

Research Article

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Effects of the combined usage of nanomaterials and steel fibres on the workability, compressive strength, and microstructure of ultra-high performance concrete<https://doi.org/10.1515/ntrev-2021-0029>

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Abstract: Using nanomaterials to enhance concrete performance is of particular interest to meet the safety and functionality requirements of engineering structures. However, there are few comprehensive comparisons of the effects of different nanomaterials on the properties of ultra-high performance concretes (UHPCs) with a compressive strength of more than 150 MPa. The aim of the present study was to assess the coupling effects of nanomaterials and steel fibres on the workability and compressive performance of UHPC. Three types of nanomaterials, nano-SiO₂ (NS), nano-calcium carbonate (NC), and carbon nanofibre (CNF), were each added into UHPC mixes by quantity substitution of the binder; two types of steel fibres were investigated; and two mixing methods were used for casting the UHPC. In addition, the effect of curing age (7 or 28 days) on the compressive performance of the mixtures was considered. Comprehensive studies were conducted on the effects of these test variables on the fluidity, compressive strength, failure mode, and microstructure. The results show that the combination of these nanomaterials and steel fibres can provide good synergetic effects on the compressive performance of UHPC and that the addition of CNF results in a greater enhancement than the addition of NS or NC. The addition of NS, not CNF or NC, has a considerable negative influence on the fluidity of the UHPC paste. It is suggested that reducing the agglomeration of the nano-

materials would further improve the performance of the resulting UHPC.

Keywords: ultra-high performance concrete, nanomaterials, steel fibres, mixing method, fluidity, compression

1 Introduction

With continued modernisation, the requirements for the safety and functionality of engineering structures are increasing rapidly [1]. To meet these requirements, the development of ultra-high performance concretes (UHPCs) has accelerated in the last two decades [2]. Commonly, UHPC is defined as a cementitious material that is reinforced by fibre and that has compressive and tensile strengths greater than 150 and 5 MPa, respectively [3]. Compared with normal-strength and high-strength concretes, UHPC has many advantages, including an ultra-high compressive strength and excellent durability [4]. Due to the superior mechanical properties of UHPC, the utilisation of UHPC in bridge engineering, has received increasing attention in recent years [5]. The advantages of using higher-strength concrete in structures include reducing member sizes and building dead loads, offering an attractive alternative to traditional concrete.

Although UHPC is less porous than normal-strength concrete, a relatively weak interfacial transition zone (ITZ) still exists [6]. The strength and ductility of fibre-reinforced concrete mainly depend on the properties of the micro- and nanoscale structures, especially at the fibre-matrix interface. Therefore, it is essential to engineer the microstructure of the ITZ to enhance fibre-matrix bonds in UHPC [7]. Currently, there are three main ways to improve the bond at the fibre-matrix interface as follows: (1) densification of the cementitious matrix using supplementary cementitious materials, nanoparticles, and high temperature curing [8]; (2) enhancement of mechanical anchorage through the use of deformed fibres [9]; and (3) improvement in fibre-matrix friction by surface treatment [10].

Nanomaterials as fine particles with a form between those of macrosubstances and clusters possess small-size

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effects, surface effects, graining effects, and macroscopic tunnelling effects [11]. How to introduce nanomaterials into concrete has become an issue constantly being explored by concrete material researchers in practice. In recent years, the development of nanotechnology has accelerated [12]. Due to the new uses of nanoparticles, there is an interest in the investigation of the effect of nanoparticles, especially in concrete and cement mortar [13]. Among these nanomaterials, nano-SiO₂ (NS) [14], nano-calcium carbonate (NC) [15], and carbon nanofibre (CNF) [16] have been considered the most effective additives to enhance the mechanical performance and durability of cement-based products [17]. Researchers have conducted many experiments to investigate the properties of UHPC with NS [18]. The results showed that NS promotes the hydration reaction due to its high surface activity and form more calcium–silicate–hydrate (C–S–H) gels [19]. It is well accepted that NS can act as a nano-filler, which develops the strength of the C–S–H gels and strengthens the ITZs between the paste and aggregates [20]. Additionally, NS undergoes a pozzolanic reaction in cementitious media and generates a micro-filling effect [21]. Thus, the compressive strengths of mortars with NS particles were higher than those of mortars containing silica fume at 7 or 28 days.

NC is a type of nanomaterial that prepares favourable sites for nucleation of hydration products and consequently develops hydration reactions [22]. In addition, NC behaves as nanofiller, thereby improving the strength of a cement-based matrix. Mendoza *et al.* [23] added NC into cement paste and observed a decreased flowability and shortened setting time of the resulting fresh cement paste. Some researchers also reported similar results [24]. They also found that the compressive strength of UHPC increased with the addition of NC at ages of 7 and 28 days.

CNF, a relatively expensive nanomaterial, has attracted the attention of civil engineers [25]. Some studies on the performance of concrete with CNF pointed out that the presence of homogeneously dispersed CNF increased the compressive strength and compensated for the autogenous shrinkage of concrete [26]. This phenomenon

could be attributed to the CNF filling the nanopores and bridging the nanocracks, therefore strengthening the ITZ and densifying the microstructure [27]. These findings indicate that the presence of CNF refines the microstructure of concrete [28].

It is noted that many reported studies have focused on the effects of nanomaterials on the performance of conventional concrete, but limited information is presented on the combined usage of nanomaterials and steel fibres in UHPC [29]. To effectively use nanomaterials in UHPC applications, it is essential to study its workability and mechanical properties. The objective of this work is to improve the mechanical performance of UHPC with the addition of nanomaterials and steel fibres. The coupling effects of nanomaterials and steel fibres are examined on the workability and compressive behaviour of UHPC. A series of cubic specimens were cast by considering different types of nanomaterials and steel fibres as well as different mixing methods. The fluidity, compressive strength, and failure mode of modified UHPC are analysed. A mechanistic study was conducted, using scanning electron microscopy (SEM), on the microstructure of UHPC with nanomaterials. The flowchart is shown in graphical abstract.

2 Materials

2.1 Cementitious materials

The cementitious materials (the binder) used in this study mainly consisted of ordinary Portland cement with a compressive strength grade of 52.5 MPa and silica fume, both in compliance with the Chinese standards. Quartz flour was also considered as the cementitious material in this study due to its activity. The quartz flour had particle sizes ranging from 10 to 45 µm. Table 1 presents the properties of the cement, silica fume, and quartz flour.

Table 1: Properties of the cement, silica fume, and quartz flour

Materials	Size (µm)	Density (g/cm ³)	Substance (%)						Loss on ignition (%)
			SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	SO ₃	MgO	
Cement	5.0–30.0	3.10	19.60	5.0	68.00	3.50	2.30	0.70	1.70
Silica fume	0.10–1.00	0.30	98.50	0.3	0.20	0.02	0.10	0.50	2.14
Quartz flour	10.0–45.0	2.63	99.66	—	0.01	—	—	0.01	0.09

Table 2: Properties of the nanomaterials

Materials	Appearance	Size (nm)	Length (μm)	Purity (%)	Specific surface area (m^2/g)
NS	White powder	20	—	>99.0	145–160
NC	White powder	10–100	—	>98.5	28
CNF	Black powder	50–200	1–15	>95.0	18

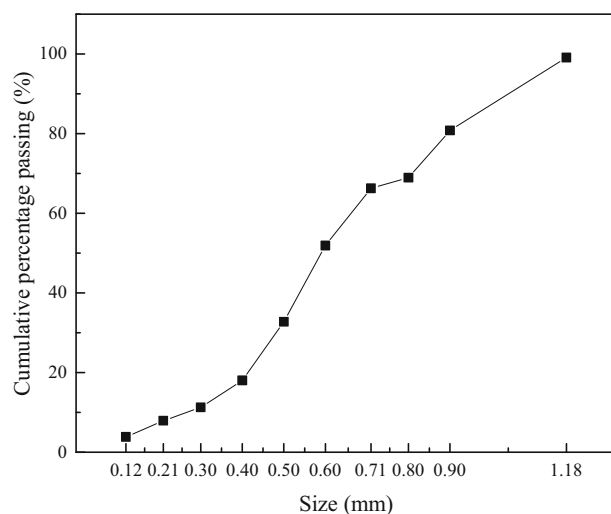
Table 3: Properties of the silica sand

Aggregate	SiO_2 content (%)	Whiteness (%)	Fineness modulus	Water content (%)	Lost in ignition (%)
Silica sand	97.96	90.30	0.93	0.20	0.12

Three types of nanomaterials (provided by XFNANO, China), NS, NC, and CNF, were prepared to partially replace the above binder. The properties of these nanomaterials are shown in Table 2.

2.2 Aggregates

The fine aggregate used in the UHPC mixtures in this study was silica sand with the properties given in Table 3. The silica sand was composed of crushed quartz particles of coarse (0.60–1.18 mm), medium (0.40–0.60 mm), and fine (0.12–0.40 mm) grades, in proportions of 48.7, 33.2, and 18.1%, respectively. The results of the sieve analysis of the silica sand are shown in Figure 1. No coarse aggregate was used in the UHPC mixtures. Figure 2 shows the particle size distribution of the particle materials used in the mixture.

**Figure 1:** Particle size distribution of the silica sand.

2.3 Steel fibres

Two types of copper-plated steel fibres, straight steel fibre (type I) and hooked-end steel fibre (type II), were used in this study, as shown in Figure 3. Both steel fibres were from the same manufacturer (SHRS, China) and were

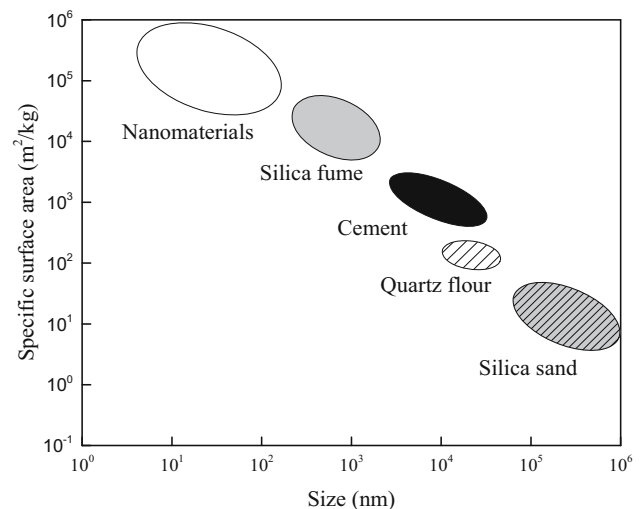
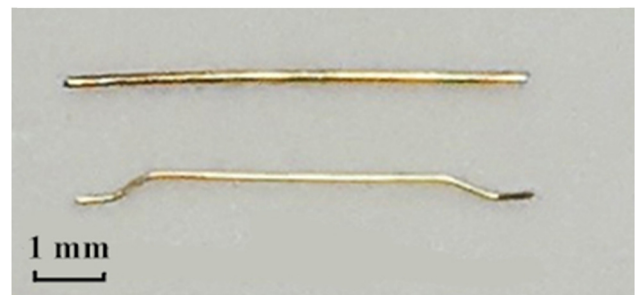
**Figure 2:** Distribution of material sizes.**Figure 3:** Steel fibres.

Table 4: Properties of the steel fibres

Fibre type	Tensile strength (MPa)	Density (g/cm ³)	Elastic modulus (GPa)	Fibre number (10 ⁴ /kg)
Straight fibre	2,000	7.85	210	30
Hooked-end fibre	2,000	7.85	210	27

13 mm in length and 0.2 mm in diameter. The detailed properties of the steel fibres are listed in Table 4.

2.4 Additives

A powder polycarboxylate-based superplasticizer with high performance was used to control the actual amount of water added to the mixture and also to improve the initially low workability. The properties of the superplasticizer are shown in Table 5. Prior to being put into the mixtures, the powder polycarboxylate superplasticizer was mixed with tap water for 3 min at a mass ratio of 1:3 to form a liquid solution.

3 Experimental programme

3.1 Mixture design

Nine groups of UHPC mixtures were prepared in this study, with a water-to-binder (w/b) ratio of 0.18, as detailed in Table 6. Regardless of the fibre type, steel fibres were added to the mixtures at 2.5% by volume for all groups. Following the suggestions on the optimum dosage in ref. [4], the nanomaterials NS and NC were used to replace 3% of the binder by mass, while CNF was used to replace only 0.15% of the binder by mass due to its expensive price. Two mixing methods, designated Method a and Method b, were compared in this study, which will be introduced in the next section. In addition, the effect of curing age (7 or 28 days) on the compressive performance of the mixtures was considered.

Table 5: Properties of the superplasticizer

Appearance	Water reducing (%)	Chloride content (%)	Water content (%)
Creamy-white powder	20	0.002	2.0

3.2 Specimen preparation

A total of 54 cubic specimens with a size length of 100 mm were cast from the nine groups (Table 6) of UHPC mixtures in plastic moulds. The six cubic specimens made from each group of UHPC were divided into two batches, which were tested after 7 and 28 days of curing.

All the mixtures were prepared using a 30 L horizontal mixer at room temperature (approximately about 25°C). Considering whether the nanomaterials were pretreated, two mixing methods were investigated in this study. Two different mixing methods are shown in Figure 4. In Method a, the nanomaterials were not pretreated and were directly added into the mixtures as powder. The mixing procedure of Method a is as follows: all the powders (cement, silica fume, quartz flour, or nanomaterials) and silica sand were first mixed under dry conditions for 5 min; the prepared superplasticizer solution was added to and mixed with the powders for 3 min, and then the remaining water was continuously introduced and mixed for 2 more minutes; and the steel fibres were then dispersedly added and the mixing was continued for 4 more minutes. In Method b, the nanomaterials were pretreated to form dispersions before being added to the UHPC mixtures. Following the pretreatment method of nanomaterials reported by Meng *et al.* [30], the nanomaterials were put in a polycarboxylate superplasticizer solution and then stirred with an electric drill mixer for 3 min at a high speed of 600 rad/min to form a mixture dispersion. The three dispersions with different nanomaterials are shown in Figure 5. The NS dispersion was a milky viscous colloid, while the CNF dispersion was a thick black liquid, and the viscosity of the former was lower than that of the latter. Note that the NC dispersion exhibited a low solubility in the polycarboxylate superplasticizer solution, and most of the NC floated on the surface of the solution.

Method b has a mixing procedure similar to Method a, except that in Method b, the nanomaterials as a dispersion with superplasticizer solution were added to the mixtures after the mixing of the powders (cement, silica fume, and quartz flour) and silica sand, while the nanomaterial powders were directly added into the mixtures in Method a.

Table 6: Mix proportions of UHPC (kg/m³)

Group	Cement	Silica fume	Quartz flour	Nanomaterials (type)	Coarse sand	Medium sand	Fine sand	Superplasticizer powder	Water	Steel fibre (type)	Mixing method
Ref-I	674.21	168.55	202.26	—	480.00	327.00	179.00	10.45	188.10	196.25 (I)	a
Ref-II	674.21	168.55	202.26	—	480.00	327.00	179.00	10.45	188.10	196.25 (II)	a
NS3-I-a	653.98	168.55	202.26	20.23 (NS)	480.00	327.00	179.00	10.45	188.10	196.25 (I)	a
NS3-I-b	653.98	168.55	202.26	20.23 (NS)	480.00	327.00	179.00	10.45	188.10	196.25 (I)	b
NS3-II-b	653.98	168.55	202.26	20.23 (NS)	480.00	327.00	179.00	10.45	188.10	196.25 (II)	b
NC3-I-a	653.98	168.55	202.26	20.23 (NC)	480.00	327.00	179.00	10.45	188.10	196.25 (I)	a
NC3-I-b	653.98	168.55	202.26	20.23 (NC)	480.00	327.00	179.00	10.45	188.10	196.25 (I)	b
NC3-II-b	653.98	168.55	202.26	20.23 (NC)	480.00	327.00	179.00	10.45	188.10	196.25 (II)	b
CNF0.15-II-b	653.20	168.55	202.26	1.01 (CNF)	480.00	327.00	179.00	10.45	188.10	196.25 (II)	b

Notes: I and II denote straight and hooked-end steel fibres, respectively. Ref denotes the control mixture, which did not incorporate nanomaterials. NS3, NC3, and CNF0.15 denote the nanomaterials mass substitution ratios of 3, 3, and 0.15%, respectively. a and b denote mixing method a and b, respectively.

After pouring the fresh concrete into the moulds, the moulds were vibrated for 1 min on a vibration table to remove any air bubbles trapped inside. The wet specimens were sealed in the moulds with plastic film and stored in the laboratory at room temperature for the first day. They were then demoulded and cured at 25°C and $98 \pm 2\%$ RH until the test age (7 or 28 days).

3.3 Tests and instrumentation

In this study, the fluidity of fresh UHPC mixtures was measured with a jump table according to the Chinese standard GB/T 2419-2005 [31]. The procedures of this method were as follows: first, a mini-lump cone was filled with UHPC paste on an automatic jolting table; second, the cone was lifted vertically to allow the paste to flow evenly on the table for 25 times; finally, two diameters perpendicular to each other were determined and the mean value was reported.

The cubic specimens were tested under axial compression loading at room temperature (approximately 25°C) according to the Chinese standard GB/T 50081-2019 [32]. The compression testing was conducted by the Italian MATEST C088-01 material testing machine with a capacity of 4,000 kN. The axial load, controlled by the displacement, was applied at a speed of 0.2 mm/min. The load and displacement data were collected with a data acquisition system during the compression tests.

Field emission SEM was conducted on a Hitachi SU8220 to observe the microstructure with a working distance of 4 mm and voltage from 0.5 to 30 kV. The UHPC samples were extracted from the inside cracked surface of the specimens and had a size of less than 1 cm³. These samples were stored in sealed plastic bags before SEM observation. In addition, a gold sputter coating was applied to make the samples electronically conductive, which enabled the microstructures and microscale damage to be observed with SEM.

4 Results and discussion

4.1 Fluidity

It is well accepted that the incorporation of steel fibre could reduce the fluidity of the UHPC and increase the air content in the fresh state and increase the porosity in

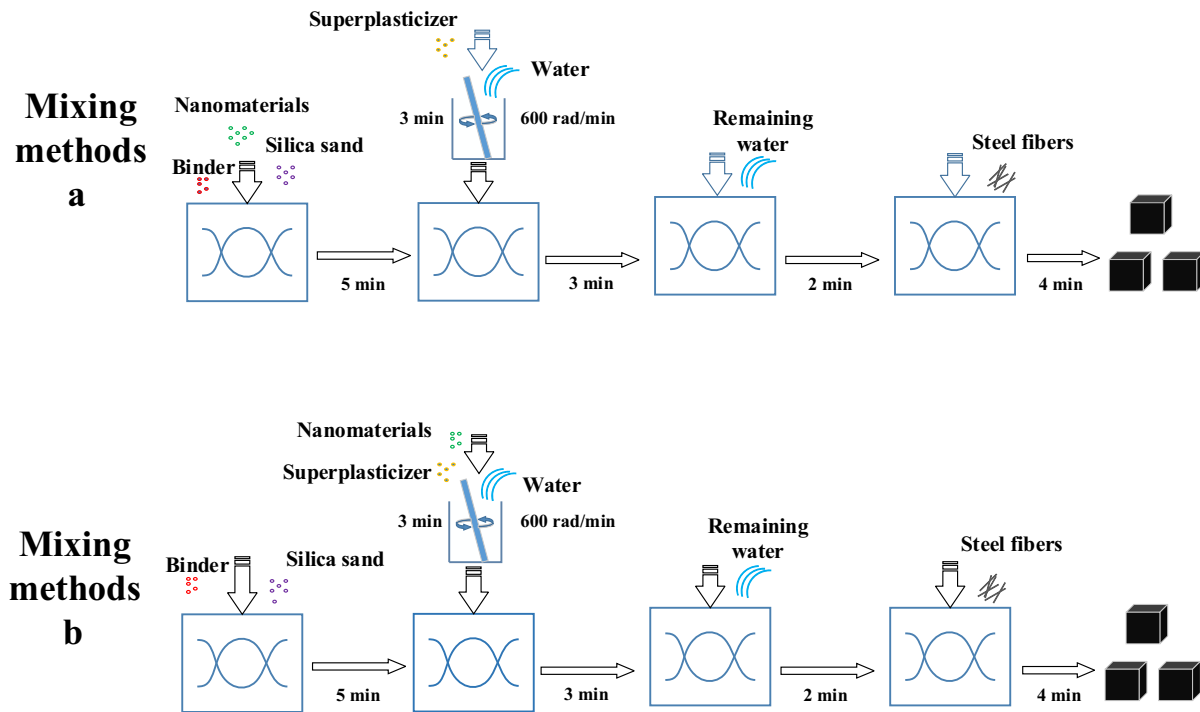


Figure 4: Mixing methods of UHPC.

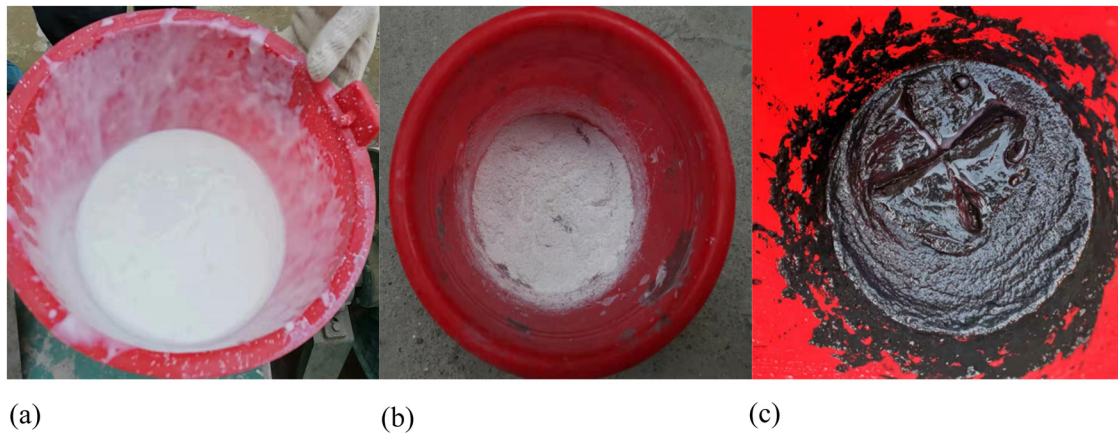


Figure 5: Nanomaterial dispersion. (a) NS dispersion, (b) NC dispersion, and (c) CNF dispersion.

the hardened state [33]. As reported by Chang and Zheng [34], the fluidity of UHPC paste has an approximately linear relationship with the steel fibre volume fraction. This could be attributed to the skeleton effect of the fibres blocking the other particles during the flow [35]. Figure 6 shows the influence of the steel fibre type on the fluidity of UHPC paste. Hooked-end steel fibres exhibit a more detrimental effect on the fluidity of UHPC paste than the straight steel fibres do. The reason for this is that the curved hooked-end of the steel fibre (type II) forms a groove with a straight section (Figure 3), which constrains the flow of the fresh mixture in the groove to a certain

extent, as illustrated in Figure 7. The hooked ends could increase the friction between the fibres and aggregates and thus increase the matrix coherence, consequently reducing flowability. In addition, a change in fibre shape leads to a strengthening effect among fibres, which makes fibres prone to cluster [36]. Figure 6 also demonstrates that the fluidity of the UHPC paste was reduced by less than 10% by replacing the straight steel fibre with hooked-end steel fibre. This finding indicates that the effect of the steel fibre type on the workability of this UHPC paste is slight. It is noted that although the directions of steel fibres have strong influence on the fluidity of UHPC, as

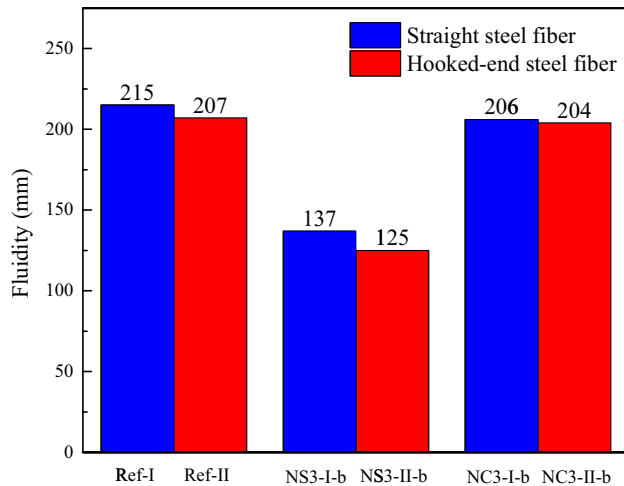


Figure 6: Effect of steel fibre type on UHPC paste fluidity.

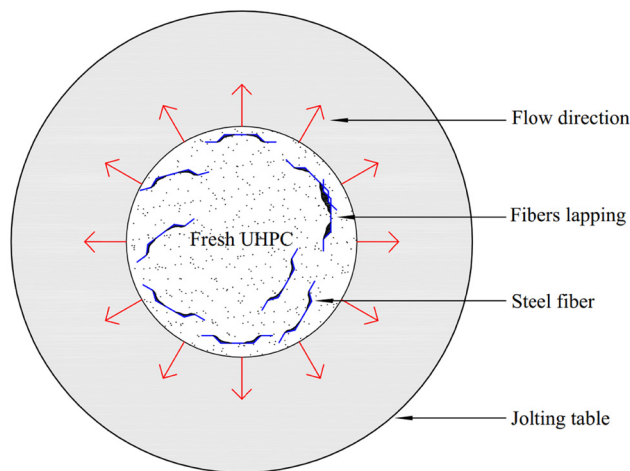


Figure 7: Flow diagram of fresh UHPC with steel fibres on a jolting table.

well as its mechanical properties, it is difficult to control the fibres' direction by mixing. Commonly, the distribution of the steel fibres is considered to be uniform. Thus, the direction effect of the steel fibres is not discussed in this study.

Figure 8 shows the effects of nanoparticles on the fluidity of fresh UHPC with straight steel fibres. The fluidity of the fresh UHPC with NS, NC, and CNF decreased by 28, 2.8, and 4.6%, respectively. There are two reasons for this change in fluidity. First, nanoparticles fill in the voids of the mixture and replace some of the filling water, resulting in an increase in the free water in the mixture, which is beneficial for the fluidity, as reported by Kong *et al.* [37]. Second, the nanomaterials have a larger specific surface area and a higher surface energy than the cement; consequently, more water will be adsorbed on the surfaces

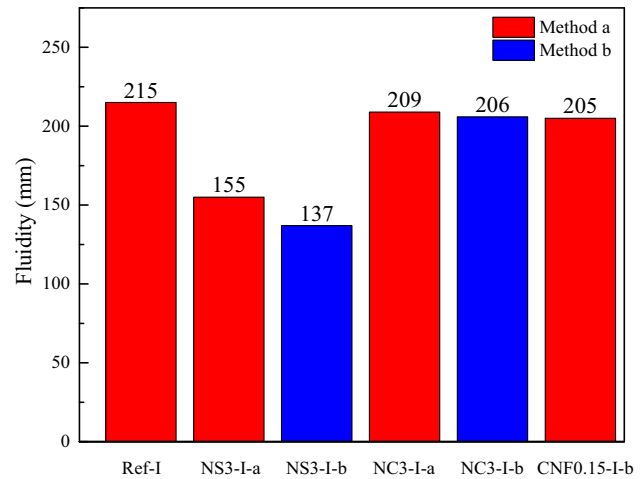


Figure 8: Effects of nanomaterials and mixing methods on UHPC paste fluidity.

of the nanomaterial particles, which significantly reduces the free water among the particles in the mixture. As shown in Figure 8, the second reason plays a greater role in the decrease in fluidity. It is worth noting that the fluidity of UHPC doped with NS was much lower than that of the other groups. This is because the specific surface area of NS is much larger than that of NC and CNF, as shown in Table 2. This agrees well with the findings of Li *et al.* [38].

Figure 8 also demonstrates the effect of the mixing method on the fluidity of UHPC paste. Compared with those made by Method a, the UHPC paste made by Method b exhibited a lower fluidity. As shown in Figure 8, when the mixing method changed from Method a to Method b, that is, the nanomaterials were dispersed in polycarboxylate superplasticizer solution by Method b, the fluidity of the UHPC paste made with NS and NC decreased by 10 and 1%, respectively. This result could be attributed to the fact that compared with those in Method a, the nanomaterials in Method b more easily contacted free water in the polycarboxylate superplasticizer solution, and more water was adsorbed on the surface of the nanomaterial particles, resulting in a further decrease in the fluidity. Korpa *et al.* [39] reported similar experimental results.

4.2 Compressive strength

4.2.1 Effect of nanomaterials

Figure 9 shows the influence of adding nanomaterials on the compressive strength of UHPC. The 7 days compressive strength of UHPC incorporated with NS (Method a),

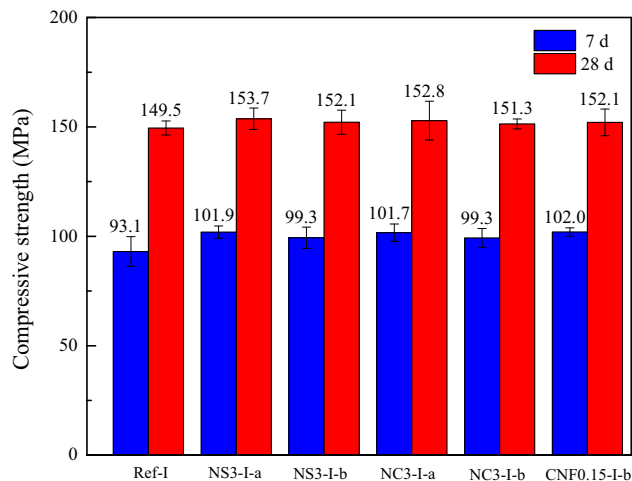


Figure 9: Effects of nanomaterials and mixing methods on the compressive strength of UHPC.

NC (Method a), and CNF increased by 9.5, 9.2, and 9.6%, respectively. There are two possible reasons for this improvement in strength due to the addition of nanomaterials. First, the small-size effect of nanomaterials can increase the bulk density of powder materials and make the inner structure denser [40]. The other reason is that the surface effect of the nanomaterials can rapidly increase the surface atomic number and surface energy of the particles, and this high surface energy could make them highly active and easy to combine with other atoms to obtain stability [22]. Due to their interactions with unsaturated electron clouds near unsaturated bonds, nanomaterials can combine with the main hydration product of Portland cement, such as calcium silicate hydrate (C–S–H) [41,42], to form a space network structure and then optimize the internal structure of the UHPC with nanomaterials, consequently improving the mechanical properties of the UHPC. In addition, NS has pozzolanic activity and can react with calcium hydroxide to produce additional C–S–H, which is beneficial for enhancing the strength and density of hardened cement-based pastes. Regarding the role of adding CNF, Figure 9 shows that the 7-day compressive strength of the UHPC with CNF was higher than that of the UHPC with NS or NC, although the CNF content was only 0.15%. This improvement could be attributed to the coupling action of the filling and bridging effects of the CNF [43,44].

4.2.2 Effect of curing age

Compared with the 7 days compressive strength, the 28 days compressive strength exhibited a smaller improvement

with the addition of nanomaterials. As shown in Figure 9, the addition of 3% NS and NC improved the 28 days compressive strength of UHPC by 2.8 and 2.2%, respectively. This result could be attributed to the fact that relatively few hydration products formed in the early stage of curing; thus, the nanomaterials can be used to fill the internal pores of concrete and even contact the C–S–H structure to produce a denser network structure. However, in the later stage of curing, the hydration process generally finished, and the flocculation effect of the nanomaterials was more dominant than the filling or pozzolanic effects. Moreover, nanomaterials may absorb a large amount of water to form agglomeration phenomena and cover the surface of cement particles to hinder hydration. This is the reason why the improvement in the 28 days compressive strength is insignificant. Yu *et al.* [45] reported similar experimental results and pointed out that the agglomeration of NS is detrimental to the later strength of UHPC. To improve the performance of UHPC with NS, Kong *et al.* [46] added a small amount of a naphthalene-based superplasticizer into the mixture, but the agglomeration of NS particles could not be modified well.

4.2.3 Effect of mixing method

Figure 9 also presents the influence of the mixing method on the compressive strength of the UHPC with nanomaterials. A comparison of the strength results of the UHPC made by Method a with those made by Method b indicates that these two methods could result in similar compressive strengths for the UHPC with NS or NC, and the former is a more effective alternative to the latter in terms of the mechanical properties. That is, using Method b to disperse the nanomaterials in polycarboxylate superplasticizer solution may weaken the strength enhancement of UHPC with the addition of nanomaterials. This phenomenon arises mainly because it is difficult to effectively disperse the nanomaterials in the polycarboxylate superplasticizer solution with this method; in contrast, it may cause the agglomeration of nanomaterials, resulting in a reduction in strength. These findings indicate that an effective method for preventing the agglomeration of nanomaterials in the mixture is critical to improve the positive effect of nanomaterials on the performance of UHPC.

4.2.4 Effect of steel fibre type

The influence of steel fibre type on the compressive strength of the resulting UHPC is presented in Figure 10.

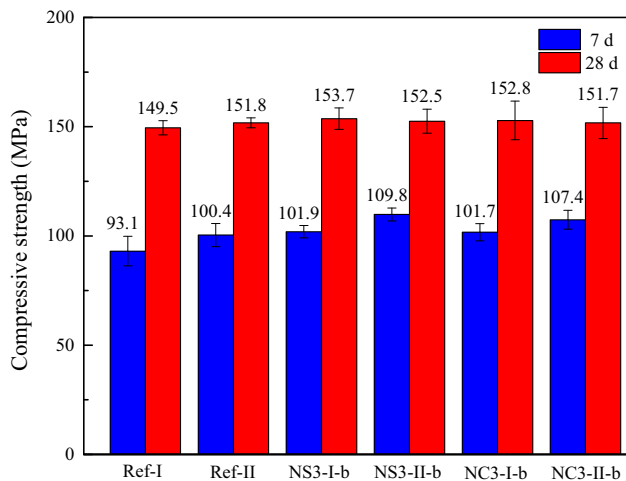


Figure 10: Effect of steel fibre type on the resulting UHPC compressive strength.

Compared with those with straight steel fibres, the 7 days compressive strength of the Ref group, NS group, and NC group with hooked-end steel fibres increased by 8.5, 9.9, and 6.4%, respectively, while the 28 days compressive strength was not affected significantly, as presented in Figure 10. These observations could be explained as follows. When the early hydration reaction of concrete is not

sufficient, many internal defects remain in the concrete. At this stage, hooked-end steel fibres can bridge the internal structure of concrete more effectively than straight steel fibres can, which inhibits the development of internal cracks. However, with the improvement in the hydration degree and the strengthening of the internal structure, the effect of the fibre end shape on the concrete compressive behaviour decreases.

4.3 Failure mode

The failure modes of the UHPC specimens during axial compression testing are presented in Figure 11. During loading, the failure processes of all the specimens were similar. Figure 11 also shows that there were no obvious changes in the failure mode of the UHPC specimens, regardless of the differences in the steel fibres, nanomaterials, and mixing processes used. In the process of failure, cracks first appeared in the surface layer of the middle part of the UHPC cube; then, the cracks developed from the middle to both ends, and the surface concrete bulged. Finally, the vertical main crack propagated through the specimen along the edge. After the cracking ended,

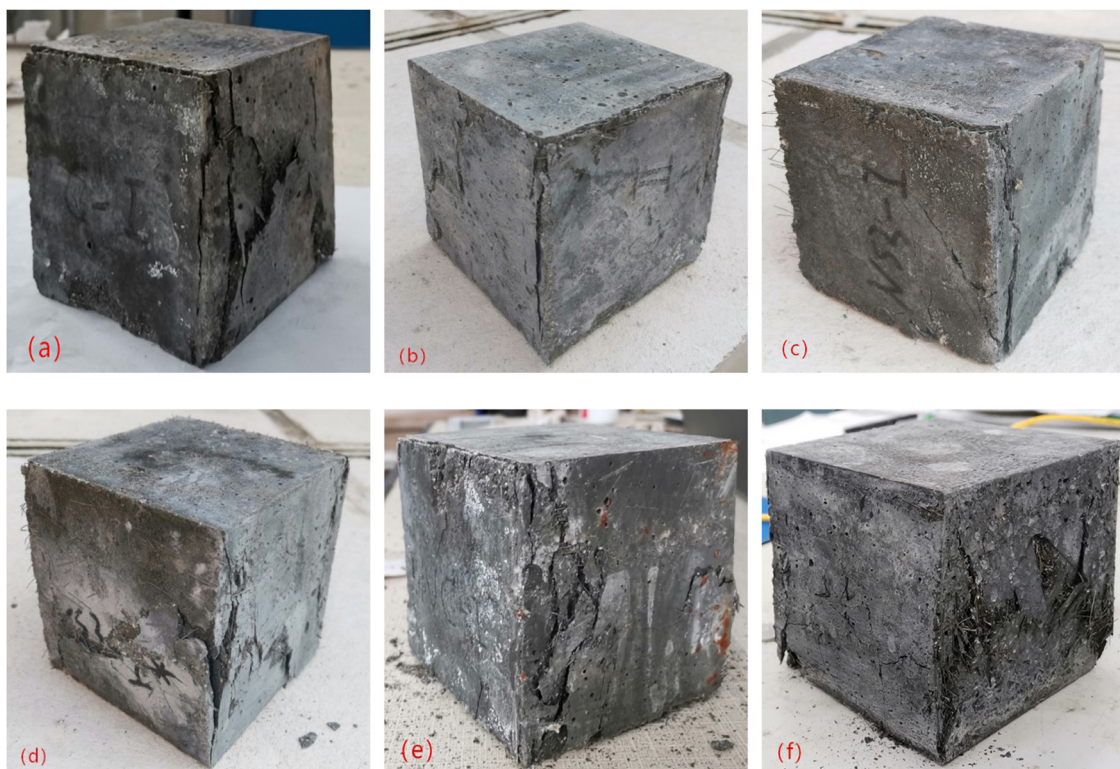


Figure 11: Failure mode of UHPC specimens: (a) Ref-I, (b) Ref-II, (c) NS3-I-a, (d) NS3-I-b, (e) NC3-I-b, and (f) CNF0.15-I-b.

there was a continuous but quiet cracking sound, and small debris fell from the surface of the specimen. Compared with the rapid brittle failure following cracking of the high-strength concrete without steel fibre, as reported in earlier literature [47], the UHPC tested in this study exhibited a better ductility, indicating the significance of the steel fibre in the UHPC. This finding also verifies that steel fibres can effectively reduce the stress concentration at the crack tips, dissipate the failure energy within the concrete, and increase the ductility of the concrete.

4.4 Microstructure

Figure 12 presents the microstructure of UHPC without nanomaterials after 28 days of curing based on SEM experiments. It can be seen that C–S–H gel was the main hydration product to enhance the strength and density of the UHPC; however, because of the low w/b ratio of the slurry, only a small amount of ettringite formed because ettringite requires a considerable amount of crystal water to form during the hydration process. Figure 12 also shows that the structure of the UHPC was dense, which contributed to the large defects being filled by microsilica powder and hydration products. The microcracks in the UHPC mainly initiated at the ITZ of the C–S–H and aggregate. Notably, the C–S–H was relatively intact, but

there were still some defects and some micropores less than $1\mu\text{m}$ in diameter, which had a negative effect on the strength of the UHPC, as shown in Figure 12.

When NS was added to the UHPC, the calcium/silica ratio and water/silica ratio in the mixture changed, and the C–S–H gel appeared to be a network structure while the edge part was fibrous, as shown in Figure 13. Thus, the hydration products of the cement paste with NS formed a network skeleton structure, as reported by Chang and Fang [48]. Actually, the high specific surface energy of NS can not only react with $\text{Ca}(\text{OH})_2$ to form secondary hydrates, which can induce the formation of new C–S–H, but also make C–S–H grow in a needle-like columnar shape and thus reduce the pore space in the cement paste. In addition, the filling effect of NS could increase the density of the slurry and improve the mechanical properties of the cured UHPC.

The microstructure of typical specimens with NC is illustrated in Figure 14. A comparison of Figure 12 with Figure 14 shows that the addition of NC could make the structure of UHPC denser, suggesting that NC can promote the hydration level of cement and accelerate the hydration process. This result is in accordance with previous analogous investigations [24]. This could be attributed to the fact that the addition of NC particles can adsorb Ca^{2+} released during C_3S hydration and change the enrichment and orientation of $\text{Ca}(\text{OH})_2$ in the interface, consequently increasing the content of C–S–H in

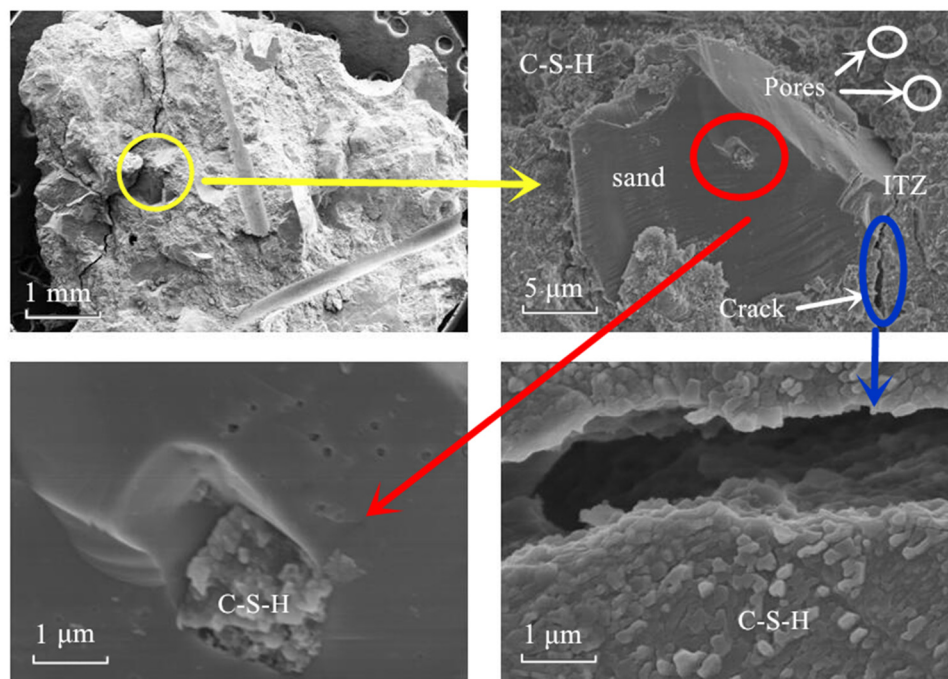


Figure 12: Microstructure of the UHPC without nanomaterials at 28 days.

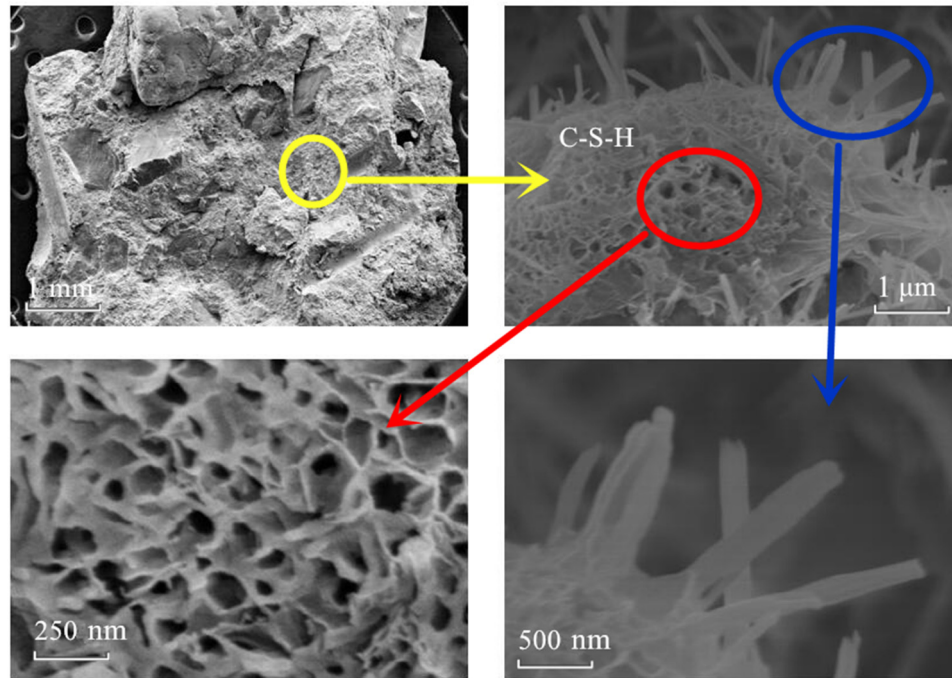


Figure 13: Microstructure of the UHPC with NS at 28 days.

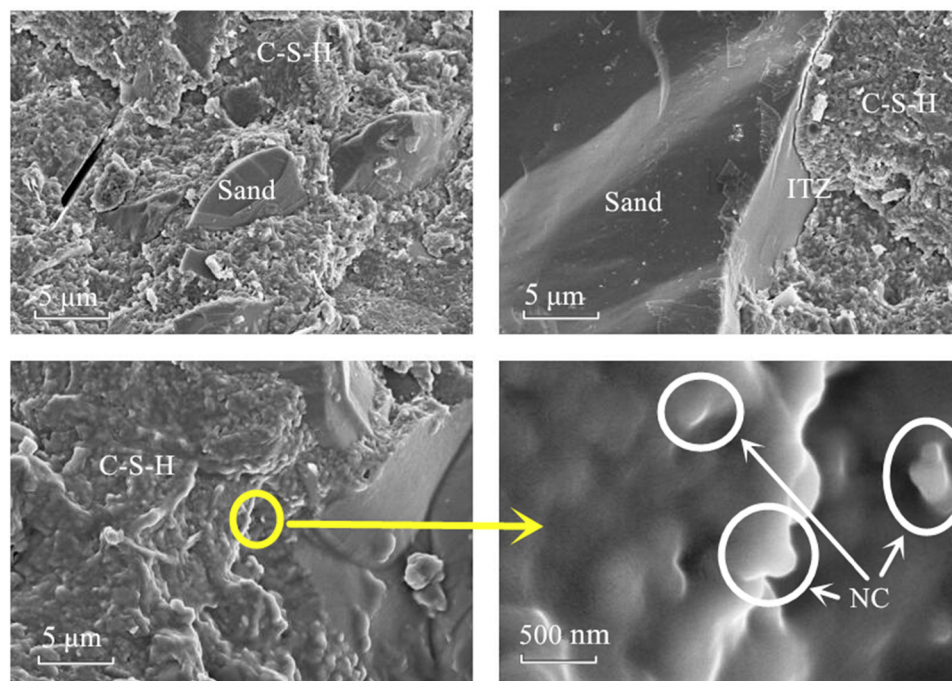


Figure 14: Microstructure of the UHPC with NC at 28 days.

the paste. However, there was some NC on the surface of the paste, as shown in Figure 14, indicating the agglomeration effect of the nanomaterial.

Figure 15 shows the microstructure of the UHPC with CNF. An SEM image at the interface between the CNFs and the surrounding cement matrix is shown in Figure 15.

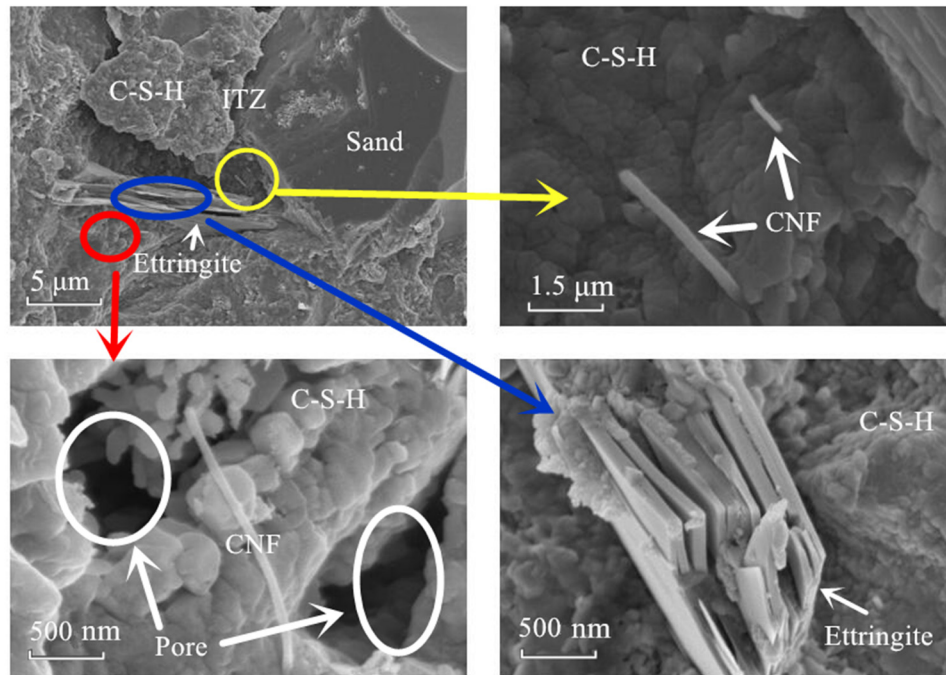


Figure 15: Microstructure of the UHPC with CNF at 28 days.

Most of the CNF was completely embedded in the C–S–H. CNFs not only penetrated the hydration products to fill the fine pores of the C–S–H structure but also connected the cement paste and the ITZ. Therefore, CNF can play a coupling role of bridging and filling, thus inhibiting the expansion of microcracks between the C–S–H and ITZ. These results also indicate the enhancement of the compressive strength of the resulting UHPC, as discussed in Section 4.2.1.

5 Conclusion

An experimental study was conducted to investigate the workability and compressive behaviour of UHPC with nanomaterials. The effects of nanomaterial type, steel fibre type, and mixing method on the fluidity, compressive strength, failure mode, and microstructure of UHPC were examined. The following conclusions can be made:

- (1) The combination of nanomaterials and steel fibres can provide good synergetic effects on the mechanical performance of UHPC, i.e. the nanomaterials and steel fibres are mainly responsible for matrix reinforcement and anti-cracking, respectively.
- (2) The addition of NC or CNF has a slight influence on the fluidity of the UHPC paste, while adding NS into UHPC can cause a great reduction in the mixture

fluidity. For example, a 3% NS replacement of the binder by mass reduced the fluidity of the UHPC by 28%. This finding could be attributed to the fact that the specific surface area of NS is much larger than that of NC and CNF.

- (3) The mixing method has an impact on the fluidity of the UHPC paste to a certain extent. Compared with the method of directly adding nanomaterial powder into the mixtures (Method a), the method of adding nanomaterials into the mixtures as a dispersion with a superplasticizer solution (Method b) could improve the fluidity of UHPC by 1–8% according to the nanomaterial type.
- (4) Compared with straight steel fibres, hooked-end steel fibres can increase the early compressive strength of the resulting UHPC by 6–10% but decrease the fluidity of the UHPC paste with different nanomaterials by 1–8%.
- (5) Due to the coupling action of the filling and bridging effects, CNF can provide more improvement than NS and NC, while how to balance the high cost of CNF in the concrete design is the key problem that engineers need to consider.
- (6) Compared with NS, NC can provide a similar improvement in the compressive strength of UHPC with steel fibre. Similar to the fluidity of UHPC paste, the compressive strength of cured UHPC is not greatly affected by the tested mixing method – Method a or Method b.

It is suggested that an effective method to prevent the agglomeration of nanomaterials in the mixture is critical to improve the positive effect of nanomaterials on the fluidity and mechanical properties of UHPC.

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