The filler effects of TiO_2 nanoparticles in concrete

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Abstract: The effect of limewater on compressive strength permeability of TiO_2 nanoparticles binary blended concrete has been investigated. TiO_2 nanoparticles with partial replacement of cement by 0.5, 1.0, 1.5 and 2.0 weight percent have been used as reinforcement. Curing of the specimens has been carried out in water and saturated limewater for 7, 28 and 90 days after casting. The results indicate that TiO_2 nanoparticles up to maximum replacement level of 2.0% produces concrete with improved compressive strength when the specimens cured in saturated limewater with respect to the specimens cured in water. TiO_2 nanoparticles can improve the filler effect and also the high pozzolanic action of fine particles increases substantially the quantity of strengthening gel. Although the limewater reduces the strength of concrete without nanoparticles, curing the specimens in saturated limewater results in more strengthening gel formation in TiO_2 nanoparticles blended concrete causes high strength.

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Key words: TiO_2 nanoparticle; compressive strength; concrete.

1. Introduction

There are few reports on incorporation of nanoparticles in cement-based concrete. Li et al. [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-SiO_2 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-SiO_2 particles by adding rice husk ash to blended concrete has been reviewed by Naji Givi et al. [2]. Several researchers have demonstrated that the finer the TiO_2 particle sizes in micron level, the higher the strength. But there is a lack of knowledge on the effects of ultra fine and nano-size particles on concrete's properties. Lu and Young [3] achieved high strengths on compressed samples, and Richard and Cheyrezy [4] developed Reactive Power Concretes (RPCs). 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]. Kuo et al. [6] investigated the properties of waterworks sludge ash cement paste incorporating SiO_2 nanoparticles. In their work, the flowability of the cement pastes has been considered and it has been shown that the flowability of the concrete decreases by increasing the nanoparticle amount. Lin and Tsai [7] investigated the influences of nano-materials on the microstructures of sludge ash cement paste. They noticed that the amount of crystallization in the hydrates increased with the increased quantities of nano-material added. Furthermore, denser crystallizations, smaller pore sizes, and a decreased number of pores were observed with the addition of nano-material results in decreasing water permeability.

Previously, a series of works [8-15] has been conducted on cementitious composites reinforced by different nanoparticles evaluating the mechanical properties of the composites. In this work, the influence of nano-TiO_2 on compressive strength and water permeability of binary blended concrete cured in water and limewater has been investigated.

2. Materials and Methods

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.

Nano–TiO_2 with average particle size of 15 nm was used as received. The properties of nano-TiO_2 particles are shown in Table 2.

Crushed limestone aggregates were used to produce self-compacting concretes, with gravel 4/12 and two types of sand: one coarse 0/4, for fine aggregates and the other fine 0/2, with a very high fines content (particle size < 0.063 mm) of 19.2%, the main function of which was to provide a greater volume of fine materials to improve the stability of the fresh concrete.

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

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	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/cm^3

Table 2. The properties of nano-TiO_2

Diameter (nm)	Surface Volume ratio (m^2/g)	Density (g/cm^3)	Purity (%)
15 ± 3	155 ± 12	< 0.13	>99.9

Table 3. Mixture proportion of nano-SiO_2 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-SiO_2] ratio of 0.40, sand 492 kg/m^3, and aggregate 1148 kg/m^3

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-TiO_2 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 [17]. 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/m^3. 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-TiO_2 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 workability following the mixing procedure. Cubes of 100 mm edge for compressive strength tests were cast and compacted in two layers on a vibrating table, where each layer was vibrated for 10 s [18]. 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^o C prior to test days. The strength and water permeability tests of the concrete samples were determined at 7, 28 and 90 days.

Compressive test were done in accordance to the ASTM C39 Standard. Again, compressive tests were carried out on triplicate specimens and average compressive strength values were obtained.

3. Results and discussion

The compressive 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 compressive strength increases with nano-TiO_2 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-TiO_2 particles decreases the compressive strength to a value which is near to the control concrete. This may be due to the fact that the quantity of nano-TiO_2 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 [18]. Also, it may be due to the defects generated in dispersion of nanoparticles that causes weak zones. The high enhancement of compressive 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-TiO_2 particles. As a consequence, the hydration of cement is accelerated and larger volumes of reaction products are formed. Also nano-TiO_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 compressive strength of C0-LW and N-LW series. The results show that the replacement of cement by TiO_2 nanoparticles up to 2.0

Wt% (N4-LW) in N-LW series produces concrete with high strength with respect to N-LW control concrete. By comparison the compressive 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 compressive strength of the C0-LW series in smaller than the corresponding strength of C0-W series. This may be due to more formation of crystalline $Ca(OH)_2$ in the presence of limewater which reduces the compressive strength in C0-LW series with respect to C0-W series. On the other hand, the compressive strength of the N-LW series is more than those of N-W series. Lime reacts with water and produces $Ca(OH)_2$ which needs to form C-S-H gel. When TiO_2 nanoparticles react with $Ca(OH)_2$ 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 $Ca(OH)_2$. The compressive strength of N-W and N-LW series should be compared from two viewpoints. The first viewpoint is that the compressive strength of N-LW series increases by partial replacement of cement with TiO_2 nanoparticles up to 2.0 wt% (N4-LW) while for N-W series it increases by partial replacement of cement with TiO_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-TiO_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 compressive strengths of the N-W and N-LW series after 28 days of curing is relatively high while this difference in compressive strength after 90 days of curing is not high. This may be due to formation of crystalline $Ca(OH)_2$ in N-LW series after the 28 day causes reduction in compressive strength. In the other words, curing of the TiO_2 nanoparticles blended concrete in saturated limewater after 28 days is completely suitable to achieve high strength especially with high weight percent of nanoparticles.

Table 4. Compressive strength of nano-TiO_2 particle blended cement mortars

		Compressive strength (MPa)		
Sample designation	nano-TiO_2 particle (%)	7 days	28 days	90 days
C0-W (control)	0	27.3	36.8	42.3
N1-W	0.5	30.8	41.9	45.5
N2-W	1.0	31.9	43.4	46.9
N3-W	1.5	31.5	42.5	45.9
N4-W	2.0	28.7	39.3	44.8
C0-LW (control)	0	27.0	35.4	39.8
N1-LW	0.5	31.3	43.0	43.2
N2-LW	1.0	32.8	45.7	45.8
N3-LW	1.5	35.9	48.1	48.6
N4-LW	2.0	38.1	49.9	50.3

Water to binder [cement + nano-TiO_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-TiO_2 particles blended concrete had higher compressive strength compared to that of the concrete without nano-TiO_2 particles. It is found that the cement could be advantageously replaced with nano-TiO_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-TiO_2 particles content was achieved with 1.0% replacement for the specimens cured in water 7, 28 and 90 days.

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