 minutes until the mixture became flowable. The flow value was measured in accordance with ASTM C230 [12] within 30 seconds to ensure the workability.

The fresh mix was cast into 50 mm cube molds and 40 mm × 40 mm × 160 mm prism molds. All molds were covered with plastic sheets to prevent evaporation of water during the initial curing. The specimens were demoulded after 24 h and were then cured in water at room temperature for mechanical characterization. Compressive and flexural strength were determined in accordance with ASTM C109 [13] and ASTM C38 [14], respectively. The flexural strength, f_t, was calculated based on the following equation:

$$f_t = 0.0028\,P \qquad (2)$$

where P = maximum load, N

3.0 RESULTS AND DISCUSSION

3.1 Effect of Chemical Composition of Cement

Cement is the main constituent in concrete which directly reflects the compressive strength of concrete. Three different types of Type I ordinary Portland cement were utilized in this study with a control w/c ratio of 0.28, and the findings are as presented in Figure 3. UHPCC made of Cement-C achieved a 28 days compressive strength of 110 MPa, while the UHPCC made of Cement-B recorded the highest compressive strength on both 7 days and 28 days with 109 MPa and 120 MPa, respectively. This is due to the higher C3S and C2S content in Cement-B (as shown in Table 2), which contribute towards better strength development. It was concluded that the compressive strength of UHPCC are significantly influenced by the chemical composition of the cement and the total combination of C3S and C2S is essential to achieve better strength development characteristics.

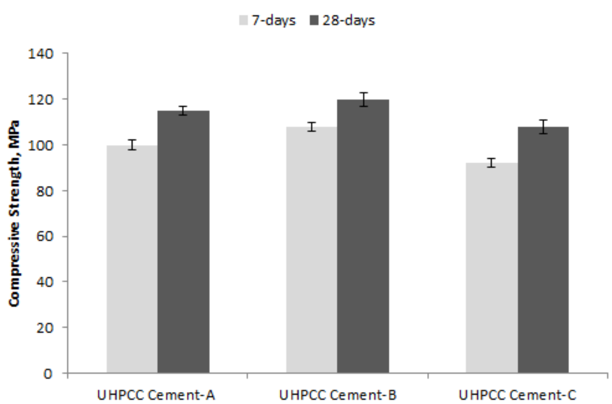


Figure 3 Compressive strength of UHPCC made of different types of cement at 7 and 28 days of age

3.2 Effect of Water-Cement Ratio

Theoretically, a lower w/c ratio will lead to higher strength. Three different UHPCC mixes with w/c ratio of 0.28, 0.25 and 0.20 were prepared with Cement-B. Figure 4 shows that UHPCC mix with w/c ratio of 0.28 recorded the lowest strength; while the UHPCC with w/c ratio of 0.20 recorded the highest strength with 125 MPa at 7 day and 152 MPa at 28 days. A higher w/c ratio will contribute to a lower strength due to the resulting porous cement paste and create more water-filled pore space [15]. Figure 5 shows the flexural strength recorded at 28 days, and the ratio of 28th day flexural strength (f_t) to the 28th day compressive strength (f_{cu}). Theoretically, the f_t/f_{cu} ratio is approximately about 10% [15, 16]. The mix with w/c ratio of 0.20 achieved the highest flexural strength of 11.3 MPa, but with the lowest f_t/f_{cu} ratio of 7.4%. Concrete is brittle in nature. Therefore, UHPCC mix with a much denser matrix and higher strength will result in enhancement to the brittleness of the composite [16, 19].

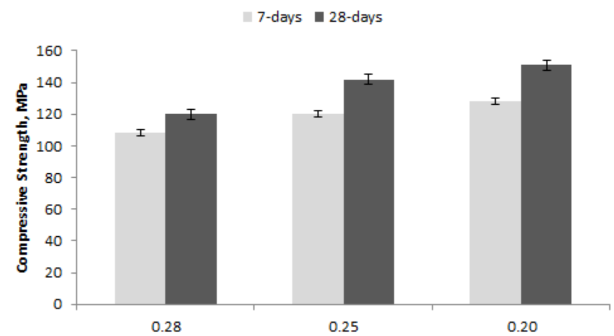


Figure 4 Compressive strength of UHPCC made of different water-cement ratio at 7 and 28 days of age

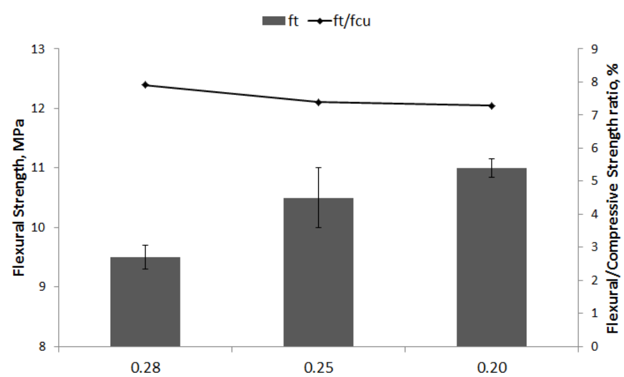


Figure 5 Flexural strength and flexural/compressive strength ratio of UHPCC produced with different water-cement ratio at 28 days of age

3.3 Effect of CNT Types and Dispersion Methods

3.3.1 Compressive Strength

Preliminary findings indicated that UHPCC with w/c ratio of 0.20 achieved the highest 28 days compressive strength. Hence, this mix design was further enhanced with CNT by using two variations of CNT. It can be observed from the results (Figure 6) that UHPCC made of CNT-A recorded the lowest compressive strength of 113 MPa at 7 days and 138 MPa at 28 days. This might be caused by the poor dispersion and instability of the CNT after ultrasonication. The improved version of CNT-A blended with surfactant (Figure 1) shows a much stable dispersion, achieved a higher compressive strength, but was still inferior in terms of strength compared to the mix without CNT. On the other hand, CNT-B was dispersed homogenously under ultrasonication without any surfactant (Figure 1) and achieved the highest strength, with a compressive strength of 135 MPa at 7 days and 158 MPa at 28 days. The presence of surfactant in the dispersion process affected the CNT surface properties, where the surfactant is likely to form a coat on the CNT surface and weaken the bonding of CNT and the cement matrix [7, 16].

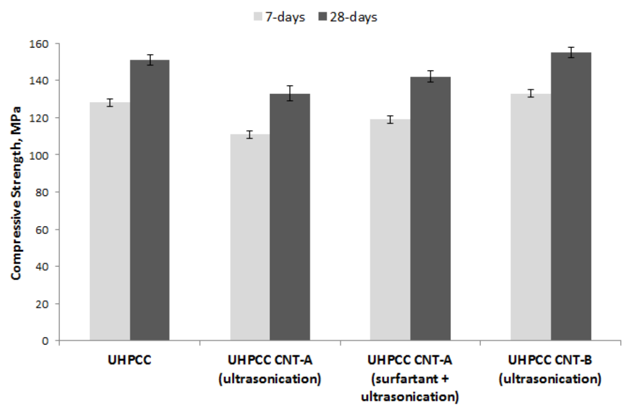


Figure 6 Compressive strength of UHPCC with different CNT variations

Microstructural analysis is essential to understand the presence and contribution of CNT in the UHPCC matrix. The presence of CNT also provided better bridging in the matrix, as shown in Figures 7 and 8. It can be observed from Figure 7 that CNT-A likely "agglomerated" in the matrix. Poor dispersion of CNT-A will greatly affect the microstructure of the matrix and lower the compressive strength (Figure 6). A stable and good dispersion of CNT-B will make significant contribution to the strength improvement. Figure 7 and 8 also indicate the variation in the characteristics of CNT-A and CNT-B, i.e. being formed with different dimensional grading. CNT-A consisted of generally uniform nano-diametered tubular fibers of about 40 nm, while CNT-B was formed with a wider range of 90-190 nm diametered tubular fibers. The FESEM analysis also illustrated the good bridging characteristics between CNT-B and the UHPCC matrix, whereas CNT-A agglomerated in the matrix and may not have effective bridging with the surrounding matrix [17].

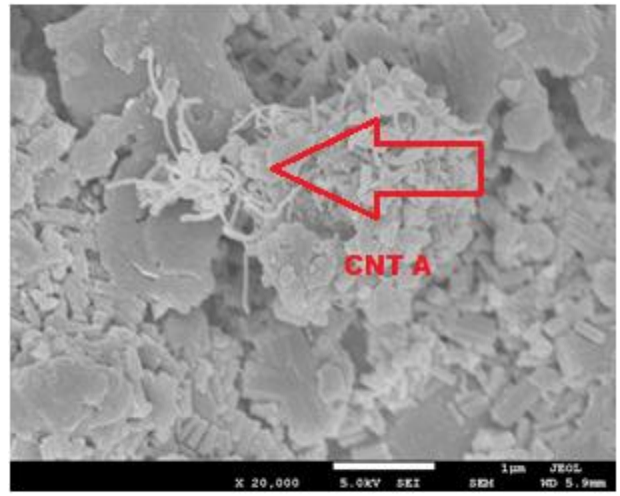


Figure 7 FESEM micrograph of CNT-A in the UHPCC matrix

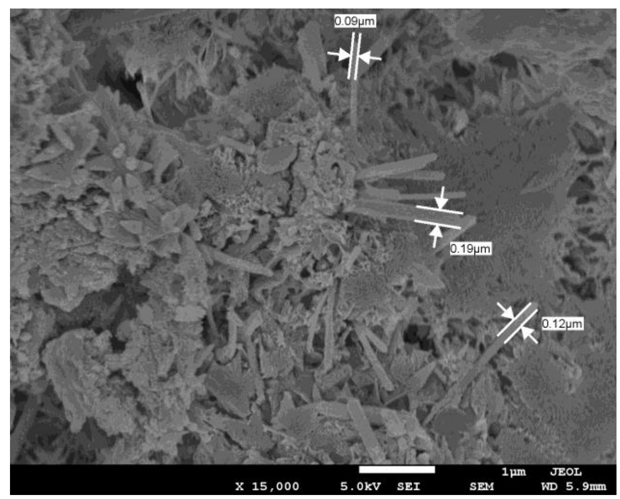


Figure 8 FESEM micrograph of CNT-B in the UHPCC matrix

3.3.2 *Flexural Strength*

Generally, flexural strength can be lower in a denser UHPCC matrix (Figure 5). The presence of CNT strengthens the matrix and delays the propagation of cracks at the nano-scale. Unlike the compressive strength, both UHPCC with CNT-A and UHPCC with CNT-B showed positive improvement on the flexural strength, as presented in Figure 9. UHPCC with CNT-B achieved the highest flexural strength of 20 MPa, a 60% enhancement compared to the control. This is clearly evident that CNT-B provided an effective bridging capacity with the surrounding matrix, as shown in Figure 8. CNT-B with larger diameter grading provided excellent bridging at nano-scale to enhance the toughness of the UHPCC matrix. The specimens enhanced with CNT managed to record flexural strength percentage to be higher than the theoretically predicted value of 10%. The reinforcement of both CNT-A and CNT-B shows a positive trend with a higher flexural tensile strength.

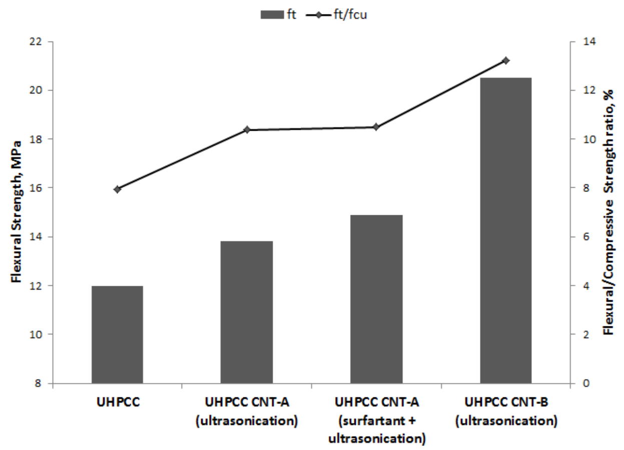


Figure 9 Flexural strength of UHPCC with different CNT variations

Figure 10 concludes the overall findings of UHPCC with CNT-A and UHPCC with CNT-B. The addition of CNT-A contributes adverse effect on the compressive strength due to improper dispersion, but contributed positively on the flexural strength due to the enhancement of nano-particle at nano-scale [19, 20]. CNT-B contributed on both compressive and flexural strength due to a much stable dispersion and better CNT characteristic. Under the mechanism of flexural bending, the CNT with nature formation diameter and length in the nano-range provide effective solution to enhance and increase the toughness of the matrix [20]. The properties of CNT is a major factor which can enhance the properties of the cementitious composite.

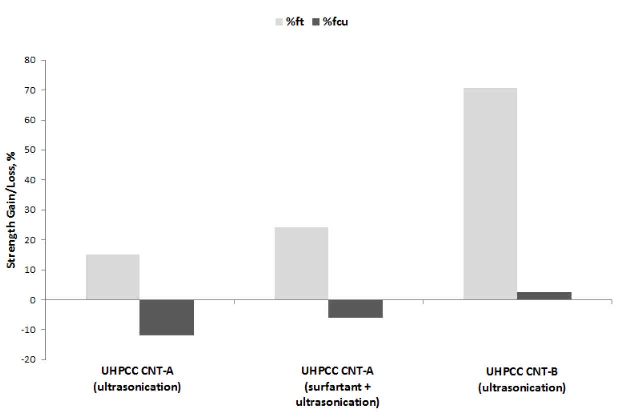


Figure 10 The effect of CNT-A and CNT-B on the strength characteristic of this study

4.0 CONCLUSIONS

This study proposed a simpler version of UHPCC mix design to incorporate CNT, with compressive strength higher than 150 MPa under normal curing conditions, and discussed the effect of CNT on the strength characteristics of UHPCC. The cement with higher C_3S and C_2S combination is favorable to produce the UHPCC. A good and stable dispersion of CNT is the key to optimize the positive characteristic of nano-particles.

The findings from this research also indicated that even though the use of CNT as nano-reinforcement, in some cases, resulted in some minor negative effect to the compressive strength (decrease in the compressive strength of up to 12%), the flexural strength was improved significantly (more than 60%) compared to the control UHPCC mix. The overall findings indicated that the presence of CNT strengthens the matrix and delays the propagation of cracks at nano-scale and further enhances the post-crack behavior of the composite.

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