NEW CONSTRUCTION MATERIALS COMBINING SELF-CLEANING AND HEAT STORAGE PROPERTIES

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ABSTRACT

Following growing awareness concerning indoor air quality and energy efficiency, two different solutions became prominent in this research field: latent heat storage capabilities (for energy savings) and photocatalytic mortars (for elimination of air pollutants and self-cleaning). Indoor air quality in buildings is now going far beyond the simple indoor temperature regulation. Aspects like contamination of the indoor air by pollutants, are gaining importance and being included into building regulations. These functionalities, heat storage and self-cleaning, have been always considered separately, so the products available so far only include one. With the increasing demand for new and more innovative materials, future research will tend to include several functionalities in one single product.

Within this work a new multifunctional mortar combining energy storage, self-cleaning and air depolluting capabilities has been developed. The paper discusses the manipulation of mortars microstructure, by studying the microstructural modifications with different amounts of PCM (phase change material) and nanoparticles of titanium dioxide. Using the correct combination of both additives, the mechanical strength will not be compromised. The paper demonstrates that it is possible to develop new advanced mortars for building applications, more complex and with multiple functions, opening a new field of opportunities for the construction sector.

INTRODUCTION

A study conducted by Tong et al in 2016 demonstrates how indoor air quality is affected by external pollution in urban environments (Tong, Chen et al. 2016). Indoor air quality and thermal comfort can have a significant impact in human health and productivity (Jantunen 2007, Nicol and Humphreys 2007). Good comfort levels are usually settled at the design stage by introducing solutions for climatic control (heating and cooling) and ventilation systems. The main problem lies in the need to increase the air renovation rate to achieve lower particulate and pollutant concentrations. This outdoor air has a different temperature and this will force the heating or cooling systems to use energy to re-establish thermal comfort.

Construction materials can play an important role in reducing the final energy costs and increasing indoor air quality (Lucas, Ferreira et al. 2013, Lucas, Ferreira et al. 2013). Traditionally this can be made by using materials with better insulating properties and lower emissions (Petter 2011). However, this does not solve the problem of having outdoor pollutants inside the building neither contribute effectively to eliminate them without ventilation. Recent research in the field of functional construction materials resulted in new solutions, such as heat storage and self-cleaning, for indoor air cleaning and thermal control. An important limitation however of these new materials, is the inability to provide more than one functionality at the same time, what limits the application of these products in the construction industry.

This works focus on the development of a new type of mortar with combined depolluting, self-cleaning and heat storage properties aiming, in particular, application for building's renovation. This solution reduces air renovation rates while maintaining good quality levels for the indoor air, leading to lower energy demands for heating/cooling.

Photocatalytic, self-cleaning mortars

The photocatalytic effect of titanium dioxide has been known for more than 70 years (Goodeve and Kitchener 1938). The most common crystalline forms of titanium dioxide are anatase and rutile. The anatase, for its excellent photocatalytic abilities, is widely used in air and water cleaning systems (Diamanti, Paolini et al. 2015).

Titanium dioxide has a band gap energy of 3.2 eV, corresponding to a wavelength of 385 nm. Electron-hole pairs are generated when titanium dioxide is irradiated with light within this wavelength. Equations 1 to 3 show the 3-step reaction process involved in photocatalysis (Fujishima, Zhang et al. 2008):

$$TiO_2 + hf \rightarrow TiO_2 + e^- + h^+ \quad (1)$$

$$e^- + O_2 \rightarrow O_2^- \quad (2)$$

$$h^+ + H_2O \rightarrow HO + H^+ \quad (3)$$

Where hf is the energy required to move an electron to the conduction band, e^- is the electron in the conduction band and h^+ is the electron hole. The high oxidizing and reducing ability of TiO_2 makes it unique for photocatalytic applications. It is commonly used in degradation of organic pollutants and aromatic compounds, solar energy conversion, self-cleaning and anti-fog surfaces.

TiO_2 exhibit a good efficiency when it comes to remove several air pollutants. It works best for concentrations between 0.01 and 10 ppmv, presenting itself as a good solution for indoor air cleaning, with concentrations falling within this range. The possibility to incorporate titanium dioxide nanoparticles in construction materials (cement, plaster, concrete, etc.) has been investigated and its feasibility has been demonstrated (Maury and De Belie 2010).

The photocatalytic reaction takes place on the surface of these materials where the adsorption of the gaseous pollutants occurs. 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 cycle.

In this study, a common pollutant in urban areas NOx, was selected to determine the mortars' photocatalytic efficiency (Ballari, Hunger et al. 2010). The degradation of NOx can be divided in several chemical reactions:

$$NO + OH^{\bullet} \rightarrow NO_2 + H^+ \qquad (4)$$

$$NO + O_2^- \rightarrow NO_3^- \qquad (5)$$

$$NO_2 + OH^{\bullet} \rightarrow NO_3^- + H^+ \rightarrow HNO_3 \qquad (6)$$

The O^{2-} and $OH^{\bullet}$ radicals are formed during the activation process of the photocatalyst as described in reactions 1 to 3, react with the pollutant gas producing NO_2 and HNO_3. These are environmentally benign substances, not harmful to human health (Fujishima, Zhang et al. 2008). Besides being able to clean the air, mortars incorporating TiO_2 are also able to self-clean by degrading any organic substance that contaminates the surface. This has been demonstrated by Ruot et al. using a solution of Rhodamine B as contaminant (Ruot, Plassais et al. 2009).

Latent heat storage in PCM-mortars

The application of materials that can contribute to reduce energy demand is considered one of the top priorities for both new and renovated buildings. Materials with latent heat storage capabilities can contribute to save energy by reducing the operation time of the heating and cooling systems (Sharma and Sagara 2005). Several companies already have commercially available cement and gypsum-based mortars with heat storage capability, however, these products are destined for new buildings only. The development of a mortar with a suitable composition for historic buildings will improve their energy performance helping them to fit into new buildings regulations (Lucas, Ferreira et al. 2010).

Phase Change Materials (PCM) are formed by a capsule of polymethyl methacrylate (PMMA) containing paraffin waxes which are able to store and release heat. When the temperature inside the room is higher than the phase transition temperature (Tg) of the paraffin, an endothermic reaction occurs and heat is stored. If the temperature decreases below Tg, the same amount of heat will be released through an exothermic reaction.

Heat storage and self-cleaning have been always considered separately. With the increasing demand for new and more innovative materials, future solutions will necessarily pass by including several functionalities in one single product (Salonitis, Pandremenos et al. 2010). In this work a multifunctional mortar combining energy storage and self-cleaning capabilities was developed through the study of the microstructural modifications with different amounts of PCM (phase change material) and nanoparticles of titanium dioxide. The paper demonstrates that with careful manipulation of the mortars' internal structure it is possible to develop new advanced mortars for building applications, more complex and with multiple functions. This opens a new field of opportunities for the construction sector.

EXPERIMENTAL

Materials and formulations

The mortar mixture was prepared using hydrated lime as binder and sand as fine aggregate. The phase change material (Micronal DS 5008) comprises a paraffin mixture encapsulated in a polymethylmethacrylate (PMMA) shell, with an average particle size of 6 µm, transition temperature of 23ºC and enthalpy 135 kJ/kg. The titanium dioxide, a photocatalytic additive, is a commercial product (Evonik P25), consisting of 85% of anatase and 15% rutile having a specific surface area of 50±15 m^2 g^{-1}. It was added to the mixtures 1 wt.% of a plasticizer (Glenium 51), with a density around 1.067-1.107 g/cm^3 and a total solid content of 28.5 - 31.5 wt.%. Mixing water content was keep in a level that assured proper workability for each composition.

Lucas et al. studied the effect of PCM and TiO_2 in lime, gypsum and cement based mortars. Supported by these previous works the compositions tested in this paper contained 20 to 30% PCM and 2.5 to 5% TiO_2. The mortars have a constant binder aggregate ratio of 1:2 (weight).

The samples for the mechanical strength tests were prepared following the procedure described in the European Standard EN 1015-11. The tests were carried out after a curing time of 90 days with a temperature of 20 ºC ± 2 ºC and 65% ± 5% of relative humidity. The pore size and pore distribution were determined using a mercury intrusion porosimeter (AutoPore IV Micromeritics) working in the pressure range from 4 kPa to 228 MPa and intrusion in pores between 6 nm and 360 µm.

The test developed to assess the heat storage capability was designed to simulate as closely as possible the real application conditions. Test cells placed inside a climatic chamber were submitted to a specific temperature cycle. The minimum temperature of 10°C was the starting point and the maximum value of 40°C was reached at a constant rate of 0.5 ºCmin^{-1}. The highest and lowest temperatures were kept constant for 10 minutes and this cycle was repeated during 24 hours. The test cells made with an insulating material (extruded polystyrene) were coated on the inside with a mortar layer of 3 mm. During the test, thermocouples placed outside and inside the boxes to monitor the temperature inside the cells with PCM and the reference sample box. The temperature cycle forces the PCM to change phase (around 23 to 25ºC) and it is possible to determine the impact of the heat storage capability of the mortar. The multifunctional mortars were submitted to cyclic thermal tests to determine if the use of multiple additives can influence the thermal behaviour.

To conduct the photocatalytic test, a specific setup using NOx as pollutant was developed. NOx is a common pollutant gas present inside buildings and in urban areas in concentrations around 1 ppmv. This value was selected as the initial concentration for the laboratory tests conducted in this study. Several authors also used this concentration and this would facilitate comparisons with related studies. NOx (10 ppmv) was diluted in standardized air, to obtain the desired concentration. Gas inlet measured with mass flow controllers was injected to the chamber at a constant flow rate of 1 l/min. The reaction took place inside the stainless steel chamber. The cylinder with a 35 dm^3 capacity is completely sealed and the glass window on the top allowed the light from the 300-Watt solar lamp (OSRAM UltraVitalux), placed at 1m from the sample, to irradiate the mortar. During the tests, a thermocouple and a humidity sensor monitored temperature and relative humidity and the values remained steady at 20 ºC and 40% respectively. Excessive temperature can affect the photocatalytic measurements making difficult to distinguish the degradation effect from an overheating phenomena. A chemiluminescence analyser (AC-30 M, Environment SA) measured the concentration of the outlet gas.

A blank reference and TiO_2 containing samples were tested at NOx concentration in air of 1 ppmv after stabilization to ensure complete saturation in order to prevent any absorption effect from the sample and reactor walls. The photocatalytic efficiency was determined by equation 7.

$$NO_{X\,removed} = \frac{[NO_X]_{TiO_2} - [NO_X]_{blank}}{[NO_X]_{TiO_2}} \times 100 \qquad (7)$$

where,

$[NOx]_{TiO2}$ is the final pollutant concentration after the irradiation test

$[NOx]_{blank}$ is the NOx concentration for the blank test (0% TiO_2).

RESULTS AND DISCUSSION

Mechanical strength and pore distribution

The mechanical strength is higher for the formulation with maximum content of PCM (30%) and 2.5 % of titanium dioxide, as shown in Figure 1. If we compare the results when the additives are used separately with the combined formulations, it can be concluded that, generally, the combination of two additives present better results. This can be a consequence of better particle packaging inside the mortar matrix, but also resulting from a fluidizing effect of PCM, that allowed the introduction of TiO_2 without degrading the hardened state behaviour of these samples with combined additives. Combining microcapsules (PCM) with nanoparticles (TiO_2) results in complex internal microstructures (Figure 2).

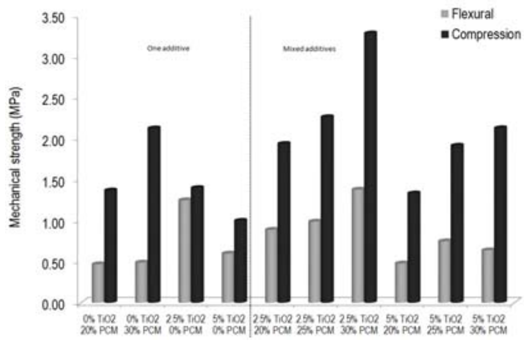

Figure 1 – Mechanical strength of the compositions tested

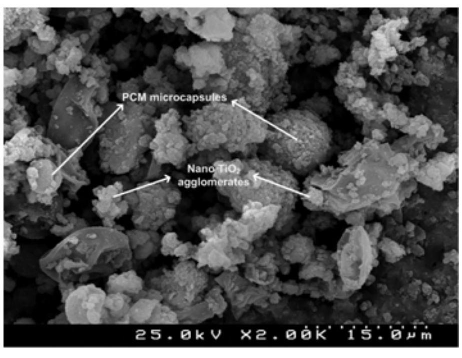

Figure 2 – Internal microstructure of a mortar containing PCM and TiO_2

The analysis of pore size distribution contributes for a better understanding of impact on the mortar microstructure. For 2.5% of photocatalytic additive (Figure 3), increasing the PCM content reduces the macropores (above 5 µm) and lead to an increase of micropores (0.5 to 5 µm) and nanopores (below 0.1 µm) achieved by better accommodation of additives into the internal microstructure.

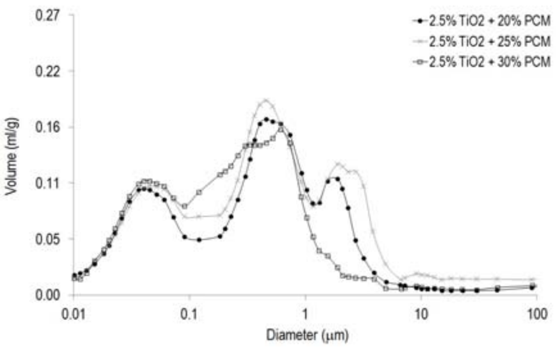

Figure 3 – Pore distribution for mortars containing 20-30%PCM and 2.5% TiO_2

Lucas et al., have observed this effect in PCM containing mortars and it is noticeable in the PCM mortars pore distribution in Figure 4 (Lucas, Ferreira et al. 2013). PCM act as counterbalance for the detrimental effect of titanium dioxide nanoparticles as a very fine material addition. According to Figure 5, the compositions containing only titanium dioxide exhibit a high content of pores above 10 µm however when PCM is added, these pores are eliminated.

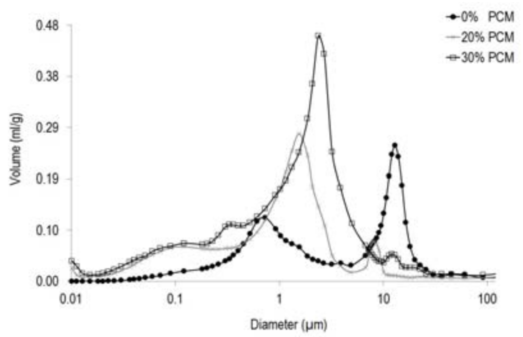

Figure 4 – Pore distribution for mortars with 0-30% PCM

With 5% of TiO_2, the compensation from the PCM microcapsules is still evident, though less effective, due to the excess of nanoparticles (Figure 6). The high volume of macropores present in the 20% PCM formulation disappeared when PCM content increases and the volume of nanopores become higher. However, a parallel effect occurs with 5% titanium dioxide that was not present with 2.5%, the presence of a high porosity, above 8 µm. These bigger pores can explain why the composition with 2.5% TiO_2 and 30% PCM performs better compared to the 5% TiO_2 and 30% PCM combination, since total porosity and average pore size are similar in both.

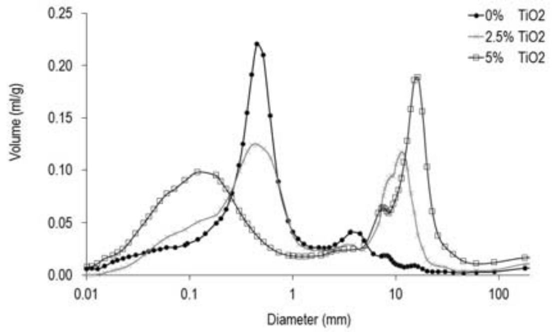

Figure 5 – Pore distribution for mortars with 0-5% TiO_2

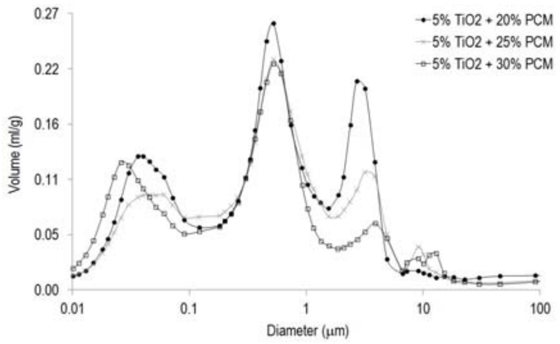

Figure 6 – Pore distribution for mortars containing 20-30%PCM and 5% TiO_2

Table 1 – Average pore size and total porosity for PCM/TiO_2 compositions with 2.5% TiO_2

<table>
<tr><th></th><th>%</th><th>Pore average size (µm)</th><th>Total porosity (%)</th></tr>
<tr><td>TiO2</td><td>2,5</td><td rowspan="2">0,076</td><td rowspan="2">31,6</td></tr>
<tr><td>PCM</td><td>20</td></tr>
<tr><td>TiO2</td><td>2,5</td><td rowspan="2">0,088</td><td rowspan="2">36,3</td></tr>
<tr><td>PCM</td><td>25</td></tr>
<tr><td>TiO2</td><td>2,5</td><td rowspan="2">0,068</td><td rowspan="2">31,6</td></tr>
<tr><td>PCM</td><td>30</td></tr>
</table>

Table 2 – Average pore size and total porosity for PCM/TiO_2 compositions with 5% TiO_2

<table>
<tr><th></th><th>%</th><th>Pore average size (µm)</th><th>Total porosity (%)</th></tr>
<tr><td>TiO2</td><td>5</td><td rowspan="2">0,095</td><td rowspan="2">39,0</td></tr>
<tr><td>PCM</td><td>20</td></tr>
<tr><td>TiO2</td><td>5</td><td rowspan="2">0,094</td><td rowspan="2">35,8</td></tr>
<tr><td>PCM</td><td>25</td></tr>
<tr><td>TiO2</td><td>5</td><td rowspan="2">0,067</td><td rowspan="2">33,8</td></tr>
<tr><td>PCM</td><td>30</td></tr>
</table>

Tables 1 and 2, show that pore size distribution plays a more important role in mechanical strength than total porosity and average pore size.The ideal combination that has achieved better mechanical strength was the mortar with 30% of PCM and 2.5% of titanium dioxide.

Latent heat storage

Figure 7 and Figure 8 exhibit the behavior of the PCM/TiO_2 mortars when submitted to the test in the climatic chamber. For mortars containing 2.5% of TiO_2, when the temperature increases, the efficiency is similar for 20 and 30% of PCM, which can be observed by the same temperature reduction relative to the outside temperature.

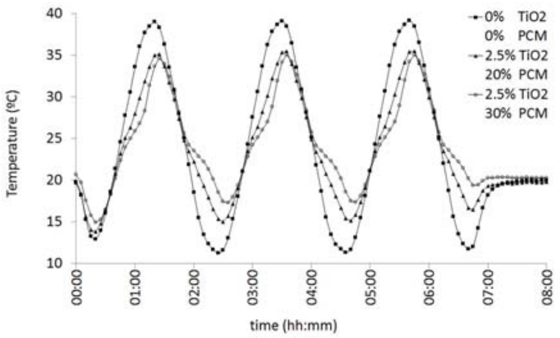

Figure 7 – Thermal tests for the 2.5% TiO_2 mortars with 20-30% PCM

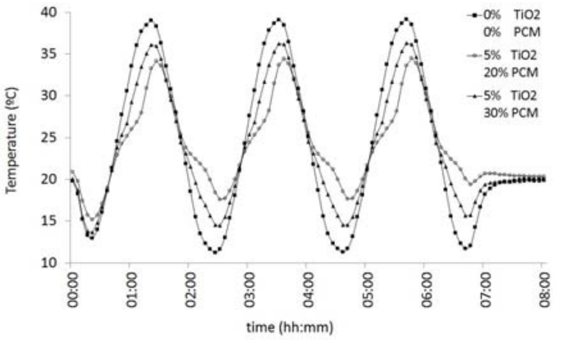

Figure 8 – Thermal tests for the 5% TiO_2 mortars with 20 to 30% of PCM

During the cooling cycle in this simulation, the composition with 30% is slightly more effective. A change in the internal porosity does not play an important role, because the amount of nanopores (below 0.1 µm) is the same for both mortars. The porosity between 0.5 and 1 µm present in the 30% PCM mortar is high enough to assure an effective heat exchange, since the critical limit to delay the heat transfer in PCM mortars is below 0.5 µm (Lucas, Ferreira et al. 2013).

When the amount of titanium dioxide nanoparticles increase to 5% an interesting phenomena appears. The mortar with 20% PCM is more efficient than the one with 30%. This event shows the importance that the internal pore distribution play in the heat transfer. The strong reduction in macropores for the 30% PCM-5% TiO_2 composition, when the content of nanopores (< 0.1 µm) and micropores (0.5 to 5 µm) remains the same, determines the heat efficiency differences between this composition and the 30%PCM-2.5% TiO_2 formulation. However, an improvement in latent heat storage performance for the mortars with 5% of TiO_2 is not enough to compensate the loss in mechanical strength. It is clear that a good compromise between hardened state properties and heat transfer must be advantageous for the durability of the mortar.

Photocatalytic efficiency

The photocatalytic tests demonstrate that an increase in the titanium dioxide content does not necessarily translates into an increase in efficiency (Fig. 9) (Lucas, Ferreira et al. 2013). The excess of catalyst contributes in fact to a decrease of the degradation rate in 5% compositions. While for the 2.5% of TiO_2, an increase in PCM does not compromise the overall photocatalytic efficiency, when using 5%, the increase in PCM reduces the degradation rate. The strong decrease in pores above 1 µm for the composition with 30% of PCM diminishes the amount of catalytic agent exposed to the NOx and can explain the difference for 20 to 30% PCM, when the TiO_2 content remains the same.

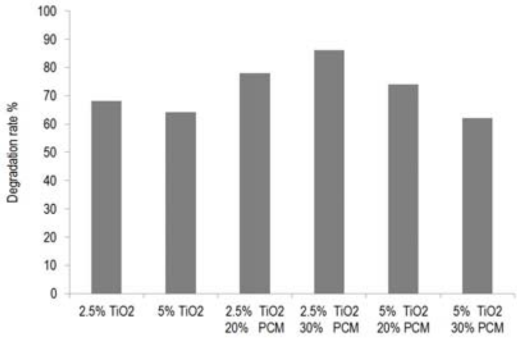

Figure 9 – Photocatalytic tests of the TiO_2/PCM mortars

CONCLUSIONS

The results presented in this work confirmed that microstructural modification can open new possibilities in the development of construction materials with multiple functionalities. Combining micro and nano-size components does not necessarily mean that hardened state properties will be compromised. It was demostrated in this paper that a good understanding of the microstructural changes involved can lead to an optimization of compositions without compromising their functionality. This opens a new field of opprotunities for new, innovative and sustainable materials.

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