

## The effects of limewater on flexural strength of TiO<sub>2</sub> nanoparticles binary blended palm oil clinker aggregate-based concrete

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**Abstract:** Malaysia is the largest producer and exporter of palm oil in the world. However the palm oil refineries also produce tones of waste products known as palm oil clinker or POC. POC is normally disposed of in landfill or incinerated, incurring costs and causing negative environmental impact, such as pollution. Therefore the appropriate use of POC can help preserve the environment from undesirable effects, while at the same time contributes to cost reduction for the palm oil industry. The effect of limewater on flexural strength permeability of TiO<sub>2</sub> nanoparticles binary blended concrete has been investigated. TiO<sub>2</sub> 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<sub>2</sub> nanoparticles up to maximum replacement level of 2.0% produces concrete with improved flexural strength when the specimens cured in saturated limewater with respect to the specimens cured in water. TiO<sub>2</sub> 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<sub>2</sub> nanoparticles blended concrete causes high strength.

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**Key words:** TiO<sub>2</sub> nanoparticle; flexural strength; palm oil clinker; lightweight concrete.

POC produced in the boiler when the burning process of husk fiber and shell of palm oil. This burning process is the phase to generate the energy in order to generate the plant boiler in palm oil mill. According to Tay (1991) about 20 % by weight of ash and other residues (i.e. clinker) are produced after the burning process. The clinker turned as abundance of the factory compared to ash. Researches in palm oil industry had been discovered the uses of the palm oil fuel ash (POFA) either as commercial construction material or as fertilizer for the palm oil plant. Also, the ashes turn to potential usage as a detergent. Less of research of POC caused a large amounts of untreated waste and finally contribute of contaminate land, water and air.

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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 Cheyreyzy [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<sub>2</sub> 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<sub>2</sub> on flexural strength and water

permeability of binary blended concrete cured in water and limewater has been investigated.

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

Material	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> 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/cm<sup>3</sup>

Table 2. The properties of nano-TiO<sub>2</sub>

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

Table 3. Mixture proportion of nano-SiO<sub>2</sub> particles blended concretes

Sample designation	nano-SiO <sub>2</sub> particles	Quantities (kg/m <sup>3</sup> )	
		Cement	SiO <sub>2</sub> 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<sub>2</sub>] ratio of 0.40, sand 492 kg/m<sup>3</sup>, and aggregate 1148 kg/m<sup>3</sup>

## 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<sub>2</sub> with average particle size of 15 nm was used as received. The properties of nano-TiO<sub>2</sub> particles are shown in Table 2.

The clinkers forms are usually flaky and irregular with rough and spiky broken edges. The POC for this study was collected from a palm oil mill factory located at Kahang, Kluang. To ensure a better bonding with the clay, the clinker has been ground to powder form before combined together with clay and cement.

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<sub>2</sub> 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<sup>3</sup>. 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<sub>2</sub> 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 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 [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° C prior to test days. The strength and water permeability tests of the concrete samples were determined at 7, 28 and 90 days.

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

## 3. Results and discussion

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-TiO<sub>2</sub> 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<sub>2</sub> particles 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-TiO<sub>2</sub> 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 flexural

strength in the N series blended concrete are due to the rapid consuming of Ca(OH)<sub>2</sub> which was formed during hydration of Portland cement specially at early ages related to the high reactivity of nano-TiO<sub>2</sub> particles. As a consequence, the hydration of cement is accelerated and larger volumes of reaction products are formed. Also nano-TiO<sub>2</sub> particles recover the particle packing density of the blended cement, directing to a reduced volume of larger pores in the cement paste.

Table 4. Flexural strength of nano-TiO<sub>2</sub> particle blended cement mortars

Sample designation	nano-TiO <sub>2</sub> particle (%)	Flexural strength (MPa)		
		7 days	28 days	90 days
C0-W (control)	0	4.2	4.4	4.7
N1-W	0.5	4.7	5.0	5.4
N2-W	1.0	5.3	5.3	6.0
N3-W	1.5	4.8	5.1	5.5
N4-W	2.0	4.6	4.9	4.8
C0-LW (control)	0	4.0	4.1	4.2
N1-LW	0.5	5.0	5.6	5.7
N2-LW	1.0	5.7	6.1	6.2
N3-LW	1.5	6.0	6.4	6.4
N4-LW	2.0	6.5	6.8	6.9

Water to binder [cement + nano-TiO<sub>2</sub>] ratio of 0.40

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

Table 4 also shows the flexural strength of C0-LW and N-LW series. The results show that the replacement of cement by TiO<sub>2</sub> 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 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 Ca(OH)<sub>2</sub> 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 Ca(OH)<sub>2</sub> which needs to form C-S-H gel. When TiO<sub>2</sub> nanoparticles react with Ca(OH)<sub>2</sub> 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)<sub>2</sub>. 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 TiO<sub>2</sub> nanoparticles up to 2.0 wt% (N4-LW) while for N-W series it increases by partial replacement of cement with TiO<sub>2</sub> 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<sub>2</sub> 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 Ca(OH)<sub>2</sub> in N-LW series after the 28 day causes reduction in flexural strength. In the other words, curing of the TiO<sub>2</sub> nanoparticles blended concrete in saturated limewater after 28 days is completely suitable to achieve high strength especially with high weight percent of nanoparticles.

### Conclusions

The results show that the nano-TiO<sub>2</sub> particles blended concrete had higher flexural strength compared to that of the concrete without nano-TiO<sub>2</sub> particles. It is found that the cement could be advantageously replaced with nano-TiO<sub>2</sub> 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<sub>2</sub> particles content was achieved with 1.0% replacement for the specimens cured in water 7, 28 and 90 days.

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