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Thermal and mechanical characteristics of cement nanocomposites

Abstract: Widespread applications and advantages of different types of composite materials have drawn researchers' attention toward the science and technology of composites. Among these materials, cementitious composites have a special place, as they have many applications in various fields of structural and civil engineering. Due to the importance of cementitious composites and their behavior, investigation of their properties is of great importance. Thus in the present study, thermal and mechanical properties of the self-compacting cementitious composites containing different fractions of nano TiO_2 have been investigated. Mechanical properties were assessed through compressive, split tensile and flexural tests. The thermal properties were assessed through thermogravimetric analysis (TGA) and conduction calorimetry tests. Accelerated peak appearance in conduction calorimetry tests and more weight loss in thermogravimetric analysis could indicate that TiO_2 nanoparticles could lead to strength development at earlier ages and improve the properties of the self-compacting cementitious composites.

Keywords: cementitious composites; conduction calorimetry; mechanical properties; nano TiO_2; TGA.

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1 Introduction

Portland cement-based binders are the primary active components of cementitious composites used in most modern construction. The other components are water, and both fine and coarse aggregates. Binders are made from Portland 'clinker' ground together with a little calcium sulfate, and frequently also contain fine mineral powders such as limestone, pozzolan (typically volcanic ash), fly ash (usually from coal-burning power plants), and granulated blast furnace slag. Such powders are referred to as supplementary cementitious materials (SCMs) as they are used to replace some of the more expensive types of clinker. Chemical admixtures such as superplasticizers (SP) and air-entraining agents can be added in small amounts to modify the properties of a cementitious composite for specific applications. One of the cementitious composites is self-compacting concrete (SCC) that is used to facilitate and ensure proper filling and good structural performance of restricted areas and heavily reinforced structural members. Many researchers have used SCC containing admixtures to satisfy the great demand for fines needed for this type of cementitious composites, thereby improving its mechanical, rheological and durability properties in comparison with normal vibrated concrete (NVC).

There are a few works on incorporating nano particles into cementitious composites to achieve improved physical and mechanical properties which most of them have focused on using SiO_2 nano particles in mortars and cement-based materials [1–3], normal concrete [4, 5], and high performance self-compacting concrete [6].

Incorporating of TiO_2 nanoparticles has been addressed in some of the works considering the properties of NVCs [7]. The flexural fatigue performance of concrete containing TiO_2 nanoparticles for pavement has been studied experimentally by Li et al. [8]. They showed that the flexural fatigue performance of concretes containing TiO_2 nanoparticles is improved significantly and the sensitivity of their fatigue lives to the change of stress is also increased. In addition, the theoretical fatigue lives of concretes containing TiO_2 nanoparticles are enhanced in different extent. With increasing stress level, the enhanced extent of the theoretical fatigue number is increased [8]. The abrasion resistance of concrete containing TiO_2 nanoparticles for pavement has been experimentally studied [9]. The abrasion resistance of concretes containing TiO_2 nanoparticles is significantly improved. The enhanced extent of the abrasion resistance of concrete is decreased by increasing the content of TiO_2 nanoparticles [9]. The hydration kinetics of titania-bearing tricalcium silicate phase has been studied [10]. Nano-TiO_2-doped tricalcium silicate (C3S) was obtained by repeated firing of calcium carbonate and quartz in the stoichiometric ratio of 3:1 in the presence of varying amounts of titanium dioxide from 0.5% to 6% by weight. The study revealed that the presence of up to 2% TiO_2 has an inhibiting effect on the rate of hydration of C3S [10].

In the present study, thermal and mechanical properties of self-compacting concrete as a type of cementitious composite has been investigated in which TiO_2 nanopowder was added into the binder from 0% to 5%. Thermal properties w evaluated by thermogravimetric analysis (TGA) and conduction calorimetry tests. Mechanical properties were assessed through compressive, split tensile and flexural tests.

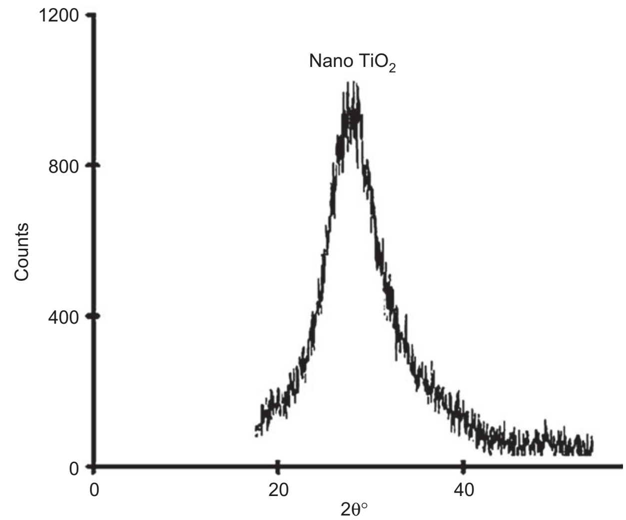

Figure 2 XRD spectrum of TiO_2 nanoparticles.

2 Materials

An ASTM Type II Portland cement (PC) was used to produce the various SCC mixtures. TiO_2 nanoparticles were used as a cement replacement by an amount of 1 up to 5 wt%. Scanning electron microscopy (SEM) micrograph and powder X-ray diffraction (XRD) spectrum of TiO_2 nanoparticles are shown in Figures 1 and 2. Properties of the nanoparticles are also presented in Table 1.

The coarse aggregate used was limestone gravel with a nominal maximum size of 12.5 mm. As fine aggregate, a mixture of silica aggregate sand and crushed limestone (as filler) was used with a maximum size of 4.75 mm. All aggregates in this research were used in dry form and the aggregates are a mixture of eight particle sizes of fine and coarse aggregates. A polycarboxylic-ether type SP with a specific gravity of 1.06–1.08 was employed to achieve the desired workability in all concrete mixtures This SP is according to ASTM C494 for which the physical properties are presented in Table 2. Furthermore viscosity modifying agent (VMA) for better stability was used.

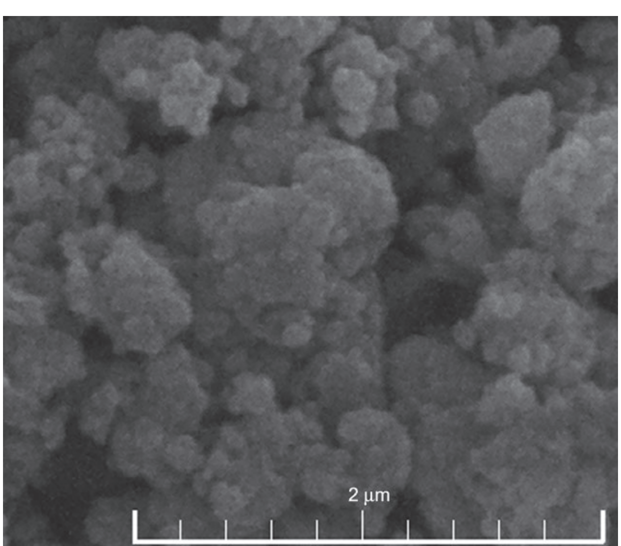

Figure 1 SEM micrograph of TiO_2 nanoparticles.

3 Mix proportions and preparation of the specimens

A total of six concrete mixtures were designed with a constant water/binder (w/b) ratio of 0.38 and a total binder content of 450 kg/m^3. Concrete mixtures were prepared with 0, 1, 2, 3, 4 and 5 wt% of cement replacement by TiO_2 nanoparticles. The mixture proportions of concrete and binder paste are given in Table 3.

As the SP plays a very important role in the flowability of SCC mixes, a modified mixing procedure was adopted

Appearance	White powder
Purity	99.5%
Grain size	20±5
Specific surface area	>120
Apparent density	0.3
pH Value of aqueous suspended matter	7–8 (untreated type)
Loss of weight in drying (%)	≤0.5
Loss of weight in burning (%)	≤1.0

Table 1 Properties of nano TiO_2.

Form	Viscous liquid
Color	Light brown
Relative density	1.06–1.08 @ 20°C
pH	6.6
Viscosity	128±30 cps @ 20°C
Transport	Not classified as dangerous
Labeling	No hazard label required

Table 2 Physical properties of poly-carboxylic ether 4.

to benefit from the action of adsorption of molecules of poly-carboxylic ether based SP on the cement particles for all the mixes. SCC mixtures were prepared by mixing the coarse aggregates, fine aggregates and powder materials (cement and nanoparticles) in a laboratory drum mixer. The powder material and aggregates were mixed in dry form for 2 min. Then half of the water containing the whole amount of SP was poured and mixed for 3 min. Thereafter, about 1 min rest was allowed and finally rest of the water containing VMA was added into the mixture and mixed for 1 min [6].

4 Mechanical tests

Mechanical tests aimed to determine the mechanical properties including the compressive and splitting tensile strengths of the concrete specimens. Compressive strength values were measured according to BS-1881 [11] on 150×150×150 mm cubes with two specimens for each concrete mix on 7, 28 and 90 days of curing. The splitting tensile strengths were determined on 7, 28 and 90 days on cylinders measuring 100 mm diameter and 200 mm height and cured in water until the date of the test according to the ASTM C496 [12]. Flexural tests were performed conforming to the ASTM C293 standard on 50×50×200 mm cubes [13]. Two specimens of each mixture were tested and the mean value was reported.

5 Tests of thermal properties

5.1 Conduction calorimetry

The test was performed on an isothermal calorimeter, at 22°C for a maximum of 70 h. Fifteen grams of cement was mixed with water and a different amount of TiO_2 nanoparticles (1, 2, 3, 4 and 5%) as partial replacement of the cement before introducing it into the calorimeter cell.

5.2 Thermogravimetric analysis (TGA)

A thermogravimetric analysis (TGA) test was conducted so that the weight loss of the concrete specimens due to heating can be determined. A simultaneous thermal analyzer equipped with a data acquisition system was used for the tests. Specimens which were cured for 28 days were heated from 110°C to 650°C, at a heating rate of 4°C/min in an inert N_2 atmosphere.

6 Results and discussion

6.1 Mechanical properties

Mechanical properties of SCC-N mixtures including the compressive, flexural and split tensile strength results are given in Table 4. This table presents the average of the compressive and flexural strengths as determined from two cubic specimens and splitting tensile strength as reported from two cylindrical specimens at each age.

The results show that the compressive strength increases by adding TiO_2 nanoparticles up to 4 wt% replacements and then decreases, although adding 5 wt% TiO_2 nanoparticles produces specimens with higher compressive strength with respect to SCC-N specimens with

No	Concrete ID	w/b	Cement	TiO_2 nanoparticles	Filler	Fine aggregate	Coarse aggregate	SP	VMA
			(kg/m^3)						
1	SCC-N0	0.38	450	–	177	1003	578	2.5	2
2	SCC-N1	0.38	445.5	4.5	177	1003	578	2.5	2
3	SCC-N2	0.38	441	9	177	1003	578	2.5	2
4	SCC-N3	0.38	436.5	13.5	177	1003	578	2.5	2
5	SCC-N4	0.38	432	18	177	1003	578	2.5	2
6	SCC-N5	0.38	427.5	22.5	177	1003	578	2.5	2

Table 3 Mix proportions of the concrete specimens.

No	Concrete ID	Compressive strength (Mpa)			Splitting tensile strength (Mpa)			Flexural strength (Mpa)		
		7	28	90	7	28	90	7	28	90
										Days
1	SCC-N0	36.4	51.8	53.1	2.9	3.6	3.9	3.4	3.9	5.1
2	SCC-N1	38.2	54.5	55.3	3.1	3.9	4.3	3.6	4.3	5.6
3	SCC-N2	39.7	57.7	59.1	3.3	4.3	4.7	3.8	4.7	5.8
4	SCC-N3	42.3	60.3	63.2	3.6	4.6	5.2	4.1	5	6.5
5	SCC-N4	44.6	63.2	67.4	3.9	4.9	5.7	4.5	5.6	6.8
6	SCC-N5	43.2	61.5	63.8	3.7	4.7	5.5	4.4	5.3	6.6

Table 4 Mechanical properties of SCC-N mixtures.

1, 2 and 3 wt% TiO_2 nanoparticles. The reduced compressive strength by adding more than 4.0 wt% TiO_2 nanoparticles may be due to the fact that the quantity of TiO_2 nanoparticles presented 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. Also, it may be due to the defects generated in the dispersion of nanoparticles that causes weak zones. The higher compressive strength in the mixtures containing nanoparticles with respect to control specimens may be as a result of the rapid consumption of crystalline $Ca(OH)_2$ which are quickly formed during the hydration of Portland cement specially at the early ages as a result of the high reactivity of TiO_2 nanoparticles. As a consequence, the hydration of cement is accelerated and larger volumes of reaction products are formed. Also TiO_2 nanoparticles recover the particle packing density of the blended cement, leading to a reduced volume of larger pores in the cement paste. However, as indicated, the larger volume of TiO_2 nanoparticles than 4.0 wt% reduces the compressive strength due to a reduction of hydrated lime in addition to the deficiency which occurred during the dispersion of TiO_2 nanoparticles in the cement paste.

Kondo and Yoshida [14] have studied the hydration behavior of C3S. To compare the rate of hydration, the thickness of the reacted layer was calculated from the data of the particle size distribution and the data of the degree of hydration. It was reported that in the early period, the rates of hydration of C3S and its solid solution are considered to be a kind of autocatalytic reaction [14]. In the case of Ti-bearing C3S, the initial hydration period is prolonged, but the degree of hydration at 1–3 days is high because of the rapid autocatalytic hydration. Kondo and Yoshida [14] have also studied the hydration by monitoring the setting of mortar and its strength at various intervals. It was observed that the setting of mortar made with C3S occurs within a few hours after mixing, whereas the setting of C3S with TiO_2 is occurred after approximately 10 h. The split tensile strength of pure C3S at 1 day was much higher than that of the Ti-doped specimen. The strength of the Ti-bearing specimen at 3 days was almost double that of pure C3S. Higher strengths were noticed at 28 and 90 days for the Ti-bearing specimen than the pure C3S [14]. It was also reported that when alite or C3S contains TiO_2 [15], the reaction within 1 day is retarded, but the subsequent reaction is remarkably accelerated. It can be seen that the reactivity is increased because of the substitution of Ti for Si in the structure of C3S, but the retardation of the initial period in the C3S and alite-containing Ti may be attributed to the difficulty of the growth of nuclei of more stable hydrate formed in the impermeable coating [14].

Table 4 also shows the split tensile strength and the flexural strength of the SCC series. Similar to the compressive strength, the split tensile strengths and the flexural strengths of all SCC-N specimens are more than those of the mixtures without nanoparticles. In addition, the split tensile strength and the flexural strength of SCC-N series is increased by adding TiO_2 nanoparticles up to 4 wt% and then it is decreased, similar to the compressive strength results.

The strength growth for nanoparticles addition up to 4 wt% is evident from the results. Several studies have been conducted on flexural strength of cementitious composites reinforced by nanoparticles and some possible reasons have been represented to show the increment of flexural strength: (a) when a small amount of the nanoparticles is uniformly dispersed in the cement paste, the nanoparticles act as a nucleus to tightly bond with cement hydrate and further promote cement hydration due to their high activity, which is favorable for the strength of cement mortar [16]; (b) the nanoparticles among the hydrate products will prevent crystals from growing which are positive for the strength of cement paste [17]; (c) the nanoparticles fill the cement pores, thus increasing the strength.

Mixture	Total heat (kJ/kg)	First peak		Second peak	
		Time (h)	Rate (W/kg)	Time (h)	Rate (W/kg)
SCC-N0	405	3	0.95	28.5	5.45
SCC-N1	391	2.8	0.9	27.2	5.34
SCC-N2	380	2.6	0.84	26	5.13
SCC-N3	366	2.4	0.76	25.5	4.85
SCC-N4	343	2.2	0.65	25.1	4.62
SCC-N5	349	2.3	0.69	25.3	4.71

Table 5 Calorimetric results of SCC specimens.

Nano-TiO_2 can contribute in the hydration process to generate C–S–H through reaction with $Ca(OH)_2$ [18].

6.2 Conduction calorimetry

Table 5 shows the conduction calorimetry of the specimens. Two signals can be distinguished on all test results: a peak corresponding to the acceleration or post-induction period, associated with the precipitation of C–S–H gel and CH, and a shoulder related to a second, weaker signal with a later peak time, associated with the transformation from the ettringite (AFt) to the calcium monosulfoaluminate (AFm) phase via dissolution and reaction with $Al(OH)^{4-}$ [19]. The numerical values corresponding to these two signals (heat release rate, peak times) and the total released heat are shown in Table 5. The time period over the total heat was measured until the heat release rate was below 1% of the maximum of the second peak.

Table 5 shows that increasing the percentage of TiO_2 nanoparticles up to 4.0 wt% in the pastes accelerates peak times and drops heat release rate values. This is indicative of acceleration in initial cement hydration due to the higher content of TiO_2 nanoparticles. TiO_2 nanoparticles as a pozzolan can accelerate the cement hydration and hence increase the heat release rate. As stated above, the appearance of the peaks in conduction calorimetry tests are due to CH and C3H compounds formation in the cement paste. When TiO_2 nanoparticles partially added to cement paste, the acceleration in formation of CH and C3H would result in more rapid appearance of the related peaks.

6.3 Thermogravimetric analysis

Table 6 shows the thermogravimetric analysis results of SCC-N specimens measured in the 110°C–650°C range in which dehydration of the hydrated products occurred.

Mixture	Weight loss (%) (110°C–650°C)
SCC-N0	13.5
SCC-N1	14.2
SCC-N2	15.9
SCC-N3	16.7
SCC-N4	17.5
SCC-N5	17.1

Table 6 Weight loss (%) of the pastes in the range of 110°C–650°C for SCC specimens.

The results show that after 90 days of curing, the loss in weight of the specimens is increased by increasing TiO_2 nanoparticles in the mixtures up to 4 wt%. Again, the results obtained for conduction calorimetry, show the increase in weight loss which could be due to more formation of CH and C3H compounds in the cement paste.

7 Conclusion

The following conclusions may be obtained from the present study:

1. Compressive, splitting tensile and flexural strengths improved rather significantly in the mixtures containing TiO_2 nanoparticles which may be due to accelerated C–S–H gel formation as a result of the increased crystalline $Ca(OH)_2$ amount at the early ages.
2. From the microstructure point of view, more refined microstructure and smaller pores may be achieved by the addition of TiO_2 nanopowder that can lead to enhanced mechanical properties of the cementitious composites.
3. TiO_2 nanoparticles could accelerate the appearance of the first peak in conduction calorimetry test that is related to the acceleration in formation of hydrated cement products.

4. Thermogravimetric analysis shows that TiO_2 nanoparticles could increase the weight loss of the specimens when partially added to cement. More rapid formation of hydrated products in presence of TiO_2 nanoparticles could be the reason for more weight loss.

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