

Optimum flexural strength of binary blended concrete in presence of SiO₂ nanoparticles as nanofillers

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Abstract: Flexural strength of SiO₂ nanoparticle blended cementitious composite cured in saturated limewater have been optimized. SiO₂ nanoparticles with partial replacement of cement by 0.5, 1.0, 1.5 and 2.0 weight percent have been used as reinforcement. To determine the strength of cement pastes, the specimens were cured in two different media (water and saturated limewater) for 7, 28 and 90 days. The results showed that SiO₂ nanoparticles could improve the mechanical properties of concrete. It has been obtained that curing in saturated limewater for 28 days and afterwards in water until 90 days, produces more strengthened cementitious composite than those cured only in water or saturated limewater for 90 days. Excess Ca(OH)₂ crystals which forms after 28 days when the specimens cured limewater reduces the effect of C-S-H gels which form until the 90 days hence negatively impacts the mechanical properties of the specimens. On the other hand, curing the specimens in water after 28 days produces more C-S-H gel results in a cementitious composite with higher strength.

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Optimum flexural strength of binary blended concrete in presence of SiO₂ nanoparticles as nanofillers. Journal of American Science 2011;7(9):985-989. (ISSN: 1545-1003). <http://www.americanscience.org>, 126

Key words: SiO₂ nanoparticle; flexural strength; cementitious composite; curing medium; optimal strength.

1. Introduction

Portland cement-based binders are the primary active components of cementitious composites used in most modern construction. The other components are water and both fine and coarse aggregate. Binders are made from Portland 'clinker' ground together with a little calcium sulfate, and frequently also contain fine mineral powders such as limestone, pozzolan (typically volcanic ash), fly ash (usually from coal-burning power plants) and granulated blast furnace slag. Such powders are referred to as supplementary cementitious materials (SCMs) since they are used to replace some of the more expensive clinker. Chemical admixtures such as superplasticisers and air-entraining agents can be added in small amounts to modify the properties of a cementitious composite for specific applications.

There are several reports on incorporation of nanoparticles in NVCs which most of them have focused on using SiO₂ nanoparticles [1-10] and TiO₂ nanoparticles [11, 12]. There are a few studies on incorporating nano-Fe₂O₃ [13], nano-Al₂O₃ [14], and nanoclay particles [15, 16]. Additionally, a limited number of investigations are dealing with the manufacture of nanosized cement particles and the development of nanobinders [17]. Previously, a series of works [18-25] has been conducted on cementitious composites by adding different nanoparticles evaluating the mechanical properties of the composites. Nanoparticles can act as heterogeneous nuclei for cement pastes, further accelerating cement hydration because of

their high reactivity, as nano-reinforcement, and as nano-filler, densifying the microstructure, thereby, leading to a reduced porosity. The most significant issue for all nanoparticles is that of effective dispersion.

SiO₂ nanoparticles have been found to improve concrete strength [11, 12, 26], to increase resistance to water permeability [27], and to help control the leaching of calcium [28], which is closely associated with various types of concrete degradation. SiO₂ nanoparticles, in addition, have been shown to promote the hydration reactions of C₃S as a result of the large and highly reactive surface of the nanoparticles [10, 29]. SiO₂ nanoparticles have been found to be more efficient in enhancing strength than silica fume [30, 31]. Adding 10% SiO₂ nanoparticles with dispersing agents has been observed to increase the flexural strength of cementitious composites at 28 days by as much as 26%, compared to only a 10% increase with adding 15% silica fume [10]. Even the addition of small amounts of SiO₂ nanoparticles has been observed to increase the strength results in improving the 28 day flexural strength by 10% and flexural strength by 25% [2]. However, these results depend on the production route and conditions of synthesis of SiO₂ nanoparticles (e.g., molar ratios of the reagents, the type of reaction media, and duration of the reaction for the sol-gel method) and that dispersion of SiO₂ nanoparticles in the paste plays an important role. SiO₂ nanoparticles not only behaved as nanofiller to improve the microstructure but also as an activator to accelerate pozzolanic reactions [30].

Table 1. Chemical and physical properties of Portland cement (Wt. %)

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Loss on ignition
Cement	21.89	5.3	3.34	53.27	6.45	3.67	0.18	0.98	3.21

Specific gravity: 1.7 g/cm³

Table 2. The properties of nano-SiO₂

Diameter (nm)	Surface Volume ratio (m ² /g)	Density (g/cm ³)	Purity (%)
15 ± 3	160 ± 12	< 0.14	>99.9

Table 3. Mixture proportion of nano-SiO₂ particles blended concretes

Sample designation	nano-SiO ₂ particles	Quantities (kg/m ³)	
		Cement	SiO ₂ nanoparticles
C0 (control)	0	450	0
N1	0.5	447.75	2.25
N2	1.0	445.50	4.50
N3	1.5	443.25	6.75
N4	2.0	441.00	9.00

Water to binder [cement + nano-SiO₂] ratio of 0.40, sand 492 kg/m³, and aggregate 1148 kg/m³

In this work, the influence of nano-SiO₂ on flexural strength, flexural strength and split tensile strength binary blended cementitious composite cured in water and saturated limewater for different ages has been investigated. The optimum replacement level of SiO₂ nanoparticles has been determined in different curing media has been obtained and the method for achieving the optimum strength using a combination of two curing media has been discussed.

2. Materials and Methods

Ordinary Portland Cement (OPC) conforming to ASTM C150 [32] standard was used as received. The chemical and physical properties of the cement are shown in Table 1. The nanoparticle size distribution pattern of the used OPC has been illustrated in Fig. 1.

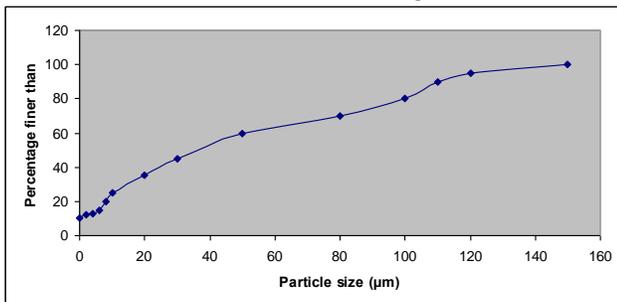


Fig.1. Particles distribution pattern of ordinary Portland cement.

SiO₂ nanoparticles with average particle size of 15 nm and 45 m²/g Blaine fineness producing from Suzhou Fuer Import & Export Trade Co., Ltd was used as received. The properties of SiO₂ nanoparticles are shown in Table 2. Scanning electron micrographs (SEM) and

powder X-ray diffraction (XRD) diagrams of SiO₂ nanoparticles are shown in Figs. 2 and 3.

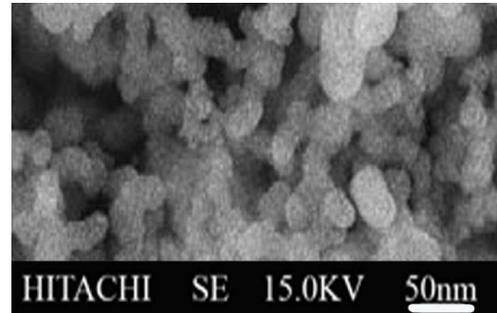


Fig. 2. SEM micrograph of SiO₂ nanoparticles.

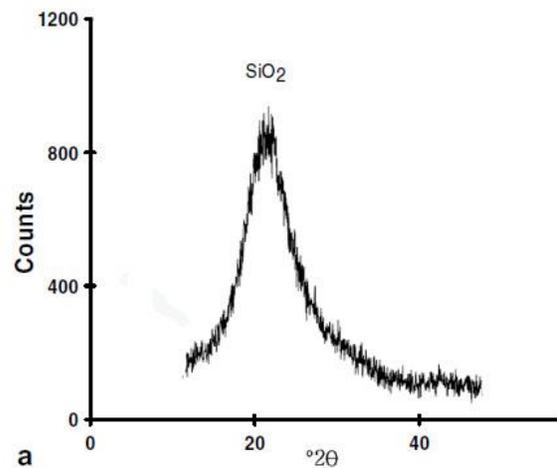


Fig. 3. XRD analysis of SiO₂ nanoparticles.

Table 4. Flexural strength of nano-SiO₂ particle blended cement mortars

Sample designation	nano-SiO ₂ particle (%)	Flexural strength (MPa)		
		7 days	28 days	90 days
C0-W (control)	0	4.2	4.4	4.7
N1-W	0.5	5.0	5.3	5.5
N2-W	1.0	5.5	5.8	6.2
N3-W	1.5	5.2	5.6	5.9
N4-W	2.0	4.8	5.0	5.2
C0-LW (control)	0	4.0	4.1	4.2
N1-LW	0.5	5.3	5.9	6.0
N2-LW	1.0	6.0	6.5	6.6
N3-LW	1.5	6.4	6.8	6.8
N4-LW	2.0	6.9	7.2	7.3
C0-LW-W (control)	0	4.0	4.1	4.3
N1-LW-W	0.5	5.3	5.9	6.4
N2-LW-W	1.0	6.0	6.5	6.9
N3-LW-W	1.5	6.4	6.8	7.5
N4-LW-W	2.0	6.9	7.2	8.1

Water to binder [cement + nano-SiO₂] ratio of 0.40

W denotes the specimens cured in water and LW denotes to those cured in saturated limewater

Locally available natural sand with particles smaller than 0.5mm and fineness modulus of 2.25 and specific gravity of 2.58 g/cm³ was used as fine aggregate. Crushed basalt stored in the laboratory with maximum size of 15 mm and specific gravity of 2.96 g/cm³ was used as coarse aggregate.

Two series of mixtures were prepared in the laboratory trials. Series C0 mixtures were prepared as control specimens. The control mixtures were made of natural aggregates, cement and water. Series N were prepared with different contents of nano-SiO₂ particles with average particle size of 15 nm. The mixtures were prepared with the cement replacement of 0.5%, 1.0%, 1.5% and 2.0% by weight. The water to binder ratio for all mixtures was set at 0.40. The aggregates for the mixtures consisted of a combination of crushed basalt and of fine sand, with the sand percentage of 30% by weight. The binder content of all mixtures was 450 kg/m³. The proportions of the mixtures are presented in Table 3.

Series N mixtures were prepared by mixing the course aggregates, fine aggregates and powder materials (cement and nano-SiO₂ particles) in a laboratory concrete drum mixer. The powder material in the series C0 mixtures was only cement. They were mixed in dry condition for two minutes, and for another three minutes after adding the water. Cubes with 200 mm × 50 mm × 50 mm edges for flexural strength were cast and compacted in two layers on a vibrating table, where each layer was vibrated for 10 s [33]. The moulds were covered with polyethylene sheets and moistened for 24 h. Then the specimens were demoulded and cured in water (N-W series) and saturated limewater (N-LW series) at a temperature of 20° C prior to test days. The strength tests of the concrete samples were determined at 7, 28 and 90 days. A series of the specimens were cured in saturated limewater for 28 days and then cured in water until 90 days (N-LW-W series) after casting and then were tested.

Flexural strength of nano-SiO₂ particles blended concrete cubes was determined as per ASTM C 293 [34] after 7, 28 and 90 days of moisture curing. Tests were carried out on triplicate specimens and average flexural strength values were obtained.

For thermogravimetric analysis (TGA), A Netzsch model STA 409 simultaneous thermal analyzer equipped with a Data Acquisition System 414/1 programmer was used. Specimens which were cured for 90 days were heated from 100 to 650 °C, at a heating rate of 4 °C/min and in an inert N₂ atmosphere.

Scanning electron microscopy (SEM) investigation was conducted on a Hitachi apparatus. Secondary electron (SE) imaging was used to study the samples, which were prepared under conditions that ensured their subsequent viability for analytical purposes.

3. Results and discussion

3.1. Flexural strength

The flexural strength results of series C0-W and N-W mixtures are shown in Table 4. Comparison of the results from the 7, 28 and 90 days samples shows that the flexural strength increases with nano-SiO₂ particles up to 1.0% replacement (N2-W) and then it decreases, although the results of 2.0% replacement (N4-W) is still higher than those of the plain cement concrete (C0-W). It was shown that the use of 2.0% nano-SiO₂ particles in N-W series decreases the flexural strength to a value which is near to the control concrete. This may be due to the fact that the quantity of nano-SiO₂ particles (pozzolan) present in the mix is higher than the amount required to combine with the liberated lime during the process of hydration thus leading to excess silica leaching out and causing a deficiency in strength as it replaces part of the cementitious material but does not contribute to strength [36]. Also, it may be due to the defects generated in dispersion of nanoparticles that causes weak zones. The

high enhancement of flexural strength in the N series blended concrete are due to the rapid consuming of $\text{Ca}(\text{OH})_2$ which was formed during hydration of Portland cement specially at early ages related to the high reactivity of nano- SiO_2 particles. As a consequence, the hydration of cement is accelerated and larger volumes of reaction products are formed. Also nano- SiO_2 particles recover the particle packing density of the blended cement, directing to a reduced volume of larger pores in the cement paste.

Table 4 also shows the flexural strength of C0-LW and N-LW series. The results show that the replacement of cement by SiO_2 nanoparticles up to 2.0 Wt% (N4-LW) in N-LW series produces concrete with high strength with respect to N-LW concrete. By comparison the flexural strength results of C0-W and C0-LW series, it shows that after 7, 28 and 90 days of curing the concrete in the saturated limewater, the flexural strength of the C0-LW series is smaller than the corresponding strength of C0-W series. This may be due to more formation of crystalline $\text{Ca}(\text{OH})_2$ in the presence of limewater which reduces the flexural strength in C0-LW series with respect to C0-W series. On the other hand, the flexural strength of the N-LW series is more than those of N-W series. Lime reacts with water and produces $\text{Ca}(\text{OH})_2$ which needs to form C-S-H gel. When SiO_2 nanoparticles react with $\text{Ca}(\text{OH})_2$ produced from saturated limewater, the content of C-S-H gel is increased because of high free energy of nanoparticles which reduces significantly when reacts by $\text{Ca}(\text{OH})_2$. The flexural strength of N-W and N-LW series should be compared from two viewpoints. The first viewpoint is that the flexural strength of N-LW series increases by partial replacement of cement with SiO_2 nanoparticles up to 2.0 wt% (N4-LW) while for N-W series it increases by partial replacement of cement with SiO_2 nanoparticles up to 1.0 wt% (N2-W) and then decreases. Once more this confirm the more C-S-H gel formation in the presence of saturated limewater in which the quantity of nano- SiO_2 particles (pozzolan) present in the mix is close to the amount required to combine with the liberated lime during the process of hydration thus leading to lesser silica leaching out with respect to the specimens cured in water. Second viewpoint is that the difference between flexural strengths of the N-W and N-LW series after 28 days of curing is relatively high while this difference in flexural strength after 90 days of curing is not high. This may be due to formation of crystalline $\text{Ca}(\text{OH})_2$ in N-LW series after the 28 day causes reduction in flexural strength. In the other words, curing of the SiO_2 nanoparticles blended concrete in saturated limewater after 28 days is completely suitable to achieve high strength especially with high weight percent of nanoparticles.

3.5. Thermogravimetric analysis results

Table 5 shows the weight loss measured in the 100-650 °C range in which dehydration of the hydrated products occurred. The results show that after 90 days of

curing, the loss in weight of the specimens is increased by increasing the nanoparticles content in concretes. This is more evident in N2-W and N4-LW series. This may be due to more formation of hydrated C-S-H gel in N2-W and N4-LW series.

Table 5. Weight loss (%) of the pastes in the range of 110-650 °C after 90 days of curing.

Mixture	Total heat
	kJ/kg
C0-W (control)	12.2
N1-W	11.7
N2-W	11.9
N3-W	11.8
N4-W	11.6
C0-LW (control)	12.7
N1-LW	11.5
N2-LW	11.2
N3-LW	10.8
N4-LW	10.5

Water to binder [cement + nano- SiO_2] ratio of 0.40

W denotes the specimens cured in water and LW denotes to those cured in saturated limewater

Conclusions

The results show that the nano- SiO_2 particles blended concrete had significantly higher strength (flexural, split tensile and flexural strength) compared to that of the concrete without nano- SiO_2 particles. It is found that the cement could be advantageously replaced with nano- SiO_2 particles up to maximum limit of 2.0% with average particle sizes of 15 nm when the specimens cured at saturated limewater for 28 days. The optimal level of nano- SiO_2 particles content was achieved with 1.0% replacement for the specimens cured in water 7, 28 and 90 days. The optimized strength of nanoparticles blended concrete was achieved by partial replacement of 2.0 wt% cement with SiO_2 nanoparticles which was cured for 28 days in saturated limewater and then in water until 90 days.

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8/25/2011