Construction and Building Materials 148 (2017) 261–272

Contents lists available at ScienceDirect

Construction and Building Materials

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

Physical-mechanical properties of mortars with addition of TiO_2 nanoparticles

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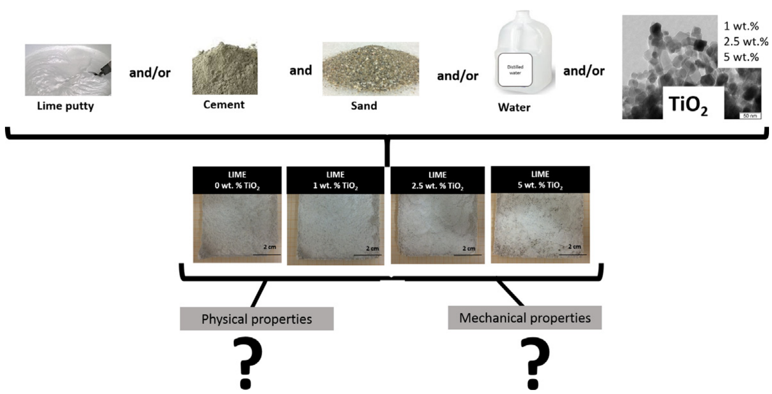
HIGHLIGHTS

- Lime-, cement- and lime & cement-based mortars containing TiO_2 have been investigated.
- Physical-mechanical properties induced by the introduction of TiO_2 were studied.
- Higher TiO_2 content leads higher open porosity and water accessible coefficients with exceptions.
- Global colour change showed a direct relation with the TiO_2 content.
- Mechanical properties were inversely related with the hygric properties.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 December 2016
Received in revised form 20 April 2017
Accepted 5 May 2017
Available online 13 May 2017

Keywords:
Nanocrystalline anatase
Titanium dioxide
Lime
Cement
Mortar
Chemical property
Physical-mechanical property

ABSTRACT

Lime-, cement- and lime & cement-based mortars, containing different proportions of nanocrystalline TiO_2 (1, 2.5 and 5 wt%) and fine aggregates of silicate nature have been investigated with the aim to improve the knowledge in terms of their chemical, physical and mechanical properties. The influence on the physical-mechanical properties induced by the addition of TiO_2 were evaluated through measurement of chromatic parameters, open porosity, water absorption coefficient at atmospheric pressure, P-wave velocity, material loss by peeling test and microdrilling resistance and compared to the reference mortars ones, i.e., without the TiO_2 nanoparticles addition. Moreover, stereo and electronic microscopy were used to study the morphology, the mineralogical and chemical composition of each mortar formulation. Fourier transform infrared spectroscopy was also applied to gather qualitative information on the chemistry of some of the characteristic components of the mortar.

The results suggest that the physical-mechanical properties of the studied mortars were influenced by the TiO_2 nanoparticles addition. Furthermore the influence of the TiO_2 on the properties of the studied mortars is also dependent on the nature of the binder used. Nevertheless, in general terms, the global colour change showed a direct relationship with the TiO_2 content. Regarding the hygric properties, mortars with higher addition of TiO_2 content showed higher open porosity and water absorption coefficients, but an exception for the cement-based mortar with 2.5 wt% was detected. The values obtained in the mechanical properties evaluated were inversely related with the hygric parameters.

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http://dx.doi.org/10.1016/j.conbuildmat.2017.05.040
0950-0618/

1. Introduction

The protection and conservation of Cultural Heritage (CH) is an important issue affecting countries worldwide. Increasing deterioration of its materials, among which are natural stone and mortars, is causing great concern. The urban environment, and the air quality in particular, as well as biological colonization, may cause or accelerate the deterioration of several heritage elements. In order to prevent the biodeterioration and soot deposition on CH objects, which alter both their aesthetical aspect and their physical–chemical properties, chemical procedures such as water repelling and cleaning products are commonly used as conservation treatments for historic monuments [1]. Nevertheless, some of these chemical products, namely water repellents, do not promote a long term protection and they need to be periodically re-applied [2]. Moreover, cleaning procedures and the ageing of protective coatings may cause themselves further changes on those materials. Therefore in order to avoid or at least to reduce aesthetical and physical–chemical deteriorations, those maintenance actions should be minimised, considering their potential invasiveness and environmental impact. So, new technologies focused on this prevention has been developed during the last years and a special focus has been given to innovative nanomaterials [3–7].

The nanocrystalline TiO_2 mainly of anatase form has been used in construction materials (concrete, mortars and stone basically) in order to provide a self-cleaning property due to its photocatalysis [3–7]. Several reviews have been published on self-cleaning action of TiO_2 and mainly discuss its photocatalytic activity [8–10]. Moreover, anatase is a good alternative to conventional biocides because it is non-toxic [6]. The introduction of anatase in CH conservation have widened to surfaces with self-cleaning and bactericidal properties in order to avoid biological colonization and fuel soot deposition [6,7,11]. It is known that black crust and biological colonization are some of the deterioration patterns derived from the interaction between the mortar or stone with the contaminant agents and the biological activity [12]. The photocatalysis is the acceleration of a photochemical reaction breaking down organic pollutants, volatile organic compounds and bacterial membranes by means of a catalyst interacting with light of sufficient energy [11]. Later, with the removal of the reaction products from the active sites, the catalyst becomes active again, making it capable of accomplishing a new photocatalytic process [13].

Regarding to the self-cleaning evaluation of the mortars with anatase addition, considerable research has been devoted to prevent biological colonization or fuel soot deposition by using this product mainly as a coating [14,15]. Nevertheless, some research has been focused on the addition of anatase during the common process of mortar manufacturing [6,7,16]. In what concerns anatase as aqueous solutions applied directly on the mortar surfaces, it achieved a satisfactory soot oxidation [14] and avoided the biological development on outside mortar walls [6]. A solution of TiO_2 in deionised water was also tested on white mortars to evaluate the degradation of *Rhodamine B* and tobacco [17], where photocatalytic efficiency was demonstrated to be dependent on the type of contaminant. Regarding the direct addition of nanocrystalline anatase powder during the manufacturing process of the mortar, Fonseca et al. determined that this procedure achieved a more satisfactory protection and self-cleaning property against lichen development than the application of conventional biocides [6].

When a mortar is used as a repair mortar, it must respect the features of the originally applied materials in terms of chemical, mechanical and physical properties in order to avoid a rapid and significant deterioration in a short time [18–23]. It is highly recommended every repair mortar to exhibit good compatibility and appropriate strength with the ancient mortars. Nevertheless, little if any attempts appear to have been made to evaluate the influence of added TiO_2 on the chemical, mechanical and physical properties of mortars made up with different binders. Therefore, this study focuses on the assessment of the effects of the introduction of different concentration of TiO_2 nanoparticles on the properties of lime-, cement-, lime & cement-based mortars.

2. Materials and methods

2.1. Materials and proportions

Mortars with two different binders were tested: (i) A commercial 5 years aged slaked lime putty supplied by CTS Srl Spain, and according to indications of the manufacturer it had a water content of 45 ± 5% and was composed of CaO (88.0–95.0%), MgO (0.0–0.5%) and $SiO_2 + Al_2O_3 + Fe_2O_3$ (0.1–0.3%). (ii) A Portland cement CEM II/B-L 32.5N (according to Ref. [24]). Their chemical composition was confirmed by energy dispersive X-ray Fluorescence spectrometry (XRF, Siemens SRS 3000) and the results are presented in Table 1.

The titanium dioxide, TiO_2, used as a photocatalyst additive, is a commercial product P25 AG D-60287 from Degussa, consisting of predominantly nanocrystalline anatase (3/1, anatase/rutile ratio) with specific surface area of 50 $m^2\,g^{-1}$ (a relative large surface area). Transmission Electron Microscopy (TEM, Hitachi 8100) was used to examine size and morphology of TiO_2 nanoparticles. The TiO_2 nanoparticles consist of both spherical and hexagonal disk-like shapes with an average grain size about 30 nm (Fig. 1). Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum 65) was also used to characterize these nanoparticles and confirmed the predominance of anatase (the peak observed at 452 cm^{-1} corresponds to a characteristic Ti-O vibration of the anatase).

In this study, a commercial siliceous aggregate from BIC S.L. (Spain) was used. The aggregate was passed through a sieve analysis in accordance to the requirements of Ref. [25]. The particle size distributions of this aggregate in compliance with Ref. [26] are presented in Fig. 2, where the suitability of the gradation of the tested aggregate as a mortar aggregate was evaluated by comparing the obtained gradation curve with the suggested particle size ranges according to Ref. [27]. This aggregate has a fineness modulus of 2.45 and a maximum diameter of 2.36 mm.

A total of 12 mortar formulations were considered for the characterization of some physical-mechanical properties of mortars with addition of TiO_2 nanoparticles (Table 2). Mortars were prepared adapting the methodology proposed by Refs. [6,28]. For each formulation (in Table 2, L for lime-based mortars, C for cement-based mortars and LC for lime & cement-based mortars), different TiO_2 concentrations added to the total solid content were tested: 0, 1, 2.5 and 5 wt%, with respect to the dry mixture. The three mortars formulations were prepared using a weight proportion binder/aggregate ratio of 1/3. For each condition 3 samples were prepared. The components were manually mixed, without any previous treatment. Then, distilled water (if necessary) was added and the fresh materials were prepared using a laboratory mixer. The water/binder ratio (w/w) for the cement mortars was fixed at 0.45 [29]. Considering the free water already present in the lime

Table 1
Average chemical composition of slaked lime putty and Portland cement CEM II detected by XRF (%). n.d.: no detected.

Compound	Lime putty (%)	Cement (%)
CaO	97.00	n.d.
$CaCO_3$	n.d.	48.52
SiO_2	0.68	26.3
Al_2O_3	0.36	12.3
SO_3	1.19	2.96
Fe_2O_3	0.168	3.89
K_2O	0.03	2.59
MgO	0.40	1.7
TiO_2	0.018	0.47
Na_2O	0.031	0.39
P_2O_5	0.03	0.21
Cl	0.01	0.009
Cr_2O_3	n.d.	0.0073
MnO	0.0083	0.039
NiO	n.d.	0.009
CuO	0.006	0.0009
ZnO	n.d.	0.012
SrO	0.004	0.0269
BaO	n.d.	0.059
V_2O_5	0.016	0.008
ZrO_2	n.d.	0.0057