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Effect of Titanium Dioxide on Properties of Cement Mortar Blended Periwinkle Shell Ash

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Abstract : Pozzolana cement/concrete has been identified with the problem of early strength development by many researchers, this was due to the slow pozzolanic reactions in pozzolana mortar/concrete, which also denies its usage where early strength is of paramount. To arrest this, several additives are being added to enhance its early strength development. The introduction of titanium dioxide (TiO_2) at different percentage replacements of 2%, 4%, 6% and 8% of the weight of cement on the optimum dosage of periwinkle shell ash as adopted from the work of Olusola & Akaninyene (2012) serve as control specimen (0%TiO_2) in this research with a designed mortar of grade 7.5N/ mm^2 at 28days. This study therefore, examine the effect of titanium dioxide (TiO_2) on the properties of cement mortar blended periwinkle shell ash (PSA). The rheological properties and the compressive strength were carried out at 3, 7, 14 and 28days. Decreased in consistency for the mortar was observed as TiO_2 percentage increases when compared with the control. Likewise, the initial and final setting time of the mortar decreases as the percentage replacement of TiO_2 increases. The compressive strength tends to increase by increasing the amount of TiO_2 compared to the control up to 6% replacement of TiO. It was concluded that the addition of TiO_2 to mortar mixes reduces the measured flow in accordance with ASTM: C 1437– 07. It therefore, improves the rheological properties of the cement mortar, and the compressive strength was increased with the inclusion of TiO_2 at almost all the percentages with 6% TiO_2 as the optimum dosage.

Keywords: Periwinkle shell ash; titanium dioxide; rheological properties; compressive strength

1.0 Introduction

The production of Portland cement characterizes the production of mortar/concrete as one of the major contributors to global warming with the excessive carbon dioxide released during the production process of cement as well as aggregates (Malhotra, 2002). To deal with this major issue of CO_2 emissions, considerable efforts are being taken worldwide to improve on the strength and durability performance of concrete through the use of pozzolanic materials. In making more effort for cost-efficient and environmentally acceptable materials for construction, the call for sustainability globally supported by the American Concrete Institute (ACI) has also encouraged the development and application of new construction materials which are locally available, renewable, and environmentally friendly. Recently, there has been a growing interest in the use of agricultural wastes as pozzolans. Some of the pozzolans of agricultural waste origin include sawdust ash (Sumaila & Job 1999; Udoeyo & Dashibil 2002), rice husk ash (Zhang & Malhotra 1996), corn cob ash (Adesanya 2001; Adesanya and Raheem 2009), palm oil fuel ash (Tangchirapat et al. 2009) and periwinkle shell ash (Badmus et al. 2007; Job et al. 2009; Koffi 2008).

Many researchers over decades proved the suitability of pozzolanic materials such as periwinkle shell ash (PSA) which is an agricultural waste in the production of concrete to partially replaced ordinary Portland cement. Ekop, Adenuga, and Umoh, (2013), also reported that, researchers in Nigeria in recent times have made use of periwinkle shell both for construction and non-construction purposes. The use of periwinkle shell ash (PSA) as partial replacement of cement in concrete has been extensively investigated in recent years. It is generally proved by researchers that pozzolana concrete encountered certain challenges out of which is poor/low early strength and durability issues as related to permeability properties. Generally, pozzolana as partial replacement of cement in mortar/concrete have been reported to have low strength gain especially during the early ages, this is a situation that makes it usage not feasible where early strength is of paramount importance (Akaninyene & Olusola, 2012).This is due to the slow pozzolanic reactions in PSA mortar/concretes, since pozzolanic reaction depends on the liberation of calcium hydroxide from cement hydration, the effect became much more beneficial to compressive strength development of concrete at later ages (Kolapo & Akaninyene, 2012). This deficiency of slow strength gain especially during the early ages will deny PSA concrete to be suitable in the construction where early strength is of paramount importance such as offshore structures, highly strength performing concrete and where concrete permeability is highly required. The reduction of porosity is essential to guarantee the strength and durability of the structure, (Juliana, 2006).

Similarly, researches have been carried out to improve the strength and permeability properties of concrete through the use of nano materials such as titanium oxide in concrete matrix. It is proved that, Nano iron oxide (NanoFe_2O_3) and Nano silicon dioxide (NanoSiO_2) particles fills the pores and also reduce the contents of $Ca(OH)_2$ within the hydration period (Li, 2004). These effects are responsible for the improvement of mechanical properties of mortar/concrete with Nano-particles. It was also confirmed that the pozzolanic activities of fly ash can significantly improve by the application of Nano SiO_2, which was concluded that the use of Nano SiO_2 leads to an increase of both early age and ultimate strength of high-volume fly ash concrete (Li, 2004). The use of nanotechnology materials while being incorporated in constructional structures would not only help in prolonging their lifetime, but would also keep a check on the energy spent by them and at the same time gauging their reactions and reacting to different agents like fire, corrosion, water penetration, fractures, cracks, etc. Researches shows that the incorporation of nanomaterials in mortar/concrete production contributes in filling the pores in mortar/concrete, thereby increasing the density and subsequently the strength of mortar/concrete right from early to later age. It also improves the strength of mortar/concrete produced with pozzolanic materials at the same time improves the permeability properties of mortar/concrete in general. It is expected that the introduction of nano materials in the PSA blended mortar will enhance it early strength development. Therefore, this study investigates the effect of incorporation of TiO_2 in cement mortar produced with periwinkle shell ash as partial replacement of cement.

2.0 Methodology

2.1 Materials

Ordinary Portland cement (OPC) was in conformity to NIS 444, (2001) was used. The Periwinckle shell ash (PSA) was processed from the calcination of periwinkle shells collected from Jos, Plateau state of Nigeria, at a temperature of 800°C. The ash was grounded and sieved with 45μm size. The titanium dioxide (TiO_2) was supplied from Odibest chemical company zaria in a powdered form. The TiO_2 was a company processed powder from Germany. The powder is pure silky white in colour with no specific smell. The fine aggregate was that of river-bed and the sieve analysis (Table 1) revealed that it falls within zone 2 fine aggregate (Figure 1).

The physical properties and physical appearance of the PSA and TiO_2 were presented in Tables 2, plate I and Plate II. While the particle size distribution values of TiO_2 powder and chemical properties of cementitious materials obtained by XRF analysis were presented in table 3 and 4 respectively.

Table 1. Sieve analysis of fine aggregate

Sieve size	ASTM C33 Finer limit	ASTM C33 coarser limit	Weight of aggregate retained (gm)	% of total weight retained	Cumulative % of total weight retained	% Passing
10mm	100	100	0	0.0	0.0	100
4.75mm	100	95	0	0.0	0.0	100
2.36mm	100	80	159.0	15.90	15.90	84.1
1.18mm	85	50	324.3	32.43	48.33	51.7
600µm	60	25	308.7	30.87	79.20	20.8
300µm	30	5	134.3	13.43	92.63	7.4
150µm	10	0	58.0	5.80	98.43	1.6
75µm	-	-	12.3	1.23	99.66	0.34
Pan	-	-	3.4	0.34	100	0.0

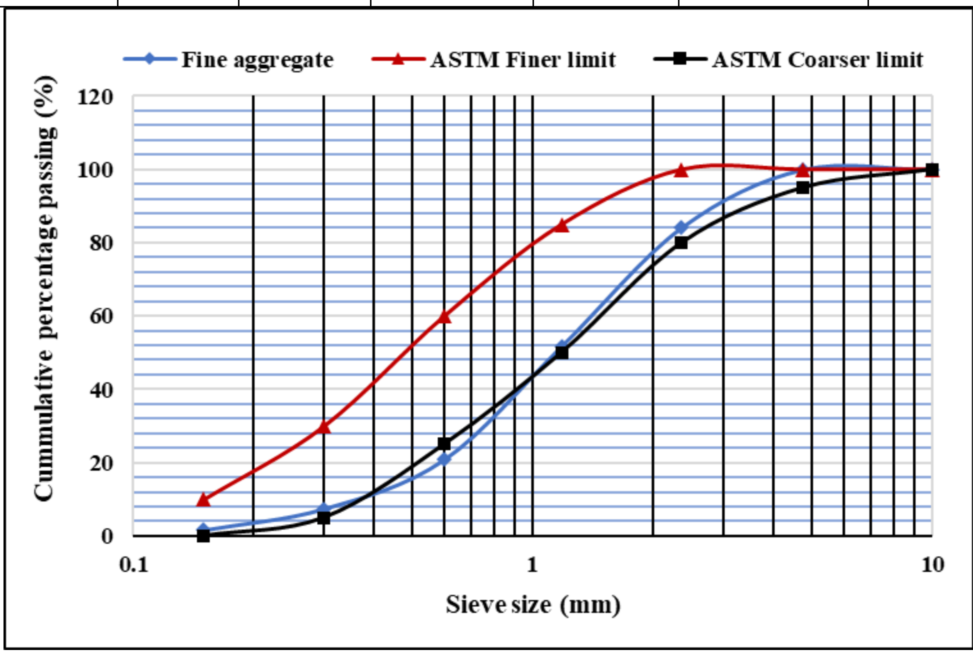

Figure 1; Sieve analysis graph.

Table 2. Physical properties of materials

Properties	Cement	PSA	Fine aggregate	TiO_2
Fineness modulus	-	-	2.71	-
Coefficient of uniformity	-	-	2.48	
Particle size	-	-	-	0.2912-0.672
Purity	-	-	-	98%
Specific Gravity	3.12	2.14	2.64	3.89
Consistency (%)	27.70	-	-	-
Soundness	-	0.08	1.00	-
L.O.I	-	-	-	0.13%

Physical appearance of PSA and TiO_2

Plate I; Periwinkle shell ash (PSA)

Plate II; Titanium dioxide (TiO_2)

Table 3; Particle size distribution values of TiO_2 powder

No	Diameter (μm)	q(%)	retained weight
20	0.161	0.000	0.000
22	0.197	0.510	0.677
24	0.269	2.936	4.917
26	0.338	9.842	20.673
28	0.446	16.458	50.989
30	0.584	13.267	80.934
32	0.766	6.539	95.186
34	1.006	1.287	99.337
36	1.318	0.165	100.00

Table 3; Chemical Properties of Cementitious Materials obtained by XRF Analysis

Constituents	Cement	PSA	TiO_2
Fe_2O_3	3.05	4.08	0.51
Al_2O_3	5.85	8.89	0.25
SiO_2	20.06	33.20	0.32
P_2O_5	0.17	0.04	-
SO_3	2.71	0.16	-
K_2O	0.97	0.10	-
CaO	62.44	46.6	0.20
TiO_2	0.28	0.06	98.72
SnO_2	-	1.0	-
MgO	1.93	-	-
Na_2O	0.14	-	-
LOI	1.09	4.06	1.34

2.2 Proportioning and mixing of constituents

A mortar grade $7.5N/mm^2$ at 28 days was designed using the Department of Environment (DOE) Method. The optimum dosage of PSA used was 10% adopted from the work of Olusola & Akaninyene (2012) which serves as the control specimen (0%TiO_2). A design was made for 12 cubes for having 0%, 2%, 4%, 6%and 8% replacements of TiO_2. A water/cement ratio of 0.5 was adopted.

The ingredients (cement, PSA, TiO_2 and water), were manually mixed on an impermeable platform. The blended cement, PSA and TiO_2 was spread on already measured sand, and mixed thoroughly before water was added. Mixing was assumed to be completed when a homogenous mix was obtained.

3.0 Workability Test on Fresh Mortar

3.1 Flowability test

The flow table test was conducted in accordance with standard test method for flow of cement mortar ASTM C230 (2001). The degree of flowability of the mortar mixes for both control (0% 0% TiO_2) and TiO_2 mortar were determined by flow table as shown in plate IIIa, IIIb, and IIIc.

Plate IIa

Plate IIb

Plate IIc. (Plate II a-c Showing the flowability test of the mortar produced).

3.2 Setting time test

The initial setting time and final setting time was carried out in accordance with standard test method for setting time of cement mortar ASTM C191 (2001). The degree of initial and final setting time of the mortar mixes for both control (%TiO_2) and TiO_2 mortars were determined using vicat apparatus as shown in plate IV.

Plate III; Setting time of mortar

3.2 Casting and curing of specimens for test

Cast iron moulds of 50mm x 50mm x 50mm were used to produce the mortar cubes. The moulds were thoroughly cleaned and oiled to allow for easy removal of mortar cubes. The mortar was placed in approximately three equal layers and each layer was rammed with 25 strokes of 50mm round ended rod. The cubes were de-moulded at 24 hours, and immersed in water curing tanks kept at a temperature of 29.0 ± 1.0 up to 28days.

3.3 Compressive strength test

The compressive strength test was carried out in accordance with ASTM C109 (2001)/C109M (2001), Standard test method for compressive strength of hydraulic cement mortars. The total of 60 samples specimens of control (10% PSA as adopted) and TiO_2 mortar of 50 x 50 x 50 were produced. 12 sample specimens were for control (0% TiO_2) which is 10 % PSA as adopted and 48 sample specimens were for TiO_2. All the sample specimens were crushed at saturated surface dry condition. The crushing was carried out at 3, 7, 14, and 28 days respectively, using the hydraulic crushing machine of 1000kN capacity in Abubakar Tafawa Balewa University, Building Department concrete laboratory. The failure load recorded was divided by the cross-sectional area to obtain the compressive strength.

4.0 Results and Discussion

4.1 Rheological properties

4.1.1 Flow Table Test

The flow table test was conducted based on 2%, 4%, 6%, and 8% replacement of TiO_2 to the mortar with constant 10% PSA. The results were compared with that of control samples of 10% PSA and 0% TiO_2. The comparison was used to ascertain the extent to which the TiO_2 affect the flowability of the mortars. The result was shown in Figure 2.

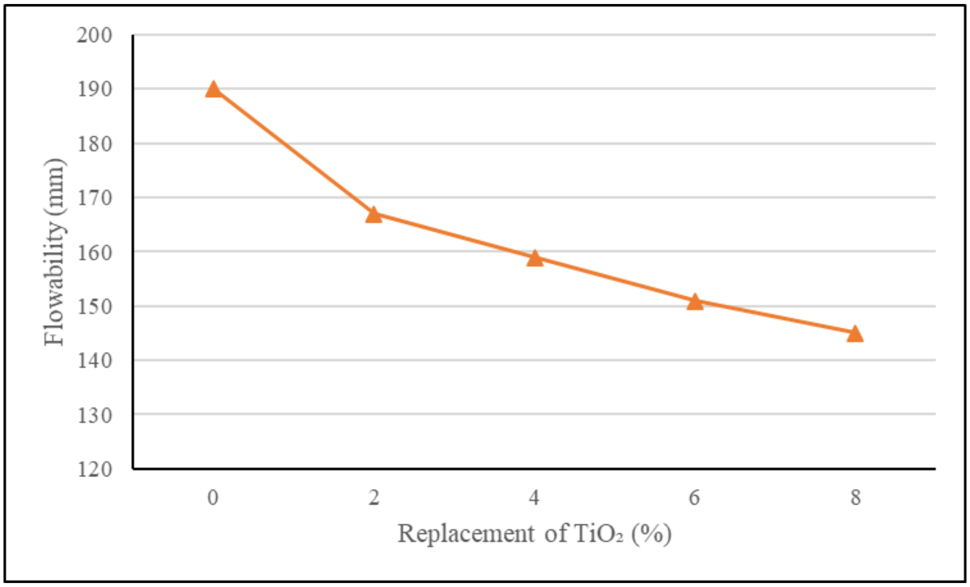

Figure 2; Flow table test results for the mortars

The figure shows decrease in consistency for the mortar as TiO_2 percentage increase when compared with the control. The percentage decrease in consistency of the mortar when compared with the control were 12.1%, 16.3%, 20.5% and 23.7% for 2%, 4%, 6% and 8% replacement of TiO_2 respectively. This reason for the tread may be attributed to the capacity of TiO_2 to absorb the mixing water (hydrophilic material) and the high specific surface area of the TiO_2.

4.1.2 Setting Time

The results of setting time were conducted based on 2%, 4%, 6%, and 8% replacement of TiO to the mortar with constant 10% PSA were compared with that of control samples of 10% PSA and 0% TiO_2. The comparison was used to ascertain the extent to which the TiO_2 affects the setting time of the mortars. The results of the percentage replacement of TiO_2 to the PSA mortar were shown in Figure 3.

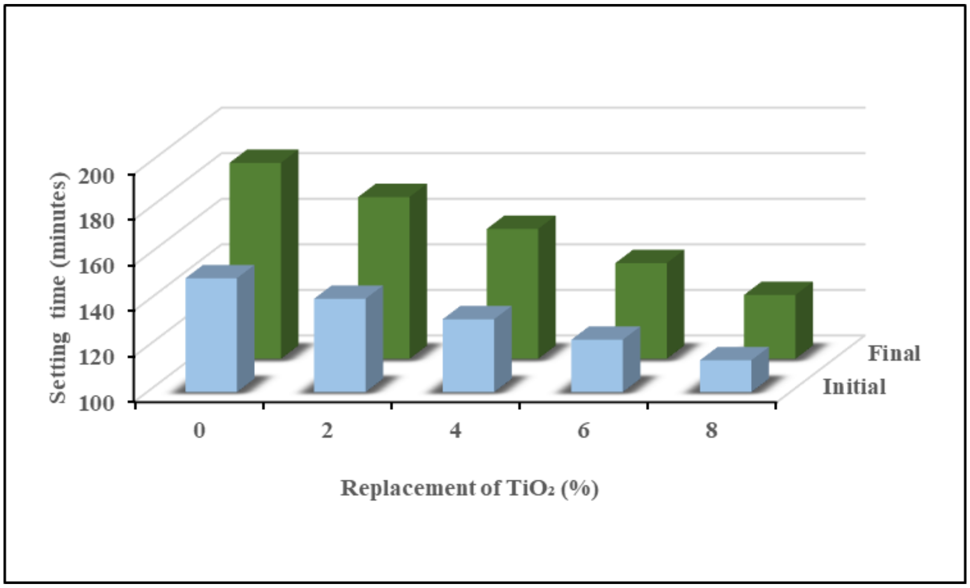

Figure 3; Setting time results

The Figure shows the initial and final setting time of 2%, 4%, 6% and 8% replacement of TiO_2 to the mortar. It was clearly shown that the initial and final setting time of the samples decreases as the percentage replacement of TiO_2 increases. The percentage decrease in initial and final setting time between the control specimen compared 8% and 6% TiO_2 mortars were 24%, 31.2% and 18%, 23% respectively. While the percentage decrease in initial and final setting time between the control sample to 4% and 2% TiO_2 were 12%, 15.6% and 26%, 8.1% respectively. This may be attributed to the cementitious composites due to its role as an accelerator (Mahmud and Mohammed, 2022).

4.1.3 Result of Compressive Strength Test

The results of the compressive strength test based on 2%, 4%, 6%, and 8% replacement of TiO_2 to the mortar with constant 10% PSA were compared with that of control samples of 10% PSA and 0% TiO_2. The comparison was used to ascertain the extent to which the TiO_2 affect the strength of the hardened specimens. The results were shown in Figure 4.

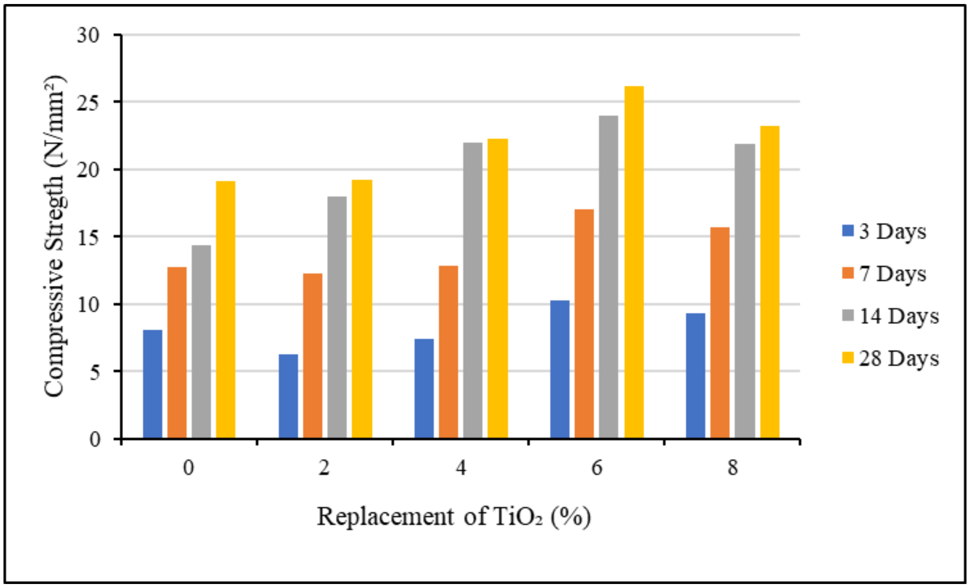

Figure 4. Compressive strength test at 3, 7, 14, and 28days

Figure 4 also shows the average compressive strength of all samples at all ages of 3, 7, 14, and 28days. The compressive strength tends to increase by increasing the amount of TiO_2 compared to the control up to 6% replacement of TiO_2. The percentage increase in strength between control (0%) and 6% for 3, 7, 14 and 28days was 21.4%, 25.5%, 40%, and 27% respectively. This could be attributed to the presence of TiO_2 nanoparticles that lead to more formation of hydrated products. The increase in compressive strength could also be attributed to the facts that titania nanoparticles enhance the microstructure properties by improving the homogeneity, enhancing the compaction and reducing the pore volume and size of cement-based materials. While the mortar starts dropping in compressive strength when the percentage of TiO_2 was increased to 8%. The percentage decrease in strength from 6% to 8% TiO_2 replacement for 3, 7, 14 and 28days was 8.9%, 8.0%, 87%, and 11.3% respectively. This may be attributed to the amount of titania nanoparticles required to liberate with cement during hydration was exceeded by increasing the pore volume and size of cement-based material. It could also be related to the agglomeration and bad dispersion of nanoparticles which lead to weak zones.

5.0 Conclusion

1. The addition of TiO_2 to mortar mixes reduces the measured flow in accordance with ASTM: C 1437 (2007). It therefore, improves the rheological properties of the cement mortar.
2. The initial and final setting time of mortar was carried out in accordance to ASTM C403 and found increased with the increase in TiO_2 at all percentages, therefore increase in early strength development.

3. The compressive strength of mortars was tested in accordance with ASTM C109/C109M (2016) and found increased with the inclusion of TiO_2 at all percentages except 2 and 4 replacement. it with established that the 6% TiO_2 was the optimum dosage with respect to early strength development.

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