Thermal properties of TiO2 nanoparticles binary blended cementitious composites

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Abstract: Widespread applications and advantages of different types of composite materials have drawn the researchers' attention toward the science and technology of composites. Among theses materials, cementitious composites have a special place, since they have many applications in various fields of structural and civil engineering. Due to importance of cementitious composites and their behavior, investigation of their properties is of great importance. Thus in the present study, one of these properties, i.e. thermal properties of the self compacting cementitious composites containing different fractions of TiO2 nanoparticles have been investigated. The thermal properties were assessed through thermogravimetric analysis (TGA) and conduction calorimetry tests. Accelerated peak appearance in conduction calorimetry tests, more weight loss in thermogravimetric analysis could indicate that TiO2 nanoparticles could improve the properties of the self compacting cementitious composites
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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) since they are used to replace some of the more expensive clinker. Chemical admixtures such as superplasticizers 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 several few works on incorporating nano particles into cementitious composites to achieve improved physical and mechanical properties which most of them have focused on using SiO2 nano particles in mortars and cement-based materials [1–3], normal concrete [4,5], and high performance self compacting concrete [6].

Incorporating of TiO2 nanoparticles has been addressed in some of the works considering the properties of NVCs [7]. The flexural fatigue performance of concrete containing TiO2 nanoparticles for pavement has experimentally been studied by Li et al. [8]. They showed that the flexural fatigue performance of concretes containing TiO2 nanoparticles is improved significantly and the sensitivity of their fatigue lives to the change of stress is also increased. In addition, the theoretic fatigue lives of concretes containing TiO2 nanoparticles are enhanced in different extent. With increasing stress level, the enhanced extent of theoretic fatigue number is increased [8]. The abrasion resistance of concrete containing TiO2 nanoparticles for pavement has been experimentally studied [9]. The abrasion resistance of concretes containing TiO2 nanoparticles is significantly improved. The enhanced extent of the abrasion resistance of concrete is decreased by increasing the content of TiO2 nanoparticles [9]. The hydration kinetics of titania-bearing tricalcium silicate phase has been studied [10]. Nano-TiO2-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% TiO2 has an inhibiting effect on the rate of hydration of C3S [10].

In the present study, thermal properties of self compacting concrete as a type of cementitious composites have been investigated in which TiO2 nanoparticles were added into the binder by 0 to 5%. Thermal properties were evaluated by thermogravimetric analysis (TGA) and conduction calorimetry tests.

2. Materials

An ASTM Type II Portland cement (PC) was used to produce the various SCC mixtures. TiO2 nanoparticles were used as cement replacement by 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 Figs. 1 and 2.

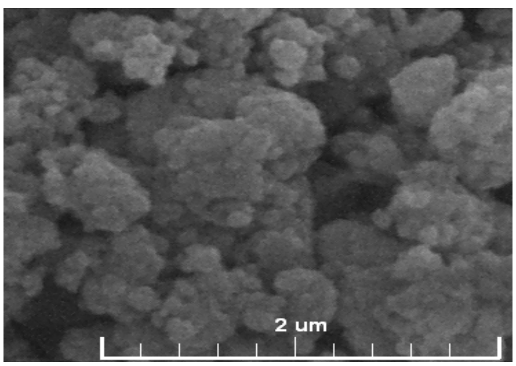

Fig. 1. SEM micrograph of TiO2 nanoparticles

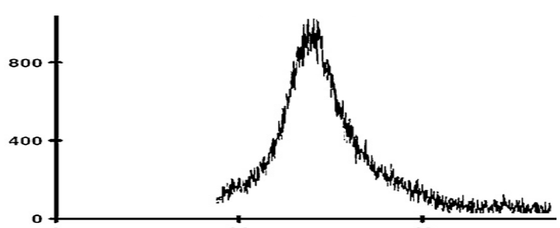

Fig. 2. XRD spectrum of TiO2 nanoparticles

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 superplasticizer (SP) with a specific gravity of 1.06 to 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 1. Furthermore viscosity modifying agent (VMA) for better stability was used.

Table 1. Physical properties of poly carboxylic ether 4

form	viscous liquid
color	light brown
Relative density	1.06 – 1.08 @ 20°C
pH	6.6
Viscosity	128 +/ - 30 cps @ 20°C
Transport s	Not classified as dangerou
Labeling	No hazard label required

3. Mix proportions and preparation of the specimens

A total number of 6 concrete mixtures were designed with a constant water/binder (w/b) ratio of 0.38 and 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 2.

Table 2. Mix proportions of the concrete specimens

No	Concrete ID	w/b	Cement (kg/m3)	TiO2 nanoparticles	Filler	Fine aggregate	Coarse aggregate	Sp	VMA
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

Since the SP plays a very important role in the flowability of SCC mixes, a modified mixing procedure was adopted to take the benefit of 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 minutes. Then half of the water containing the whole amount of Super plasticizer was poured and mixed for 3 minutes. After that, about 1 minute rest was allowed and finally rest of the water containing VMA was added into the mixture and mixed for 1 minute [6].

4. Tests of thermal properties

4.1. Conduction calorimetry

The test was performed on a isothermal calorimeter, at 22◦C for a maximum of 70 h. Fifteen grams of cement was mixed with water and different amount of TiO2 nanoparticles as a partial replacement of the cement before introducing it into the calorimeter cell.

4.2. Thermogravimetric analysis (TGA)

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 to 650ºC, at a heating rate of 4ºC/min and in an inert N_2 atmosphere.

5. Results and discussion

5.1. Conduction calorimetry

Table 3 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 monosulphoaluminate (AFm) phase via dissolution and reaction with $Al(OH)^{4-}$ [11]. The numerical values corresponding to these two signals (heat release rate, peak times) and the total released heat are shown in Table 3. 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 3. Calorimetric results of SCC specimens.

Mixture	Total heat (kJ/kg)	First peak		First 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 3 shows that increasing the percentage of TiO_2 nanoparticles up to 4.0wt% in the pastes accelerates peak times and drops heat release rate values. This is indicative of acceleration in initial cement hydration due to higher content of TiO2 nanoparticles. TiO_2 nanoparticles as a pozzolan can accelerate the cement hydration and hence increase the heat release rate. As it is 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 [5].

5.2. Thermogravimetric analysis

Table 4 shows the thermogravimetric analysis results of SCC-N specimens measured in the 110–650 ◦C range in which dehydration of the hydrated products occurred.

Table 4. Weight loss (%) of the pastes in the range of 110–650◦C for SCC specimens.

Mixture	Weight loss % (110-650˚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

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, such as the results obtained for conduction calorimetry, the increase in weight loss could be due to more formation of CH and C3H compounds in the cement paste [5].

6. Conclusion

The following conclusions may be obtained from the present study:

- TiO_2 nanoparticles could accelerate the appearance of the first peak in conduction calorimetry test which is related to the acceleration in formation of hydrated cement products.
- 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 of more weight loss

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