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# Multiple effects of nano-$SiO_2$ and hybrid fibers on properties of high toughness fiber reinforced cementitious composites with high-volume fly ash

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ABSTRACT

This article explores multiple effects of nano-$SiO_2$ and hybrid fibers on the flowability, microstructure and flexural properties of high toughness fiber reinforced cementitious composites. Only a little negative influences of nano-$SiO_2$ and hybrid fibers on the flowability are observed. SEM and MIP analysis reveal that nano-$SiO_2$ results in much smaller pore size in the composites. However, the porosity increases gradually with nano-$SiO_2$ addition. Three-point bending test results show that nano-$SiO_2$ increases the flexural strength of the composites with nearly equivalent deformability, but higher strength of the matrix leads to wider cracks. Due to larger volume fraction and higher modulus, hybrid fibers effectively mitigate this adverse influence on crack width and further enhance the flexural strength. The composites reinforced with 1.4% steel fiber and 2.5% polyvinyl alcohol (PVA) fiber exhibit the best flexural properties in the test. Finally, a simplified model is proposed to illustrate the reinforced mechanism of steel-PVA fibers.



## 1. Introduction

On account of highly brittle property in conventional cement based materials, high toughness fiber reinforced cementitious composites have widely attracted research interests in recent years. Based on micromechanical principles, Li, Wu and Leung [1–3] firstly designed this kind of material and named it engineered cementitious composites (ECC). During the last thirty years, the material has been widely investigated in Europe, South Africa, Japan and China, which was termed strain-hardening cement-based composites (SHCC) [4], ultra high performance fiber reinforced cementitious composites (UHPFRCC) [5–7] and ultra high toughness cementitious composites (UHTCC) [8], respectively. The composites exhibit remarkable pseudo-strain-hardening and multiple-cracking behaviors [9–11]. The ultimate tensile strain can exceed 3% and the corresponding crack width can be controlled smaller than 0.1 mm [12]. Recently high-volume fly ash, the industrial by-product in fuel power plant, has been selected to replace part of cement in UHTCC [13–15]. It can benefit the environment by allaying pollution and modify the interface between fiber and matrix, so the tensile ductility and crack width of UHTCC are effectively improved [16]. Generally the ratio between fly ash and cement in concrete is about 0.1–0.2, but the volume fraction of fly ash in this composites is 1.0–1.5 times of cement. Because of large volume fraction and low activity, fly ash seriously reduces the hydration rate. The loose microstructure leads to the decrease of chlorion penetration resistance and early strength [17,18]. However, in order to increase the structure life and reduce the construction period, many important constructions, such as high-rise building, bridge and nuclear plant, require materials to perform excellent durability and high early strength. Hence, it is necessary to compensate the effects of high-volume fly ash on hydration and further improve the properties of UHTCC by other ways.

The focus of this problem is to deal with the low activity of high-volume fly ash. Zhu et al. successfully improved the strength of UHTCC by replacing part of fly ash with slag due to its higher activity [19]. Actually, it is also beneficial to accelerate the pozzolanic reaction of fly ash by using nanoparticles. Nowadays, several researchers [20–22] added nano-$SiO_2$ (0.5–4% by weight) into cementitious composites and found that the mechanical properties and microstructures were both dramatically improved. Nano-$SiO_2$

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can accelerate the pozzolanic reaction especially at early ages and react with $Ca(OH)_2$ to generate large quantities of hydrated calcium silicate (C-S-H) gels [23–25]. The generated C-S-H gels gradually fill the detrimental pores in the matrix, so the microstructure can be modified. Moreover, nanoparticles effectively improve the interface transition zone and provide stronger bond between the matrix and fibers, resulting to better mechanical properties of materials [20,26–28]. However, higher matrix strength may make its initial cracking stress exceed the maximum fiber bridging stress, so crack width will become larger. To compensate this influence, physical property and volume fraction of fibers should be carefully considered when designing the composites.

Different fibers in lengths and modulus have been applied in the cementitious composites. It is concluded that UHTCC with low modulus fibers generally exhibits low strength, high deformability and large crack width, while high modulus fibers are expert in high strength, low ductility and fine cracks [29–31]. In hybrid fibers reinforced composites, the mechanical properties are further improved [32–34]. Ahmed et al. demonstrated that Polyethylene (PE) fiber could increase the tensile strain and steel fiber was beneficial to improve the ultimate tensile strength [35], whereas steel–PE hybrid composites exhibited lower flexural strength than steel–PVA hybrid composites [36]. Furthermore, the effect of different volume fractions on the mechanical properties under the same steel-PVA fiber proportion was also explored by Soe et al. [37]. It can be noticed that high and low modulus fibers are suitably combined to give play to their respective advantages in cementitious composites [38,39].

In this study, the matrix and fibers were adjusted to reduce the negative effects of fly ash and improve the properties of UHTCC. The main object is to produce one kind of high strength and excellent ductility composites which is different from conventional UHTCC. Hence, nano-$SiO_2$, PVA fiber with low modulus and steel fiber with high modulus were all applied in the study. The flowability of UHTCC was investigated firstly. Then the influences of nano-$SiO_2$ on the microstructure and pore size distribution were analyzed by SEM and MIP. Flexural properties of the composites with nano-$SiO_2$ and hybrid fibers were tested in the three-point bending experiment. In order to illustrate the roles and pull-out mechanism of hybrid fibers in the composites, a simplified model for steel-PVA fiber was proposed finally.

## 2. Materials and experimental methods

### 2.1. Materials

UHTCC consisted of cementitious binders, ultra-fine sand, nano-$SiO_2$, PVA fiber and steel fiber. Cementitious binders mainly contained cement and high-volume fly ash. The cement utilized was P·O 52.5, corresponding to the Chinese standard GB175-2007. The chemical and physical properties of the cement and fly ash are provided in Table 1. Fig. 1 is the particle size distribution of fly ash. It can be found that the size range of the most particles was between 2 and 100 μm, and the average diameter was only 20.16 μm. The diameter and density of ultra-fine sand prepared for the mixture were around 0.1 mm and 2.62 g/cm$^3$ respectively. The used type of nano-$SiO_2$ had extremely high specific surface area and several hydroxyl groups on the surface. Hydroxyl groups could enhance the hydrophilicity of nano-$SiO_2$ and beneficial to the homogeneous dispersion of nano-$SiO_2$. Fig. 2 is the scanning electron micrographs (SEM) diagram of nano-$SiO_2$. The specific properties of nano-$SiO_2$ and fibers are summarized in Table 2 and Table 3. The content of nano-$SiO_2$ addition was 0, 1%, 3% and 5% by weight of cementitious binders. The volume fractions of PVA and steel fiber were 2.0%, 2.5% and 1.0%, 1.2%, 1.4%, respectively. Mix proportions of the composites are listed in Table 4.

**Table 1**
Chemical properties of the cement and fly ash.

| Compositions | Cement (wt%) | Fly ash (wt%) |
|---|---|---|
| CaO | 59.85 | 5.98 |
| $SiO_2$ | 21.90 | 56.48 |
| $Al_2O_3$ | 6.78 | 28.79 |
| $Fe_2O_3$ | 3.79 | 3.11 |
| MgO | 3.68 | 2.03 |
| $SO_3$ | 2.12 | – |
| $K_2O$ | 1.08 | 1.47 |
| $Na_2O$ | 0.80 | 2.14 |
| Loss on ignition | 1.99 | 1.55 |

### 2.2. Mix procedure and specimen preparation

Cement, fly ash and ultra-fine sand were premixed in Hobart mixer without water firstly. To obtain the uniform dispersion of nano-$SiO_2$ particles, hot water at 60 centigrade was used to dissolve nanoparticles under stirring at high speed. Then dispersible emulsion powder, nearly 1% by weight of nano-$SiO_2$, was added and mixed for 1.5 min. Following this step, the nano-$SiO_2$ suspension was poured into the Hobart mixer with the rest of water, superplasticizer, PVA and steel fibers, stirring more than 10 min. In the end, it could be found that fresh UHTCC was seriously viscous like liquid plasticine and fibers were not balled in the matrix.

The fresh composites were cast into the three-point bending moulds used in the test, the dimension of which was 40 mm × 40 mm × 160 mm. In order to reduce the air bulbs in the matrix, all the specimens were cast in 2 layers. The specimen underwent the vibration for about 30 s after casting every layer. When the cast was completed, plastic sheets were applied to cover the specimens and prevent the evaporation of the moisture from the composites. After curing 24 h in the lab, the specimens were demolded and put into the standard curing room at 95% relative humidity and 20° centigrade.

### 2.3. Experimental methods

#### 2.3.1. Flowability of UHTCC

As UHTCC did not contain coarse aggregates, the workability of composites was tested according to the Chinese standard GB/T

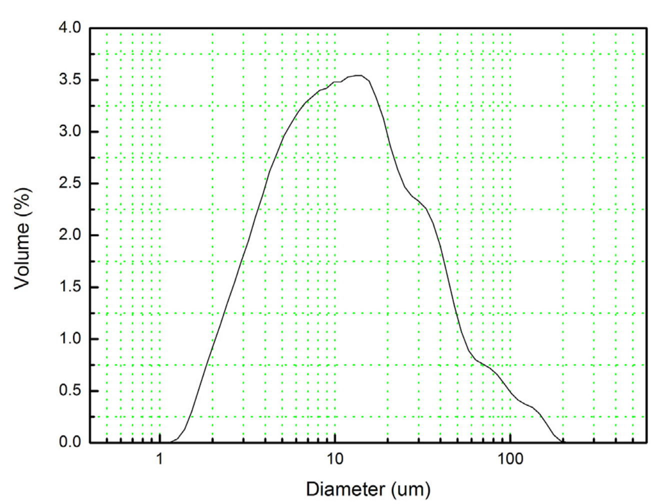


**Fig. 1.** Particle size distribution of fly ash.