NEW CONSTRUCTION MATERIALS COMBINING SELF-CLEANING AND HEAT STORAGE PROPERTIES

Sandra S. Lucas

1University of Greenwich, Faculty of Engineering and Science, Chatham, UK, s.lucas@gre.ac.uk

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 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 et al. 2013, Lucas 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 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 et al. 2008):

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 + e^- + h^+ \quad (1)
\]

\[
e^- + \text{O}_2 \rightarrow \text{O}_2^- \quad (2)
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \text{HO} + \text{H}^+ \quad (3)
\]
Where \(h\text{f}\) 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 NO\(_x\), was selected to determine the mortars’ photocatalytic efficiency (Ballari, Hunger et al. 2010). The degradation of NO\(_x\) can be divided in several chemical reactions:

\[
NO + OH^* \rightarrow NO_2 + H^+ \quad (4)
\]

\[
NO + O_2^- \rightarrow NO_3^- \quad (5)
\]

\[
NO_2 + OH^* \rightarrow NO_3^- + H^+ \rightarrow HNO_3 \quad (6)
\]

The O\(^2\) and OH\(^*\) 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 (T\(_g\)) of the paraffin, an endothermic reaction occurs and heat is stored. If the temperature decreases below T\(_g\), 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 23°C 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 m² g⁻¹. It was added to the mixtures 1 wt.% of a plasticizer (Glenium 51), with a density around 1.067-1.107 g/cm³ 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 10ºC was the starting point and the maximum value of 40°C was reached at a constant rate of 0.5 ºC/min. 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 dm³ capacity is completely sealed and the glass window on the top allowed the light from the 300-Watt solar lamp (OSRAM UltraVitalux), placed at 1 m 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 TiO2 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.

\[
NOX_{removed} = \frac{[NOX]_{TiO2} - [NOX]_{blank}}{[NOX]_{TiO2}} \times 100
\]

where,

- \([NOX]_{TiO2}\) is the final pollutant concentration after the irradiation test
- \([NOX]_{blank}\) is the NOx concentration for the blank test (0% TiO2).

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 TiO2 without degrading the hardened state behaviour of these samples with combined additives. Combining microcapsules (PCM) with nanoparticles (TiO2) results in complex internal microstructures (Figure 2).

![Figure 1 – Mechanical strength of the compositions tested](image1)

![Figure 2 – Internal microstructure of a mortar containing PCM and TiO2](image2)
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.

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.

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.

<table>
<thead>
<tr>
<th>%</th>
<th>Pore average size (µm)</th>
<th>Total porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ 2,5</td>
<td>0,076</td>
<td>31,6</td>
</tr>
<tr>
<td>PCM 20</td>
<td>0,088</td>
<td>36,3</td>
</tr>
<tr>
<td>TiO$_2$ 2,5</td>
<td>0,068</td>
<td>31,6</td>
</tr>
<tr>
<td>PCM 30</td>
<td>0,067</td>
<td>33,8</td>
</tr>
</tbody>
</table>

Table 1 – Average pore size and total porosity for PCM/TiO$_2$ compositions with 2.5% TiO$_2$
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.

**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.

**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 demonstrated 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 opportunities for new, innovative and sustainable materials.
ACKNOWLEDGEMENTS
This work has been supported by the project PTDC/ECM/72104/2006, funded by the Foundation for Science and Technology (FCT) and the project 13265 R08132 from REF 2016, University of Greenwich.

REFERENCES


