INVESTIGATION OF MECHANICAL AND PHYSICAL PROPERTIES OF MORTARS CONTAINING SILICA FUME AND NANO-SiO$_2$

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ABSTRACT
It has been found that physical properties of concrete, particularly strength and permeability significantly depend on its pore structure. Ultra fine particles of nano-SiO$_2$ fill the voids of CSH structure and provide more homogenous distribution of hydrated products. This effect of nano-SiO$_2$ enhances the durability of cement composites as well as the strength. In this paper, influence of nano-SiO$_2$ on different properties of cement mortar was investigated in comparison with silica fume (SF) as a well-known active pozzolan. Different amounts of nano-SiO$_2$ (0, 1%, 3%, 5%, 7% and 9%) were incorporated into the ordinary cement mortar. Mechanical properties, shrinkage, water absorption of the specimens were determined. Results showed that the optimal content of Nano-SiO$_2$ in plain cement mortar was around 7%. Nano-SiO$_2$ particles were more effective in developing higher mechanical strength and lower water absorption than that of SF. Yet the mortar containing nano-SiO$_2$ experienced higher shrinkage than that of SF mortar.

Keywords: cement mortar, mechanical properties, nano-SiO$_2$, silica fume, shrinkage

1. INTRODUCTION
High strength concrete and mortar with high strength and durability properties offer many advantages. They have been gradually replacing normal strength concrete due to their improved mechanical characteristics and low permeability. With such outstanding characteristics they can be utilized in structure, exposed to severe loading or influenced by environmental conditions, for instance large bridges and offshore constructions [1,2].

Silica fume has been widely used as a supplementary cementing material for producing high performance concrete. It is used to enhance the strength and durability of concrete. It has been reported that use of SF as a cement replacement increased sulfate and acid resistance and decreased chloride permeability of concrete. When SF is added to cement/concrete, it acts as a filler to fill the gaps between cement particles resulting in finer pore structure. Also more CSH gel can be formed in SF concrete due to the reaction that occurs between the silica in SF
and the Ca(OH)$_2$ in hydrating cement (pozzolanic reaction)[3,4]. Recently with the help of advanced nanotechnology developments, nano-SiO$_2$ with finer particles size and higher pozzolanic activity has been introduced. Studies have shown that incorporating nano-SiO$_2$ into cement based materials improved mechanical properties of the products. Qing Ye [5] reported that nano-SiO$_2$ improved the bond strength of paste-aggregate interface. Additional studies have also concluded that pozzolanic activity of nano-SiO$_2$ was much greater than that of silica fume [6]. The abrasion resistance of concrete containing nano-SiO$_2$ was studied by Hui Li [7]. He suggested that nano-SiO$_2$ was valuable for enhancing abrasion resistance of pavement. Gengig Li [8] showed that nano-SiO$_2$ added to high-volume fly ash high-strength concrete could improve short and long term strengths. K. Lin [9] reported that nano-SiO$_2$ particles could potentially improve the negative influences caused by sewage sludge ash (SSA) replacement mortar. It has been found that when nano-SiO$_2$ particles are uniformly dispersed in cement paste they will accelerate cement hydration due to their high activity [10]. Owing to the unique properties of nano-SiO$_2$ it seems that it has a potential to be utilized in production of high strength concrete. Hence more assessments are necessary to ensure usage possibility of nano-SiO$_2$ in cement based materials. Accordingly, in the present experimental study, Nano-SiO$_2$ particles were incorporated into ordinary cement mortar and compressive strength, flexural behavior, water absorption and shrinkage of these composites were investigated. Results were compared with mortar containing 10% silica fume.

### 2. MATERIALS AND METHOD
**Materials:** In this study, ordinary Portland cement type I, silica fume, nano-SiO$_2$ particles and tap water were used. SF used in this experiment contained 91.1% SiO$_2$ with average particles size of 7.38 µm. The chemical compositions of SF and cement were analyzed using an X-ray microprobe analyzer and listed in Table 1. In order to achieve the desire fluidity and better dispersion of nano particles, a polycarboxylate ether based superplastizer was incorporated into all mixes. Natural river sand was used with the fraction of sand passing through 1.18 mm sieve and retaining on 0.2mm. The specific gravity of sand was 2.51 gr/cm$^3$. Basic material properties of nano-SiO$_2$ are given in Table 2.

**Table 3: Chemical composition of cement and silica fume**

<table>
<thead>
<tr>
<th>Chemical compositions (%)</th>
<th>Items</th>
</tr>
</thead>
<tbody>
<tr>
<td>L.O.I SO$_4$ MgO CaO Fe$_2$O$_3$ AL$_2$O$_3$ SiO$_2$</td>
<td></td>
</tr>
<tr>
<td>1.35 0.45 4.8 61.5 2.76 3.68 21.5</td>
<td>O.P.C.</td>
</tr>
<tr>
<td>2.1 0.45 .6 2.24 2 1.55 91.1</td>
<td>S.F.</td>
</tr>
</tbody>
</table>

**Table 2: Basic material properties of nano-SiO$_2$**

<table>
<thead>
<tr>
<th>Item</th>
<th>Diameter (nm)</th>
<th>PH value</th>
<th>Composition (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>50</td>
<td>10</td>
<td>SiO$_2$(30%) + H$_2$O(70%)</td>
</tr>
</tbody>
</table>
Table 4: Mix proportion of the specimens

<table>
<thead>
<tr>
<th>No</th>
<th>Sand/Binder</th>
<th>Water/Binder</th>
<th>% Content (by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>O.P.C.</td>
</tr>
<tr>
<td>NS0</td>
<td>2.75</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>NS1</td>
<td>2.75</td>
<td>0.5</td>
<td>99</td>
</tr>
<tr>
<td>NS3</td>
<td>2.75</td>
<td>0.5</td>
<td>97</td>
</tr>
<tr>
<td>NS5</td>
<td>2.75</td>
<td>0.5</td>
<td>95</td>
</tr>
<tr>
<td>NS7</td>
<td>2.75</td>
<td>0.5</td>
<td>93</td>
</tr>
<tr>
<td>NS9</td>
<td>2.75</td>
<td>0.5</td>
<td>91</td>
</tr>
<tr>
<td>SF10</td>
<td>2.75</td>
<td>0.5</td>
<td>90</td>
</tr>
</tbody>
</table>

Methods: Cement mortars containing SF or nano-SiO₂ were prepared with the same flowing capacity through the adjustment of superplastisizer (Table 3). The water/binder and sand/binder ratios of all mixtures were 0.5 and 2.75 respectively, where the binder weight is the total weight of cement, SF or nano-SiO₂. The amount of SF replacement in mortar (SF mortar) was fixed at 10% which is an acceptable range and is used most often. In order to achieve the desired properties, it is essential to disperse nano particles uniformly. Accordingly, mixing was carried out in a rotary mixer as follows:

1. The nano-SiO₂ particles were stirred with 90% of mixing water at high speed and for about 1 min.
2. The Cement and SF were premixed for 30 s. Then dry mixed cement and SF were added to the mixture. After adding, the mixer was allowed to run for 1 min at medium speed.
3. The sand was gradually added at 30s while the mixer was running at medium speed.
4. The superplastisizer and remaining water were added and stirred at high speed for 30s.
5. The mixture was allowed to rest for 90s. Then mixing was continued for 2 min at high speed.

After mixing, the samples were cast into the 50×50×50 mm cubes for compressive and water absorption tests and 50×50×200 beams for flexural and shrinkage tests. The compressive samples were placed in two layers. Each layer was tamped 32 times in about 10s using a hard rubber mallet following the procedure of ASTM C-109 [11]. The flexural samples also were placed in two layers and each layer was tamped 12 times in 4 rounds as per ASTM C-348 [12]. After 24 hours the specimens were removed from the molds and cured in water at 23±2 °C for 7, 28, 60 and 90 days. The specimens were tested using a hydraulic testing machine under load control at 1350 N/s for compressive test and 44N/s for flexural test. The absorption test was carried out on two 50 mm cubes. Saturated surface dry specimens were kept in an oven at 110°C for 72 h. After measuring the initial weight, specimens were immersed in water for 72h. Then the final weight was measured and the absorption was reported to assess the mortar permeability of mortar in this study.
3. RESULTS AND DISCUSSION

**Compressive strength:** Figure 1 shows the variation in the compressive strength of mortars. It can be seen that the compressive strength of cement mortar with nano-SiO$_2$ is higher than that of plain cement mortar and gradually increases with an increase in the amount of nano-SiO$_2$. It is obvious that increase in the nano-SiO$_2$ content beyond 7% did not change the compressive strength significantly. It is found that large amounts of nano-SiO$_2$ decrease the compressive strength of the composites instead of improving it. Because when the content of nano-SiO$_2$ is large, nano particles are difficult to disperse uniformly. Therefore, they create a weak zone in the form of voids, consequently the homogeneous hydrated microstructure can not be formed and a lower strength will be probable [13]. Also it can be observed that the compressive strength of the specimens containing 5%, 7% and 9% nano-SiO$_2$ (Mixtures NS5, NS7, NS9) are higher than that of the SF mortar. This indicates that nano-SiO$_2$ has a higher pozzolanic activity and is more valuable in reinforcement of mortar than that of SF.

![Compressive strength of different cement mortars](image)

**Flexural strength:** Flexural strength test results are shown in Figure 2. Results show that nano-SiO$_2$ is more effective in developing flexural strength than that of SF. From the results it can be concluded that the optimum nano-SiO$_2$ content in ordinary cement mortar ranges between 5% and 7%.

Two fundamental mechanisms can be deduced for strength enhancement by nano-SiO$_2$:

1) **Strength enhancement by matrix densification and paste-aggregate interfacial zone refinement**
2) **Strength enhancement by reduction in the content of Ca (OH)$_2$.**

The first strengthening mechanism is called the filler effect. The micro filling effect of nano-SiO$_2$ is one of the important factors for the development of dense concrete/mortar with very high strength, because small amount of air content significantly decreases the strength of the mortar. Nano-SiO$_2$ particles, due to their
small size act as a filler to fill into the interstitial spaces inside the skeleton of hardened microstructure of cement paste to increase its density as well as the strength [14]. The filling effect of nano-SiO$_2$ is also valuable for generating strong transition zone. It has been reported that the microstructure of the transition zone between cement paste and aggregates strongly influences the strength and durability of concrete [15]. Nano-SiO$_2$ particles reduce the wall effect in the transition zone between the paste and the aggregate and strengthen this weaker zone due to the higher bond between those two phases. It should be mentioned that the silica fume causes reduction in the volume of large pores and increases the mortar strength too, but as the size ratio between filler and the aggregates is one of the main parameters that strongly affects the strengthening caused by filling effect, and thanks to the high size ratio between nano-SiO$_2$ and cement grains, the filling effect of nano-SiO$_2$ particles is more obvious. The second strengthening mechanism is the pozzolanic activity. Pozzolans are defined as siliceous or siliceous and aluminous materials that in themselves possess little or no cementing property but in finely dispersed form in the presence of moisture chemically react with calcium hydroxide at ordinary temperature to form compound possessing cementitious properties. Two major products of cement hydration are calcium silicate hydrate (CSH) and calcium hydroxide (CH) respectively. Calcium silicate hydrate which is produced by hydration of C$_3$S and C$_2$S plays a vital role in mechanical characteristics of cement paste. Whereas calcium hydrate which is also formed by hydration of cement does not have any cementing property. It contains about 20-25% of the volume of the hydration products. Calcium hydrates due to their morphology are relatively weak and brittle. Cracks can easily propagate through regions populated by them, especially at the aggregate cement paste matrix interface [16]. Nano-SiO$_2$ reacts with Calcium hydrates formed during hydration of cement rapidly and produces calcium silicate hydrate with cementitious properties which is beneficial for enhancement of strength in concrete/mortar.

![Figure 2. Flexural strength of different cement mortars](image-url)
Both nano-SiO$_2$ and SF belong to pozzolanic materials, however results showed that the pozzolanic activity of nano-SiO$_2$ was much greater than that of SF. A possible reason for this observation could be nucleation effect. Nano-SiO$_2$ due to its high specific surface serves additional nucleation sites for precipitation of the hydration products whereby chemical reactions are accelerated [17]. Moreover it has been suggested that the surface of pozzolan can adsorb many Ca$^{2+}$ ions and that lowering of the concentration of the calcium ions accelerates the rate of dissolution of C$_3$S that increases the rate of hydration [18]. Owing to the higher specific surface of nano particles they adsorb more Ca$^{2+}$ ions and accelerate the rate of hydration more effectively.

**Figure 4. Shrinkage behavior of different cement mortars**

Shrinkage: Shrinkage is a common phenomenon generally encountered in almost every cementitious product due to contraction of total mass upon loss of moisture. It is sometimes accompanied by development of cracks specially in such members whose surface area to volume ratio is large [19,20]. These cracks serve as conduits for salt and water. The saline solution comes in contact with reinforcing steel and promotes corrosion. Corrosion causes expansion of steel and inevitably pop-outs occur in the concrete cover, Thereby reducing the strength and service life of the concrete [21]. In view of the importance of the volume changes due to shrinkage this section is devoted to the study of the influence of nano-SiO$_2$ on the drying shrinkage of ordinary mortars. Prismatic specimens with 50×50×200 mm dimensions were prepared. The first measurement was taken using a length comparator with a precision of 2µm after 24 h of mixing, while the rest of measurements were taken at different ages of 3, 7, 14, 21, 28, 35, 42 days. The specimens were cured in the laboratory environment. The average temperature in the laboratory was 27±3 °C. The shrinkage behavior of mortars containing different amounts of nano-SiO$_2$ in comparison with SF mortar is presented in Figure 3. Results showed that both SF mortar and mortar containing nano-SiO$_2$ experienced higher shrinkage than that of ordinary cement mortar. Moreover it can be seen that the drying shrinkage of mortars with nano-SiO$_2$ is higher than that of SF mortar.
and increases with increasing nano-SiO₂ content. The increase in the drying shrinkage of mortar containing nano-SiO₂ might be due mainly to refinement of pore size and increase of mesopores volume which is directly related with the shrinkage due to self desiccation. Moreover nano-SiO₂ particles act as an Activator to accelerate cement hydration, therefore the degree of hydration increases as the amount of nano-SiO₂ increases and the autogenous shrinkage related to chemical shrinkage also increases [22].

**Water absorption:** The absorption characteristics indirectly represent the porosity through an understanding of the permeable pore volume and its connectivity [23]. In order to investigate the effect of nano-SiO₂ particles on cement mortar permeability, water absorption test was carried out at the curing age of 28 days. The absorption values of mortars are listed in Table 4. It is clear that presence of pozzolanic material in cement mortar decreased the water absorption value. Nano-SiO₂ was more effective in reduction of permeability than that of SF. The increase of impermeability caused by nano-SiO₂ can be attributed to two concomitant phenomena:

i. Nano-SiO₂ particles generate a large number of nucleation sites for the hydration products and induce a more homogenous distribution of CSH and hence less pore structure [24].

ii. Nano-SiO₂ particles block the passages connecting capillary pores and water channels in cement paste [25].

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Water absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS0</td>
<td>6.12</td>
</tr>
<tr>
<td>NS3</td>
<td>5.11</td>
</tr>
<tr>
<td>NS5</td>
<td>4.35</td>
</tr>
<tr>
<td>NS7</td>
<td>4.23</td>
</tr>
<tr>
<td>SF10</td>
<td>5.18</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS
An experimental study was carried out to investigate the effect of nano-SiO₂ on the physical and mechanical properties of mortar. Based on the experimental results, following conclusions can be drawn:

1. Noticeable increase was observed in compressive and flexural strength of ordinary cement mortar upon adding nano-SiO₂, however high amounts of nano-SiO₂ had a negative effect on mechanical properties especially flexural strength. From the results it can be concluded that the optimum nano-SiO₂ content in ordinary cement mortar ranges between 5% and 7%.

2. The effect of nano-SiO₂ on drying shrinkage of mortar was significant. The mortar samples containing nano-SiO₂ experienced higher values of drying shrinkage compared to reference mortars. This effect was more prominent for larger amounts of nano-SiO₂.

3. The absorption characteristics which indirectly reflect the porosity showed that nano-SiO₂ particles decreased the water absorption of cement composites by
pore filling and pozzolanic effects. Also it was observed that nano-SiO₂ particles were more effective in the reduction of permeability than that of SF.

REFERENCES
5. Qing Y., Zenan Z., Deyu K., Rong S.C., Influence of nano-SiO₂ addition on properties of hardened cement paste as compared with silica fume, Construction and Building Materials 2007, 21, 539-545.