Composites: Part B 44 (2013) 40–47

Contents lists available at SciVerse ScienceDirect

Composites: Part B

journal homepage: www.elsevier.com/locate/compositesb

# Formulation of mortars with nano-$SiO_2$ and nano-$TiO_2$ for degradation of pollutants in buildings

L. Senff [a,b,*], D.M. Tobaldi [b], S. Lucas [c], D. Hotza [d], V.M. Ferreira [c], J.A. Labrincha [b]

[a] Materials Science and Engineering Graduate Program (PGMAT), Federal University of Santa Catarina (UFSC), 88040-900 Florianópolis, SC, Brazil
[b] Materials and Ceramics Engineering Department/CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
[c] Department of Civil Engineering/CICECO, University of Aveiro (UA), 3810-193 Aveiro, Portugal
[d] Department of Chemical Engineering (EQA), Federal University of Santa Catarina (UFSC), 88040-900 Florianópolis, SC, Brazil

ARTICLE INFO

*Article history:*
Received 12 January 2012
Received in revised form 13 June 2012
Accepted 11 July 2012
Available online 20 July 2012

*Keywords:*
A. Smart materials
B. Rheological properties
A. Ceramic-matrix composites (CMCs)

ABSTRACT

This paper reports on the design of cement mortars that use nano-$SiO_2$ (nS) and nano-$TiO_2$ (nT) particles, aiming to improve the durability of traditional building materials while giving new functionalities (aerial decontamination of pollutants). Samples with 0–2 wt.% nS, 0–20 wt.% nT, 0.45–7 wt.% superplasticizer (SP) and 0.45–0.58 water/binder weight ratio were prepared. The formulations of mortars were defined according to rheology and flow table measurements, then showing suitable workability. The temperature of hydration, compressive strength, water absorption, and photocatalytic degradation of pollutants ($NO_x$ and Orange II dye) were also evaluated. In general, the rheological behavior and the temperature of hydration changed in distinct levels, depending on the dosage and type of nanoadditives, but nT influenced more significantly the results. However, such differences were not identified on the compressive strength and water absorption. In addition, $NO_x$ photocatalytic degradation up to 1 h under solar light ranged from 65% to 80%, while Orange II degradation after 9 h under visible light changed from 18% to 50%.



## 1. Introduction

The recent developments conducted by nanoscience and nanotechnology are changing our world. For instance, the use of nanoparticles can make our homes cleaner and stronger, as well as retain energy from the sun for later release [1]. In addition, the wide range of products manufactured from nanotechnology, such as electronics to communication, aerospace, medicine, energy, construction and consumer goods is almost limitless [2] and the estimative is that the annual market of components of nanotechnology will reach $1 trillion by 2015 [3].

The application of nanotechnology in the civil engineering related industry can play an important role in the quality of building materials (strength, durability and lightness), creating multifunctional coatings or paintings as well as components such as sensors or other devices [4,5]. In addition, it allows us understanding the phenomena that occurs at nano-scale, opening the overall competitiveness in the market [6].

Currently, many investigations have been made on the use of nanoparticles of silica (nS) and titania (nT) in cementitious materials, but less common nanoparticle (e.g. $ZnO_2$) have been also utilized in concrete [7]. In general, the presence of nS accelerates the chemical reactions during initial hydration [8–10] while the reaction with calcium hydroxide (CH) [8,11,12] increases the amount of calcium silicate hydrate (C–S–H) produced at later ages [13]. As a consequence, the microstructure becomes more compact [11,14], while the mechanical properties are improved [8,9,11,14,15]. Concerning nT particles, the investigations mainly describe their known photocatalytic action, used for environmental pollution remediation, self-cleaning and self-disinfection [16]. In general, the performance is enhanced by the use of finer $TiO_2$ particles more effectively than by using higher dosages in the mixtures [17]. However, the use of fine particles might negatively affect the rheological properties and the hardened properties of mortars [18]. Instead of internal use in the bulk, active particles are normally applied on the external surface, in paints or renders, since the catalytic action needs light stimulation. The improvement of porosity and surface roughness of the layer assures higher exposure specific area and as a consequence air purification is more effective [19]. The use of $TiO_2$ nanoparticles as coating for concrete pavement seemed not to affect the wear resistance of the surface [20], while the deficiency in dispersion of nanoparticles decreases the benefits on the split tensile strength and percentage water absorption [21]. In addition, the use of a mixture of anatase and rutile have been reported to be more efficient than pure ana-

* Corresponding author at: Materials Science and Engineering Graduate Program (PGMAT), Federal University of Santa Catarina (UFSC), 88040-900 Florianópolis, SC, Brazil. Fax: +55 48 37219687.
*E-mail address:* lsenff@gmail.com (L. Senff).

1359-8368/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compositesb.2012.07.022

tase containing formulations [22], but the degradation rate of the photocatalysts decreases when the relative humidity enhances [17]. From the reported indications, the use of nS and nT containing cementitious coatings has received considerable attention. However, the photocatalytic performance of mortars that were formulated in a way that also assures desirable workability in a rheometer and flow table is not reported, and that was one of the main objectives of the current work.

The spread on table is the traditional method utilized in the civil construction to determine the workability of mortars. The use of the flow table is widespread around the world, since it is easier to operate and the results can be obtained quickly. However, it does not allow evaluating the behavior of material under different deformation rates. In addition, it is not possible to quantify the yield stress and plastic viscosity separately that are important parameters to define the rheological behavior of a fluid. As a consequence, the characterization is incomplete and not accurate, despite being popular worldwide. Thus, specific rheometers have been developed and utilized lately. In general, fresh mortar or concrete can be considered as a fluid material, where the initial resistance to the flow caused by contacts between particles is represented by yield stress, while the plastic viscosity controls the movement afterwards [23]. In addition, rheometer allows measuring the rheological parameters, using different deformation rates and approaching the conditions in which the materials are submitted in real applications. Often, the rheological behavior of mortars is represented by the Bingham model,

$$\tau = \tau_0 + \mu_p \cdot \gamma \tag{1}$$

where $\tau$ (Pa) is the shear stress, $\tau_0$ (Pa) is the yield stress, $\mu_p$ (Pa s) is the plastic viscosity and $\gamma$ ($s^{-1}$) is the shear rate. The Bingham model may be also expressed through torque ($T$, in N mm) as a function of rotation speed ($N$, in $min^{-1}$) by the following equation:

$$T = g + h \cdot N \tag{2}$$

where $g$ (N mm) and $h$ (N mm min) are directly proportional to the yield stress and plastic viscosity, respectively [24].

Therefore, this paper reports the influence of nanomaterials on fresh and hardened state properties of mortars, focusing the effects of nS and nT additions on their rheological behavior. Additionally, compressive strength, temperature of hydration, and the photocatalytic activity – considering degradation of $NO_x$ (gas–solid phase) and Orange II (OII, liquid–solid phase) – were also measured. The objective is to modify traditional materials in order to contribute for the overall environmental performance of buildings.

## 2. Experimental

### 2.1. Materials

Portland cement (OPC type II 32.5N), according to EN 197-1 [25] was used as a binder. It has a specific surface area (SSA) of 0.43 $m^2$/g (Blaine fineness), and the chemical composition is given in Table 1. Nanotitania (nT) is composed by 80% anatase and 20% rutile (Aeroxide P25, Portugal) with SSA of ~50 $m^2$/g and average size of 21 nm. Nanosilica (nS) slurry (Levasil 200, 40 wt.%, H.C. Starck, Germany) contains 40 wt.% solids, an average size of 15 nm and SSA of 200 $m^2$/g. The particle size distribution of sand used as aggregate in the mortars ranges between 0.075 and 1.18 mm (average size of 0.45 mm), while the superplasticizer (SP) used to adjust the plasticity of fresh samples is based on a polycarboxylic (Glenium 52, Basf, Germany) and contains 20 wt.% solids.

**Table 1**
Chemical composition of Portland cement CEM II – 32.5 N.

| Component (in wt.%) | Portland cement |
|---|---|
| $SiO_2$ | 15.41 |
| $Al_2O_3$ | 3.82 |
| $Fe_2O_3$ | 2.36 |
| CaO | 59.2 |
| MgO | 1.41 |
| $SO_3$ | 2.83 |
| Loss on ignition | 14.02 |

### 2.2. Experimental design and mixture

As mentioned before, nS and nT have been used in cement based materials for different aims, but their concomitant use was not reported so far. If the high reactivity of nS might contribute to the mechanical properties and durability of the materials, the use of nT particles aims to assure self-cleaning coatings due to the photocatalytic action. However, the dosages of nS and nT particles required to reach such benefits should be well established.

In this work, mortars with suitable workability were defined from measurements in the rheometer and in the flow table. In addition, a comparative evaluation between nanoadditive-free (REF) mortars and those containing (nS + nT) blends or just one single (nS or nT) additive was tried. In order to accomplish all those variables, two experimental plans were conducted (Table 2).

In the first plan, mortars with different dosages of nS and nT were prepared. The negative impact of nS and nT on the workability was compensated by adding distinct dosages of a superplasticizer (SP) up to obtain the torque values between 65 and 80 N mm. Such values were measured after 10 s of rheology test started. This time is required by equipment to reach the maximum value of speed (100 rpm). As the dosage of nanoadditives and SP ranged simultaneously in this experimental plan, the impact caused by nS and nT is not evident and, therefore, a second experimental plan was conducted. In this case, mortars containing one single nanoadditive were produced, using the same dosage of SP utilized in the corresponding blend.

Mortars were prepared for rheology and flow table, compressive strength, water absorption tests, $NO_x$ and OII photocatalytic degradation measurements, while the effects upon hydration (temperature evolution) were tested with respective pastes (Table 2). In both experimental plans, the water-to-binder weight ratios were initially fixed as 0.58 and 0.45 for mortars and pastes, respectively. Meanwhile, the binder-to-aggregate weight ratio of mortars remained constant (1:3) and the dosage of nS and nT were calculated in relation to the weight of cement.

In general, the solid components of the blends were dry mixed inside a plastic bag for 1 min, while 50% of total SP was mixed in the water, before addition to the solids. After 1 min of mechanical mixing of all components, the process was stopped for 1 min and during this period, the remaining SP portion was added. Afterwards, the mechanical mixing was re-established for another 1.5 min.

### 2.3. Rheometry and flow table measurements

Rheometer (Viskomat NT, Fig. 1a) and flow table (Fig. 1b) were used to measure the rheological behavior and workability of fresh mortars, respectively. For the rheological measurements, the maximum rotation speed was set at 100 rpm and at every 5 min the speed was brought to zero, kept there for 30 s and then it was increased to 100 rpm again during 30 s. The rheological parameters, namely plastic viscosity ($h$) and yield stress ($g$) were obtained by the Bingham model (Eq. (1)). The workability was tested in the flow table after mechanical mixing, following EN 1015-3 [26].