Assessments of the effects of limewater on water permeability of TiO_2 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 water 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 water permeability 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.

[Farzad Soleymani. **Assessments of the effects of limewater on water permeability of TiO_2 nanoparticles binary blended palm oil clinker aggregate-based concrete.** J Am Sci 2012;8(5):698-702]. (ISSN: 1545-1003). http://www.americanscience.org. 76

Key words: TiO_2 nanoparticle; water permeability; 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_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 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_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

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.

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_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 water permeability 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.

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.

Percentage of water absorption is an evaluation of the pore volume or porosity of concrete after hardening, which is occupied by water and limewater in saturated state. Water absorption values of TiO_2 nanoparticle blended concrete samples were measured as per ASTM C 642 after 7, 28 and 90 days of moisture curing.

Velocity of water absorption is a measure of the capillary forces exerted by the pore structure causing fluids to be drawn into the body of the material [19]. In this experiment, the speed of water absorption by concrete cubes were considered by measuring the increase in the mass of samples due to water absorption at certain times when only one surface of the specimen is exposed to water. Concrete samples were dried in an oven at 50^o C for three days and then cooled in a sealed container at 23^o C for fifteen days as per ASTM C1585 after 7, 28 and 90 days of moist curing [20]. The sides of the concrete samples were covered with epoxy resin in order to allow the flow of water in one direction. The end of the samples were sealed with tightly attached plastic sheet and protected in position by an elastic band. The initial mass of the samples were taken after which they were kept partly immersed to a depth of 5mm in water as shown in Figure 1. The readings were started with the initial mass of the sample at selected times after first contact with water (typically 1, 5, 10, 20, 30, 60, 110 and 120 min) [21], the samples were removed, excess water was blotted off using paper towel and then weighed. Then they were replaced again in water for the chosen time period. The gain in mass

(Δm, m^3/m^2) at time t (s), exposed area of the specimen (a, m^2), and density of water (d), were used to obtain the rate of water absorption (I, m/s $^{1/2}$) as per the equation [20]:

$$I = \frac{\Delta m}{(a/d)} \qquad (1)$$

Coefficient of water absorption is considered as a measure of permeability of water [22]. This was measured by determining the rate of water uptake by dry concrete in a period of 1 h [21]. The concrete samples were dried at 110° C in an oven for one week until they reached to constant weight and then were cooled in a sealed container for one day. The sides of the samples were covered with epoxy resin, and were placed partly immersed in water to a depth of 5 mm at one end, and at the other end a tightly attached plastic was secured in position by an elastic band as shown in Figure 1 [21]. The amount of water absorbed during the first 60 min was calculated for TiO_2 nanoparticles blended concrete samples after 7, 28 and 90 days of moisture curing using the formula [20]:

$$Ka = \left[\frac{Q}{A}\right]^2 . \frac{1}{t} \qquad (2)$$

where Ka is the coefficient of water absorption (m^2/s), Q is the quantity of water absorbed (m^3) by the dried samples in 3600 s and A is the surface area (m^2) of concrete samples through which water penetrates.

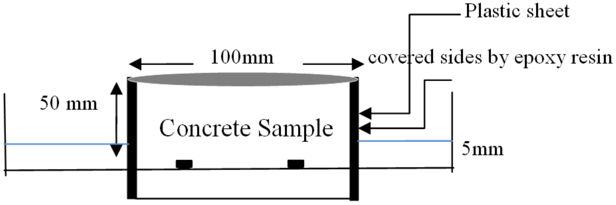

Figure 1. Velocity of water absorption and coefficient of water absorption test.

3. Results and discussion

3.1. Percentage of water absorption

The results of saturated water absorption at different ages of moist curing are shown in Table 4. As it can be seen, the percentage of water absorption of concrete samples immersed in water and saturated limewater decreases with the increase in the age of moist curing from 7 to 90 days for all series during the hardening process of the concrete. In the other words, strengthening gel formation in the presence of nanoparticles especially for the specimens cured at saturated limewater are high enough reduces the water absorption of the blended concrete. This reduction is more for N-LW series as a result of more strengthening gel formation. However this difference is not too high because of this fact that the water permeability is significantly related to the content of pores in the concrete which is equal for two N-W and N-LW series at a certain nanoparticles content.

It was observed that the reduction of water absorption was found at the 7 days curing for N series compared to C0 series. The decrease in water absorption which is related to the increase in the amount of TiO_2 nanoparticles can be resulted from the reduced amount of pores. These results were achieved because of fewer hydration products when the pozzolanic reaction is small at the early ages for C0 series reverse of the N series. On the other hand, the percentage of water absorption related to the porosity of the hardened concrete which is engaged by water in saturated state [23] was more in series C0 compared to N series at the early ages. But by increasing the age of curing to 90 days the percentage of water absorption values decreases significantly with the increase in nanoparticles content up to 2.0%. Therefore, it can be suggested that with prolonged curing, increasing the ages and percentages of TiO_2 nanoparticles in both series can lead to reduction in permeable voids. This is due to the pozzolanic action of TiO_2 nanoparticles and filler effect provided by both series of TiO_2 nanoparticles. Another finding is that the interfacial transition zone in concrete had improved due to pozzolanic reaction as well as filler effect of the TiO_2 nanoparticles. This finding is partially in confirmation of the results of the study by Bui et al. [18].

3.2. Velocity of water absorption

The velocity of water absorption of all two series is shown in Table 5. It can be seen that at 7 days of curing, there was a progressive reduction in the velocity of water absorption in series N. With increase of TiO_2 nanoparticles content up to 2.0%, an increase in the velocity of water absorption was observed but the values are still lower than the control concrete. With progressing in the curing time until 90 days the velocity of water absorption for N series at all replacement contents are quite lower than C0 series.

It is well known that mineral admixtures with fine particles can improve the filler effect and also the high pozzolanic action of fine particles increases substantially the quantity of strengthening gel. If this phenomenon joins with low water cement ratio, it can improve the microstructure in the interfacial transition zones and thus the value of C–S–H gel, then the water permeability can be considerably increased.

All these events result in more homogeneous and stronger interfacial transition zones and reduction of their thickness, with less potential of micro cracks and uniform particle distribution that lead to the grain refinement of hydrated cement paste in the interfacial transition zone [25, 26]. Hence, admixing of TiO_2 nanoparticles especially with ultra fine particles of conventional concrete may lead to rearrangement and improvement of the concrete microstructures physically and chemically. The speed of water absorption is very important to predict the service life of concrete as a structural material and to improve its performance [27].

Micro filler materials with fine particles can fill both the interfaces and the bulk paste and develop discontinuous and tortuous pore in concrete structure causing reduction in the rate of water absorption [28, 29]. Micro and macro pores present in the concrete can be completely filled up by finer particles [30]. High reactive pozzolanic materials are able to reduce the size of voids in concrete, thus, making it almost impermeable even at early ages of 7 to 28 days [31]. The connectivity of pore system is characterized by the degree of water in filled voids in the concrete mix and the hydration products of concrete after hardening. Capillary pores are known as those voids which were originally filled with mixing water in the range of 3.2– 3000 nm diameter [32]. These capillary pores can become unconnected under moist curing situation after about 3 days for concrete having w/ c of 0.4 [33]. TiO_2nanoparticles blended concrete shows a continued decrease of pore size and its continuity by increasing the curing time than ordinary Portland cement concretes.

The effect of the saturated limewater is once more related to the content of strengthening gel formation which accelerates the velocity of water absorption after 7 days of curing for N-LW series with respect to N-W series to form more strengthening gel and then decreases because of rapid formation of strengthening gel.

Table 4. Percentage of water absorption in control and TiO_2 nanoparticles blended concrete.

Mix designation	TiO_2 nanoparticles (%)	7days	28days	90 days
C0-W (control)	0	3.30	5.60	4.80
N1-W	0.5	4.09	2.29	0.88
N2-W	1.0	4.39	2.57	1.12
N3-W	1.5	4.69	2.74	1.34
N4-W	2.0	5.26	2.94	1.63
C0-LW (control)	0	3.32	5.71	4.92
N1-LW	0.5	6.10	1.50	0.60
N2-LW	1.0	6.52	1.63	0.82
N3-LW	1.5	6.89	1.79	1.15
N4-LW	2.0	7.06	1.95	1.36

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

Table 5. Velocity of water absorption ($m/s^{1/2}$) in control and TiO_2 nanoparticles blended concrete.

Mix designation	TiO_2 nanoparticles (%)	7days	28days	90 days
C0-W (control)	0	13.02	12.34	10.14
N1-W	0.5	15.15	13.87	9.03
N2-W	1.0	15.31	14.60	9.44
N3-W	1.5	14.92	14.69	9.54
N4-W	2.0	15.52	15.05	9.69
C0-LW (control)	0	13.06	12.56	10.18
N1-LW	0.5	17.56	11.15	8.30
N2-LW	1.0	17.98	11.45	8.73
N3-LW	1.5	17.32	11.87	9.22
N4-LW	2.0	17.68	12.04	9.34

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

Table 6. Coefficient of water absorption (m^2/s) in control and TiO_2 nanoparticles blended concrete.

Mix designation	TiO_2 nanoparticles (%)	7days	28days	90 days
C0-W (control)	0	9.02	2.86	1.35
N1-W	0.5	10.62	3.49	1.21
N2-W	1.0	11.10	3.87	1.27
N3-W	1.5	11.21	4.19	1.28
N4-W	2.0	11.46	4.45	1.32
C0-LW (control)	0	9.06	2.78	1.40
N1-LW	0.5	13.42	2.35	1.15
N2-LW	1.0	13.56	2.42	1.21
N3-LW	1.5	13.77	2.69	1.22
N4-LW	2.0	13.98	2.91	1.31

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

3.3. Coefficient of water absorption

The coefficients of water absorption of TiO_2 nanoparticles blended concrete samples for all series are presented in Table 6. Significant reductions in the coefficient of water absorption can be observed with increase in TiO_2 nanoparticles content up to 2.0% for series N at 7 days of curing. For series N at the same age of 7 and 28 days, the values of coefficient of water absorption are lower than those of the control concrete at all cement replacement contents. Likewise, at 90 days of curing, the coefficient of water absorption values up to 2.0% are quite lower than those of the control concrete for N series confirming that cement replacement by TiO_2 nanoparticles with prolonged curing leads to a reduction of pore spaces and permeable voids in the concrete. Again, the effect of the saturated limewater is once more related to the content of strengthening gel formation which significantly reduces the coefficient of water absorption after 7 days of curing for N-LW series with respect to N-W series.

Conclusions

The results show that the nano-TiO_2 particles blended concrete had higher flexural 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. Test results show a significant reduction in percentage of water absorption, velocity of water absorption and also coefficient of water absorption at all ages with TiO_2 nanoparticles.

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3/25/2012