Assessment of the effects of the cement paste composite in presence TiO_2 nanoparticles

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Abstract: The purpose of this study is to investigate the compressive strength and workability of concrete by partial replacement of cement with nano-phase TiO_2 particles. TiO_2 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- TiO_2 particles up to maximum replacement level of 2.0% produces concrete with improved strength. However, the ultimate strength of concrete was gained at 1.0% of cement replacement. The workability of fresh concrete was decreased by increasing the content of TiO_2 nanoparticles. It is concluded that partial replacement of cement with nanophase TiO_2 particles improves the compressive strength of concrete but decreases its workability. [Journal of American Science 2010;6(4):43-46]. (ISSN: 1545-1003).

Key words: Nanophase TiO_2 particles; concrete; compressive strength; workability.

1. Introduction

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-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 nano-SiO_2 particles by adding to blended concrete has been reviewed by Nazari et al. (2010) [2]. Several researchers have demonstrated that the finer the SiO_2 particle sizes in micron level, the higher the compressive 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 Cheyrezy [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 compressive 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/m^2 [7,8].

In this work, the influences of nano- TiO_2 on compressive strength and workability of binary blended concrete has been studied. Nanoparticles react 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- TiO_2 of a high purity (99.9%) and a high Blaine fineness value (60 m^2/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.

HPC and HSC are very useful in constructions and multistory buildings because they can decrease the cross-sectional area of the structural fundamentals.

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.

2.1.2. Nano- TiO_2 particles

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.

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

Chemical properties

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Cement	21.89	5.3	3.34	53.27	6.45
Material	SO_3	Na_2O	K_2O	Loss on ignition	
Cement	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

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/cm^3 was used as fine aggregate. Crushed basalt stored in the laboratory with maximum size of 15mm and specific gravity of 2.96g/cm^3 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- 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 [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/m^3. The proportions of the mixtures are presented in Table 3.

2.2. Preparation of test specimens

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 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^o C prior to test days. The compressive strengths tests of the concrete samples were determined at 7, 28 and 90 days. The reported results are the average of three trials.

Table 3. Mixture proportion of nano- TiO_2 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- TiO_2] ratio of 0.40, sand 492 kg/m^3, and aggregate 1148 kg/m^3

2.3. Compressive strength of nano- TiO_2 particles blended concrete

Compressive strength of nano- TiO_2 particles blended cement concrete cubes was determined as per ASTM C 39 after 7, 28 and 90 days of moisture curing.

2.4. Workability

Standard slump tests conforming to ASTM C143 were used to determine the workability of the concrete.

3. Experimental results and discussion

The compressive strength results obtained from the experimental investigations are showed in tables and the comparison between the results of workability test is presented in form of bar chart. All the values are the average of the three trails in each case in the testing program of this study. The results are discussed as follows.

3.1. Compressive strength

The compressive 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 compressive strength increases with nano- TiO_2 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- 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

[11]. 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. Compressive strength of nano- TiO_2 particle blended cement mortars

Sample designation	nano- TiO_2 particle (%)	Compressive strength (MPa) 7 days	28 days	90 days
C0 (control)	0	27.3	36.8	42.3
N1	0.5	30.8	41.9	45.5
N2	1.0	31.9	43.4	46.9
N3	1.5	31.5	42.5	45.9
N4	2.0	28.7	39.3	44.8

Water to binder [cement + nano- TiO_2] ratio of 0.40

3.2. Workability

A high-quality concrete is one which has acceptable workability (around 6.5 cm slump height) in the fresh condition and develops sufficient strength. Basically, the bigger the measured height of slump, the better the workability will be, indicating that the concrete flows easily but at the same time is free from segregation [12, 13]. Maximum strength of concrete is related to the workability and can only be obtained if the concrete has adequate degree of workability because of self compacting ability. Self-compacting repair mortars, as new technology products, are especially preferred for the rehabilitation and repair of reinforced concrete structures [14]. The water/powder (cement, fly ash, limestone filler, silica fume, nano-particles, etc.) ratio of mortar and the type of chemical admixtures should be determined, in order to place the fresh mortar without any external compaction and at the same time without causing any segregation [15]. In other words, the rheology of paste phase of self-repairing mortar should have suitable properties from flowability and segregation point of view [16–19].

The workability of C0 and N series concrete are presented in Figure 1. The figure shows the influence of nano- TiO_2 particles content on the workability of mixtures at constant water to binder ratio of 0.40. The results show that unlike the C0 series, all investigated nano- TiO_2 particles blended mixtures had low slump values and non-acceptable workability. This may be due to the increasing in the surface area of powder after adding nanoparticles that needs more water to wetting the cement particles.

With the improvement of novel plasticizers, to obtain high filling rates is possible even for compound molding systems. The fresh characteristics of concrete, strength and durability of mortars can be improved by the addition of inert or pozzolanic [20]. The selection of the amount and the type of cementitious or inert powders depends on the physical and physico-chemical properties of these powders which are affecting the performance of fresh paste such as particle shape, surface texture, surface porosity and rate of superplasticizer adsorption, surface energy (zeta potential), finest fraction content, Blaine fineness and particle size distribution.

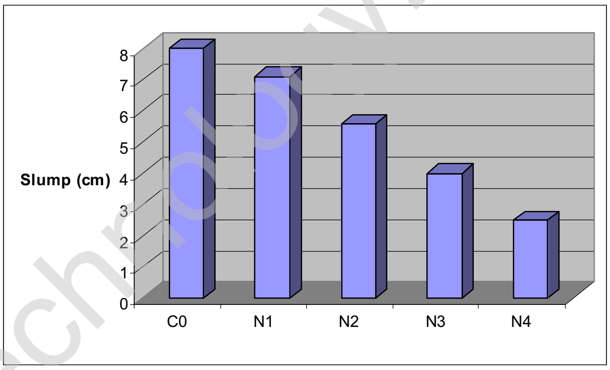

Figure 1. Particle size effects of nano- TiO_2 on workability of concrete. N1,N2,N3 and N4 are the series N blended concrete with 0.5, 1.0, 1.5 and 2.0 percent of nano- TiO_2 particles, respectively.

There is no universally accepted agreement on the effect of these factors due to the complex influence of the combination of these factors [21].

Usually, increasing the fine particles content in cements changes the rheological properties of pastes and consequently influences the workability of mortars and fresh concrete mixtures. The observed changes can be advantageous or not as a result of many factors influencing the rheology of cement pastes [22]. It is usually expected that, if the volume concentration of a solid is held constant, for a specific workability, the replacement of cement with a fine powder will increase the water demand due to the increase in surface area. This is more observed for nanoparticles blended concrete. However, in some cases, the above-mentioned conclusion is not appropriate. Lange et al. [23] obtained same results with fly ash blended concrete. But In this study, the addition of nano- TiO_2 particles decreased the fluidity and increased the water demand for normal consistency

Conclusions

The results show that the nano- TiO_2 particles blended concrete had significantly higher compressive strength compare 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. Although, the optimal level of nano- TiO_2 particles content was achieved with 1.0% replacement. Partial replacement of cement by nano- TiO_2 particles decreased workability of fresh concrete; therefore use of super plasticizer is substantial.

References

[1] Li H, Xiao HG, Yuan J, Ou J. Microstructure of cement mortar with nano-particles. Composites Part B: Engineering 2003; 35(March).
[2] Nazari A., Riahi, Sh, Khademno A., "Effects on nano- SiO_2 on mechanical properties of binary blended concrete", To be published.
[3] Lu P, Young JF. Hot pressed DSP cement paste, Material Research Society Symposium Proceedings, 1992; 245.
[4] Richard P, Cheyrezy M. Reactive powder concretes with high ductility and 200- 800 MPa compressive strength, San Francisco: ACI Spring Convention, SP 144–24, 1994.
[5] Jo BW, Kim CH, Tae G, Park JB. Characteristics of cement mortar with nano-SiO2 particles. Const Build Mater 2007; 21(6): 1351-1355.
[6] Ismail MS, Waliuddint AM. Effect of rice husk ash on high strength concrete. Const Build Mater1996; 10(1): 521-526.
[7] Sun MQ, Liu QP, Li ZQ, Hu YZ. A study of piezoelectric properties of carbon fiber reinforced concrete and plain cement during dynamic loading. Cem Concr Res 2000; 30: 1593– 1595.
[8] Sorelli L, Constantinides G, Ulm FJ Toutlemonde F. The nano-mechanical signature of Ultra High Performance Concrete by statistical nano indentation techniques. Cem Concr Res 2008; 38: 1447–1456.
[9] Zivica V. Effects of the very low water/cement ratio. Const Build Mater 2009; 23(8): 2846-2850.
[10] Bui DD, Hu J, Stroeven P. Particle size effect on the strength of rice husk ash blended gap-graded Portland cement concrete. Cem Concr Compos 2005; 27(3): 357–366.
[11] AI-Khalaf MN, Yousift HA. Use of rice husk ash in concrete. Int J Cem Compos Lightweight Concr 1984; 6(4): 241-248.
[12] Lin YH, Tyan YY, Chang TP, Chang CY. An assessment of optimal mixture for concrete made with recycled concrete aggregates. Cem Concr Res 2004; 34(8): 1373-1380.
[13] Tattersall GH, Baker PH, An instigation of the effect of vibration on the workability of fresh concrete using a vertical pipe apparatus, Magazine of Concrete Research 1989; 14 (146): 3–9.
[14] L. Courard, A. Darimont, X. Willem, C. Geers, R. Degeimbre, Repairing concretes with self-compacting concrete: testing methodology assessment, Proceedings of the First North American Conference on the Design and Use of Self-Consolidating Concrete, 2002, pp. 267–274.
[15] Felekoglu B, Tosun K, Baradan B, Altun A, Uyulgan B. The effect of fly ash and limestone fillers on the viscosity and compressive strength of self-compacting repair mortars. Cem Concr Res 2008; 36: 1719–1726.
[16] P.F.G. Banfill, The Rheology of Fresh Cement and Concrete—A Review, 11th International Cement Chemistry Congress, Durban, 2003. 13 pp.
[17] C. Lemmer, J. Hartman, T. Wolf, Rheological properties of mortars for self-compacting concrete, http://www.massivbau.tu-darmstadt.de/user/ lemmer/web/scc/LeDaCon199.htm, 13 pp.
[18] C.F. Ferraris, J.M. Gaidis, Connection between the rheology of concrete and rheology of cement paste, ACI Mater. J. (July–August 1992) 388–393.
[19] C.F. Ferraris,Measurement of the rheological properties of high performance concrete: state of the art report, J. Natl. Inst. Stand. Technol. 104 (1999) 461–478.
[20] M. Cyr, C. Legrand, M. Mouret, Study of the shear thickening effect of superplasticizers on the rheological behavior of cement paste containing or not mineral admixtures, Cem. Concr. Res. 30 (2000) 1477–1483.
[21] C.F. Ferraris, K.H. Obla, R. Hill, The influence of mineral admixtures on the rheology of cement paste and concrete, Cem. Concr. Res. 31 (2001) 245–255.
[22] S. Grzeszczyk, G. Lipowski, Effect of content and particle size distribution of high-calcium fly ash on the rheological properties of cement pastes, Cem. Concr. Res. 27 (1997) 907–916.
[23] F. Lange, N. Mortel, V. Rudert, Dense packing of cement pastes and resulting consequences on mortar properties, Cem. Concr. Res. 27 (1997) 1481–1488.

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