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Influence of partial replacement TiO2 nanoparticles on the compressive and flexural strength of ordinary cement mortar

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Abstract:

In this paper, the compressive and flexural strength together with microstructural analysis of mortar by partial replacement of cement with Nano-TiO2 particles has been studied. TiO2 nanoparticles with average diameter of 15 nm were used with four different contents of 0.25%, 0.75%, 1.25% and 1.75% by weight. the compressive and flexural strength tests were done after curing at the ages of 7-days as early age, 28-days as standard age. The Nano-cement mortar was prepared using cement-sand ratio of 1:3 by weight with water-binder ratio (w/b ratio) as 0.5. The results showed that the compressive and flexural strength of the cement mortars with TiO2 were higher than pure cement mortar. The ultimate strength of Nano-cement mortar was gained at 0.75% of cement replacement. The enhancement in compressive and flexural strength were 19.33 % and 15.1% respectively at 28 days. SEM study about the micro structure of cement mortar containing nanoparticles and ordinary cement mortar showed that TiO2 nanoparticles fills the pores completely and reduces the large crystals of Ca(OH)2 and the hydrate products are denser and compact.

1. Introduction:

Concrete is by far the most widely used construction material worldwide. Lately, various efforts were exerted to improve the environmental friendliness of concrete to make it suitable as a Green Building material. Foremost and most successful in this regard is the use of suitable substitutes for Portland cement [1].

To reduce the environmental pollution created by cement industries, the usage of cement must be limited which automatically controls the manufacture of cement. Supplementary cementitious materials are those which are added to concrete as a part of the total cementitious system to reduce the total quantity of cement to be used and most significantly to increase the strength of concrete from its normal to high strength [2].

Finer particles are being used in construction industry in recent years. Several works were performed on use of nanoparticles in concrete specimens as mineral admixtures to improve physical and mechanical properties [3]. Hui et al. (2003) [4] investigated the properties of cement mortars blended with nanoparticles to explore their super mechanical and smart (temperature and strain sensing) potentials. However, until now, research performed over the years has been mainly aimed at achieving high mechanical performance with cement replacement materials in micro level. Porro et al. (2005) [5] refers to the use of nano-silica particles as increasing the compression strength of cement pastes. Sobolev et al. (2008) [6] reported that the addition of nano-silica produced an increase in strength of 15–20%. Konsta-Gdoutos et al. (2010) [7] studied the effect of carbon nano-fibers on cement pastes (0.08% by binder mass) and observed an increase in strength.

Nazari and Riahi (2011) [8] used ZrO2 nanoparticles with an average particle size of 15 nm and reported an improvement in the flexural strength of self-compacting concrete up to 4 wt%. Increasing the nanoparticle content caused a reduction in flexural strength because of the inadequate dispersion of nanoparticles within the concrete matrix. According to Zhang and Li (2011) [9], the pore structure of concrete containing nano-TiO2 is finer than that of concrete containing the same amount of nano-SiO2.

The most significant issue in the use of nanoparticles is that of effective dispersion. Nochaiya and Chaipanich (2011) [10] also found that homogeneous dispersion can be obtained if nanoparticles are mixed with water and then subjected to ultrasound for one hour. Metaxa et al. (2012) [11] developed an ultracentrifugation concentration process for the production of highly concentrated suspensions of carbon nanotubes.

In this work, the influences of nano-TiO2 on compressive and flexural strength of mortar has been studies. 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-TiO2 of a high purity

(99.9%) and a high Blaine fineness value (60 m2/g) in order to improve the characteristics of cement mortars [12].

In this study an attempt has been made to prove that using new materials, it is possible to obtain high performance concrete (HPC) or high strength concrete (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 mixture:

2.1. Materials:

2.1.1. Nano-TiO2 particles:

Nano–TiO2 with average particle size of 15 nm obtained from (NANOSHEL-INTELLIGEN MATERIALS PVT. LTD) company/USA, was used as received. Table 1 shows the properties of nano-TiO2 particles.

Table1: The properties of nano-TiO2

Name	Titanium Oxide Nano powder
chemical composition	TiO_2
Particle size	10-20nm
pH	6.7
appearance	White powder
Specific surface area(m^2/g)	20-30
purity	>99.9%
stability	Completely stable
Reactivity	Non-reactive

2.1.2 Cement:

The cement used in this study is Ordinary Portland Cement (OPC) type I commercially known (MASS) manufactured in Al-Sulaimaniya, Iraq. Chemical and physical analysis where conducted by National Center for Laboratories and Construction Research, test results indicate that the MASS OPC complying with the Iraqi standard specification (L.O.I.S.) No. 5 / 1984 . The chemical composition and physical properties of MASS OPC are shown in Table 2.

Table2: Chemical Composition and physical properties of MASS OPC.

Item	% by weight	Spec. Limit according to (L.O.I.S) No.5:1984
SiO_2	19.5	-
Fe_2O_3	3.8	-
CaO	61.34	-
MgO	2.25	<5.00
Al_2O_3	4.79	-
SO_3	1.33	<2.80
Loss on ignition(L.O.I.)	1.41	<4.00
Time saturation factor(T.S.F.)	0.86	0.66 – 1.02
Insoluble residue(I.R.)	0.98	<1.50
Physical Properties	Test result	
Fineness (cm^2/g) by Blaine method	2731	>2300
Compressive strength for cement mortar cube (70.7)mm at, MPa 3 days 7 days	 17.15 24.54	 >15 >23
Setting time (Vicat´s method) Initial setting(min) Final setting(min)	 148 275	 >45 min <10 hrs.
Soundness using Auto clave%	0.25	<0.8

2.1.3. Aggregate:

Locally available AL–Ukhaidher, Karbalaa, Iraq, natural sand with dimeter less than 4.75 mm is used in this study which has fineness modulus (F.M.) of (2.60), bulk specific gravity (S.G.) of (2.58) and sulfate content, (SO3%) of (0.09%) by sand weight , which is conform the limit of Iraqi standard specification No. 45 / 1984.

2.2 Mixture:

Two main kinds of mixtures were prepared in the laboratory trials. First kind CM mixtures were prepared as control specimens. The control mixtures (CM0) were made of sand , cement and water (without Nano materials). Second kind NM mixtures were prepared with different contents of nano-TiO2 particles with average particle size of 15 nm. The mixtures were prepared with the cement replacement of 0.25%, 0.75%,1.25% and 1.75% by weight. For all mixtures the ratio of sand to cement was set at (3:1) , and the water to binder ratio was set at (0.5). The proportions of the mixtures are presented in Table 3.

Table3: shows the details of mixtures

Name of group	Cement%	Nano TiO2%	(water/cement) ratio	(sand/cement) ratio
CM0	100	0	0.5	3:1
NM1	99.75	0.75	0.5	3:1
NM2	98.25	1.25	0.5	3:1
NM3	98.75	1.25	0.5	3:1
NM4	98.25	1.75	0.5	3:1

3. Preparation of test specimens:

3.1. Procedure of work:

Preparation of mixtures was performed in way similar to ASTM C 305-12 [13] with some variants:

1. Weighing components, by used sensitive digital balance of 0.01gm and for nano-TiO2 other one of 0.0001gm digits.
2. If the mixture did not contained Nano-particles, cement and sand mixed manually until they reached a homogeneous appearance and then accommodated within the electrical mixer together with water and finally mechanical mixing for 3 min.
3. If the mixture contained Nano-particles, TiO2 added to 95% of the total water of the mixture and mixed by hand for 5 minutes. Then this whole was submitted to the sonication for 20 minutes to obtain a dispersion of nano-TiO2 and a better homogenization of the mixture[14]. For this purpose, was used the ultrasonic wave bath machine (Power Sonic 410) model (LUC)(220 V,50 Hz, 400 W).
4. The cement and sand (previously mixed) accommodated within the mixer together with the mixture of the water and nano-TiO2.
5. After mixing for 60 sec. 5% of water slowly added and continue mixing for another 30 sec.
6. After stopping the mixer, it remained in rest for 90 sec, and then mixed for 90 sec.
7. The mortar was removed from the mixer and poured into clean oiled molds. The densification of the samples was made in two layers on a vibrating table, where each layer was vibrated for 10sec [15]. The surface finish of the samples was performed with the aid of a spatula.
8. After molding, the molds were covered with plastic sheets to preserve their moisture and the specimens were kept for 24 hours in a chamber at room temperature about (23±1 C) .
9. Then the specimens were demolded and cured in water where they were kept until the testing ages.

3.2. Compressive strength specimens:

The compressive strength was performed according to ASTM C109-02 [16]. The compressive strength for each mixture was determined from an average of three cubic specimens (50 × 50 × 50)mm tested at the age of 7 and 28 days of curing.

3.3. Flexural strength specimens:

The flexural strength was performed according to ASTM C 511-03. The flexural strength for each mixture was determined from an average of three prism specimens (160 × 40 × 40) mm tested at the age of 7 and 28 days of curing.

3.4 SEM analyses samples:

Broken sample pieces were used for this purpose after mechanical testing was carried out (28-day test) for SEM. The SEM was performed at the department of materials engineering.

4. Results and Discussion:

4.1. Mechanical properties:

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.

4.1.1. Compressive strength:

The compressive strength results of all mixtures are shown in Table 4. Comparison of the results from the 7 and 28 days samples shows that the compressive strength increases with nano-TiO2 particles up to 0.75% replacement (NM2) and then it decreases, although the results of 1.75% replacement (NM4) is still higher than those of the ordinary cement mortar (CM0). It was shown that the use of 1.75% nano-TiO2 particles decreases the compressive strength to a value which is near to the control mixture. This may be due to the fact that the quantity of nano-TiO2 particles 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 [17]. Also, it may be due to the defects generated in dispersion of nanoparticles that causes weak zones.

Table 4: Results of the compressive strength

Name	TiO2 %	7 days (MPa)	Enhanced extent (%)	28 days (MPa)	Enhanced extent (%)
CM0	0	11.21	-	29.13	-
NM1	0.25	14.85	32.47	32.19	10.50
NM2	0.75	16.78	49.68	34.76	19.33
NM3	1.25	15.93	42.11	33.52	15.07
NM4	1.25	14.69	31.04	30.37	4.27

The high enhancement of compressive strength in the NM mixtures 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-TiO2 particles. As a consequence, the hydration of cement is accelerated and larger volumes of reaction products are formed. Also nano-TiO2 particles recover the particle packing density of the blended cement, directing to a reduced volume of larger pores in the cement paste.

4.1.2. flexural strength:

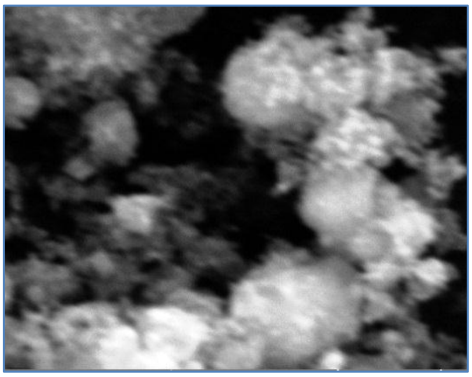
The flexural strength results of series CM0 and NM mixtures are shown in Table 5. Similar to the compressive strength, the flexural strength of the specimens increases with nano-TiO2 particles up to 0.75% replacement (NM2) and then it decreases, although the results of 1.75% replacement (NM4) is still higher than those of the ordinary cement mortar (CM0). Again, the increasing in the flexural strength is 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-TiO2 particles.

Table 5: Results of the flexural strength

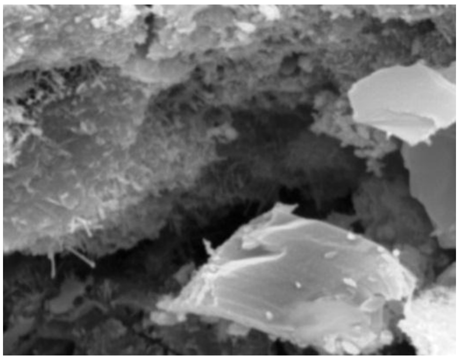
Name	TiO2 %	7 days (MPa)	Enhanced extent (%)	28 days (MPa)	Enhanced extent (%)
CM0	0	3.9	-	5.3	-
NM1	0.25	4.4	12.8	5.8	9
NM2	0.75	5.1	30.7	6.1	15.1
NM3	1.25	4.5	15.4	6.0	13.2
NM4	1.25	4.2	7.7	5.7	7.5

4.2. Microstructure analysis:

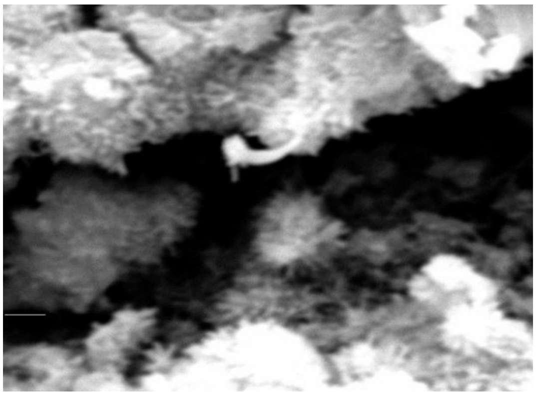
The microstructure of samples CM0, NM2 and NM4 is shown in figure 1-(a, b, and c). As shown in the figure 1-a, it can be seen in the microstructure of CM0 the ordinary cement mortar samples have large crystals of Ca(OH)2. The microstructure of ordinary cement mortar is non dense and the voids can be observed. In NM2 that have best mechanicals properties figure 1-b, with the increase of nanoparticles quantity up to 0.75%, microstructure has improved completely and achieved better density. As shown in figure 1-c, in samples containing 1.75% nanoparticles because of the agglomeration of nanoparticles voids are formed. This microstructure with the reduction of mechanical properties in NM4 samples is appropriate.



(a)



(b)



(c)

Figure 1 : SEM photo for microstructure of (a. CM , b. NM2 and c. NM4).

5. Conclusion:

With respect to the experimental results of compressive and flexural strength it is expected that adding of TiO2 nanoparticles up to 0.75% by weight of cement can act as a filler for strengthening the micro structure of cement and also reduces the quantity and size of Ca(OH)2 crystals and fill the voids of C-S-H gel structure and finally structure of hydrated product is compacted and denser. With the increase of nanoparticles quantity up to 1.75% there is decrease in nanoparticles distance and Ca(OH)2 crystal due to limited space cannot grow to appropriate size. This factor along with the agglomerated nanoparticles causes the mechanical properties of the NM4 is near from those of the ordinary cement mortar (CM0).

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تأثير اضافة جزيئات ثنائي اوكسيد التيتانيوم النانوية على مقاومة الضغط والأنحناء لمونة الأسمنت

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الخلاصة

تم دراسة مقاومة الانضغاط والانحناء بالإضافة الى التحليل البنيه المجهرية لمونة الاسمنت المستبدل جزئيا بجزيئات نانوية من ثنائي اوكسيد التيتانيوم. الجزيئات النانوية من ثنائي اوكسيد التيتانيوم ذات معدل قطر 15 نانو ميتر تم استخدامها واستبدالها جزئيا عوضا عن الاسمنت بأربع نسب مختلفة هي 0.25% , 0.75% , 1.25% و 1.75% من وزن الاسمنت. اختبار مقاومة الانضغاط ومقاومة الانحناء تم بعد 7 و 28 يوم من المعالجة في الماء. مونة الاسمنت النانوية تم تحضيرها باستخدام عامل سمنت الى رمل هو 3:1 , ماء الى الاسمنت هو 0.5. اظهرت النتاج ان مقاومة الانضغاط ومقاومة الانحناء للمونة التي تحتوي على مواد نانوية اعلى من تلك التي لا تحتوي عليها, وكانت اعلى مقاومة انضغاط ومقاومة انحناء عند نسبة استبدال 0,75% , حيث كانت نسبة الزيادة لمقاومة الانضغاط 19,33% ولمقاومة الانحناء 15,1% بعد 28 يوم. كما اظهرت الصور المأخوذة من جهاز الماسح الالكتروني المجهري للبنية المجهرية لكل العينات, ان جزيئات ثنائي اوكسيد الكاربون النانوية تملء الفراغات البينية للمونة و تقلل من حجم بلورات Ca(OH)2 ويكون الناتج من عملية الإماءة اكثف من المونة التي لا تحتوي على مواد نانوية.