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## Properties of low binder ultra-high performance cementitious composites: Comparison of nanosilica and microsilica



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#### HIGHLIGHTS

• Ultrahigh strength concrete with low powder was produced.

• Effects of nanosilica and microsilica were investigated.

• Effect of 1% of nanosilica equals to almost that of 10% microsilica.

• The highest strength properties were achieved at 2% nanosilica.

• Combined use of nanosilica and microsilica had better performance.

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#### 1. Introduction

#### ABSTRACT

This paper presents the effect of using binary and ternary blends of nanosilica (NS) and microsilica on the mechanical properties of low binder ultra-high performance cementitious composites (UHPCs). For this, two concrete groups were designed with and without silica fume by weight of cement with a constant water/binder ratio and total binder content. Commercially available NS was used in partial substitution of cement at 0%, 0.5%, 1%, 2% and 3% by weight. The results show that among different NS contents, UHPC containing 2% NS exhibited the best results of compressive strength, splitting tensile strength, modulus of elasticity, flexural strengths, load–displacement behavior and fracture energy at 90 days. The samples of UHPC containing binary cementitious materials (NS and SF) gave better results than concretes containing only NS. Additionally, the effect of 1% NS is almost equal to that 10% of SF.

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During the last 20 years, ultra-high performance concrete or cementitious composites (UHPCs) have become an introduction of the most favorable ingenious high technology types of concrete [1–3]. UHPC has been applied to many huge strategic and sensitive projects like, coupling beams in high-rise buildings, precast members, infrastructure rehabilitations, blast resistant structures, and special facilities like nuclear waste storage containers [4]. The main composition of UHPC involves a large content of cement and silica fume as binder, fine sand of 150–600  $\mu$ m sizes, and crushed quartz of about 10  $\mu$ m sizes. Very low water-to-binder ratio is also typically used in UHPC mixes resulting in reduced workability that may be managed by adding an effective superplasticizer (SP) [5,6]. In order to obtain the desired mechanical properties of UHPC, enhancing the stiffness and strength of the interfacial transition zone (ITZ) to a level comparable to that of bulk paste aggregate

\* Corresponding author. E-mail address: mgesoglu@gantep.edu.tr (M. Gesoglu). is vital. This might be achieved by using silica materials such as silica fume and (or) nanosilica, regardless of its forms that can be an amorphous state [7].

In cementitious systems, silica fume (SF) is the most commonly used amorphous silica which possesses an average particle size of about 10 times smaller than cement. It has been used in the ranges of 10–25% by weight of cement since the 1950s, thus its pozzolanic and filling effects on the concrete properties have been widely known [8]. Pozzolanic reaction of silica with calcium hydroxide forms more C–S–H gel at final stages (chemical effect) while filling the remaining voids in the fresh and partially hydrated cement paste (physical effect) increased the density of concrete [9]. Moreover, some researchers like Dunster [10] agreed that contribution of SF with concrete constituents would save the cement that accounts for sustainability of economic and environmental development.

Nano technology has attracted considerable interest due to the new potential uses of particles in nanometer scale associated with high specific surface area, high purities, and small primary particles [11]. Nano-scale SiO<sub>2</sub> seems to be the most popular nano-

particle in the researches because of its great benefits in the concrete. Nano-SiO<sub>2</sub> cannot only fill the voids between cement and silica fume particles; its high specific surface area to the volume ratio yields a high rate of pozzolanic reaction that leads to the potential for tremendous chemical activity. Recent studies have revealed that addition of nano-silica provided many significant improvement in mechanical [12], durability [13], physical [14] and micro structure of concretes [15].

Researchers have proven that the finer the silica particles the higher strength of UHPC. Nevertheless, there are divergent opinion and poor vision about the optimum percentage of the nano-sized particles when replaced with cement to produce concrete. In the case of conventional concretes, Sobolev et al. [16] reported that addition of 0.25% of SiO<sub>2</sub> nanoparticles increased the 28-day compressive and flexural strengths by as much as 10% and 25%, respectively. Zaki and Ragab [17] studied the effect of NS on the strength of self-compacting concretes with 0.35 and 0.39 water/ binder (w/b) ratios. They used NS at 0.5%, 0.7%, and 1% replacement levels by weight of cementitious materials. The measured compressive strengths at the ages of 7, 28, 90, and 365 days showed that NS used at 0.5% replacement level gave the highest results, irrespective of the testing ages. Safan et al. [18] utilized Cu-Zn nano-ferrite in producing Portland cement pastes and mortars at w/c ratios of 0.25 and 0.40, respectively. The optimum dose of nano materials was found to be 1% of cement by weight that enhanced the compressive strength of the cement paste and mortar by as high as 45%. In the study of Du and Pang [19], however, increase in the compressive strength of the mortar with 0.3 w/c ratio continued up to 1.5% of colloidal NS, thereafter the tendency seemed to be constant up to 2.0%. Nazari and Riahi [20] reported that 4% of nano-silica by weight of cement gave the best improvement in mechanical properties of self-compacting concretes at 0.4 w/b ratio.

In spite of the beneficial effects of nano-materials mentioned above, there are some researches in which the use nanomaterials was found to be insignificant on the mechanical properties of conventional concretes. According to Senff et al. [21], using nano-SiO<sub>2</sub> and nano-TiO<sub>2</sub> in making cement pastes and mortars did not lead to any significant enhancement on the compressive strength. Even in the study of Ltifi et al. [22], a lower compressive strength was monitored for the mortars with 3% nano-silica compared to the plain specimens. Furthermore, Hosseini et al. [23] and Abbas [24] observed the negative effects of high dosages of NS on workability which was attributed to dispersion problems and conglomeration of particles. Indeed, each kilogram of NS added required 0.4 kg of water to maintain the same workability.

Comparing to the other types of concrete, there is little studies on properties of ultra-high performance concrete (UHPC) containing nano materials in which the effect of such material is varying and contradictory. Rong et al. [25] stated that incorporating 3% of nano-SiO<sub>2</sub> led to the maximum compressive and flexural strengths by as high as 100% compared to the reference concretes. According to Yu et al. [26], however, the effect of nano-silica was rather little such that the mixes with 4% of nanosilica by weight of 875 kg of total binder had only 3.6 MPa higher compressive and 2.7 MPa higher flexural strengths than those of reference UHPCs. Compressive strength of UHPCs decreased from 200 to 150 MPa when Wille and Naaman [27] only substituted the Portland cement by 1% of NS in the mixtures.

#### 2. Experimental study

#### 2.1. Materials and mixture proportioning

The cementitious materials used in concrete production were ordinary Portland cement (CEM I 42.5 R) conforming to the TS EN 197 [28] (mainly based on the European EN 197-1), Silica fume (SF), and nanosilica (NS). Chemical composition, physical and mechanical properties of them are given in Table 1. Quartz aggregate with a specific gravity of 2.65 was utilized in three fractions, namely 0–0.4, 0.6–1.2, and 1.2–2.5 mm. A new-generation super-plasticizer (SP) of polycarboxilate type was used to fulfill the workability specifications in ASTM C 494 [29].

The mixture proportioning studied in the experimental program is shown in Table 2. Group 1 and 2 in the mix design codes show 0% and 10% SF respectively with a mutual NS content of 0%, 0.5%, 1%, 2% and 3%. Superplasticizer was used in varying amounts to adjust the workability enough for the mixtures. The mixtures in Table 2 were designated according to NS and SF replacement level. For example, SF0NS1 indicates the mixture containing 0% of silica fume and 1% of nanosilica.

#### 2.2. Concrete mixture proportioning, casting, and sample preparation

The mixtures were prepared by means of a special designed, vertical axis, high speed mixer which has mixing speed of as high as 470 rpm. Dry powders and aggregates were mixed with the speed of 100 rpm for about 3 min. After a half of water addition, mixture was remixed for about 5 min with the speed of 100 rpm. Finally, SP and remaining water were added to premixed material and mixing was resumed at 470 rpm for about 5 min. Fresh concretes were then poured into the molds and compacted by using a vibrating table. The specimens were then covered with polyethylene sheets and kept in the molds for 16 h at room temperature of 22 ± 2 °C. Thereafter, they were cured in standard conditions of water curing until the testing age. A typical mixture consists of three 50-mm cubes, three 100-mm cubes, and three 150-mm cubes to determine compressive strength, splitting tensile strength, and modulus of elasticity, respectively. Moreover, flexural strength and fracture energy were measured on three prisms of  $70 \times 70 \times 280$  mm dimensions.

#### 2.3. Testing methods

Compression test was conducted on 50 mm cubes at 1, 3, 7, 14, 28, 56, and 90 days with respect to ASTM C39 [30]. Splitting test was performed on 100 m cubes at 28, 56, and 90 days as ASTM C496 [31]. Static modulus of elasticity was determined on 150 cubes at 90 days in accordance with ASTM C469 [32]. For this, the cube specimens were loaded and unloaded three times up to 40% of the ultimate load determined from the compression test. The first set of readings from each cube was discarded, and the

Table 1						
Properties of Portland	cement,	silica	fume	and	nanosilica	a.

Constituent (%)	Cement	Silica fume	Nanosilica
CaO	62.12	0.45	-
SiO <sub>2</sub>	19.69	90.36	99.8
Al <sub>2</sub> O <sub>3</sub>	5.16	0.71	-
Fe <sub>2</sub> O <sub>3</sub>	2.88	1.31	-
MgO	1.17	-	-
SO <sub>3</sub>	2.63	0.41	-
K <sub>2</sub> O	0.88	1.52	-
Na <sub>2</sub> O	0.17	0.45	-
Cl	0.0093	-	-
Loss on ignition	2.99	3.11	-
Insoluble residue	0.16	-	-
Free CaO	1.91	-	-
Specific surface (m <sup>2</sup> /kg)	394 <sup>a</sup>	21,080 <sup>b</sup>	150,000 <sup>b</sup>
Specific gravity	3.15	2.2	2.2

<sup>a</sup> Blaine specific surface area.

<sup>b</sup> BET specific surface area.

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