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Multifunctional wall coating combining photocatalysis, self-cleaning and latent heat storage

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Abstract

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Mortars, one of the most common construction materials, have not received any substantial modification for many decades. This has changed in recent years; new compositions are now being developed, with new properties, using nano-additives, fibres and capsules. In this work, surfaces with new and innovative functionalities that promote energy savings and improve air quality have been developed and studied. Incorporation of phase change materials (PCM) and titanium dioxide (TiO_2) nanoparticles in construction products is currently under study by different research groups. However, these studies only address their incorporation separately. Adding new additives into the mortar's matrix can be complex-due to microstructural modifications that will influence both fresh and hardened state properties. Moving from a single additive to multiple additions, as in this study, increases the system's complexity. Only with a good understanding of the microstructural properties, it is possible to add multiple additives (including nano and microparticles) to mortars, without damaging its final quality. This work demonstrates that a higher additive content is not always a guarantee of better results; lower additions can often provide a better compromise between performance and final mechanical properties. The results presented in this paper confirmed this and show that combining PCM microcapsules and TiO₂ nanoparticles open a new path in the development of mortars with multiple functionalities. In this study, a new material with depolluting, self-cleaning and heat storage was created. For the development of new and innovative mortars, a proper balance of multiple additives, supported by the study of microstructural changes, can lead to an optimization of the compositions, ensuring that the mortar's final properties are not affected.

1. Introduction

Impact of poor indoor air quality on human health has gained interest after a clear correlation has been established between both [1]. In the United Kingdom, high levels of air pollution become a matter of great concern with the government establishing lowering these levels as one of its top priorities [2, 3]. Quality of indoor air and its perception by building's occupants is however, more than just pollutants concentration. There is a direct relationship between the perceived quality of indoor air and indoor comfort, which is strongly dependent on thermal comfort [1, 4]. This work discusses the development and study of a material able to simultaneously reduce pollutants concentration, self-clean and store/release heat.

1.1. Photocatalytic degradation of indoor pollutants

The photocatalytic effect of titanium dioxide has been studied for more than 70 years [5]. Two different catalysers are amongst the most investigated, zinc oxide (ZnO) and titanium dioxide (TiO₂) [6, 7]. TiO₂ has been applied in two different crystalline phases: rutile and anatase and has been by far, the most studied due to its high chemical stability, good efficiency and relative low cost when compared with other catalysts [8]. The

photocatalyst efficiency has improved considerably when it started to be produced in nano-sized particles [9]. Reducing the size of an additive to the nanometre scale increases its specific surface area, dramatically changing the additive's properties and reactivity [10]. Anatase, one of titanium dioxide mineral forms, for its excellent photocatalytic properties, is widely used in air and water cleaning systems [11]. Titanium dioxide has a band gap energy of 3.2 eV, corresponding to a wavelength of 385 nm. When titanium dioxide is irradiated within this wavelength, electron–hole pairs are generated. Equations (1)–(4) describe the 4-step reaction process involved in the photocatalytic process [12]:

$$\mathrm{TiO}_2 + hf \to \mathrm{TiO}_2 + e^- + h^+ \tag{1}$$

$$+ H_2 O \rightarrow OH^{\bullet} + H^+$$
 (2)

$$e^- + \mathcal{O}_2 \to \mathcal{O}_2^- \tag{3}$$

$$O_2^- + H^+ \to HO_2^{\bullet} \tag{4}$$

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 TiO₂ makes it unique for photocatalytic applications. It is commonly used for organic pollutants and aromatic compounds degradation [13, 14], solar energy conversion [15], self-cleaning [16] and anti-fogging surfaces [17].

 h^+

Titanium dioxide has the ability to react with air pollutants commonly detected in urban areas, in external and indoor air, such as VOC, NO_x, CO and SO_x; often present in concentrations as high as 1 ppm [18]. Surfaces prepared with this photocatalytic additive are able to degrade air pollutants and its application in construction materials has been extensively explored in the last decades [19–21]. Nitrogen oxides (NO_x), being common pollutants in indoor air, are amongst the preferred contaminants for testing photocatalytic degradation [19, 22]. Tests using this pollutant have been performed for concentrations between 0.01 and 10 ppmv, but usually they are conducted with concentrations around 1 ppmv [13, 23].

The possibility of incorporating titanium dioxide nanoparticles in construction materials (cement, plaster, concrete, etc) has been investigated and its feasibility has been demonstrated in previous research works [24]. The photocatalytic reaction takes place on the surface of these materials, where the adsorption of gaseous pollutants occurs. On a final stage, 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 [25].

Equations (5)–(7) describe the degradation process, where OH^- and O_2^- radicals created during the photocatalytic activation, explained above, react with NO₂ to produce HNO₃ [26]. These reaction products are environmentally benign substances, non-harmful to human health [12].

$$NO + OH^{-} \rightarrow NO_{2} + H^{+}$$
(5)

$$NO_2 + OH^- \rightarrow HNO_3$$
 (6)

$$\mathrm{NO} + \mathrm{O}_2^- + \to \mathrm{NO}_3^-. \tag{7}$$

1.2. Photocatalytic degradation of Rhodamine B (self-cleaning)

Wall coatings are especially prone to attack by algae, mould and pollutants, what contributes to an accelerated degradation of historical buildings [27]. By gaining the ability to self-clean, the mortar's durability will be improved, the building will require fewer maintenance interventions, keeping a good aesthetic appearance for a longer time. Besides reacting with indoor pollutants, titanium dioxide nanoparticles also degrade organic paints, mould and can kill bacteria [28].

N-[9-(2-Carboxyphenyl)-6-diethylamino-3-Hxanthen-3-ylidene]-N-ethyl-ethanaminium chloride, also known as Rhodamine B (figure 1) is frequently used to test self-cleaning in photocatalytic surfaces. This organic dye can realistically replicate the contamination effect of a mortar's surface and it constitutes an effective method to assess self-cleaning efficiency. Rhodamine B can undergo two different pathways when reacting with TiO₂ [29]. Rhodamine B (RhB), when activated by visible light, undergoes a dye-sensitisation process that constitutes a catalysed photoreaction (figure 2), where the organic molecule absorbs visible light photons.

These photons do not have sufficient energy to activate TiO_2 but their energy is enough to move electrons to the lowest unoccupied molecular orbital of the organic dye (reaction 8). These electrons can transfer to the conduction band of TiO_2 and a new molecular ion radical will be adsorbed on the catalyst's surface (reaction 9). This electron is then transferred to the oxygen adsorbed on the TiO_2 surface producing and oxygen radical (reaction 10).

$$RhB + h\nu \rightarrow RhB$$
 (8)

$$RhB' + TiO_2 \rightarrow RhB^+ + TiO_2 + e^-$$
(9)

$$RhB' + O_2 \rightarrow RhB^+ + O_2^{-}.$$
 (10)





Both radical species produced by this process are highly reactive and lead to a complete mineralization of the organic molecule.

1.3. Using encapsulated paraffin waxes as phase change materials (PCM)

Besides air quality levels, other factors, for example temperature, can influence indoor comfort in buildings. To maintain an adequate indoor temperature for human occupancy, HVAC systems for heating and/or cooling are usually the easiest solution, but their high-energy demand has a strong environmental impact. Looking for new and passive methods to achieve thermal comfort can reduce the buildings carbon footprint without compromising human levels of comfort.

The application of materials that can reduce energy demand is considered one of the top priorities for both new and renovated structures. Materials with latent heat storage capabilities contribute to save energy by reducing the operation time of heating and cooling systems [30]. The PCM selected for this study, are formed by a capsule of polymethyl methacrylate (PMMA) containing a mix of paraffin waxes [31].

These waxes are able to store and release heat when they undergo a phase transition from solid to liquid. 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. When the temperature rises, the PCM stores a certain amount of heat that is able to release as soon as the temperature drops below the phase change point. When the capsules are mixed with a mortar, the latent heat storage can be used to create walls capable of improving thermal indoor comfort by releasing or storing heat, delaying the start of the heating/cooling systems [32].

PCM may be applied as a passive storage media for heat and to prevent thermal damage in concrete exposed to freeze/thaw cycle [33]. The latent heat transfer, caused by PCM's melting, occurs at a temperature designated as phase change temperature. Latent heat storage (ΔQ) is therefore dependent on the enthalpy change and can be determined from equation (11):

$$\Delta Q = m \times \Delta H,\tag{11}$$

where ΔH is the enthalpy variation (*J*); and *m* the material's mass (*g*) [34].

	2.5% TiO ₂ 20% PCM	2.5% TiO ₂ 25% PCM	2.5% TiO ₂ 30% PCM	5% TiO ₂ 20% PCM	5% TiO ₂ 25% PCM	5% TiO ₂ 30% PCM
Lime	20	20	19	20	19	19
Sand	61	59	57	60	58	56
TiO ₂	2.0	2.0	1.9	4.0	3.8	3.7
РСМ	16	20	23	16	19	22

2. Ternary compositions mortar + TiO₂ + PCM—combining multiple functionalities

Heat storage and photocatalysis have always been considered separately in building systems [35, 36]. With the increasing demand for new and more innovative materials, future solutions will necessarily include several functionalities in one single product [37]. In this work, a multifunctional mortar combining energy storage, depolluting and self-cleaning capabilities was developed.

Particular attention has been given to the study of the microstructural modifications with different amounts of PCM and nanoparticles of titanium dioxide. The paper demonstrates that with careful manipulation of the mortars' internal structure it is possible to develop new advanced materials for building applications, more complex and with multiple functions. This opens a new field of opportunities for advanced building materials, where several functional additives can be combined in one single product.

3. Experimental

3.1. Materials and formulations

The mortar mixture was prepared using hydrated lime as binder and sand as fine aggregate. The PCM (Micronal DS 5008) comprises a paraffin mixture encapsulated in a PMMA shell, with an average particle size of 6 μ m, transition temperature of 23 °C and enthalpy 135 kJ kg⁻¹. 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 \pm 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 cm⁻³ and a total solid content of 28.5–31.5 wt%.

The ternary compositions were prepared using a hydrated lime and sand, with a 2:1 sand/binder weight ratio and combined amounts of titanium dioxide and PCM as described in table 1. The mortar's workability was controlled using the flow table method. The amount of water added in relation to the total weight of solid material was adjusted in order to keep the slump value constant for each composition. Lucas *et al* studied the effect of PCM and TiO₂ in lime, gypsum and cement based mortars [38, 39]. Supported by this previous work the compositions tested in this paper contain 20%–30% PCM and 2.5%–5% TiO₂. The mortars have a constant binder aggregate ratio of 1:2 (weight).

3.2. Tests

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 d under a controlled environment with a temperature of 20 °C \pm 2 °C and 65% \pm 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 of 4 kPa–228 MPa and intrusion in pores between 6 nm and 360 μ m.

The test developed to assess the thermal energy storage capability was designed to simulate service conditions as closely as possible. Test cells placed inside a climatic chamber were submitted to a preprogrammed temperature cycle (figure 3(a)).

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 °C min⁻¹. The highest and lowest temperatures were kept constant for 10 min and this cycle was repeated during 24 h. The test cells were blocks made with an insulating material (extruded polystyrene) coated on the inside with a mortar layer of 3 mm. During the test, thermocouples placed inside the boxes, monitored the temperature in the cells with PCM and the reference sample. The temperature cycle triggers the PCM's phase change (around 23 °C–25 °C) making it possible to assess the heat storage capability of these mortars. The multifunctional mortars containing PCM and TiO₂ were submitted to the same thermal test, to determine if the use of multiple additives will influence its thermal behaviour.



To conduct the photocatalytic test, was developed a specific setup using NO_x as the pollutant source. NO_x is a common pollutant in urban areas; concentrations can vary from 0.1 to 1 ppmv. This highest value was selected as the initial concentration for the laboratory tests conducted in this study. Several authors also used this concentration and this helps comparing results with related studies [40–42].

 NO_x at 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⁻¹ and the reaction takes 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 a 300 W solar lamp (OSRAM UltraVitalux), placed 1 m above the sample, to irradiate the mortar (figure 3(b)).

During the tests, a thermocouple and a humidity sensor monitored temperature and relative humidity and values remained steady at 20 °C and 40% respectively. Excessive temperature can affect the photocatalytic measurements making it difficult to distinguish the degradation effect from an overheating phenomena [43]. A chemiluminescence analyser (AC-30 M, Environment SA) measured the concentration of the outlet gas.

A blank reference and samples containing TiO₂ were tested according to the following process:

- Placement of the sample in the holder inside the chamber with the glass window covered.
- The inlet gas mixture starts to flow until NO_x reaches 1 ppmv measured by the analyser. This stabilization step assures that sample is completely saturated, preventing an absorption effect from the sample and reactor walls.
- The solar lamp is turned on, the reactor glass is uncovered, and the reaction starts. During this phase, the NO_x concentration is monitored continuously. When the concentration reaches a constant minimum level, it is considered that the reaction stopped and the sample is unable to degrade more pollutant. The reaction is completed.

The photocatalytic efficiency was determined by equation (12):

$$NO_{x_{removed}} = \frac{[NO_x]_{TiO_2} - [NO_x]_{blank}}{[NO_x]_{TiO_2}} \times 100,$$
(12)

where, $[NO_x]_{TiO_2}$ is the final pollutant concentration after the irradiation test and $[NO_x]_{blank}$ is the NO_x concentration for the blank test (0% TiO₂).

Self-cleaning properties have been assessed using a Rhodamine B degradation test [11, 44]. The samples were contaminated with a solution of 0.05 g l^{-1} applied in a circle with 10 cm diameter, corresponding to a pollutant concentration of 0.6 μ g cm⁻². The samples were placed at 1 m from the light source, a 300 W lamp from OSRAM that replicates the solar light spectrum and corresponds to an intensity of 3700 Lux on the target.

$$\%D_{a^{*}} = \frac{a_{f}^{*} - a_{0}^{*}}{a_{f}^{*}} \times 100.$$
⁽¹³⁾

The superficial decontamination has been measured by the degradation rate of the dye according to equation (13), where D_{a^*} is the degradation rate for parameter a^* , a_0^* and a_f^* are the initial and final measurement for a^* , respectively. The measurements were performed using a Konica Minolta Chroma-meter CR-400. Colorimetric measurements were taken until 3 h of exposure to the solar lamp for all compositions at the same time.

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4. Results and discussion

In this study, the mechanical properties and functional performance of the TiO₂-PCM-mortar composites were compared with the single additive formulations.

As shown in figure 4, the highest mechanical strength—combined flexural and compression—was achieved with the formulation with maximum content of PCM (30%) and 2.5% of titanium dioxide.

Comparing with results obtained for the pristine composition and when additives are used separately, it can be concluded that combining both additives does not seriously compromise the mechanical strength. There is a filing action—a direct result of the fluidizing effect of the PCM—its spherical particles compensate the water reduction caused by the introduction of titanium dioxide particles that have a very high surface area [45]. Because PCM capsules are made with a shell of PMMA the mortar can absorb more energy during loading, this also helps improving compression strength. The microstructure for mortars combining microcapsules (PCM) and nanoparticles (TiO₂) can be seen in figure 5. It is possible to see the PCM microcapsules aggregated in an almost perfect spherical shape, filling the bigger pores, with the irregularly shaped nano-TiO₂ agglomerates filling smaller voids.

The analysis of pore size distribution contributes for a better understanding of the impact of multiple additives in a mortar's microstructure. For 2.5% of photocatalytic material (figure 6), increasing the PCM







content reduces macropores (above 5 μ m) and led to an increase of micropores (0.5–5 μ m) and nanopores (below 0.1 μ m), achieved by a better internal particle packing; Lucas *et al* also observed this effect in PCM containing mortars [39]. It is noticeable in pore distribution of PCM mortars, in figure 7, how the internal pores shifted from 10–15 μ m to the 1–5 μ m range. This is a clear evidence of how the PCM can act as a compensation for the detrimental effect of adding the TiO₂ nanoparticles, increasing flexural and compression strength.

According to figure 8, the compositions containing only titanium dioxide show a high content of pores above 10 μ m but also more pores below 0.1 μ m what indicates an improved particle packing when compared with compositions with PCM only (figure 7), translated into higher flexural strength for compositions with 2.5% of TiO₂; this effect remains even when PCM is added.



Table 2. Average pore size and total porosity for PCM/TiO2 compositions	
with 2.5% TiO ₂ .	

	Pore average size (µm)	Standard deviation	Total poros- ity (%)
2.5% TiO ₂ 0% PCM	0.2531	0.0041	29.6
2.5% TiO ₂ 20% PCM	0.076	0.0053	31.6
2.5% TiO ₂ 25% PCM	0.088	0.0058	36.3
2.5% TiO ₂ 30% PCM	0.068	0.0054	31.6

Table 3. Avera	ge pore size and tot	al porosity for PC	CM/TiO ₂ composition	s
with 5% TiO ₂ .				

	Pore average size (µm)	Standard deviation	Total poros- ity(%)
5% TiO ₂ 0% PCM	0.1284	0.0044	34.0
5% TiO ₂ 20% PCM	0.0949	0.0069	39.0
5% TiO ₂ 25% PCM	0.0944	0.0058	35.8
5% TiO ₂ 30% PCM	0.0669	0.0055	33.8

With 5% of TiO₂, the buffering effect from the PCM microcapsules is still evident, though less effective due to the excess of nanoparticles (figure 9), causing a reduction in mechanical strength. The high volume of macropores present in the 20% PCM formulation disappears when the PCM content increases and the volume of nanopores become higher. However, another effect occurs with 5% titanium dioxide that was not detected with 2.5%, the presence of high porosity, with pores above 8 μ m. These pores reduce the overall mechanical strength for the 5% TiO₂ mortars, especially when only 20% of PCM is added. These bigger pores can explain why the composition with 2.5% TiO₂ and 30% PCM performs better under loading, when compared to the 5% TiO₂—30% PCM combination, since total porosity and average pore size are similar for both.

Tables 2 and 3, confirm that pore size distribution plays a more important role in mechanical strength than total porosity and average pore size.

As seen in table 3, adding 5% more of PCM reduces total porosity mainly in the range $1-10 \mu$ m resulting also in a reduction of the average pore size. Based on the analysis of the mechanical strength, it can be concluded that the mortar with 30% of PCM and 2.5% of titanium dioxide will be the one to achieve a better performance.





Figures 10 and 11 show the thermal performance of PCM/TiO₂ mortars when submitted to the climatic chamber test. For mortars containing 2.5% of TiO₂, when the temperature increases, the efficiency is similar for 20% and 30% of PCM, temperature reduction relative to the environmental temperature is almost the same for both. During the cooling cycle, the composition with 30% is slightly more effective. A change in the internal porosity does not play an important role here, because the amount of nanopores (below 0.1 μ m) is the same for both mortars. The porosity between 0.5 and 1 μ m 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 μ m [39].

When the amount of titanium dioxide nanoparticles increases to 5%, an interesting phenomenon can be observed, the mortar with 20% PCM is more efficient than the one with 30%. This result shows the importance that internal pore distribution has in heat transfer. A strong reduction in macropores for the 30% PCM-5% TiO₂ composition, when the content of nanopores ($<0.1 \mu$ m) and micropores ($0.5-5 \mu$ m) remains the same, explains the discrepancies between this composition and the 30%PCM-2.5% TiO₂ formulation. However, an improvement in latent heat storage for mortars with 5% of TiO₂ is not enough to compensate the loss in mechanical strength. For application in buildings, the coating needs to achieve a good compromise between hardened state properties and heat transfer, so 20% PCM will be more beneficial for the mortar's durability. It has been demonstrated that the presence of PCM capsules in mortars [46], even with several cooling and melting cycles, does not affect its durability—it was not observed any cracking in the mortars' layers of the cells subject to thermal cycling.

The photocatalytic tests (figure 12) demonstrate that an increase in titanium dioxide does not necessarily render an increase in efficiency [38]. Catalyst excess seems to be in fact a contributing factor to a decrease in degradation rate for 5% compositions. While for the coating with 2.5% TiO₂, an increase in PCM does not compromise the overall photocatalytic efficiency, for coatings with 5%, an increase in PCM reduces the degradation rate. The strong decrease in pores above 1 μ m for compositions with 30% of PCM lowers the





amount of catalyst exposed to NO_x and explains the difference from 20% to 30% PCM, when the TiO_2 content remains the same.

Self-cleaning efficiency is a separate process, assessed in this study by surface contamination with Rhodamine B. The mechanism responsible by the degradation of organic surface contaminants is different from the pollutants degradation process in photocatalysis, as it has been described in a previous section. Because mortars are inherently porous, it was expected that the study would be influenced by the absorption of dye at the surface. Higher pores, particularly the ones above 1 μ m and higher porosity, can cause a higher absorption rate of the RhB during contamination. With a lower concentration of dye exposed to radiation, the degradation rate will be affected—less contaminant should lead to a faster degradation.

However, from the analysis of the results obtained for RhB after 3 h of irradiation with a solar lamp (figure 13), it became clear that is not possible to establish a direct correlation between degradation and pore distribution. The 2.5% TiO₂—25% PCM composition, with a very high amount of pores above 1 μ m (figure 6), shows the lowest amount of RhB degraded. At the same time, the composition with 5% TiO₂—20% PCM, with also a high volume of pores above 1 μ m, is the second best result for RhB degradation. The main difference between these two compositions is the total porosity, much higher in the 5% TiO₂—20% PCM what seems to confirm that higher number of pores will keep less RhB at the surface, hence the higher degradation rate. However, this observation is contradicted by the tests with 2.5% TiO₂—30% PCM that shows the highest degradation while having the lowest total porosity and a very low percentage of pores above 1 μ m.

The immediate conclusion will be that the adsorption phenomenon at the surface of the mortar, caused by its intrinsic porosity plays a very important role in the degradation process of the organic dye and it seems to influence the results. Nonetheless, this apparent inconsistency observed for the composition 2.5% TiO_2 —30% PCM is in line with the results obtained for the NO_x degradation so, it can be pointed out that the explanation should be the same. This means that the best composition for self-cleaning is also the best composition NO_x



degradation, which is the one that combines the lowest total porosity, the lowest amount of pores above 1 μ m and enough catalyst to avoid partial deactivation caused by electron–hole recombination [38].

Although each composition shows a different degradation rate for the RhB after 3 h of exposure, all compositions containing TiO_2 were completely clean, with all dye removed from the surface, after 8 h under the solar lamp (figure 14). This shows that mortars can be effective for self-cleaning even when small amounts of TiO_2 are added and the presence of another additive, in this case a PCM for latent heat storage, does not affect its ability to degrade the dye.

Surface contamination has been applied with success and it is considered an expedite and simple method to assess self-cleaning in mortars.

These results show though, that further extensive study regarding the combined effect of surface adsorption, microstructure and dye reaction pathway has to be conducted to have a comprehensive understanding of the superficial decontamination in photocatalytic mortars.

5. Conclusions

The results presented in this work confirmed that combining micro-sized PCM and nano-sized TiO_2 opens new possibilities to develop mortars with multiple functionalities such as self-cleaning and heat storage. The microstructural modifications do not necessarily mean that hardened state properties will be compromised. Previous research demonstrated that both additives (PCM and TiO_2) maintain their functionality for long periods of time, compatible with the service life expectancy of the building in which they will be applied. Good understanding of microstructural changes in new and innovative mortars can lead to an optimization of compositions without compromising their functionality. This opens a new field of research in the development of multifunctional advanced materials for construction.

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