

Improvement the mechanical properties of the cementitious composite by using TiO₂ nanoparticles

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Abstract: In this Paper, the split tensile and flexural strength together with the setting time of concrete by partial replacement of cement with nano-phase TiO₂ particles has been studied. TiO₂ nanoparticles with the average diameter of 15 nm were used with four different contents of 0.5%, 0.1%, 1.5% and 2.0% by weight. The results showed that the use of nano-TiO₂ particles up to maximum replacement level of 2.0% produces concrete with improved split tensile strength. However, the ultimate strength of concrete was gained at 1.0% of cement replacement. The flexural strength of fresh concrete was increased by increasing the content of TiO₂ nanoparticles. The setting time of fresh concrete was decreased by increasing the content of TiO₂ nanoparticles. It is concluded that partial replacement of cement with nanophase TiO₂ particles improves the split tensile and flexural strength of concrete but decreases its setting time. [Journal of American Science 2010;6(4):98-101]. (ISSN: 1545-1003).

Key words: Nanophase TiO₂ particles; concrete; split tensile strength; flexural strength.

1. Introduction

Concrete is a newer construction material compared to steel and stone. Use of concrete in constructions and buildings may have begun less than a century ago. But in recent century, very wide and effective research has seen on improving the properties of concrete with incorporating wide range of supplementary cementing materials such as pozzolans and nanoparticles due to increasing the use of concrete from decade to decade. Recently, nanotechnology has attracted great scientific attention because of the new potential uses of particles in nanometer (10⁻⁹ m) scale. This may be due to the nanoscale size of particles being able to result in significantly improved properties from predictable grain-size materials of the same chemical composition. As a consequence, industries can be able to design new and novel products and to re-engineer many existing products that function at unprecedented levels.

There are few reports on incorporation of nanoparticles in cement-based concrete. Hui Li et al. (2003) [1] investigated the properties of cement mortars blended with nanoparticles to explore their super mechanical and smart (temperature and strain sensing) potentials. Also useful applications of nano-SiO₂ are addressed by the Fuji Chimera Research Institute (2002). However, until now, research performed over the years has been mainly aimed at achieving high mechanical performance with cement replacement materials in micro level. Recently, the effect of micro-SiO₂ particles by adding rice husk ash to blended concrete has been reviewed by Naji Givi et al. (2010) [2].

Several researchers have demonstrated that the finer the SiO₂ particle sizes in micron level, the higher the tensile strength. But there is a lack of knowledge on effects of ultra fine and nano-size particles on concrete's properties. Lu and Young [3] achieved 800 MPa strengths on compressed samples, and Richard and Cheyrez [4] developed Reactive Power Concretes (RPCs) ranging from 200 to 800 MPa and fracture energies up to 40 kJ m⁻². The development of an ultrahigh strength concrete was made possible by the application of DSP (Densified System containing homogeneously arranged ultra-fine Particles) with super plasticizer and silica fume content [5].

The definition of high performance concrete (HPC) and high strength concrete (HSC) have been changing from time to time. Until the late 1960s 35 MPa and 42 MPa were considered as HSC while in the mid 1980s 55 MPa concrete was considered as HSC. Perhaps by the end of this century, 150 MPa will be branded as HSC [6]. Production of HPC and HSC are a challenge and depends upon so many factors. Also In the last 15 years Ultra High Performance Concrete (UHPC) has become a vanguard product in industrial and structural applications gratitude to outstanding properties, such as tensile strength of 150–200 MPa, tensile strength of 8–15 MPa with significant remaining post-cracking bearing capacity, and remarkable fracture energy of 20–30 kJ/m² [7,8].

In this work, the influences of nano-TiO₂ on flexural and tensile strength together with the setting time of binary blended concrete have been investigated. Alumina

component reacts with calcium hydroxide produced from the hydration of calcium silicates. The rate of the pozzolanic reaction is proportional to the amount of surface area available for reaction. Therefore, it is possible to add nano-TiO₂ of a high purity (99.9%) and a high Blaine fineness value (60 m²/g) in order to improve the characteristics of cement mortars [5]. In this study an attempt has been made to prove that using new materials, it is possible to obtain HPC or HSC with slight increase in cost.

2. Materials and Methods

2.1. Materials and mixtures

2.1.1. Cement

Ordinary Portland Cement (OPC) obtained from Holcim Cement Manufacturing Company of Malaysia conforming to ASTM C150 standard was used as received. The chemical and physical properties of the cement are shown in Table 1.

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

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

Specific gravity: 1.7 g/cm³

2.1.2. Nano-TiO₂ particles

Nano-TiO₂ with average particle size of 15 nm was used as received. The properties of nano-TiO₂ particles are shown in Table 2.

Table 2. The properties of nano-TiO₂

Diameter (nm)	Surface Volume ratio (m ² /g)	Density (g/cm ³)	Purity (%)
15 ± 3	150 ± 12	< 0.12	>99.9

2.1.3. Aggregates

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

2.1.4. Mixture proportioning

A total of 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-TiO₂ 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 [9]. 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 550kg/m³. The proportions of the mixtures are presented in Table 3.

Table 3. Mixture proportion of nano-TiO₂ particles blended concretes

Sample designation	nano-TiO ₂ particles	Quantities (kg/m ³)	
		Cement	nano-TiO ₂ particles
C0 (control)	0	550	0
N1	0.5	547.25	2.75
N2	1.0	544.50	5.50
N3	1.5	541.75	8.25
N4	2.0	539.00	11.00

Water to binder [cement + nano-TiO₂] ratio of 0.40, sand 492 kg/m³, and aggregate 1148 kg/m³

2.2. Preparation of test specimens

Series N mixtures were prepared by mixing the course aggregates, fine aggregates and powder materials (cement and nano-TiO₂ 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. Slumps of the fresh concrete were determined immediately to evaluate the flexural strength following the mixing procedure. Cylinders with the diameter of 150 mm and the height of 300 mm for split tensile strength and cubes with 200 mm × 50 mm × 50 mm edges for flexural strength tests were cast and compacted in two layers on a vibrating table, where each layer was vibrated for 10 s [10]. The moulds were covered with polyethylene sheets and moistened for 24 h. Then the specimens were demoulded and cured in water at a temperature of 20° C prior to test days. The tensile strengths tests of the concrete samples were determined at 7, 28 and 90 days. The reported results are the average of three trials.

2.3. Split tensile strength of nano-TiO₂ particles blended concrete

Split tensile test was carried out in accordance to the ASTM C 496-90 standard. After the specified curing period was over, the concrete cylinders were subjected to split tensile test by using universal testing machine. Tests were carried out on triplicate specimens and average split tensile strength values were obtained.

2.4. Flexural strength of nano-TiO₂ particles blended concrete

Flexural test were done in accordance to the ASTM C293 Standard. Similar to the tensile tests, flexural tests were carried out on triplicate specimens and average flexural strength values were obtained.

3.4. Setting time of nano-TiO₂ particles blended concrete
Setting time of the specimens was regulated according to the ASTM C191 standard.

3. Experimental results and discussion

3.1. Split Tensile strength

The split tensile strength results of series C0 and N mixtures are shown in Table 4. Comparison of the results from the 7, 28 and 90 days samples shows that the split tensile strength increases with nano-TiO₂ particles up to 1.0% replacement (N2) and then it decreases, although the results of 2.0% replacement (N4) is still higher than those of the plain cement concrete (C0). It was shown that the use of 2.0% nano-TiO₂ particles decreases the split tensile strength to a value which is near to the control concrete. This may be due to the fact that the quantity of nano-TiO₂ 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 [11]. Also, it may be due to the defects generated in dispersion of nanoparticles that causes weak zones.

Table 4. Split Tensile strength of nano-TiO₂ particle blended cement mortars

Sample designation	nano-TiO ₂ particle (%)	Split Tensile strength (MPa)		
		7 days	28 days	90 days
C0 (control)	0	1.5	1.8	2.3
N1	0.5	2.3	2.6	2.9
N2	1.0	2.8	3.0	3.3
N3	1.5	2.6	2.7	3.0
N4	2.0	1.9	1.9	2.4

Water to binder [cement + nano-TiO₂] ratio of 0.40

The higher the split tensile strength in the N series blended concrete are due to the rapid consuming of Ca(OH)₂ which was formed during hydration of Portland cement specially at early ages related to the high reactivity of nano-TiO₂ particles. As a consequence, the hydration of cement is accelerated and larger volumes of reaction products are formed. Also nano-TiO₂ particles recover the particle packing density of the blended cement, directing to a reduced volume of larger pores in the cement paste. However, the value of split tensile strength in the specimens is not high and better reinforcements such as needle-type nanoparticles are requested.

3.2. Flexural strength

The flexural strength results of series C0 and N mixtures are shown in Table 5. Similar to the tensile strength, the flexural strength of the specimens increases with nano-

TiO₂ particles up to 1.0% replacement (N2) and then it decreases, although the results of 2.0% replacement (N4) is still higher than those of the plain cement concrete (C0). Again, the increasing in the flexural strength is due to the rapid consuming of Ca(OH)₂ which was formed during hydration of Portland cement specially at early ages related to the high reactivity of nano-TiO₂ particles.

Table 4. Flexural strength of nano-TiO₂ particle blended cement mortars

Sample designation	nano-TiO ₂ particle (%)	Flexural strength (MPa)		
		7 days	28 days	90 days
C0 (control)	0	4.2	4.4	4.7
N1	0.5	4.9	5.1	5.6
N2	1.0	5.6	5.5	6.1
N3	1.5	5.1	5.4	5.7
N4	2.0	4.5	5.1	5.0

Water to binder [cement + nano-TiO₂] ratio of 0.40

3.3. Setting time

The obtained results from the initial and final setting times of the cement mortars with nano-TiO₂ particles are shown in Figures 1 and 2, respectively. Figures 1 and 2 shows that by increasing the volume fraction of nanoparticles, the setting time is decreased indicating that nano-TiO₂ has a faster hydration reaction speed than did the cement, because nano-TiO₂ is characterized by its unique surface effects, smaller particle sizes, and higher surface energy [12]. Smaller particle sizes allow a rapid increase in surface area leading to a fast rise in the number of surface atoms. These surface atoms are highly active and unstable, which results in a faster reaction speed. Hence, a cautious approach should be taken for the setting time of the paste during the utilizing of nano-TiO₂ [12].

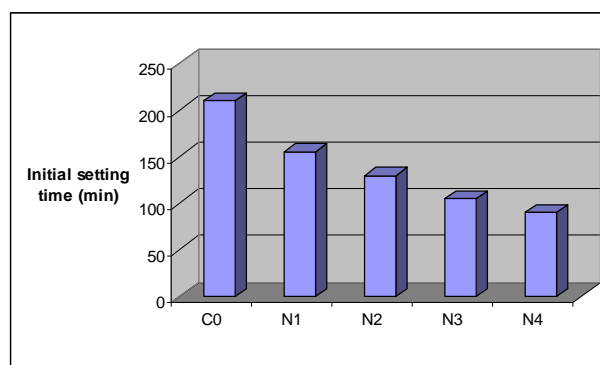


Figure 1. Influence of nano-TiO₂ particles on the initial setting time of cement paste.

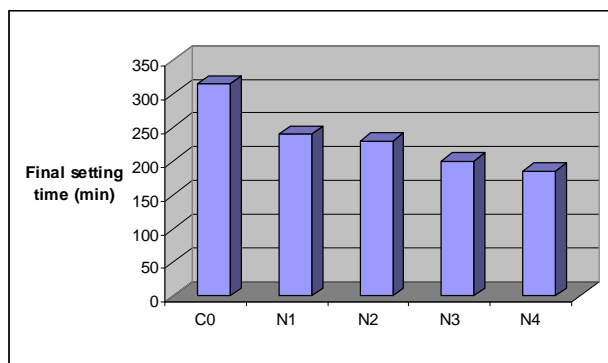


Figure 2. Figure 1. Influence of nano-TiO₂ particles on the initial setting time of cement paste.

Conclusions

The results show that the nano-TiO₂ particles blended concrete had higher split tensile and flexural strength compare to that of the concrete without nano-TiO₂ particles. It is found that the cement could be advantageously replaced with nano-TiO₂ particles up to maximum limit of 2.0% with average particle sizes of 15 nm. Although, the optimal level of nano-TiO₂ particles content was achieved with 1.0% replacement. However, the split tensile strength of the concrete could be improved by using more suitable reinforcements such as needle type nanoparticles.

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