Multifunctional smart concretes with novel phase change materials: mechanical and thermo-energy investigation

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Abstract.

Energy performance in buildings and integrated systems represents a key aspect influencing anthropogenic emissions worldwide. Therefore, novel multifunctional materials for improving envelope thermo-energy efficiency through passive techniques are presently attracting notable researchers' effort. In this view, the integration of phase change materials (PCM) into structural concrete showed interesting effects in enhancing the material thermal capacity while keeping proper structural strength. This work presents a multiphysics thermo-mechanical investigation concerning innovative concretes incorporating paraffin-based PCM suitable for structural-thermal multifunctional applications in high-energy efficiency buildings. Both classic microPCM-capsules and the novel more pioneering macroPCM-capsules with 18°C phase transition temperature are used for the new composite preparation. Results confirm the thermal benefits of PCM and demonstrate that the addition of PCM reduces the mass density of concrete by almost twice PCMs weight. Average compressive strength decreases with increasing the amount of PCM, but its coefficient of variation is not as negatively affected, which is promising in terms of structural reliability. Indeed, a 1% weight content of microPCM and macroPCM results in reduced coefficients of variation of the compressive strength, determining an increase in characteristic compressive strength. This benefit might be associated to both a filler effect of the PCM and to a positive thermal interaction between inclusions and cement hydration products. The multifunctional analysis showed promising performance of PCM-based macro-capsules as aggregates, even if their concentration is relatively minor than the classic micro-capsules already acknowledged as effective additives for high energy efficient cement-based materials.

Keywords: Phase change materials; thermal-energy storage; cement-based composites; structural concrete; smart multifunctional materials; thermo-energy building envelope analysis.

1. INTRODUCTION

In recent years, the increasing awareness of the final energy need associated with the building sector in terms of both resource and energy consumption and of CO_2 and NO_x emission has been triggering a huge research effort aimed at developing more energy efficient constructions, since they are responsible for around the 40% of the final energy use in Europe and the same percentage in terms of primary energy worldwide [1] [2]with increasing demand in residential buildings and urban areas in general [3][1]-[6].

The production of the so called “near-zero energy” or “net-zero energy” buildings and settlements, which can guarantee an effective and optimized distributed renewable energy use and the required flexibility within the demand side has become an urgent priority [7],[8], [9]. Active and passive measures aimed at providing good indoor environmental quality while achieving energy and cost-efficient buildings are being continuously improved and newly developed. In particular, the manufacturing of highly efficient passive techniques for increasing the thermal mass and insulation of a construction by means of new materials produces a huge amount of solutions, which can be used in order to limit the heat transmission through the building envelope [10]. Nevertheless, such techniques generally concern non-structural components and the more their effectiveness increases, the more relevant becomes the problem of limiting the thermal penalties (e.g. thermal bridges, etc.) through the structural members of the building [10],[3][1]. In this context, the use of thermal energy storage materials, being able to store heat to be used later on under varying temperature conditions within structural elements, can provide them with more efficient thermal-energy behavior [6],[11]. Three types of thermal energy storage technologies can be distinguished: sensible, latent and thermochemical energy storage. Sensible storage is achieved by increasing the temperature of the storage medium, while in thermochemical storage a high amount of energy is stored by means of a reversible chemical reaction [6],[12]-[17]. Lastly, latent heat storage takes advantage of the phase change transition of a material, e.g. mostly solid-liquid transformation, such as the one occurring in phase changing materials (PCMs), in order to store a large amount of latent heat in the form of phase change enthalpy, at a constant temperature [12]. The possibility of storing heat at constant temperature makes latent heat storage materials particularly attractive for the integration in building structural components, where they can both stabilize the composite material temperature and reduce the deterioration caused by frequent thermal expansion and contraction.

This paper presents a multiphysics thermo-mechanical investigation concerning innovative concretes incorporating paraffin-based PCM suitable for structural-thermal multifunctional applications aimed at improving the operative performance of building and integrated energy systems. Two types of PCM encapsulation are considered, namely micro-encapsulation and a type of macro-encapsulation that was never proposed before for application in structural concrete. Therefore, the brand-new concrete composite is compared to more classic PCM-filled concretes and new potentialities are discussed while enhancing the whole environmental performance of such material, from both mechanical and thermal-energy perspective. The rest of the paper is organized as follows. Firstly, a literature overview on the use of PCMs as multifunctional additives in concrete is presented in Section 2. Then, materials and samples developed within this work are presented in Section 3. The experimental methodology is described in detail in Section 4, while test results are presented in Section 5 and discussed in Section 6. Finally, the paper presents the main findings and conclusions.

2. BACKGROUND ON CONCRETE WITH PCM

In principle, every material can be considered as a phase change one, yet, not all of them can be used in common building applications. As a matter of fact, in order to be effectively integrated into construction components (e.g. buildings and integrated energy systems), phase change materials need to guarantee at least three basic requirements: a large melting enthalpy, an adequate phase change temperature and a limited volume change during phase transition. Furthermore, some additional properties like thermal conductivity and safety, and various technical and economic aspects, e.g. cost of production and modality of use, must be considered when choosing the appropriate phase change material [12]-[17].

The scientific interest about PCMs has been considerably growing over the last decade, due to the increase of the available products at reasonable costs, with promising areas of utilization in building applications [18]. Examples of integration of PCMs are walls, ceilings, roofs, windows, in addition to construction materials or structural elements [19]-[21]. The incorporation of PCMs typically decreases the mass density of the resulting materials, which determines the achievement of lighter building structures [6]. Given its high potential in terms of increased melting heat, and in spite of the difficult material selection process, the use of latent heat storage materials such as PCMs has been thoroughly investigated by the scientific community [22]-[26]. In particular, a huge piece of literature focused on the combination of suitable phase change materials with cementitious materials, although several aspects related to the mechanical performance of PCM-filled concrete still need to be clarified [27],[28] and PCM capsules in existing papers present comparable characteristics and therefore the same limitations, while new kinds of bigger capsules may enhance the PCM quantity within the structural element without compromising its mechanical performance and acting as PCM-filled aggregate. Therefore, this kind of scientific effort is still needed and may be of interest for the improvement of the thermo-environmental performance of new constructions built with potentially adaptive concrete also since the same concrete is, by any means, the most widespread construction material worldwide [28],[29]. It is relatively inexpensive and easy to handle and cast. Furthermore, because of its composition and structure, it possesses high thermal mass and can easily integrate small multifunctional aggregates in substitution of natural aggregates within its cementitious matrix [29],[30]. Literature studies identify two main phase change materials which can be effectively integrated in concrete for building applications: (i) organic, generally paraffin and fatty acids, and (ii) inorganic PCMs, e.g. salt hydrates. Nevertheless, the high volume changes and the potential subcooling associated to most of inorganic PCMs, oriented researchers' attention towards the use of the former kind of phase change materials in combination with concrete [31].

Literature shows that the addition of PCMs provides the cementitious materials with enhanced heat storage and thermal performance, but has also negative effects on mechanical properties, such as lower strength, uncertain long-term stability and lower fire resistance [6],[32]. Such a negative impact could be minimized using suitable PCMs and the employment of appropriate incorporation methods, and also by adding more innovative micro- and nano-fillers, such as carbon nanotubes [33], able to enhance their mechanical performance without compromising their thermal storage properties. Among PCMs materials, organic PCMs appear to be especially promising in this perspective [32],[34].

The integration of phase change materials within a cementitious matrix can be pursued via immersion [34],[35], impregnation [25],[36], and direct mixing [36]-[38]. This last method, which can prevent leakage phenomena, involves PCM encapsulations within a container having stable chemical properties before its incorporation in concrete. Different research studies show that direct mixing produces a significant improvement in the composite thermal behavior, while preserving acceptable mechanical performance [36],[39] and even reducing thermal stresses in different concrete components [40],[41]. In particular, the inclusion of PCM in concrete is known to produce a decrease in the thermal conductivity value and an increase in terms of specific heat, proportional to the amount of PCM included in the mixture [14],[15].

As already mentioned, most literature studies focus on the use of microencapsulated PCM [40],[41]. As an example, Hunger et al. [14] produce self-compacting concretes with different amounts of PCM and investigate their mechanical properties, while Thiele et al. [38] evaluate both thermal and mechanical properties of microencapsulated PCM concrete walls. Dehdezi et al. [42] study the thermal, mechanical and microstructural properties of concrete containing different quantities of microencapsulated PCM highlighting that PCMs remain undamaged during mixing but they break under loading, producing voids and crack opening weak points. Concrete compressive and flexural strength decreases with the increase of the PCMs dosage. In particular, the average decrease of compression and bending strength for specimens with over 3.0% PCM fillers is generally higher than 50% of the original strength capacity [14],[44]-[45]. However, mechanical properties compatible with structural applications are reported in the literature, such as in Cabeza et al. [45],[46] where PCM-concrete reaches a compressive strength of 25 MPa and a tensile strength larger than 6 MPa. Similarly, Lecompte et al. [46] show that the highest investigated PCM amount, up to 29.5% in volume, provides concretes with compressive strength suitable for their utilization as load bearing or self-supporting solid blocks. The fillers are micro-encapsulated paraffin materials. The compressive strength and the initial stiffness of concretes filled with inclusions are directly related to the volume fraction and compressive strength of the fillers [47][48]. PCM inclusions generally degrade the mechanical properties of cement-based composites [47],[49]; however, a critical ratio of stiff/soft inclusion volume fractions could be identified to formulate stiffness-equivalent cement-matrices containing PCMs. PCM microcapsules also reduce the rate and extent of water sorption of cement mortar composites [48]. Snoeck et al. [50] observe that PCMs are innovative fillers for concrete structures to promote thermal comfort and diminish thermal cracking [50]. They study five different types of encapsulated PCMs with sizes from 17 to 300 µm and melting points between 18 and 28 °C. The decrease in workability is found to be acceptable, i.e. up to 5% in weight of PCM addition. The compressive strength reduces significantly above the amount of 3% PCM. However, the strength of PCM-filled concrete results suitable for many applications and all those experiments concerned commercial microencapsulated PCM, typically BASF Micronal microcapsules [50], additives into the concrete recipe.

Yang et al. [51] study the mechanical performance of PCM-filled concretes, including compressive strength, elastic modulus and shrinkage, investigating also the properties of the material in the liquid phase. The phase change materials are introduced in the cementitious material within a heat storage powder based on silica powder. The mechanical tests are conducted at two different temperatures - one below the melting point (23°C) and one above (40°C), at 7 and 28 days of curing, in six different proportions. Higher PCM amounts produce lower specific weights, compressive strengths and elastic moduli and higher drying shrinkage of PCM-filled concrete. The composite materials are tested with varying temperature and PCM phase, showing that PCMs in liquid phase are softer than in solid phase: the compressive strength and elastic modulus are smaller, while the effect of the phase of PCM on the drying shrinkage is not significant. Literature studies also show that the presence of mineral aggregates reduces the degradation of the mechanical properties of PCM-filled cementitious materials and the presence of PCM in concretes has a limited influence on the fracture properties [52]. PCM microcapsules are also found feasible to produce Self Compacting Concretes (SCC), if utilized as a replacement of the marble powder [14].

The inclusion of macroencapsulated PCM in concrete is an almost unexplored field, basically because of the high influence of bigger aggregates on concrete failure. The embedded capsules, as a matter of fact, act as big voids and can negatively affect concrete mechanical properties. For such a reason, different literature studies try to somehow circumvent the problem by using peculiar kinds of capsules. As illustrative examples, Dong et al. [53] develop steel balls as PCM containers to be included in the cementitious matrix, while Memom et al. [54] use macro-encapsulated paraffin-lightweight aggregate (LWA) to develop a normal weight aggregate concrete (NWAC) which uses what can be considered as a hybrid between impregnation and direct mixing technique. Structural concretes with macroencapsulated organic PCMs were also recently studied in [55], where innovative 22 mm in diameter steel balls with attached clamps were proposed as PCM macrocapsules for partial or total substitution of coarse aggregates. While the clamps were seen apt to mitigate concrete strength reduction due to PCM inclusion, material's reliability in terms of statistical dispersion of its properties was not sufficiently investigated.

The use of lightweight aggregates as carrier units for PCM is also investigated by Shafiri and Sakulich [56]. They use three different PCMs with melting temperatures of -10 °C, 6 °C, and 28 °C and investigate the so-produced concrete ability to increase the occupant comfort in buildings and to decrease the material deterioration. In particular, the direct addition of PCM in cementitious materials has negative effects on the hydration reaction and consequently results in a reduction of mechanical performance. The use of LWA to incorporate PCM in the cementitious matrix is found able to prevent such a drawback. Also, the saturation of LWA by PCM enhanced the mechanical and thermal stability of the material [57]. Cui et al. develop macroencapsulated lauryl alcohol lightweight aggregates to be used in TES-concrete [58].

Moving ahead from such background of novel and smart concrete for sustainable and high energy efficient applications in buildings [59], this work investigates two possibilities of developing a sort of *low structural mass-high thermal mass* concrete using a new type of PCM-based additive, which is, by any means, an intermediate solution between the more rigid polymer microcapsule of PCM and the traditionally known macrocapsule filled with large quantities of PCM. In fact, such a new patented relatively big capsule (i.e. diameter of 3 to 5 mm) consists of an original double encapsulation system creating a microcapsules’ core included into a matrix–type configuration [60] that has been never tested before when incorporated into construction materials like structural concrete, as the purpose of this work. In order to clarify its effect even when compared to better known PCM based additives, the novel composite concrete is also benchmarked against multifunctional concrete doped with more traditional microencapsulated PCM included in the mix design in the same concentration of the brand new macrocapsule. New potentialities for improving PCM-filled cement based materials are therefore highlighted from a both thermal and mechanical point of view.

3. MATERIALS AND METHODS

The samples for the mechanical and the thermal investigations were realized with normal (i.e., without PCM), microPCM-filled and macroPCM-filled concrete. The samples' shapes and dimensions were conceived specifically for the subsequent research tests. This section presents the adopted phase change materials, the mix designs of the investigated concretes and the fabrication procedures of the samples.

3.1. Phase Change Materials

Two different types of phase change materials have been selected as additives for standard concrete to obtain a passive thermal regulation multifunctional composite concrete: micro- and macro-encapsulated PCMs produced by Microtek Laboratories.

MicroPCM consists of an interior PCM material within an external shell wall. The core material is a paraffin-wax with heat absorption capabilities and able to keep a specific temperature. The PCM content in each capsule is about 85-90 wt.% with respect to the whole weight. The capsule walls are made of a stable and inert polymer. They look like a white powder with a mean particle size between 14 and 24 μm (Fig. 1(a) and 1(b)). The melting point of the PCM is 18°C.

PCM macrocapsules are beads with diameters between 3 and 5 mm containing a plurality of microcapsules of microPCM suspended in a gelling agent solution of polysaccharide alginate. The PCM content in the beads is around 80%. Macrocapsules appear as white solid spheres with a density slightly less than 1000 kg/m^3. Fig. 1 depicts both microPCM and macroPCM schematic representation as small internal circles (i.e. the microcapsules containing PCM) and the circumscribed circle as the gelling agent solution constituting the structure of the macrocapsules. The same paraffin based PCM, with a melting point of 18 °C, is contained in the microcapsules as well as in the macrocapsules (i.e. the yellow content of microcapsules in Figure 1).

Figure 1. a) MicroPCM; b) macroPCM spherical beads; and c) representation of a PCM spherical bead (the inner circles are microcapsules containing PCM)

3.2. Mix design of the new PCM-filled concrete

Seven different mixes have been prepared, with different amounts of microPCM and macroPCM: both fillers have been added in the amounts of 1%, 3% and 5% with respect to the whole weight of the composite. It should be noted that, for a fixed weight, classic microcapsules resulted in a higher quantity of PCM with respect to the new macrocapsules due to the different composition of the fillers and a relatively higher capsulation material in the novel macrocapsules configuration, e.g. the alginate gelling solution and the microcapsules themselves. A stardard (aforementioned “normal”) concrete without PCM has been also prepared for comparative purposes.

All mix designs are summarized in Table 1. The PCMs were introduced in addition to the reference mix design. The water/cement ratio chosen for the normal concrete was 0.45. The PCM-filled composites had the same ratio, except for those with 5% PCM, which needed a slightly higher amount of water to warrant a workability comparable to that of the other ones. For them, the water/cement ratio was 0.5. Mix designs of composites with 5% PCM also needed greater quantities of plasticizer. The cement was pozzolanic type 42.5. Sand and gravel with nominal dimensions from 0 to 4 mm and from 4 to 8 mm, respectively, were used as aggregates. Such coarse aggregates' dimensions were chosen taking into account the geometry of the specimens to be fabricated.

Table 1. Mix designs of fabricated Normal concretes, with microPCM and macroPCM

Components (kg/m^3)	without PCM	with microPCM			with macroPCM		
		1%	3%	5%	1%	3%	5%
Cement	524	511	486	447	511	486	446
Water	234	228	218	223	228	218	223
Sand	951	927	882	817	927	882	817
Gravel	638	622	592	548	622	592	548
PCM	-	24	71	102	24	71	102
Plasticizer	2.6	2.6	2.4	6.8	2.6	2.4	4.5
w/c	0.45	0.45	0.45	0.50	0.45	0.45	0.50

3.3. Preparation procedures

The preparation of all composite specimens was carried out according to the same design procedure. First of all, the dry components of concrete (cement, sand and gravel) were mixed in the proper proportion (Fig. 2a). Then, the PCMs were added (Fig. 2b). Successively, after the addition of water and plasticizer, the compound was carefully mixed (Fig. 2c). A further amount of plasticizer was added to achieve the comparable workability, so as to provide samples with the same surface roughness. After reaching the proper consistency, the mixtures were poured into oiled molds and gently compacted in order to get an improved homogeneity of the filler distribution in the concrete matrix (Fig. 2d). After 48-72 hours, the specimens were unmolded for curing (Fig. 2e).

The samples were cubes of 100×100×100 mm^3 and square prisms with a base side of 190 mm and a thickness of 50 mm. Figure 2 shows the schematic preparation process of the PCM-filled concretes.

Figure 3 represents the structure of the PCM-filled concretes compared with the standard concrete. The figure illustrates the peculiar impact of the two different geometrical configurations of microPCM and macroPCM in the cementitious composite.

Five cubes and a slab were made for each type of concrete with 1, 3 and 5% of both microPCM and macroPCM, for a total of thirty-six samples. Regarding normal concrete, eight cubes and a plate were fabricated. A total of forty-five samples were made available for both mechanical and thermal tests.

Figure 2. Preparation procedures of concrete samples with microPCM and macroPCM.

Figure 3. Sketch of the internal structure of normal, microPCM-filled and macroPCM-filled concrete.

After mixing, both microPCM and macroPCM capsules were visually found to be intact since no oily surface in the concretes were observed.

In order to qualitatively assess the effectiveness of the proposed fabrication procedures, the internal structure of the hardened concretes after cracking was investigated using a Scanning Electron Microscope type FESEM, model Supra 25, Zeiss (Fig. 4). Figure 4a) shows the texture of a fragment of concrete doped with 5% macro-encapsulated PCM. Figure 4 c) shows the PCM microcapsules into a macrocapsule. Figures 4b) and d) are magnified images of a concrete piece with 5% microPCM. From the figures, the dispersion of the microcapsules in the concrete matrix appears evident.

Figure 4. SEM images of (a,c) concrete with 5% macroPCM and (b-d) concrete with 5% microPCM, at different magnifications.

4. EXPERIMENTAL PROCEDURES

A campaign of experimental tests was carried out on the concretes to study their physical, mechanical and thermal properties during the PCMs' phase transition with different amounts of PCM and to benchmark such properties against those of standard concrete, as presented in this section.

4.1 Mechanical tests

After laboratory curing, the hardened cubes were weighed and their volume was determined by measuring the average values of the three linear dimensions of each sample, following the EN 12390-3:2002 standard [61]. The obtained values permitted to derive the punctual and the average density of the different concrete samples, and to calculate the standard deviations of the measurements.

After collecting dimensional and weight properties of all the samples, the hardened cubes were subjected to uniaxial compression tests using a Controls Advantest machine, model 50-C7600 with a maximum capacity force of 5000 kN and a servo-hydraulic control unit model 50-C 9842 with a power of 750 W and maximum pressure of 700 bar. The internal vertical and horizontal dimensions of the test chamber of the Advantest machine were 520 mm and 425 mm, respectively. Each sample was placed at the center of the pressure rectified steel plate, instrumented with three linear displacement transducers positioned at 120 degrees.

Tests were carried out by application of compressive loads, under displacement control, from the elastic state up to the rupture and to the post-peak behavior. This allowed to investigate the complete constitutive behavior of the materials, including peak resistance and unstable post-peak branch, so as to assess the ultimate strain of concrete and, hence, its ductile properties in compression. The test speed was 2 μm/s, in agreement with the EN 12390-3 standard [61], with a limit displacement of 5000 μm. Figure 5 shows the instrumentation setup for the mechanical tests (Fig. 5a), which includes the press (on the left), the adjacent central control unit, and the data acquisition system (on the right). Figure 5b reports a detailed view of the cube positioning, where the two front displacement transducers are visible. The third LVDT was located behind the sample.

Figure 5. Experimental setup for mechanical tests: (a) testing machine and data acquisition system, (b) cubic concrete sample during uniaxial compressive test, instrumented with three displacement transducers.

In order to gain a quantitative picture of the mechanical properties of the investigated concretes and of their feasibility as structural materials, the tested specimens were compared in terms of average compressive strength, R_m, characteristic compressive strength, R_{ck}, and strain ductility, μ_c.

The characteristic compressive strength is particularly meaningful, as this represents the standard value used in technical codes to characterize concrete structural class. As it is well-known, the characteristic strength is defined as the strength value that has a 95% probability of exceedance or, in other words, that is not reached by 5% of the tested samples. According to the relevant literature on the topic, R_{ck} was determined as follows:

$$R_{ck} = R_m - k \cdot s \tag{1}$$

where R_m is the average strength among the investigated samples for each typology of concrete, s is the standard deviation, and k is a coefficient depending on the number of tested samples. According to the literature [62], k was assumed equal to 3.40 and 2.75 for a number of specimens of 5 and 8, respectively. For an infinite number of samples, k would assume the value of 1.64, which corresponds to the assumption of a Gaussian distribution for the compressive strength of concrete. The characteristic strength can be equivalently written as:

$$R_{ck} = R_m(1 - k \cdot CV) \tag{2}$$

where $CV = s/R_m$ is the coefficient of variation of the compressive strength. This, in fact, is a very important quantity in view of the use of the composite concretes for structural applications, as it is closely related to the structural reliability and the repeatability of the properties of the new developed composite material, i.e. the lower the *CV* of a structural material, the higher its structural reliability. Achieving values of *CV*, in the present case estimated by testing 5 equivalent samples per each typology, comparable to those typically expected for normal concrete is here taken as a confirmation of the repeatability of the properties of the investigated composite concretes.

The assessment of the strain ductility of the investigated concretes is carried out through the evaluation of the average stress-strain curves obtained from the experiments. In particular, strain ductility, μ_c, is computed as:

$$\mu_c = \frac{\varepsilon_{cu}}{\varepsilon_{cp}} \tag{3}$$

where ε_{cp} is the unit strain corresponding to the peak resistance and ε_{cu} is the strain corresponding to the ultimate condition conventionally evaluated as the strain corresponding to a 20% reduction in strength with respect to the peak resistance in the unstable branch.

4.3 Environmental thermo-physical tests

The thermo-physical characterization of the samples was carried out by means of an ATT DM340SR climatic chamber equipped with a test compartment ($601 \times 810 \times 694$ mm^3) inside which it is possible to obtain a temperature- and humidity-controlled environment in the range -40-to-180°C

±1°C and 10-to-98% ±3% of RH. The chamber is also equipped with 12 PT100 thermocouples, which can be used to measure the thermal profile of the samples inside the compartment during the climatic simulation of user-defined hygrothermal cycles. The simulation of realistic dynamic environment in a controlled chamber ensured the high stability of the tests compared to field experiments, and the repeatability of the same experiments.

During the experimental campaign, the seven 190×190×50 mm^3 concrete samples, i.e. the 1%, 3% and 5% macroPCM, the 1%, 3% and 5% microPCM and the normal concrete samples, were placed inside a specifically designed sample holder. Such a device was built using 10 cm thick XPS panels, assembled in order to completely protect five surfaces of the sample out of six, i.e. the four sides and the bottom surface, and leave the only upper surface exposed to the controlled environment of the chamber (Figure 6).

Four of the PT100 sensors were used to monitor the thermal behavior of each sample: one probe was placed in the centre of the bottom surface, one probe in the centre of the upper surface, and the remaining two probes were positioned in the centre of two parallel sides of the sample, as shown in Figure 6.

Figure 6. Schematic representation of the experimental setup.

The previously described experimental setup was developed in order to assure that the heat transfer could take place only through the bottom surface of the specimen via conduction through the sample thickness itself, and that such heat transfer was not directly influenced by the external temperature fluctuations of the controlled environment.

During the thermal dynamic environmental tests, all the samples were exposed to the same thermal program consisting of five subsequent segments each one lasting eight hours, characterized by a fixed RH value of 50%, and by two different temperature set points, i.e. 26°C and 10°C, centred on the nominal phase change temperature of 18°C, characterizing the adopted PCMs. The complete imposed hydro-thermal profile is described in Fig.7.

Figure 7. Imposed hydro-thermal cycle.

Three different measurements were carried out by conditioning three samples at a time inside the chamber. Each measurement investigated the thermal behavior of one of the three amounts of microPCM and macroPCM concretes and of the normal sample, always taken as reference (Figure 8). Table 2 reports the experimental cycles carried out in this campaign.

Table 2. Thermal cycle measurements.

Measurement	Sample 1	Sample 2	Sample 3
1	Normal	5% macroPCM concrete	5% microPCM concrete
2	Normal	3% macroPCM concrete	3% microPCM concrete
3	Normal	1% macroPCM concrete	1% microPCM concrete

Figure 8. View of the environmental simulation chamber before starting a test.

The experimental tests in the environmental simulation chamber were aimed at verifying that phase change of PCM effectively takes place at the expected temperature within the composite concretes and to qualitatively verify that an increase in PCM content results in a higher phase change enthalpy and, consequently, in a more significant modification of the thermal response in comparison to normal concrete.

5. RESULTS

The results of the experimental campaign are presented and discussed in this section. The mechanical tests are examined, at first, while the thermo-energy investigation is presented afterwards and followed by the discussion of all results.

5.1. Results of mechanical tests

Before presenting the results of the mechanical characterization tests, the mass density of concretes with PCM inclusion is worth investigating. Owing to the low density of the PCMs micro- and macro-capsules, the mass density of the PCM-filled concretes is seen to rapidly decrease with the increase of the filler content for both microPCM and macroPCM. Figure 9(a) summarizes mean values and standard deviations of the mass density for each type of modified concrete. Samples with 5% in weight of PCM exhibit a density reduction of about 11% compared to normal concrete (Fig. 9(b)). This circumstance makes them suitable for their utilization as lightweight concretes whenever a structural dead load reduction is desirable. Average mass density values are also reported in Table 3 containing mechanical test results and presented later on in the paper.

In regards to axial compression tests, the first aspect that is worth of investigation is the fracture pattern after crushing. As illustrative examples, Figure 10 shows such a pattern for concrete samples with 5% microPCM and 5% macroPCM after mechanical testing. All samples showed a typical bi-pyramidal fracture, indicating a good behavior of the concretes. However, detail views of the samples in Figure 10 indicate the presence of several small fractures. Furthermore, it has to be observed that concretes with 5% macroPCM exhibit various macrocapsules on the fracture surface, representing local weak points of the material, as confirmed by the circumstance that some of these PCM macrocapsules are cracked. This last circumstance was also verified through microscope investigation of the PCM macrocapsules close to the fracture surface, using the same equipment described in Section 3. As an example, Figure 11 shows a picture taken with a microscope Bresser, type Biolux NV, with magnifications up to 1280X, after the axial compression test, where the crack of the macrocapsule is clearly visible.

Figure 9. Variation of concrete density (a) with standard deviation at different amounts of microPCM and macroPCM, and (b) related to the different type of PCM

Figure 10. Fracture patterns and detail view of concrete samples after uniaxial compression test, (a-b) with 5% microPCM, and (c-d) macroPCM.

Figure 11. Fragment of crushed concrete with 5% macroPCM

In terms of constitutive stress-strain behavior, all concrete samples showed a typical non-linear curve, with the peak resistance followed by the decaying unstable branch. Focusing, at first, on the peak compressive strength, Figure 12 shows the results of all the tested samples without PCM and with microPCM and macroPCM. These results show, already at a first glance, that the compressive strength tends to decrease with the increase of the amount of PCM fillers into the concrete, which is consistent with other literature works [14],[43],[44] and is a consequence of the lower strength of PCM shells and capsules compared to fine and coarse aggregates. In more quantitative terms, concretes with microPCM exhibit a reduction in average compressive strength equal to 1.6, 33.6 and 43.1% using 1%, 3% and 5% weight contents of fillers, respectively. Concretes with 1, 3 and 5% macroPCM showed average strength reductions of 3.5%, 17.4% and 33.6%, respectively. It is therefore noted that the strength reduction is almost consistent for both types of PCM fillers, although literature studies reported that microcapsules, if not in large amounts, provide higher specific area and can act as nucleation sites stimulating cement hydration, resulting in a beneficial effect for the mechanical properties of the material [63]-[65].

Table 3 summarizes the main results of the axial compression tests and, in particular, the values of the average compressive strength of the seven types of composites, their coefficient of variation, and their characteristic compressive strength and, for the sake of completeness, their average density already discussed above. Average and characteristic compressive strength of the investigated concretes are also reported in Figure 13. The results summarized in Table 4 highlight that the CV of normal concrete is equal to 0.09, which compares well with the typical range of 0.10-0.15 reported in the literature [62]. Values of CV of concretes with PCM resulted smaller or equal than 0.09 with the only exception of the composite concrete with the largest content of macroPCM capsules. In this case, the CV is equal to 0.14, which depends on the peculiar fracture of the samples with local concentration of fillers, but is still within the acceptable range for concrete [62]. Overall, the low values of CV characterizing the composite concretes demonstrate their good reliability properties and the good repeatability of their properties. Notably, concretes with 1% weight contents of microPCM and macroPCM exhibit CV values equal to 0.02, therefore much smaller than the 0.09 of normal concrete. This reduction in CV results in both cases in an increased characteristic strength corresponding to an increased structural class from C25/30 of normal concrete to C28/35 of composite concrete. This beneficial effect associated to small PCM addition, being consistently observed with both microPCM and macroPCM, might be conceivably associated to the filler effect and to some positive thermodynamic interaction between inclusions and cement hydration products [63]. As an additional remark on the obtained results, despite the reduction in compressive strength, it should be highlighted that all composite concretes have reached structural classes compatible with their use as structural concretes, even though the C12/15 class is only applicable for massive structures without or with very low reinforcement and C16/20 class for simply reinforced structures. However, based on the presented results, higher classes of concrete incorporating 5% of microPCM or macroPCM could be conceivably obtained by starting from a basic concrete corresponding to a class greater than C25/30.

The last relevant aspect to be considered is the strain ductility of the tested concretes. Figure 14 shows the stress-strain curves obtained as averages among the different tested specimens. These average curves, for each type of tested concrete, are obtained by computing the mean stress for a fixed strain. The diagrams highlight an increase in the elastic modulus of the concrete specimens with higher strength. The curves also evidence that all concretes exhibit a similar behavior after peak, resulting in comparable ductile properties. The resulting ductility values, evaluated through Eq. (3), are summarized in Table 4. As expected, normal concrete exhibits the highest ductility of 2.38. Nevertheless, the ductility reduction consequent to the inclusion of PCM is relatively marginal and, in any case, there is no clear trend of ductility decrease with increasing PCM content as concretes with 5% weight contents of microPCM and macroPCM exhibit the largest ductility values after normal concrete equal to 1.98 and 2.04, respectively. Therefore, the novel macrocapsule typology is able to preserve this mechanical performance relatively better than the classic microcapsulated PCM additives.

Figure 12. Compressive strength of all the samples without and with micro and macroPCM

Figure 13. (a) Average compressive strength with standard deviation intervals, and (b) characteristic compressive strength of the tested concretes without PCM, and with micro and macroPCM

Table 3. Compressive strengths and densities of concrete composites tested

Sample	Mean Compressive	CV	Characteristic Compressive Strength	Mean Density (kg/m^3)

	Strength (MPa)		(MPa)	
Normal	44.39	0.09	33.52	2265
1% macroPCM	42.82	0.02	39.84	2192
1% microPCM	43.67	0.02	41.16	2233
3% macroPCM	36.65	0.04	31.70	2117
3% microPCM	29.46	0.09	20.60	2057
5% macroPCM	29.48	0.14	15.03	2023
5% microPCM	25.25	0.04	21.80	2018

Figure 14. Stress-strain curves of the complete uniaxial compression tests on concrete without PCM, and with microPCM and macroPCM.

Table 4. Values of peak force, F_{peak}, peak strain, ε_{cp}, the strain corresponding to the decrease of 20% of the peak force after peak, ε_{cu}, and their ratio, μ_c, referring to the mean curves for the seven different types of concrete

Sample	**F_{peak} (kN)**	ε_{cp} **(millistrain)**	ε_{cu} **(millistrain)**	μ_c
Normal	433.3	4.44	10.56	2.38
1% macroPCM	426.8	4.94	8.66	1.75
1% microPCM	433.6	4.93	9.17	1.86
3% macroPCM	365.5	3.77	6.80	1.80
3% microPCM	292.2	4.65	8.38	1.80
5% macroPCM	292.5	4.54	9.25	2.04
5% microPCM	251.1	5.01	9.93	1.98

5.2. Results of environmental thermo-energy tests

The thermo-physical tests are aimed at performing a qualitative analysis in dynamic experimental conditions of the phase change taking place within the PCM micro and macrocapsules so as to confirm the achieved thermal benefits in the incorporation of PCMs in concrete.

Results from the thermo-physical tests show that during the thermal cycle, all the samples follow the imposed temperature waveform. Nevertheless, the temperature profiles do not perfectly resemble the same waveform, as a consequence of the high thermal inertia of concrete (Fig. 15 and

Fig. 16). Furthermore, it is noteworthy that samples containing microPCM or macroPCM within their matrix are associated to a peculiar behavior in the temperature range 17-to-12°C during the descending ramp and in the range 15-to-18°C as the temperature set point increases. In particular, a deflection in the thermal profile with respect to the reference trend of the neat concrete sample is noted, the amount of which increases with the increasing amount of PCM in the composite. Such a deflection can be associated to the phase change taking place in the dispersed microPCM concrete and macroPCM concrete, where the paraffin with a melting point at 18°C is included. The first deflection of the analysed profile can be associated to the solidification of the PCM, while the second one to the melting phenomenon. During these intervals, the PCM-doped concretes decrease their temperature at a lower rate, since part of the thermal energy is stored in the latent storage medium in order to break or create molecular bonds in the lattice. The massive PCM effect is visible for up to 3 hours in the macroPCM concrete with 5% of macrocapsules and up to about 2 hours in the PCM-concrete with the same concentration of microcapsules in the solidification path, meaning that the novel macrocapsules are able to keep the PCM transition phase for a relatively longer duration within the same sample configuration, compared to more classic microcapsules with PCM inside. In fact, the same concentration of macrocapsules is able to sprawl the phase changing process up to several hours, by keeping a more constant temperature for the typically required time in building environment applications. In particular, the first temperature decrease was observed after 3 hours, while 2 hours were required by the micro-capsulated PCM concrete sample with the same PCM concentration, i.e. 5%. Additionally, the phase change influenced the thermal progress of the samples up to 9 hours (at the 25th hour of the dynamic transition test), where the highest concentration samples reached the same temperature of the base case sample without PCM.

Figure 17 depicts the thermal behavior of the highest and the lowest PCM-concentrations samples when compared to the thermal behavior of the standard normal concrete without PCMs, as measured within the environmental simulation chamber. As anticipated, phase change events are clearly visible during the course of the cycle, in proximity to the transition phase temperature. Also, in the plot of Figure 17 the highest PCM concentration samples, i.e. with 5% of microPCM and macroPCM, exhibit the largest deviations in temperature compared to normal concrete, which result into large area cycles, as a consequence of the energy absorbed and released in phase change transition by the composite materials. On the contrary, the lowest PCM concentration samples, i.e. with 1% of microPCM and macroPCM, exhibit a thermal behavior that is very similar to that of normal concrete resulting in small area cycles being the relation between the temperature of normal concrete and that of composite concrete almost linear.

Figure 15. Normal, macroPCM 1%, macroPCM 3% and macroPCM 5% concretes thermal profiles monitored by the PT100 probe at the bottom of the sample.

Fig. 16 Normal, microPCM 1%, microPCM 3% and microPCM 5% concretes thermal profiles monitored by the PT100 probe at the bottom of the sample.

Fig. 17 Thermal profile of the highest and the lowest PCM-concentration concrete versus the standard concrete thermal profile, as measured within the environmental simulation chamber.

6. DISCUSSION

New composite concretes have been developed by including varying concentrations and geometries of classic and brand-new capsules filled with phase change materials, aimed at increasing the thermal capacity of such concretes around the building environment thermal applications maintaining, as much as possible, their structural performance. A multipurpose experimental characterization has been carried out by means of traditional and innovative procedures, aimed at characterizing the physical features of the composite material, its mechanical performance and its thermal enhancement during the phase changing cycles. In particular, an innovative PCM macrocapsule configuration was tested as an intermediate solution between the well-known microcapsules [49] and the classic macro-boxes with large quantities of PCM inside. More in details, microcapsules with paraffin having the phase change temperature at 18°C were firstly included with varying weight concentration up to 5%. Then, the same concentration recipes were designed for another concrete with a novel kind of macrocapsule never tested before within the building environment, made of a macro-aggregation containing therein a plurality of microcapsules filled with PCM.

The results of the experimental campaign demonstrate that the incorporation of PCM as additive can be compatible with a structural use of the resulting composite concretes, while providing, at the same time, significant thermal energy benefits, despite the relatively minor PCM quantity compared to the classic microcapsules included into the cement based mix design. Experiments show that PCMs reduce the mass density of concrete by a factor that is about twice their percentage weight content, so that 5% of PCM correspond to 11% reduction in weight, leading to a lightweight and high-thermal mass concrete. Average compressive strength decreases with increasing amount of PCMs, which was also observed in other literature studies, but its coefficient of variation seems to be substantially unaffected by PCM addition, which is promising in terms of structural reliability of the material. A small amount of PCM, equal to 1% with respect to the total weight of the composite, even resulted in reduced coefficients of variation of the compressive strength, both for micro- and macroencapsulated PCM, which determined an increase in characteristic compressive strength resulting in an improved structural class from C25/30 to C28/35. Ductility, expressed in terms of ratio between the ultimate compressive strain and the compressive strain at peak resistance, is only marginally affected by PCM addition and its reduction does not seem to increase with increasing the content of PCM.

Thermo-physical tests conducted within an environmental simulation control chamber highlighted that the innovative PCM macrocapsules demonstrate to have equivalent behavior with respect to the microcapsules when added to the concrete mix design up to 3% of concentration and, again, equivalent performance with respect to all the PCM-doped samples, despite the relatively minor PCM content (80 wt.%) compared to classic microcapsules (85-90 wt.%). The thermal analyses performed by means of an innovative dynamic environmental test showed how the concretes with PCM were effectively behaving as thermal buffers, and increasing benefits were observed with increasing concentration. The PCM effect was able to produce the expected buffering effects for about 9 hours after the phase change starting, in the highest concentration samples, demonstrating how such composite material could be effective on a daily basis thermal fluctuation. Therefore, the PCM macrocapsules can produce key thermal benefits, despite the relatively lower PCM concentration in the microcapsules than in the macrocapsules, demonstrating how further investigation should be carried out for enhancing the performance (both thermal and mechanical) of such promising macrocapsule novel configuration. Additionally, such selected macrocapsules could also represent an effective way to reduce the microcapsules filler effect and the consequent cement hydration increase [61]. Promising further developments of the same macrocapsules will be carried out in order to make such material suitable to replace concrete aggregates, by optimizing its mechanical properties.

7. CONCLUSIONS

PCMs represent an effective doping solution for increasing the thermal capacitance and overall thermal energy performance of materials to be integrated into building envelope and energy systems. In this paper, novel composite concretes incorporating a new kind of PCM macrocapsules aggregating classic microcapsules are tested for multifunctional structural and energy efficient applications in the building sector. To this aim, the novel composites are developed and tested from both mechanical and thermo-energy points of view, and the key final innovative considerations are highlighted as the main original contribution of the work.

The study has focused on the use of two different types of paraffin-based PCM with transition phase temperature at 18°C, namely micro-encapsulated ones, recently investigated by some authors, and novel macro-encapsulated ones, whose application in buildings is still pioneering and was unexplored so far. The idea of such macrocapsules was motivated as possible additive to include in novel concretes, and therefore with the purpose of massive application in building structural elements, while non-structural ones have been extensively explored so far (e.g. PCM in gypsum, plaster, etc. [47],[48]).

Various cubic concrete specimens, as well as plate specimens, with inclusion of different weight contents of phase changing materials, up to the 5% with respect to the total weight of the composite, have been manufactured and subjected to a variety of mechanical and dynamic thermal characterization tests.

The main findings of the presented experimental campaign are summarized below.

- While the addition of phase changing materials has resulted, as expected, in a decrease in average mechanical compressive strength, all investigated specimens have exhibited mechanical properties that might be compatible with a structural use, including strain ductility under compression. More specifically, starting from a basic mix design corresponding to a C25/30 class structural concrete, according to Eurocode 2, concretes with 1% weight content of PCMs have even attained a higher class, namely C28/35, owing to a significant reduction in the statistical dispersion of the axial compressive strength with respect to normal concrete, while concretes with larger contents of phase change material corresponded to progressively lower classes, with the worst results corresponding to C12/15 and C16/20 for 5% of micro- and macro-encapsulated phase change material, respectively. It should be noted that both classes might still be compatible with some structural applications, whereby C12/15 is applicable for massive structures without or with very low reinforcement and C16/20 for simply reinforced structures, but they are at the very low limit for structural applications. However, the results presented in the paper allow to infer that a structural concrete with a 5% weight content of PCMs having a target class equal to C25/30 or higher is feasible and could be achieved by increasing the strength of the basic mix design. Another remark on the results is that the increased characteristic strength of composite concretes with 1% weight PCM content has been consistently obtained using both microcapsules and macrocapsules. This is likely to be attributed to a beneficial interaction between the phase change phenomenon and the heat generated during concrete hydration process.

- The analysis of the fracture mechanisms has highlighted the typical bi-pyramidal shape for all crushed specimens and has revealed that only in the largest concentration of 5% in weight some macro-encapsulated PCM particles were broken during the tests. Notably, no significant reduction in ductility has been observed while increasing the content of PCM, as obtained from displacement-controlled axial compression tests. Moreover, the coefficient of variation of the axial compressive strength has resulted always smaller than the typical value of 0.15 characterizing normal concrete, suggesting that the special composite concretes have similar reliability and repeatability if compared to standard normal concrete, which is crucial towards their application as structural materials.
- Another important feature of the novel concretes with PCM addition is their low weight, whereby a 5% weight content of PCM resulted in about an 11% reduction in mass density. Therefore, such innovative composite could be considered as a *lightweight high-thermal-mass concrete*, for promising thermal energy performance optimization in buildings.
- The thermal characterization tests performed by using an innovative dynamic procedure within a climatic chamber have demonstrated the occurrence of the phase transition within the composite, resulting in a significant enhancement in the equivalent thermal capacitance of the material and, consequently, in a mitigation of the temperature fluctuations of the

samples. Additionally, the increasing PCM concentration demonstrated to effectively optimize the thermal buffer effect up to 9 hours, highlighting the promising application as indoor stabilizers on a daily thermal fluctuation basis. In this view, the novel macrocapsule showed the most interesting buffering effect, which was notable for a longer time compared to the classic microcapsules, despite also the relatively minor PCM concentration in this new configuration (80 wt.% compared to 85-90 wt.%).

- Overall, the results presented in this paper allow to conclude that novel special structural concretes with enhanced thermal capacitance, with good mechanical properties in terms of compressive strength and ductility, low weight and good reliability can be achieved by incorporating micro-encapsulated or, even better, the more advanced macro-encapsulated phase changing materials into the mix. These last novel samples guaranteed promising structural and thermo-energy performance, opening the door of also structural building elements and integrated energy systems requiring adequate mechanical performances, e.g. storage tanks, geothermal boreholes etc., for possible PCM inclusion and, therefore, for achieving the observed performance benefits even in low inertia constructions.

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