Effect of Nano-Titanium on Properties of Concrete Made With Various Cement Types

Yasser Abdelghany Fawzy

Structural Engineering Department, Faculty of Engineering, Beni-Suef University, Egypt
Yasser_gaeb@yahoo.com

Abstract: This paper investigates the influence of nano- titanium on fresh property of concrete (slump), mechanical properties (compressive- splitting tensile strength).The thermal gravimetric analysis (TGA) and scanning electron microscope (SEM) of cement paste containing various cement types is also investigated. Concrete specimens were prepared with various cement Types (OPC-SRPC- blended cement with sand), water, sand and dolomite or gravel admixed with nano-titanium. The percentage of nano- titanium/ cement was 0, 0.5, 1and 2 % at w/c = 0.50. The effect of quantities of cement (250-350 and 400 Kg/m^3) on concrete properties were also considered. The results indicated that, there is no noticeable change in slump values of concrete containing OPC or SRPC, whereas, the concrete containing blended cement with sand exhibited an increase in slump values when compared to concrete made with the other cement types. Increasing the percentage of nano titanium beyond 1% led to decreases the concrete slump. Introducing nano titanium in concrete mix enhances the mechanical properties of concrete, the optimum percentage of nano-titanium in concrete mix made with OPC or SRPC or blended cement with sand is 1%.

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Keywords: Nano- titanium; concrete; cement types; compressive strength; TGA; blended cement.

1. Introduction

Recently, there are large numbers of applications of nanotechnology in the construction engineering field. Nano-materials pertaining to things on a scale of approximately to 100 nano meters (nm) (ASTM E 2456-06). Recently nano technology is being used in many applications and it has received increasing attention in building materials. Various nano materials such as nano silica, nano aluminum, nano titanium are used in concrete. The slump of concrete specimens with 1% nano titanium by cement weight do not show any significant increase, beyond with a 6% increase in slump was observed for every percent increase in TiO_2 (Scientific Co operations International Workshops on Engineering Branches, 2014). However, the use of nano materials improves the various characteristics of concrete, such as workability, strength and durability (Birgisson et al, 2012, Hao and Sun, 2014 and Jalal, M. et al, 2013). The partial replacement of cement with nano TiO_2 particles decreases the workability (Nazari, A. et al, 2010:6, pp.43-46). The addition of 1% TiO_2 by cement weight to concrete gave 18.5 % improvement in the 7 days compressive strength. This gain in strength started to decrease beyond the 1% TiO_2 with a decreasing rate of 1.34% at every 1% increment of nano titanium (Scientific Co operations International Workshops on Engineering Branches,2014). The nano particles can be very effective in improvement of both mechanical and durability of concrete (Shekan and Razzaghi, 2011).TiO_2 nano particles have lowered the compressive strength at 28 days of curing.This is probably as a result of the negative impact of TiO_2 nano particles on C_2S hydration which contributes to long term properties of hardened concrete (Behfamia and Keivan, 2013). The strength of mortar which was substituted by TiO_2 nano particles increased at early ages and decreased remarkably after 28 days of curing (Taom et al, 2012). On the other hand, some researches studied different types of nano particles including TiO_2 and announced that increasing TiO_2 nano particles up to 4% weight of cement can improve the mechanical properties of concrete (Nazari A. and Riahi S., 2010). The nano titanium particles had higher splitting tensile strength when compared to control mix, the cement could be advantageously replaced with nano titanium up to maximum limit of 2%, the optimal level of nano titanium was achieved with 1% replacement (Nazari A. et al, 2010:6, pp.98-101). It is noted that most of the study on nano titanium in concrete has been focused on the effect of nano titanium on fresh and mechanical properties of concrete and there is lack of information on the impact of nano titanium on properties of concrete containing different types of cement and microstructure of concrete, as well as, determine the optimum percentage of nano titanium used. This study focuses on the impact of nano titanium on concrete properties made with various types of cement. The percentages of nano titanium were 0, 0.5, 1 and 2%, the quantities of cement were 250,350 and 400 Kg/m^3. The w / c used for all mixes were 0.50.The effect of nano titanium on slump, compressive and splitting tensile strength, thermal gravimetric analysis (TGA) and scanning electron microscope (SEM) were investigated.

2. Experimental Program

21. Materials

Three types of cement were used in this investigation; the first type is normal Portland cement, it was delivered from "Beni- suef cement company", Type CEMI 42.5 N; the second type is SRPC, it was also delivered from "Beni- suef cement company"; the third type is blended cement with sand, it was delivered from " Al Qumia cement company". Testing of cements was carried out per the Egyptian Standard Specifications (ESS 2421/2005) for OPC and SRPCC, whereas, per the Egyptian Standard Specifications (ESS 1078/ 2005) for blended cement with sand. The chemical and physical analysis of these cement types is presented in Table 1. Nano titanium of rutile type was used as nano materials. The properties of nano-titanium is presented in Table 2. Natural siliceous sand with fineness modulus 2.73 was used as fine aggregates. Dolomite and gravel with 20 mm maximum nominal size were used as coarse aggregates; tap water was used for mixing and curing.

2.2 Mixture proportions

Thirty two mixtures were tested in this research, these mixtures were made with percentage of nano titanium to cement = 0, 0.5, 1and 2 %. Dolomite or gravel of 20 mm maximum nominal size was mixed with cement, sand, nano titanium and water. The mix constituents were 250,350 and 400 Kg cement, 1200Kg dolomite or gravel, and 600 Kg sand per cubic meter of concrete at w/c = 0.50. These constituents of concrete were mixed in mixer for two minutes, and then placed in cube moulds, 15×15×15 cm for compressive strength testing, whereas, the specimens for splitting tensile testing were cylinders 15x30 cm. Cylindrical paste specimens 5 cm diameter and 0.50 cm height were used for thermo-gravimetric analysis (TGA). Table 3 presents the masses of materials used (kg/m^3). Table 4 shows the tests that were conducted, sizes of specimens and testing ages.

Table 1: Chemical and physical analysis of cement types.

Property	OPC	SRPC	Blended cement with sand
Chemical composition, %			
SiO_2	20.56	20.42	12.65
Al_2O_3	5.59	3.79	9.46
Fe_2O_3	2.65	4.49	8.51
CaO	63.13	63.31	-
MgO	1.94	1.88	2.39
Na_2O	0.43	0.36	-
K_2O	0.22	0.19	-
SO_3	2.61	2.37	-
$CaCO_3$			57.54
MoO_2			8.35
Ca			36.38
b- physical properties			
Initial setting time, min.	135	125	100
Final setting time, min.	300	280	250
Specific surface, m^2/kg	370	360	330
Soundness, mm	2	2	3
c- compressive strength, Kg/ cm^2			
3 days	250	220	160
7 days	350	330	270

Table 2: The properties of nano titanium

Diameter (nm)	Density(g/cm^3)	Purity (%)
15	< 0.12	>99.8

Table 3: Composition of the concrete mixtures (Kg/m^3).

Mix no.	%nano titanium	w/c	Cement	sand	Total coarse aggregate	Cement type	Coarse aggregate type.
1	0	0.50	250	600	1200	OPC	Dolomite
2	0.5						
3	1						
4	2						
5	0	0.50	250	600	1200	SRPC	Dolomite
6	0.5						
7	1						
8	2						
9	0	0.50	250	600	1200	Blended cement with sand	Dolomite
10	0.5						
11	1						
12	2						
13	0	0.50	350	600	1200	OPC	Dolomite
14	0.5						
15	1						
16	2						
17	0	0.50	350	600	1200	SRPC	Dolomite
18	0.5						
19	1						
20	2						
21	0	0.50	350	600	1200	Blended cement with sand	Dolomite
22	0.5						
23	1						

Mix no.	%nano titanium	w/c	Cement	sand	Total coarse aggregate	Cement type	Coarse aggregate type.
24	2						
25	0	0.50	350	600	1200	OPC	Gravel
26	0.5						
27	1						
28	2						
29	0	0.50	400	600	1200	OPC	Dolomite
30	0.5						
31	1						
32	2						

Table 4: The specimens and age of testing

Test	Test specimens	Age of testing
Compressive strength	150 mm cube	7 and 28 days
Splitting tensile strength	Cylinder of 150 mm diameter and 300 mm height	28 days
TGA	Cylinder of 50 mm diameter and 5 mm height	28 days

2.3 Testing

In this research work, slump test was carried out on fresh concrete, whereas, the following tests on hardened concrete were carried out:

(a) Compressive strength: The compressive strength test was carried out according to the Egyptian Standard Specifications (ESS 1658/2006) at test ages of 7 and 28 days.

(b) Splitting tensile strength: The splitting tensile strength test was carried out at age 28 days according to the Egyptian Standard Specifications (ESS1658/2006).

(c) Thermo-gravimetric analysis (TGA): TGA was carried out on cylindrical cement paste specimens (50 mm diameter and 5 mm height), with different percentages of nano-titanium to cement to determine the amount of hydration product in cement mixes. These specimens were cast in PVC mould and after the end of curing period (28) days, the specimens were weighted in saturated surface dry (SSD) condition, and then the specimens were put in an electric oven with surface temperature up to 1200◦ C. The weight of specimens were recorded at various temperatures (105,250,450,600,700,900 and 950◦ C), then the weight loss resulted from the decomposition of matrix were used for calculation their different phases of hydration products (Rahman A. and Glasser F., 1989 and Abdelaziz G.E., 1998) where C-S-H decomposes at range 105-250◦, C-H decomposes at range of 450-600◦.

(d) Capillary porosity: Capillary porosity was carried out on cylindrical cement paste specimens (50 mm diameter and 5 mm height), with different percentages of nano-titanium to cement. These specimens were cast in PVC mould and after the end of curing period (28) days, the specimens were weighted in saturated surface dry (SSD) condition (W_1).The specimens were then exposed to an environment of 90.7 % relative humidity at 20 C until its attained constant weight (W_2). The 90.7 % RH was controlled using a saturated solution of barium chloride in an air tight plastic container, where the specimens were stored rested on steel mesh over the barium chloride solution(Young G..,1988). The capillary porosity was calculated using the following equation:

Capillary porosity %= $[(W_1-W_2)/ V] \times 100$,. (1)

(e) Scanning electron microscope (SEM): Scanning electron microscope (SEM) analysis was carried out for cement paste samples made with various cement types at 1% nano-titanium. The samples were dried, mounted on the SEM stub and coated with a thin conducing layer, and then the sample scanned with a narrow electron beam,which can be focused on a selected spot or area to generate X-ray photons, which interact with a silicon detector to produce electrical pulses. The count of pulses is then accumulated by a multi-channel analyzer for element analysis. The observations were made with SEM model Philips XL.30.

3. Test Results And Discussions

3.1 Slump

The effect of percentage of nano titanium on slump of concrete containing dolomite as coarse aggregate, various quantities of OPC and slump of concrete made with dolomite or gravel and OPC are presented in figs 1 and 2. It is apparent from these figures that, increasing the percentage of nano titanium beyond 1% decreases the slump values, These results are in agreement with the result obtained from previous research works [6] and are in contradictory with the result obtained from previous studies (Scientific Co operations International Workshops on Engineering Branches, 2014, Birgisson et al, 2012 and Hao and Sun, 2014). The values of slump increase by increasing the quantities of cement. It is also obvious that, the slump of concrete containing gravel is higher than those slumps of concrete made using dolomite at all tested percentages of nano titanium/ cement ratios. Figure 3 presents the slump values of concrete containing various cement types at quantities of cement = 250 and 350 Kg / m^3, it is apparent from this figure that, there is no noticeable change in slump values of concrete containing OPC or SRPC, whereas, the concrete containing blended cement with sand exhibited an increase in slump values when compared to concrete made with the other cement types. This result may be attributed to presence of lime stone in constituents of blended cement with sand which led to increasing workability of concrete by lowering the concrete viscosity.

3.2 Hydration of cement

Table 5 represents the impact of percentage nano titanium to cement on hydration products and capillary porosity of cement, it is apparent that introducing nano titanium in concrete mix increases mass loss due to C-S-H and decreases mass loss due to C-H, the maximum decomposition of weight due to C-S-H was observed at 1% percentage of nano-titanium to cement at different cement types, whereas, comparing to various cement types, OPC exhibited weight loss due to C-S-H more than those of SRPC or blended cement with sand. Capillary porosity of cement paste containing blended cement with sand was lower than those that of OPC or SRPC, in all studied cement type the minimum capillary porosity were observed at 1% nano-titanium to cement.

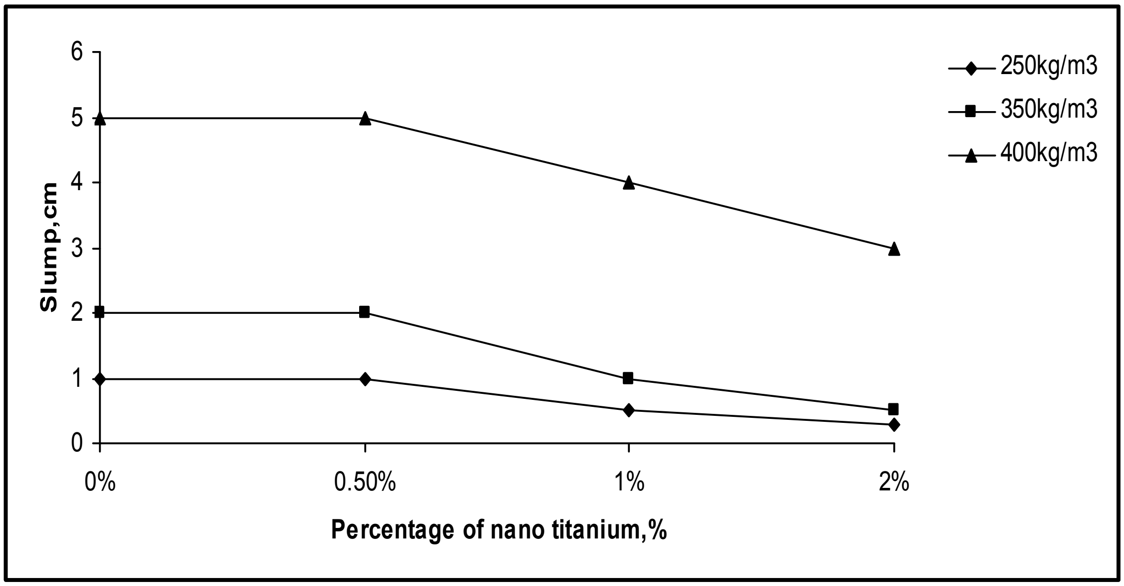


Figure 1. Effect of percentage of nano titanium on slump of concrete containing different quantities of OPC and dolomite as coarse aggregate.

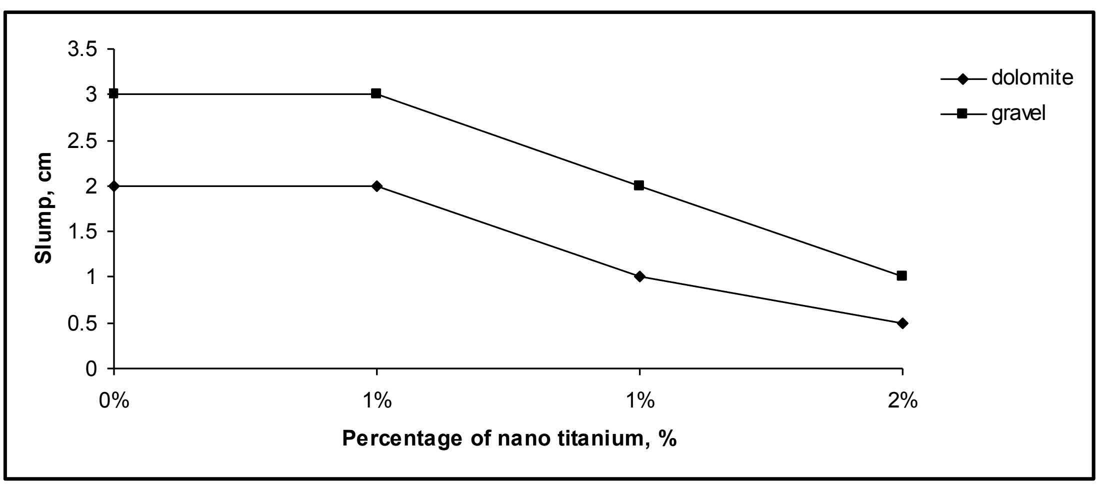


Figure 2. Effect of percentage of nano titanium on slump of concrete containing dolomite or gravel and OPC of quantity = 350 Kg/ m^3.

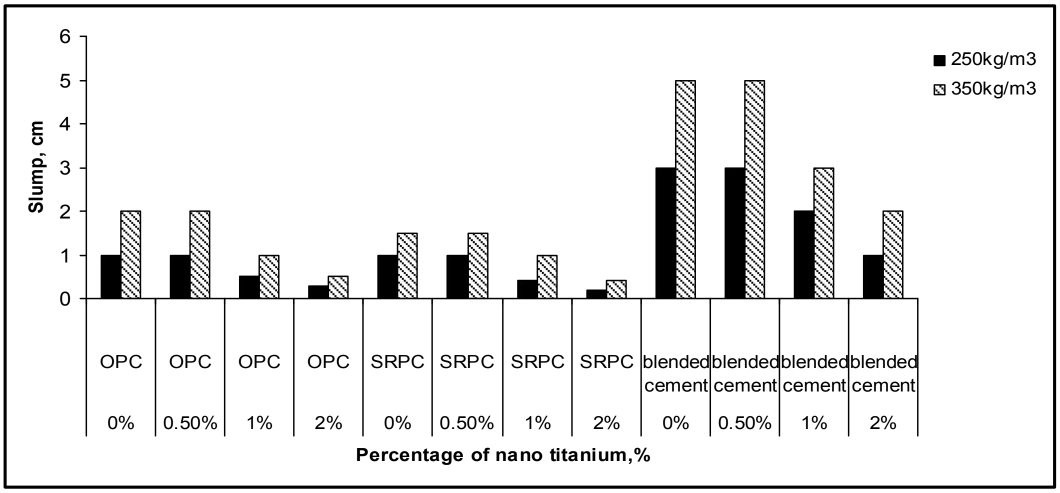


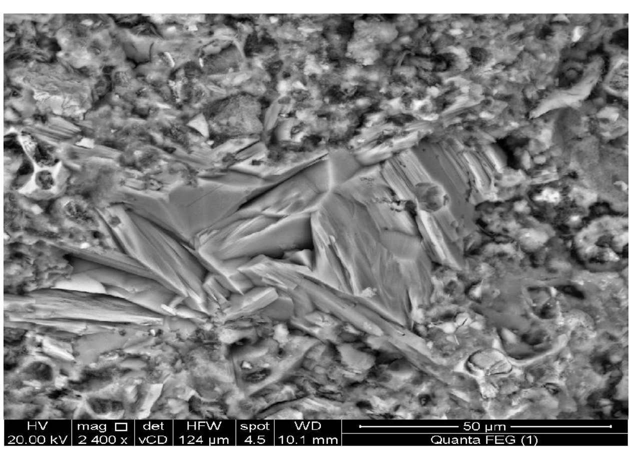
Figure 3. Effect of percentage of nano titanium on slump of concrete containing various cement types.

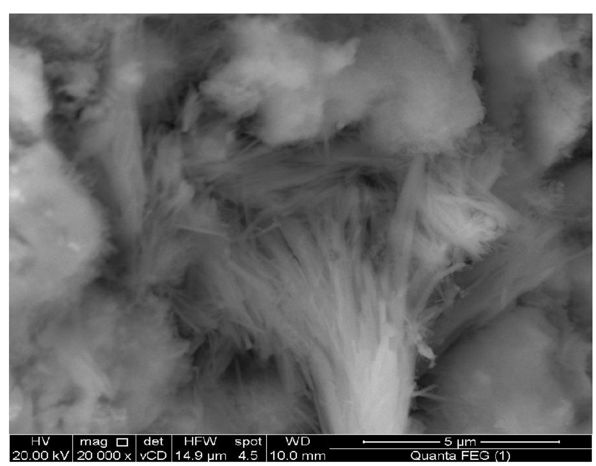
Table 5: Decompositions due to C-S-H, C-H and capillary porosity for different mixes.

Mix no.	Cement type	Nano titanium,%	Weight loss due to C-S-H,%	Weight loss due to C- H,%	Capillary porosity,%
1	OPC	0	6.0	7.7	5.6
2	OPC	0.5	6.4	6	5.2
3	OPC	1	7.6	5	3.8
4	OPC	2	7.0	5,5	4.5
5	SRPC	0	5.0	7.5	5.8
6	SRPC	0.5	5.4	6.5	5.3
7	SRPC	1	6.5	6	4
8	SRPC	2	6.0	6.3	5
9	Blended cement	0	2.5	6	4
10	Blended cement	0.5	2.7	5.5	3.6
11	Blended cement	1	3.5	5	3
12	Blended cement	2	3.1	5.2	3.5

3.3 Scanning Electron Microscope

Figure 4 shows SEM micrographs of cement paste specimens containing 1% nano titanium to cement for OPC, SRPC and blended cement with sand. It can be seen that, the amounts of C-S-H of OPC were greater than those of SRPC or blended cement with sand, the amounts of calcium carbonate was exhibited at blended cement with sand, nano titanium was observed for all studied cement types. The SEM micrographs show low porosity for blended cement with sand when compared to OPC or SRPC.





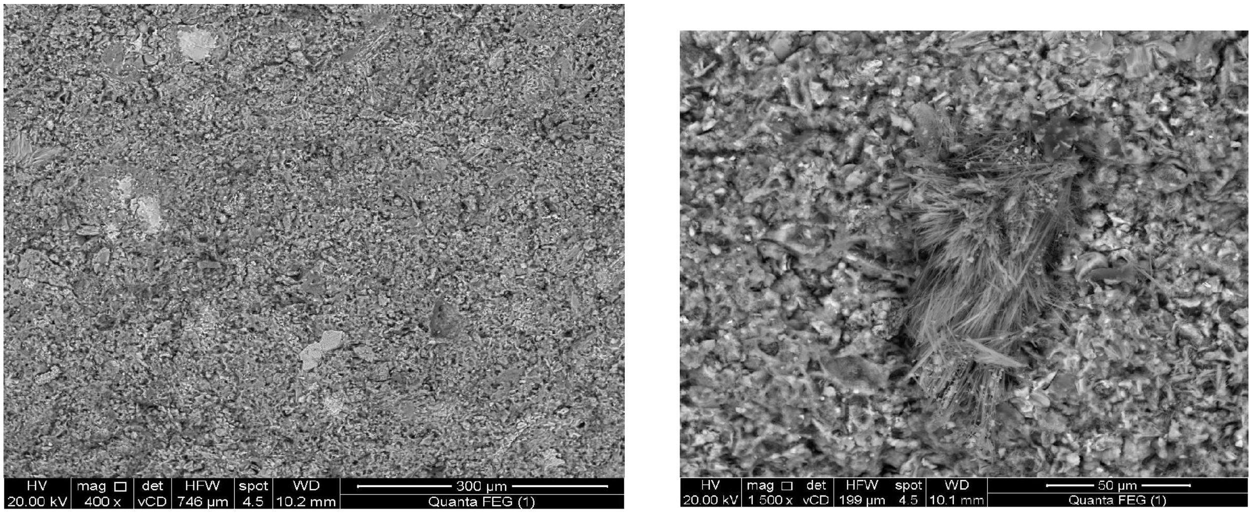


Figure 4-a, SEM of cement paste containing OPC at 1% nano-titanium.

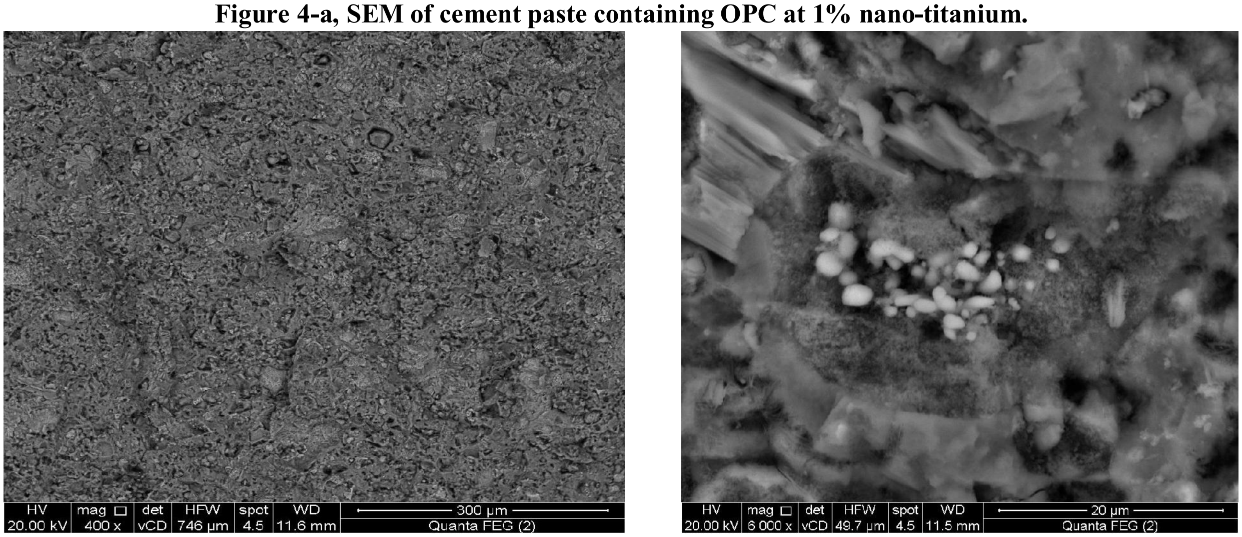
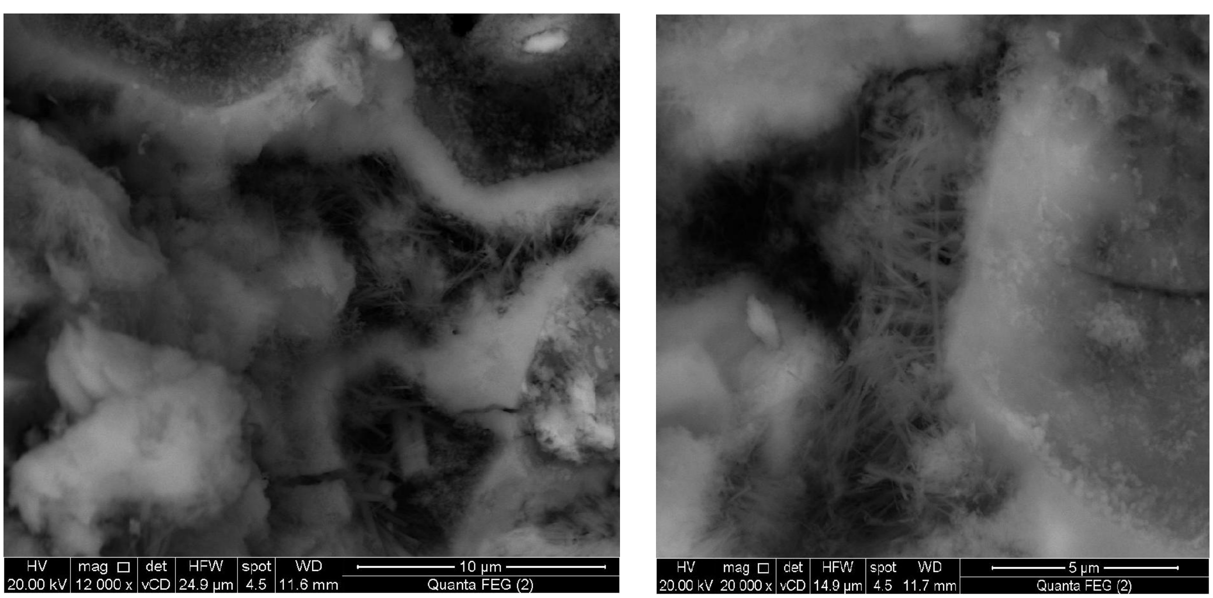


Figure 4-b, SEM of cement paste containing SRPC at 1% nano-titanium.



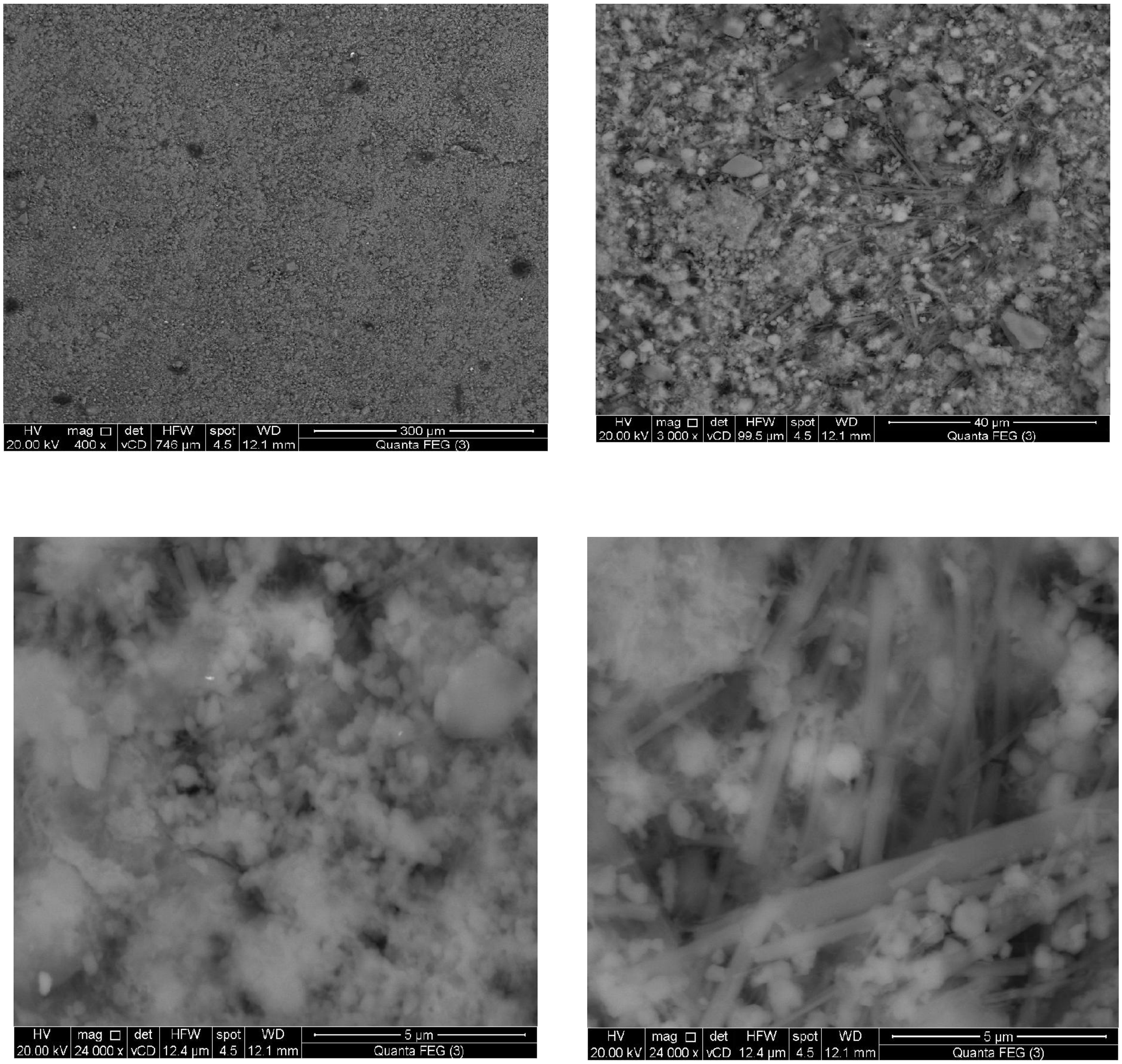


Figure 4-c, SEM of cement paste containing blended cement with sand at 1% nano-titanium

3.4 Mechanical Properties

3.4.1Compressive strength

Figures 5 to 6 represent the impact of percentage of nano titanium, % on the compressive strength of concrete containing dolomite as a coarse aggregate and various cement types (OPC-SRPC-blended cement with sand) at 250,350 Kg/m^3 cement at 7 and 28 days concrete ages. It is apparent from these figures that, the compressive strength of concrete increases by increasing concrete age, the % compressive strength at 7 days to compressive strength at 28 days were 65-85 % and 60- 75 for various cement types at 250 Kg/m^3 and 350 Kg/m^{3,} respectively. Introducing nano-titanium in concrete mixes increases the concrete compressive strength at 7 days and 28 days for different quantities of cement, the optimum % nano titanium to cement was observed at 1%, compared to control mix, 1% nano titanium led to increase the concrete compressive strength at 28 days by 50-60% and 20-30% for various cement types at 250 Kg/m^3 and 350 Kg/m^{3,} respectively. The compressive strength of concrete made with OPC was higher than those of the compressive strength of concrete containing SRPC or blended cement with sand. This result is attributed to increasing mass loss due to C-S-H of OPC, compared to those of SRPC and blended cement. Figures 7 to 8 show the impact of percentage of nano titanium, % on the compressive strength of concrete containing dolomite as a coarse aggregate and different cement types (OPC-SRPC-blended cement with sand) at 250,350 and 400 Kg/m^3 OPC at 7 and 28 days concrete ages and at 350 Kg/m^3 OPC for concrete made with dolomite or gravel.It is apparent from these figures that, the compressive strength of concrete increases by increasing concrete age, increasing the quantities of OPC led to increasing the concrete compressive strength at 7 days and 28 days, also concrete containing dolomite exhibited more compressive strength than that of gravel.

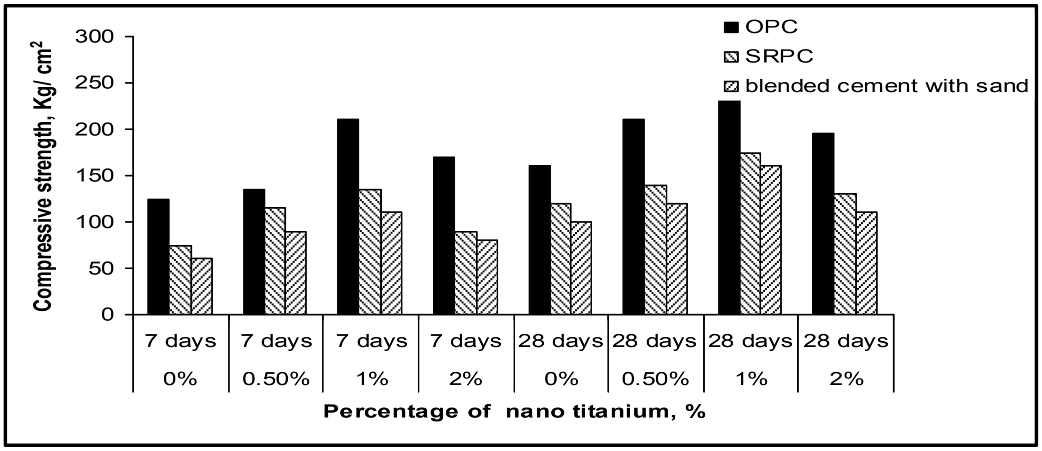


Figure 5, Effect of percentage of nano titanium on compressive strength of concrete containing 250 Kg/ m^3 of different types of cement and dolomite as coarse aggregate at various concrete ages.

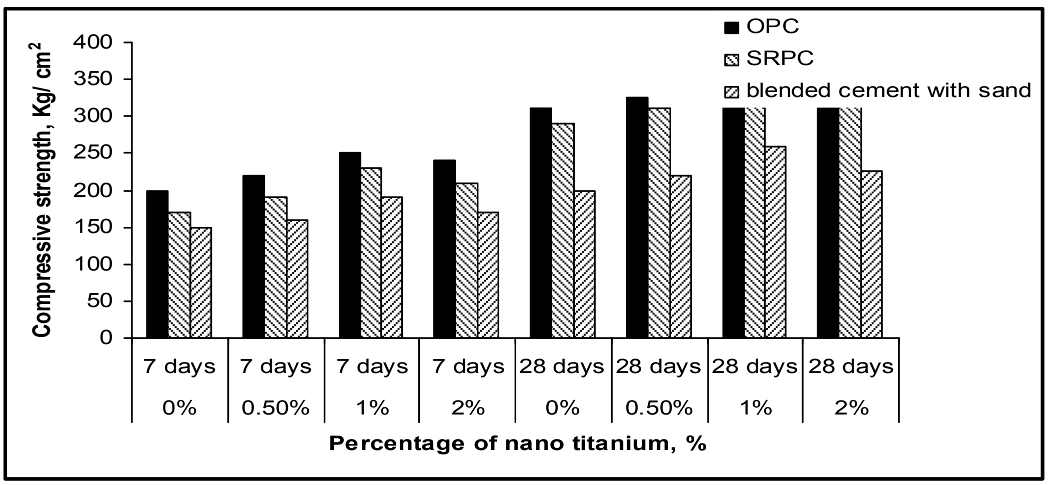


Figure 6, Effect of percentage of nano titanium on compressive strength of concrete containing 350 Kg/ m^3 of different types of cement and dolomite as coarse aggregate at various concrete ages.

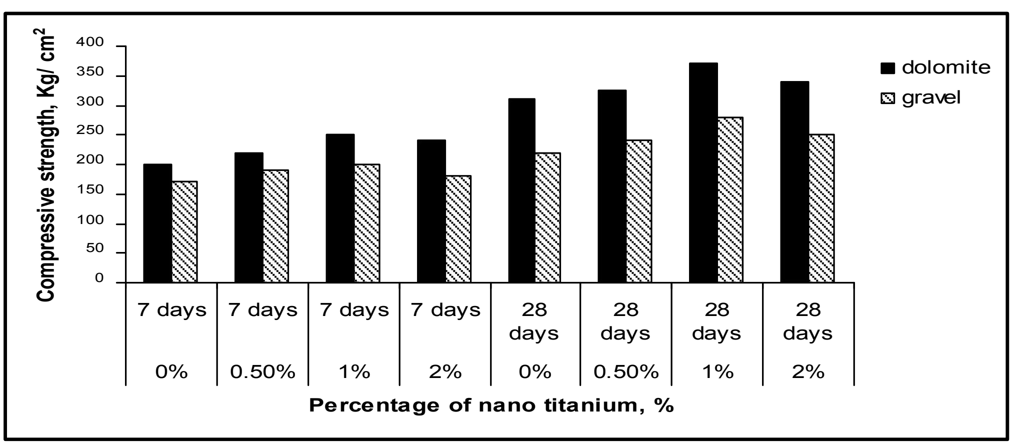


Figure 7, Effect of percentage of nano titanium on compressive strength of concrete containing 350 Kg/ m^3 of OPC and dolomite or gravel as coarse aggregate at various concrete ages.

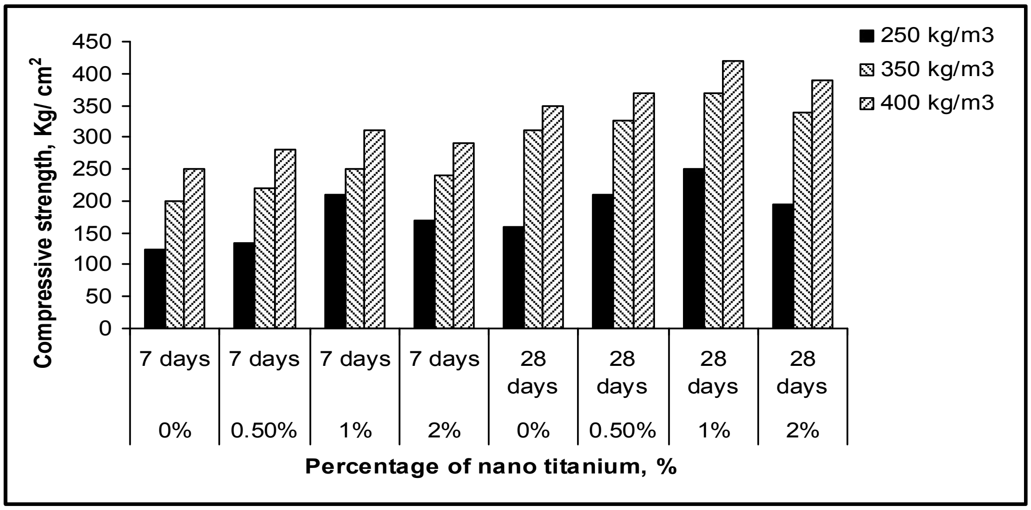


Figure 8, Effect of percentage of nano titanium on compressive strength of concrete containing different quantities of OPC and dolomite as coarse aggregate at various concrete ages.

3.4.2Splitting tensile strength

Figures 9 to 10 represent the impact of percentage of nano titanium, % on the splitting tensile strength of concrete containing dolomite as a coarse aggregate and various cement types(OPC-SRPC-blended cement with sand) at 250,350 Kg/m^3 cement at 28 days concrete age. It is apparent from these figures that the splitting tensile strength of concrete containing OPC exhibited maximum values, whereas, the minimum values of splitting tensile strength was observed at blend cement with sand, introducing nano-titanium in concrete mixes enhances the concrete splitting strength, the peak value of tensile strength was observed at 1% nano- titanium to cement. The % splitting tensile strength to compressive strength of concrete mixes containing various nano titanium ratios was 13-18% and 8-11% for 250 Kg/m^3 and 350 Kg/m^3 cement content, respectively. It is apparent from figures 11 to12 that, increasing the quantity of cement led to increasing the splitting tensile strength, for concrete made with dolomite or gravel, the splitting tensile strength increases by increasing the percentage of nano-titanium. These results are in agreement with the results obtained from compressive strength.

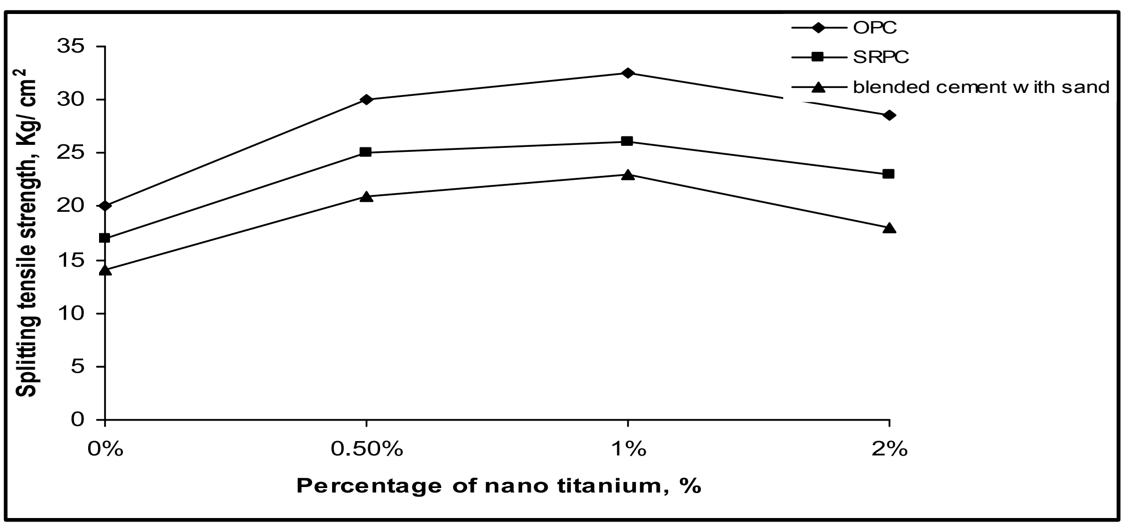


Figure 9, Effect of percentage of nano titanium on splitting tensile strength of concrete containing 250 Kg/ m^3 of different types of cement and dolomite as coarse aggregate at 28 days age.

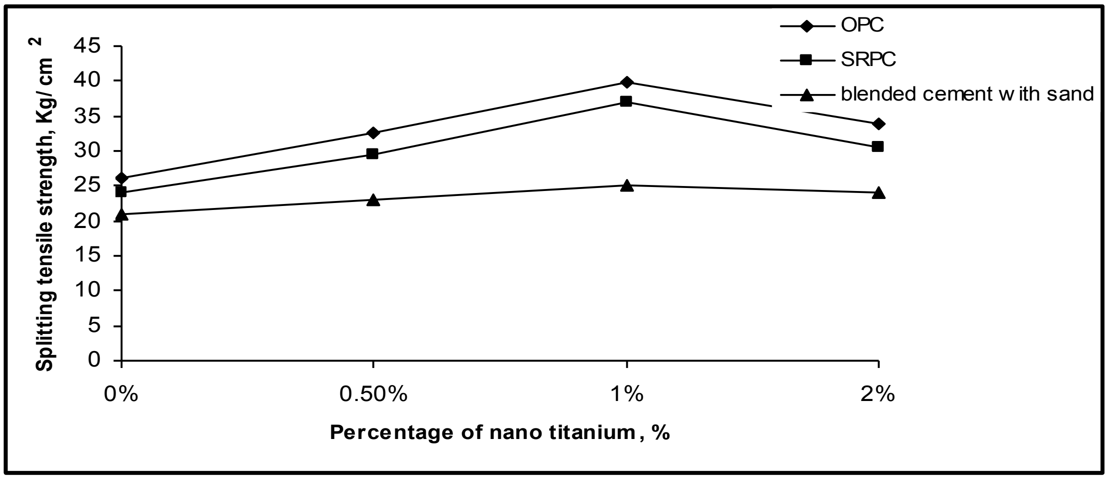


Figure 10, Effect of percentage of nano titanium on splitting tensile strength of concrete containing 350 Kg/ m^3 of different types of cement and dolomite as coarse aggregate at 28 days age.

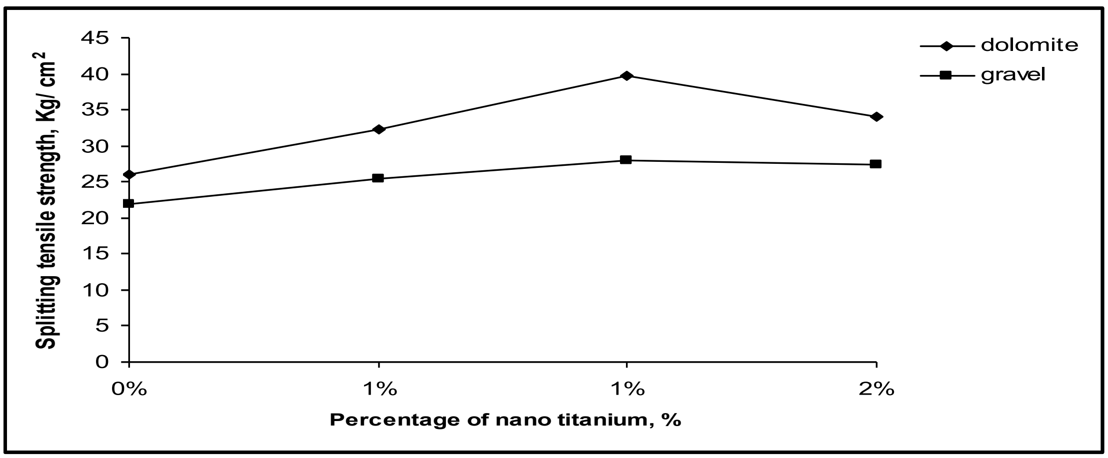


Figure 11, Effect of percentage of nano titanium on splitting tensile strength of concrete containing 350 Kg/ m^3 of OPC and dolomite or gravel as coarse aggregate at 28 days age.

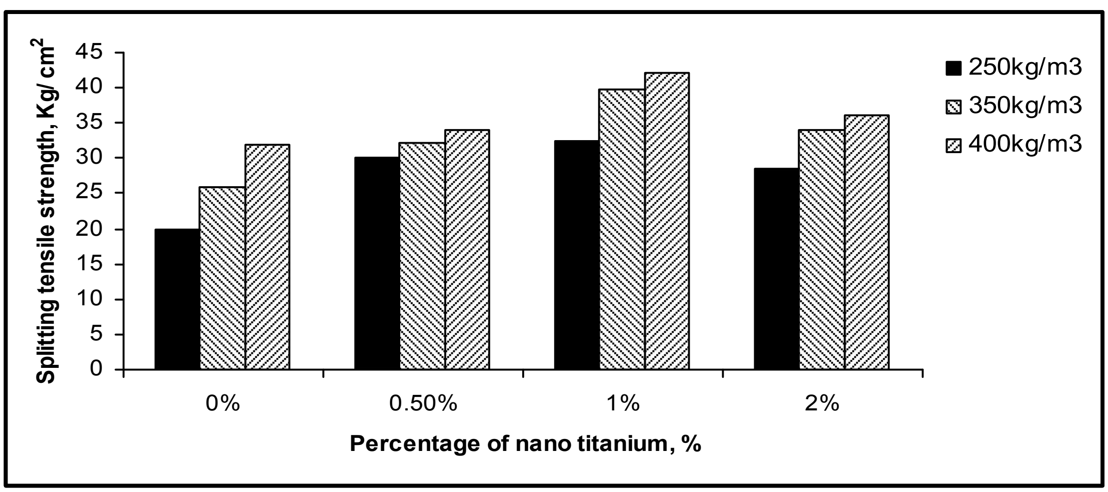


Figure 12, Effect of percentage of nano titanium on splitting tensile strength of concrete containing different quantities of OPC and dolomite as coarse aggregate at 28 days age.

4. Conclusions

From the experimental work carried out in this study, the following conclusions can be drawn: -

- There is no noticeable change in slump values of concrete containing OPC or SRPC, whereas, the concrete containing blended cement with sand exhibited an increase in slump values when compared to concrete made with the other cement types.

-Increasing the percentage of nano titanium beyond 1% led to decreases the concrete slump.

-Introducing nano-titanium in concrete mix led to enhancing the concrete microstructure.

- The compressive strength of concrete containing nano-titanium increased by increasing concrete age and quantity of cement.

- Introducing nano titanium in concrete mix enhances the mechanical properties of concrete, the optimum percentage of nano-titanium in concrete mix made with OPC or SRPC or blended cement with sand is 1%,this increase was 50-60% and 20-30% for various cement types at 250 Kg/m^3 and 350 $Kg/m^{3,}$ respectively.

-The % compressive strength of concrete made with different nano titanium ratios at 7 days to compressive strength at 28 days were 65-85 % and 60-75 for various cement types at 250 Kg/m^3 and 350 $Kg/m^{3,}$ respectively.

-The % splitting tensile strength to compressive strength was 13-18% and 8-11% for 250 Kg/m^3 and 350 Kg/m^3 cement content containing various nano titanium ratios.

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