

Experimental analysis on the functional properties of rendering mortars with superficial addition of TiO₂ nanoparticles

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ABSTRACT: Recent developments in the area of nanomaterials science and nanotechnology are changing the field of construction and building industry. The construction industry has been increasingly identified as an important market for the use of nanomaterial's since this can make buildings cleaner (minimizing the pollution effects and also reducing the building facades maintenance costs), resistant and energy efficient (thermal energy storage).

In order to contribute for the development of this area, this work aims the production of rendering plastering mortars with multifunctional properties such as photocatalytic capacity and improving thermal capabilities. Standard plastering mortars were modified by spraying titanium dioxide (TiO₂) from a water-based TiO₂ nanoparticles solution. Two mortar compositions, which are representative of rendering mortars, namely composition, 1:1:6 and 1:2:9 (cement:lime:sand) in volume, were considered. Additionally, two distinct water/binder ratios were considered to induce distinct porosities and thus to evaluate the differences on the mechanical and physical properties of the mortars after the addition of the TiO₂ nanoparticles.

Keywords: rendering mortar, TiO₂ nanoparticles, physical and mechanical properties, thermal efficiency

1 INTRODUCTION

Recent developments in the areas of nanomaterials science and nanotechnology are changing the field of construction and building industry [1]. The construction industry has been increasingly identified as an important market for the use of nanomaterial's since as they can make buildings cleaner (minimizing the pollution effects and also reducing the building facades maintenance costs), resistant and energy efficient (thermal energy storage). These are very important features in cities characterized by having a densely urban environment.

Since the discovery of the photocatalytic properties of some semiconductor materials, several investigations have been made to characterize the potential of the addition of these materials to construction materials aiming at improving the functional properties in view of achieving more sustainable materials. The photocatalytic property can be defined as the ability of a material under UV irradiation from solar light, together with the presence of water molecules, for promoting the formation of substances that have a strong oxidizing potential and win reaction to some organic and inorganic resulting in its disintegration. This development dates back the nineteen's, when several studies

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resulted in patents [2-3]. Among the semiconductor with photocatalytic properties based on oxides and sulfites, it can be highlighted the titanium dioxide (TiO_2), zinc oxide (ZnO), Tungsten oxide (WO_3), and cadmium selenide (CdSe). However, the titanium dioxide has been taken the major attention due its high photocatalytic activity, chemical stability, availability and cost (Hoffmann et al. 1995) [4]. Even though known since the sixties, the self-cleaning ability associated to photocatalytic activity only recently have been taken advantage of. The concrete with self-cleaning properties was firstly used in the church “Dives in Misericórdia” designed by architect Richard Meyer in pre-fabricated concrete blocks, made with white cement and containing TiO_2 in its composition [5]. This approach can result in the reduction of cost with the maintenance of the buildings, becoming them more sustainable. As the majority of the buildings, particularly in the south European countries have façades with rendering mortars, the study of self-cleaning abilities is privileged in case of mortars.

Besides the photocatalytic activity, the titanium dioxide (TiO_2) can promote the reduction of the contact angle between water drops and surfaces when applied in certain surfaces, like glass, becoming the surfaces hydrophilic, which contributes for the improvement of the self-cleaning ability [5].

The majority of the studies focusing on the use of TiO_2 nanoparticles in mortars considers the addition of these particles in volume, meaning that they are dispersed in the micro-structure of the mortar and can alter it. According to Maravelaki-Kalaitzaki et al. (2013) [6], the addition of nano-titania in hydraulic mortar improves the hydration process, leading to improved elasticity modulus of the mortars with nano-titania relatively to mortar without nano-titania. The hydrophylicity of the nano-titania improves the humidity retention of mortars, enhancing the adhesion to porous stones. Other study carried out by Lucas et al. (2013) [7] aiming at evaluating the photocatalytic properties of mortars by incorporating different percentages of TiO_2 nanoparticles in volume, revealed a decrease on the flexural and compressive strength of mortars when percentages of TiO_2 nanoparticles is higher than 1 wt%, essentially due to the porosity increase. It was seen that high photocatalytic activity was found for low additions of TiO_2 nanoparticles (0.5 and 1wt%). The porosity increase in mortar modified by the addition of TiO_2 nanoparticle in volume (1wt%, 3wt% and 5wt%) was also confirmed by Ruot et al. (2009) [8]. The photocatalytic ability of mortars with TiO_2 nanoparticles (in volume) was also analysed by Senff et al. (2013) [9]. In this study a combination of SiO_2 and TiO_2 nanoparticles was also evaluated for analysis of the photocatalytic activity effectiveness. The analysis of the photodegradation of organic pollutants was also investigated by Carneiro et al. (2013) [10] in asphalt admixtures either considering the TiO_2 nanoparticles as additive (addition in volume) or by considering the the TiO_2 nanoparticles as a spray coating. It was seen that the photocatalytic efficiency was achieved in both process. In case of the spray coating, the great advantage is the maintenance of the bituminous paving structure and reduction of applications costs.

In spite of the above advantages above cited, it should be mentioned that in a recent review on the application of nanomaterials in the construction industry concludes that beyond the current excitement about the possibilities of manufactured nanomaterials to enhance infrastructures, there are reasonable concerns about unintended consequences [11].

In order to contribute for the development on the use of TiO_2 nanoparticles in mortars and improve its functionality, this work focus on the analysis of rendering plastering mortars with multifunctional properties such as photocatalytic capacity and improving thermal capabilities by considering TiO_2 nanoparticles as a spray coating. Thus, standard plastering mortars surfaces were modified with TiO_2 nanoparticles by spraying a water-based TiO_2 nanoparticles solution. Two mortar compositions, which are representative of rendering mortars, namely composition, 1:1:6 and 1:2:9 (cement:lime:sand) in volume, were contemplated in the experimental study. Additionally, two distinct water/binder ratios were considered to induce distinct porosities and thus to evaluate the differences on the mechanical and physical properties of the mortars after the addition of the TiO_2 nanoparticles.

2 EXPERIMENTAL PROGRAM

As aforementioned, the major aim of the present work is the evaluation of the functional behavior of rendering mortars after the superficial addition of TiO_2 nanoparticles in a colloidal suspension in the fresh state of the mortars. The idea is that the nanoparticles can adhere in the surface during the

hardening process of the mortars. It is intended to (1) evaluate the photodegradation ability of these mortars; (2) assess of the influence of the addition of TiO₂ nanoparticles in the physical and mechanical properties of mortars; (3) access the thermal properties of stand and modified rendering mortars. The idea is that by spraying the TiO₂ nanoparticles from an aqueous solution, the surface heat transfer to the opposite surface of the wall can be reduced.

2.1. Materials

For the rendering mortars two typical mortar mixes were used, namely 1:1:6 e 1:2:9 (cement:lime:sand in volume) [12]. The cement used in the mortars was CEM II/B-L 32.5 N and the lime used was an hydrated lime. The sand used in the mortars resulted from the combination two sands available in the market, namely medium sand (M) (60%) and fine sand (F) (40%). The idea was to obtain more extensive sand that could improve the workability properties of the mortars. The particle size distribution of the sands appears to be an important influence in the quality of mortars regarding the compactness, impermeability and mechanical strength as it is directly related to the micro-structure of the mortars.. From the sieve analysis of the sands, carried out according to EN 933-1 (2000) [13], a curve grade for the original sands (M and F) and the composite sand (A) was obtained, according to what is shown in Figure1. The composite sand A presents a better distribution in terms of percentage of fine, medium and coarse aggregate particles, comparing to the sands M and F. The fineness modulus of the composite sand is 2.27, an intermediate value between 3.36 found for the sand M and 2.19 for the fine sand F. The mortar composition is shown in Table 1.

Table 1. Mortar composition

Mortar	Mix (cement:lime:sand)	w/b ratio	Flow table (mm)
M1	1:2:9	0.72	180
M2	1:1:6	0.63	180
M3	1:2:9	0.54	160
M4	1:1:6	0.50	160

The water/binder ratio considered for the mortars was defined based on the assumption that two distinct levels of workability were obtained for each mortar mix. The workability was measured by flow table, which was fixed in 160mm and 180mm. According to the results found by Haach et al. (2011) [14], it was possible to improve the workability of the mortars by increasing the quantity of water, even if it resulted in the reduction of the flexural and compressive strength of the mortars. The different levels of workability measured by the flow table tests should be associated to distinct internal structure due to the induced porosity when higher amount of water is considered [15]. The idea of using distinct flow table values was to assess the influence of the porosity of mortars on the effectiveness of the adherence of the sprayed TiO₂ nanoparticles in the surface of the mortars.

As mentioned above the water/binder ratio (*w/b*) was defined based on the flow table value obtained according to EN 1015-3 (2004) [16]. Thus, for the mortar mix 1:1:6, water/binder ratios (*w/b*) of 0.63 and 0.5 were defined corresponding to flow table values of 180mm and 160mm respectively. For the mortar mix 1:2:9, water/binder ratios (*w/b*) of 0.72 and 0.54 were defined corresponding to flow table values of 180mm and 160mm respectively. Notice that, as expected, the water quantity is higher in case of mortar 1:2:9, due to higher quantity of lime. This result is in agreement with results pointed out in literature stating that mortar mixes with lime need more water to reach the same consistency, which is essentially related to the smaller particles size found in lime than in cement and thus to higher specific surface of lime (Sébaibi et al., 2003, Reddy and Gupta, 2008) [17-18]. Thus, the increase of the amount of fine particles in lime leads to a higher water retention capacity, which is also a measure of the workability [17].

The spraying of TiO₂ nanoparticles was made in the fresh mortar after two hours of curing in order to ensure that the mortar is even in the fresh state so that it was possible to promote the adherence of

the sprayed nanoparticles. The idea consists of the possibility of obtaining a superficial thin layer of the coating that ensures the good performance of the mortars instead of waste of material by adding the nanoparticles in volume according to procedures followed by different authors [7,10]. The spraying of about 50 ml of aqueous solution of TiO₂ nanoparticles was carried out manually at 10cm of distance of the surface of the mortar by using a spraying cone with a covering area of 40cm², see Figure 2. The TiO₂ aqueous solution for the spraying had a concentration of 10 g/l and a pH of 3 and 8. According to Carneiro et al. (2013) [10], the efficiency of the photocatalytic process increase with the increase on the concentration of the aqueous solution of TiO₂ nanoparticles. However, the authors observed that for concentrations higher than 10 g/L, the aqueous solution of TiO₂ nanoparticles presented a reduced degree of dispersion, preventing the stability of the colloidal dispersion. In effect, different methods exist for the synthesizing TiO₂ nanoparticles. One of the chemical methods much used consist of the hydrothermal synthesis (carried out in a autoclave) from a precursor, the butoxide of titanium (Ti(OCH₂CH₂CH₂CH₃)₄). Nevertheless, the TiO₂ in aqueous solution tend to form aggregates and hence compromise the colloidal solution. This phenomenon is attributed fundamentally to van der Waals forces (attractive) that promote the agglomeration of the nanoparticles, avoiding the obtainment of a solution with high level of dispersion.

The common strategy to improve the dispersion level consists of using acid solutions (pH between 3 and 4) or alkaline solutions (pH between 8 and 9). The use of acid solutions allows that the nanoparticle surface acquire a positive electric charge, whereas as the alkaline solutions allow the surface nanoparticle acquire a negative electric charge. For both situations, the intensity of the Coulomb electrostatic forces (repulsive) should be higher than the van der Waals attractive forces and thus, ensure a better stability of the colloidal dispersion.

The mortar specimens with coating of nanoparticles obtained from a aqueous solution with pH equal to 3 and 8 are named as pH3 and pH8 respectively.

2.2. Characterization of the TiO₂ coatings

The morphologic characterization of the surfaces of the mortars was made through scanning electronic microscopy (SEM), complemented with the *Energy Dispersive X-Ray Spectrometer* (EDS). The scanning electronic microscopy was only carried out in two mortar specimens, namely: (1) mortar mix 1:1:6 without the addition of TiO₂ nanoparticles; (2) mortar mix 1:1:6 with the addition of TiO₂ nanoparticles from the suspension with a pH of 3. The *Energy Dispersive X-Ray Spectrometer* was also made for both specimens.

The photocatalic activity was evaluated through the measurement of the absorbance of an aqueous solution of methylene blue (MB) as a function of the time of UV irradiation. Before the degradation process, the methylene blue presents the blue colour, which progressively becomes shade off by the action of the reducing agent. The specimens were immersed in aqueous solution of methylene blue with an initial concentration of 10 g/L and then were placed in a chamber and exposed to the UV radiation (power of 12W, measured with the equipment Quantum Photo Radiometer HD9021 Delta Padova). The efficiency of the photodegradation process was evaluated during time through the concentration of MB.

For this, drop of 10 mL were removed from the MB aqueous solution and introduced in a quartz cell aiming at measuring the absorbance spectrum through the equipment Shimadzu UV-310 PC Scanning Spectrophotometeti. In this work, the measurements were made after 15, 30, 60, 90, 120, 150, 180, 210 e 240 minutes after the UV exposition.

2.3. Physical and mechanical test procedures

The physical characterization of the mortars was carried out based on absorption by water immersion after 48hours and through water absorption by capillary.

The water absorption by immersion was carried out based on the EN 394 (1993) [19]. Some cubic speciemens were sparyed in a surface by the queous solutions of TiO₂ nanoparticles. After 14 day of curing, the cubic specimens were placed at the room temperature (20 ± 2°C). After this, they were placed in a container with water at temperature of 20 ± 2°C until constant mass is achieved. The immersion of the specimens is made by phases for certain percentages of the height, *h*, being added

water up to 1/3h, 2/3h and total height after one, two and three hours in order to avoid the formation of air bubbles. The total height of water should not be higher than 20mm above the top of the specimens. The dry mass of the specimen is obtained after the placement of the specimen in oven at temperature of 105°C±5°C, being the mass between two consecutive measurements lower than 0,1% of the average of the last two measurements.

The capillary tests were carried out according to EN 1015-18 (2002) [20]. after 14 days of curing and after the drying of the specimens in an oven at a temperature of 60°C±5°C until constant mass was achieved. For this, three specimens were considered for each type of mortar. The evaluation of the possible influence of the superficial addition of TiO₂ nanoparticles was obtained by adding TiO₂ nanoparticles in the surface of the specimens in contact with water, through which the absorption by capillary is made. The specimens are isolated through the application of an impermeable material so that the unique surface in contact with water was the its bottom surface, see Figure 1. It was ensured that all the specimens tested had the same initial water immersion level, 5mm±1mm above the bottom surface of the specimens, which was kept constant during the test. Intermediate weighings of the specimens at 30, 60, 90 minutes after the starting of the test were made aiming at obtaining the water absorption by capillary with time and becoming possible the definition of the capillary absorption coefficient. After this, the specimens were weighed at each hour until almost constant values were obtained.

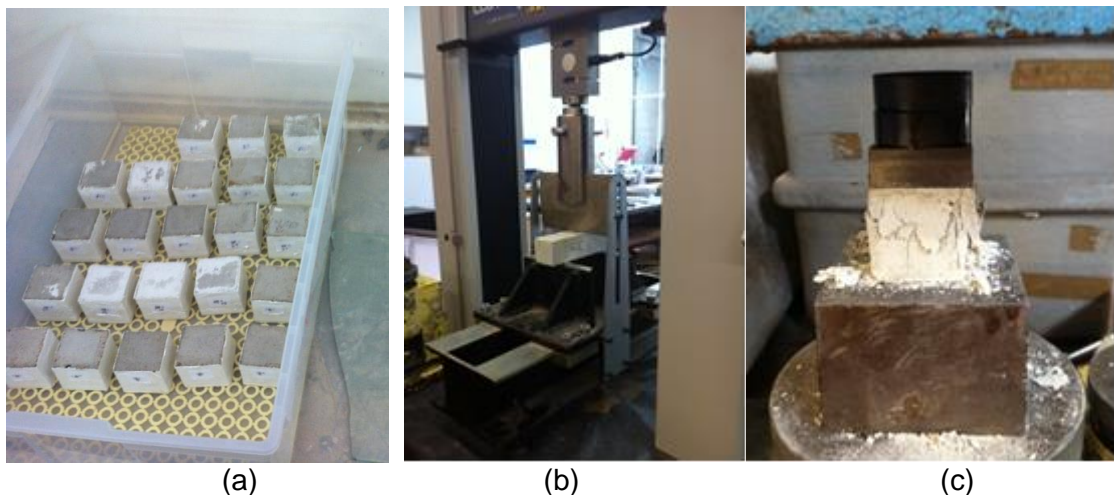


Figure 1. Experimental details: (a) capillary tests; (b) test setup for the mechanical characterization to flexure; (c) test setup for the mechanical characterization to flexure

The mechanical characterization of the mortars under study with and without the addition of TiO₂ nanoparticles was made through compression and flexural tests aiming at obtaining the compressive and flexural resistance and at evaluating also the influence of the addition of TiO₂ nanoparticles in the mechanical resistance of the mortars. The specimens were tested after 14 days of curing, similarly to what was made in the physical characterization. In the flexural tests (specimens 160x40x40 mm³), the surface where TiO₂ nanoparticles were added was the bottom surface, in which the tensile stresses induced by flexure develop, see Fig 1b. The compression tests of the mortar were then carried out according to EN 1015-11 (1999) [21] in cubic specimens (border with 50mm), sprayed at one face with TiO₂ nanoparticles. The compression tests were carried out in force control at a rate of 50 N/s until failure, see Figure 1c.

3 ANALYSIS OF RESULTS

3.1. Mortar surface morphology characterization (SEM and EDS)

The main aim of the using of the combining SEM and EDS analysis consists essentially in analyzing the degree of adherence of the spread TiO_2 nanoparticles to the mortar surface and thus, the effectiveness of the spread technique of the TiO_2 nanoparticles.

The results found for the surface with addition of the sprayed TiO_2 nanoparticles in a solution of a PH of 3 are shown in Figure 2. In case of standard mortar, it is observed that the chemical composition of the reference mortar mix is characteristic of cement and lime based mortar. The present of Au elements is attributed to the need of covering the observation surface used to ensure a good electric conductivity and prevent the possible effects of shading. In addition, it can be seen that the surface appears to be moderately uniform and regular, even if it is possible to identify zones with aggregates with higher dimension. In spite of the low amplification used, it is possible to observe that the surface presents high amount of pores, inducing a high level of porosity.

From the analysis of the surface with addition of TiO_2 nanoparticles, it can be seen that on one hand, it is possible observe from the chemical analysis that particles of TiO_2 can be identified on the surface of the mortar and, on the other hand, that they are not uniformly distributed on the surface, meaning that the spread process can be further optimized. The latter conclusion comes directly from the comparison between the EDS spectrum of zones Z1 and Z2. In fact, in the zone Z1 there is a predominance of TiO_2 elements, but this is not the case of zone Z2, where TiO_2 is present in a much lower level and predominance is given to other chemical elements characteristic of cement and lime based mortar.

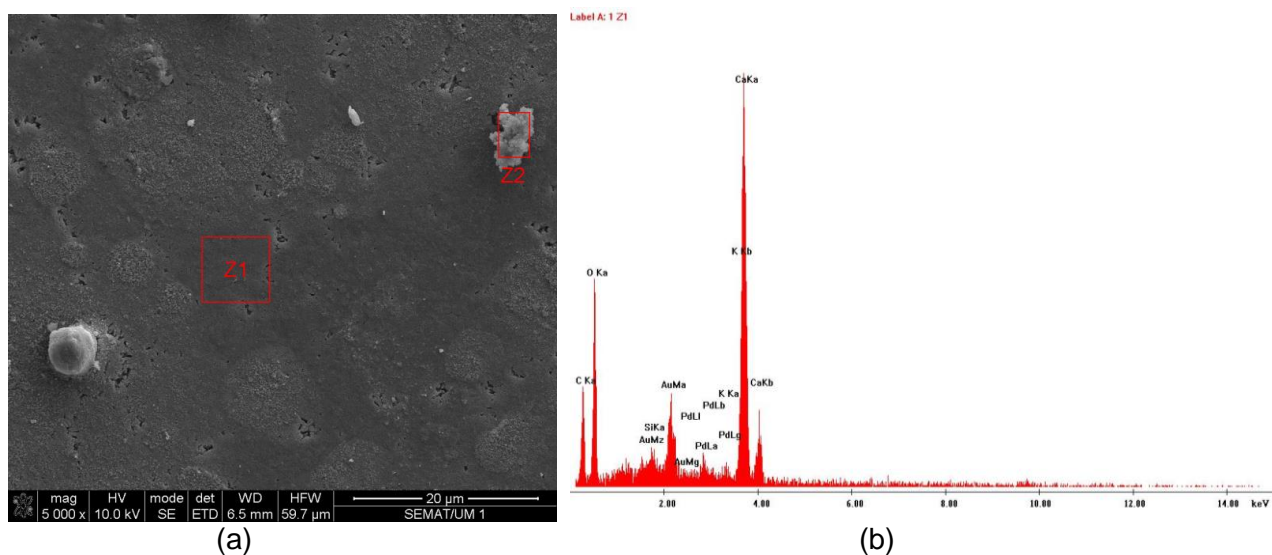


Figure 2. (a) Surface SEM micrograph and (b) EDS spectrum of the TiO_2 -coated surface mortar

3.2. Photocatalytic activity of the mortars with TiO_2 nanoparticles

As mentioned before, the photocatalytic activity of the surface modified mortars was evaluated based on the combination of the UV irradiation and time absorbance measurements. In Figure 3, it is shown the absorbance variation of the MB (organic pollutant) during the test for the mortar mix 1:1:6 with spraying of nanoparticles from an aqueous solution of TiO_2 nanoparticles having a concentration of 10g/l and a PH of 3. It is observed a decrease in absorption of the MB after UV irradiation, which is associated to its photodecomposition. From the absorption spectra of all the modified samples, it is possible to calculate the corresponding photocatalytic efficiency. Figure 3 displays the variation of the photocatalytic efficiency with time for both mortar mixes (1:1:6 and 1:2:9) modified by the spraying an aqueous solution of TiO_2 nanoparticles having a concentration of 10g/l and a PH of 3 and 8 on the mortar surface. From the analysis of the efficiency, it is observed that the photocatalytic ability of the mortars presents a high efficiency, being of approximately 70% at 240min of UV irradiation. By comparing the efficiency of the TiO_2 nanoparticles added in the distinct mortar mixes, it can be seen

that no much important differences were found, apart from the slightly lower effectiveness of the mortar mix 1:2:9 sprayed with aqueous solution of TiO₂ nanoparticles with a PH of 8 until 160mm of UV irradiation, after which similar values to the other mortar mixes were found. According to Chen and Poon (2009) [22], the photocatalytic activity of the cementitious surfaces can be increased by the consideration of glass as an aggregate aiming at serving as activator of the nanoparticles. The results presented here allow to conclude that the spraying of the an aqueous solution of TiO₂ nanoparticles at the mortar surfaces can replace the addition of nanoparticle in volume in the mortars and avoids the need of adding glass as aggregate.

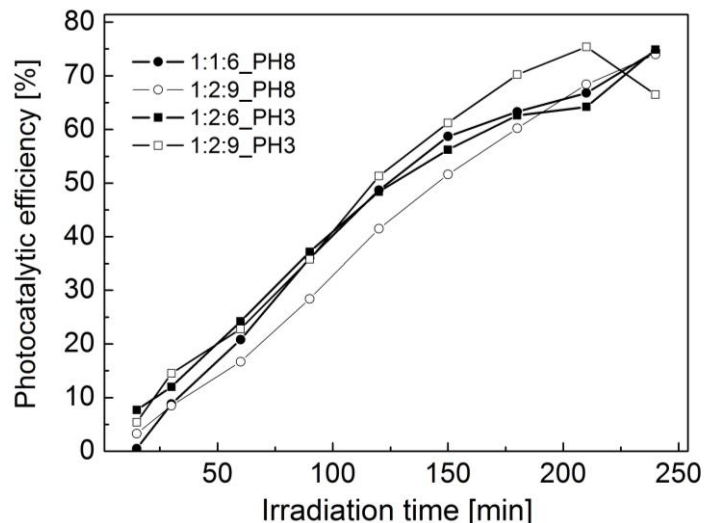


Figure 3. Photocatalytic efficiency of the different modified mortars

3.3. Physical and mechanical properties

A comparison between among the different mortars in relation to the water absorption by immersion and capillary can be made also through Figure4. From the values of the water absorption by immersion obtained for the reference mortar it is possible to observe that the mortar mix and workability are two factors affecting the water absorption. In fact, the mortar mix 1:2:9 presents higher water absorption than mortar mix 1:1:6, being the increase of about 8% for both flow table values (180mm - w/b of 0.72 and 160mm - w/b of 0.63). For both mortar mixes the increase of the value of flow table from 160mm to 180mm results in an increase of the water absorption of the order of 20%. This behavior is attributed to the higher porosity induced by the increase on the water/binder ratio (w/b) to achieve a higher workability. The increase on the sand and lime proportion on the mortar mix results also on the increase of the water absorption, which is also associated to the increase on the porosity.

Besides, the values of porosity measured by water immersion during 48 hours and the water absorption by capillary has no very significant changes, which could be associated to minor changes on the porous network of the mortars surfaces. In terms of water absorption by capillary, it is observed that the water capillary absorption decreases for lower values of w/b ratio and for mortar mix 1:1:6 when compared to mortar mix 1:2:9. It appears that the mortar mix has more influence for lower w/b ratios. In fact, there is no almost differences on the capillary absorption coefficient between mortar mix 1:2:9 and 1:1:6 when flow value is 180mm. However, the influence is considerable between the mortar mixes when the flow value is of 160mm.

In terms of the influence of the addition of TiO₂ nanoparticles, it is seen that the water absorption by immersion slightly increases with the addition of the TiO₂ nanoparticles. The percentage of the increase is almost constant when nanoparticles were added and the spread of nanoparticles in a solution with PH of 3 results always in higher value when compared to the spread of nanoparticles in a solution with PH of 8, even if the difference is very small. The effect of the addition of the

nanoparticles is not so clear when water capillary absorption is studied. There is no a clear trend for decreasing or increasing the values of water capillary absorption after the addition of nanoparticles. The water capillary absorption appears to slightly decrease with the addition of TiO₂ nanoparticles, but in case of mortar mix 1:2:9 and for a flow value of 180mm, it increases for both types of solution of the nanoparticles. Notice that this effect can not be relevant in case of the water absorption by immersion as in this case the water entrance is free in all surfaces of the specimens.

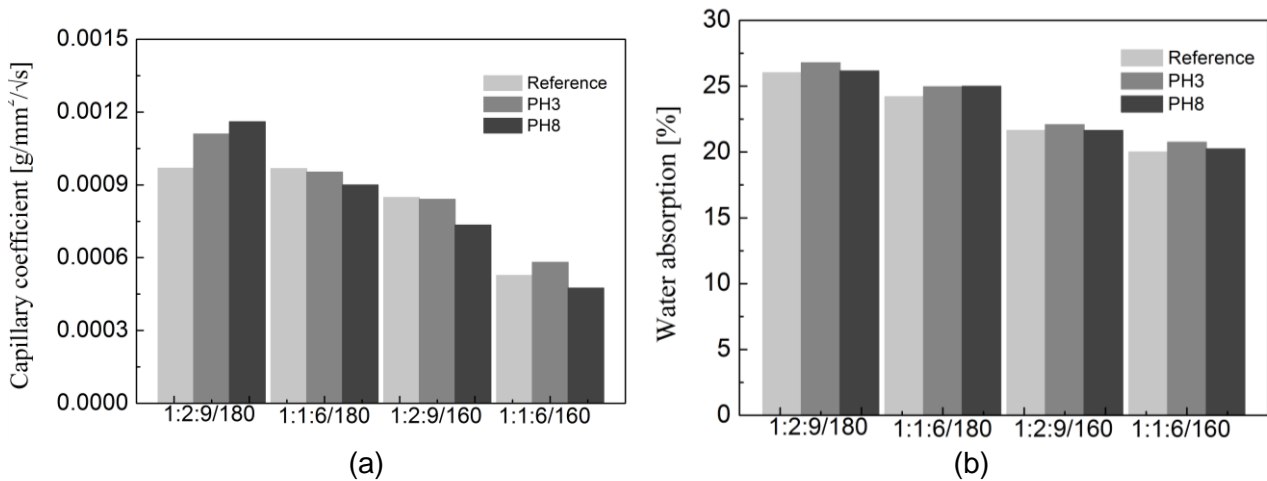


Figure 4. Evaluation of the physical properties of the distinct mortars; (a) capillary coefficient; (b) water absorption by immersion

The flexural resistance depends on the mortar mix, presenting lower values for mortar mix 1:2:9. It is possible to conclude that the increase in the lime amount in the mortar mix results in the considerable lowering of the flexural and compressive strength see Fig 5a. The w/b ratio has also an important influence on the flexural strength, being clearly lower in case of the high w/b ratios, see Figure 5b. The dependence of the mechanical properties on the w/b ratios found in this work is in accordance with other recent studies [15]. In general, the increase on the w/b ratios results in the severe decrease of the mechanical resistance, both of compressive and flexural resistance.

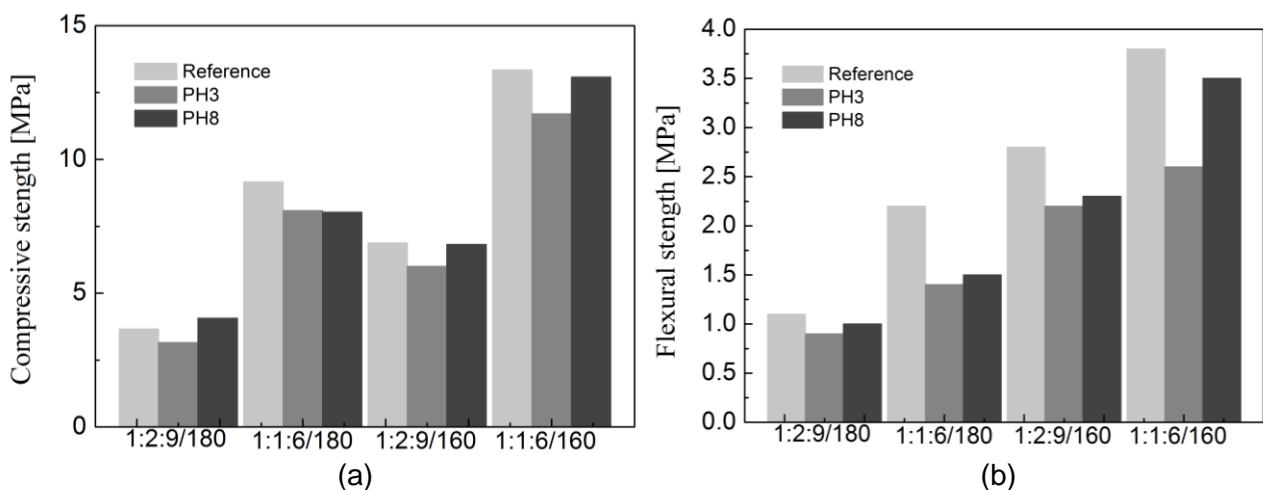


Figure 5. Evaluation of the mechanical properties of the distinct mortars; (a) compressive strength; (b) flexural strength

The increase in the w/b ratio means that there is more water between the solid particles. Consequently there are more voids in hardened condition, increasing the porosity, as previously seen leading to the decrease in the mechanical strength. There is a clear influence of the addition of nanoparticles on the flexural resistance. In general a clear decrease on the flexural strength was

observed. The decrease is slightly more evident in case of the spraying of nanoparticles from the solution with a pH of 3, even if in mortar mix 1:1:6 and a flow of 160mm, the difference is higher. The decrease is in average of 27% and 17% in case of addition of nanoparticles in a solution with a PH of 3 and 8 respectively. There is a trend for the decrease on the compressive strength of the mortars with the addition of nanoparticles, even in a lower percentage.

The lowering of the compressive strength is also higher when nanoparticles from a solution of PH of 3 are added. The lower reduction in compression should be associated to lower influence of the superficial addition of nanoparticles as the compressive resistance involves the bulk of the mortar. In relation to the flexural strength, as the maximum tensile strength occurs at the surface where nanoparticles were added and thus the change of the surface morphology is more relevant. In both cases, the reduction on the strength should be associated to the increase on the porosity of mortars. It should be mentioned that the reduction of compressive and flexural strength with the addition of nanoparticles in volume has already been mentioned by (Lucas et al., 2013) [7].

4 EVALUATION OF THE THERMAL EFFICIENCY OF COATED SURFACES

In order to evaluate the performance of the mortar surfaces two test wall models were built with the same overall dimensions. The dimensions of the test wall are 44 cm × 38 cm × 16.5 cm (width × height × thickness). Two layers compose the standard wall model, nameley: a 15 cm ceramic brick masonry wall filled by a 1.5 cm plastering mortar previously designed. The brick is horizontally perforated and is characteristic of non-loadbearing enclosure masonry walls in Portugal and various European countries [23]. The second wall model (Figure 6) is essentially the same as the previous one being the only difference the plastering mortar coated with a TiO₂ nanoparticles based thin surface layer with a thickness of about 0.8 μm (irradiated with UV lamps). By using several layers of extruded polystyrene (XPS), in which each layer is composed by two XPS plates (each have a thickness of 3 cm), all sides of the test wall (except the front and the back side) were carefully thermally insulated in order to ensure a unidirectional heat transfer. This experimental analysis consisted on monitoring over time the thermal behaviour of the test wall models, namely the TiO₂-coated mortar (modified mortar surface) and the uncoated ones (i.e. the standard model).

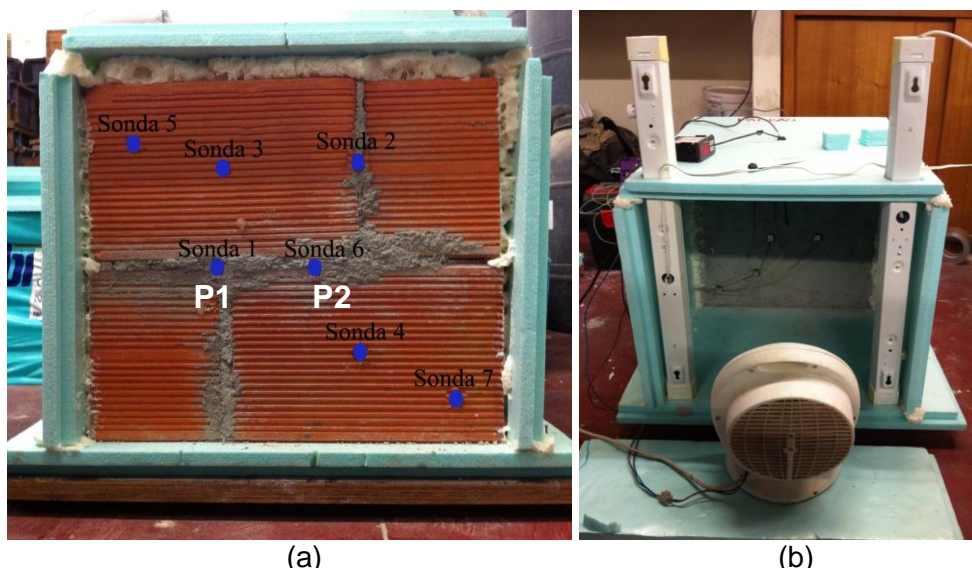


Figure 6. Experimental details about the test setup for evaluation of the thermal efficiency of the mortars; (a) uncoated surface with indication of the temperature measurement points; (b) heater used in the coated surface

In order to obtain the thermal characteristics of both test wall models, the experimental setup includes one heat flowmeter (from Hukseflux HFP01), which is fixed in the wall back face (Figure 6a), a heat source (a 120 W heating vent), surface temperature sensors (seven per face wall) located in

different positions taking into account the heterogeneous nature of brick masonry (brick, head and bed mortar joints, intersection of bed and head mortar joints) (Figure 6a), two ambient temperature sensors (one located near the heat source and the other placed in a region close to the back surface wall), a data logger (dataTaker DT 800) and a computer.

For the wall model having the external surface modified by the superficial addition of TiO₂ nanoparticles, the experimental setup also includes two UV lamps (PHILIPS TL-D 18W BLB SLV). In order to activate the semiconductor material, the light source was fixed on a support structure placed at a distance of about 30 cm from the TiO₂ coated surface wall (Figure 6b). At this distance, the UV light power intensity is about 8 W/m² (measured with a Quantum Photo Radiometer HD9021 Delta Padova). Two aspersions with water to the coated surface were made aiming at assessing the behaviour of the standard and modified mortar surfaces to the cooling of the surfaces.

The temperature profiles measured in control points P1 and P2 (Fig 6a) both in the coated and uncoated wall surfaces are presented in Figure 7. The abrupt reduction of the temperature corresponds to the spraying of the coated surfaces with water.

By comparison of the temperature profiles of the two control points, it is seen that it appears that trend for the coated surfaces modified with TiO₂ nanoparticles present slightly higher temperatures after spraying of water. As expected there is a reduction of the temperature on the uncoated surface (opposite surface to the heating) in both specimens. Also in this case the temperature appears to be slightly higher in case of the specimens with modified mortar coating. This appears that no significant thermal differences should be found for the mortar surfaces. However, this is a simple analysis of the temperature profiles in the opposite surfaces of the specimens and a more detailed analysis should be made in a further work.

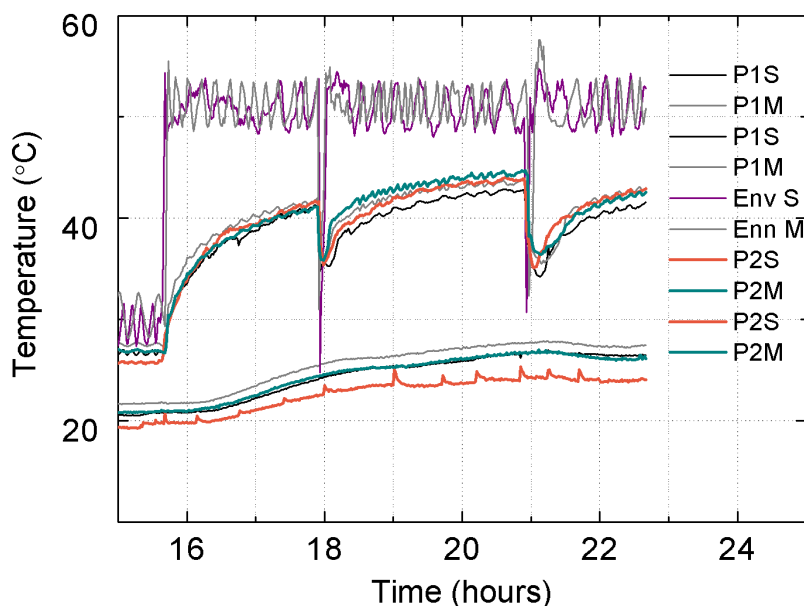


Figure 7. Profiles of temperatures measured in control points at the standard (S) and modified mortar surfaces (M): Environment of the heat surfaces (Env), Point P1 at the mortar joint and Point P2 at the intersection of the bed and head mortar joints

5 CONCLUSIONS

In order to contribute for the development on the use of TiO₂ nanoparticles in mortars and improve its functionality, this work focused on the analysis of rendering plastering mortars with multifunctional properties such as photocatalytic capacity and improving thermal capabilities by considering TiO₂ nanoparticles as a spray coating. Based on the experimental analysis carried out on the morphologic, physical and mechanical properties of the mortars, as well as on the thermal efficiency tests, the following remarks can be pointed out:

1. Based on the results of the electronic microscopy (SEM) and , it was seen that it is possible to modify the rendering mortar surfaces by spraying an aqueous solution with TiO₂ nanoparticles in the surface in the fresh state of the mortars;
2. From the evaluation of the photocatalytic activity of the modified mortars, it was possible to observe that a photo-degradation in the order of 70% after 240 minutes can be achieved.
3. The mechanical properties of mortars (compressive and flexural strenght) are influenced by the same factors, being the higher strength mortars the ones with loer quantity of lime and with lower w/b ratio, leading to lower values of flow table.
4. The spraying of TiO₂ nanoparticles at the surface of the rendering mortars leads to the reduction of the mechanical properties, even if in a lower ratio when compoared to the cases where the adition of TiO₂ nanoparticles in made in volume, as seen in the literature;
5. The water absorption of the distinct types of mortars is mostly influenced by the compositions and w/b ratios, being the differences found after the spraying of TiO₂ anopaticles not very cignificant. However, it is seen that in case of mortar 1:2:9 with the higher w/b ratio, the TiO₂ nanoparticles appears to change the cinetics of the water absorption, increasing the capillary absorption coeficients.
6. The evaluation of the thermal behavior of the rendering mortars was carried out by a test setup designed to evaluate the temperature profiles of control points in opposite surfaces of the masonry specimens (coated/uncoated, coated surface with and without sparying of TiO₂ nanoparticles). It was seen by the simple comparison of the temperature profiles that not very significant differences on the temprature profiles in the oposite surface to the heating were found, even if its appears that only slight higher tenpreature can be seen in the wall specimen coated with the TiO₂ modified mortar. With this respect a more detailed analysis is needed for more conclusive results.

REFERENCES

- [1] Wiek A, Guston D, Leeuw S, Selinand C, Shapira P. Nanotechnology in the City: Sustainability Challenges and Anticipatory Governance, *Journal of Urban Technology*, 20(2), 45-62, 2013.
- [2] Carp, O., Huisman CL, Reller A. Photoinduced reactivity of titanium dioxide, *Progress in Solid State Chemistry*, 32 (1), 33-174, 2004.
- [3] Paz Yaron. Application of TiO₂ photocatalysis for air treatment: patents overview, *Applied Catalysis B: Environmental*, 99 (3-4), 448-460, 2010.
- [4] Hoffmann MR, Martin ST, Choi W, Bahnemannt DW. Environmental applications of semiconductor photocatalysis, *Chemical Revisions*, 95, 69-96, 1995.
- [5] Pereira, J.C. Study of the behavior of TiO₂ nanoparticles in distinct suspensions, Master Thesis, Faculty of Sciences and Technology of Nova University, Lisbon, 2010. (In Portuguese).
- [6] Maravelaki-Kalaitzaki P, Agioutantis Z, Lionakis E, Stavroulaki M, Perdikatsis V. "hysico-chemical and Mechanical Characterization of Hydraulic Mortars Containing Nano-Titania for Restoration Applications, *Cement & Concrete Composites*, 36, 33-41, 2013.
- [7] Lucas S, Ferreira VM, Barrosos de Aguiar JL. Incorporation of titanium dioxide nanopartivles in mortars – Influence of microstructure in the hardened satte properties and photocatalytic activity, *Cement and Concerete Research*, 46, 112-120, 2013.
- [8] Ruot B, Plassais A, Olive F, Guillot L, Bonafous L. TiO₂-containing cement pasts and mortars: Measurements of the photocatalytic efficiency using a rhodamine B-based colorimetric test, *Solar energy*, 83, 1794-1801, 2009.
- [9] Senff L, Tobaldi DM,, Lucas S, Hotza D, Ferreira VM., Labrincha JA. Formulation of mortars with nano-SiO₂ and nano-TiO₂ for degradation of pollutants in buildings." *Composites: Part B*, 44, 40-47, 2013.
- [10] Carneiro JO, Azevedo S, Teixeira V, Fernandes F, Freitas E, Silva H, Oliveira J. Development of photocatalytic asphalt mixtures by the deposition and volumetric incorporation of TiO₂ nanoparticles, *Construction and Building Materials*, 39, 594-601.

- [11] Hanus MJ and Harris AT. Nanotechnology innovations for the construction industry, *Progress in Materials Science*, 58 (7), 1056–1102, 2013.
- [12] Gomes, N. Study of eco-efficient mortars, Master Thesis, Department of Civil Engineering, University of Minho, 2012. (In Portuguese).
- [13] EN 933-1 Ensaio das propriedades geométricas dos agregados - Parte 1." Análise granulométrica. 2000.
- [14] Haach VG, Vasconcelos G, Lourenço PB. Influence of aggregates grading and water/cement ratio in workability and hardened properties of mortars, *Construction and Building Materials*, 25, 2980-2987, 2011.
- [15] Chen X, Wu S. Influence of water-to-cement ratio and curing period on pore structure of cement mortar, *Construction and Buildings Materials*, 38, 804-812, 2013.
- [16] EN 1015-3. "Methods of test for mortar for masonry - Part 3." Determination of consistence of fresh mortar (by flow table). 2004.
- [17] Sébaïbi Y, Dheilly RM, Quéneudec M. Study of the water-retention capacity of a lime–sand mortar: influence of the physicochemical characteristics of the lime. *Cement and Concrete Research*, 3(5), 689–96, 2003.
- [18] Reddy, B. V. V., Gupta, A. Influence of sand grading on the characteristics of mortars and soil–cement block masonry, *Construction and Building Materials*, 22 (8), 2008, p.1614-1623.
- [19] EN 394, Especificação LNEC. Determinação da absorção de água por imersão. 1993.
- [20] EN 1015-18 (2002) "Methods of test for mortar for masonry - Parte 18." Determination of water absorption coefficient due to capillary action of hardened mortar. 2002.
- [21] EN 1015-11, Methods of test for mortar for masonry - Parte 11, Determination os flexural and compressive strength of hardened mortar. 1999.
- [22] Chen J, Poon C-H. Photocatalytic construction and building materials: From fundamentals to applications, *Building and Environment* 44, 1899-1906, 2009.
- [23] Lourenço, P.B., Vasconcelos, G., Medeiros, P., Gouveia, J. Vertically perforated clay brick masonry for loadbearing and non-loadbearing masonry walls, *Construction and Building Materials*, 24 (11), 2317-2330, 2010.