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Nano-encapsulation of phase change materials: from design to thermal performance, simulations and toxicological assessment

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Abstract

The paper presents the results of an experimental activity aimed at producing and characterizing a nano-encapsulated PEG600 (PCMs) into a silica shell. The nano-encapsulation was meant to be useful to improve the material's suitability to integration in building components. The (300 ± 15) nm nanoparticles that were produced underwent a full characterization of their thermal performances. An enthalpy of fusion as high as 66.24 kJ/kg, in a tight melting temperature range (20-21°C) was obtained, making the material suitable for thermal energy storage in buildings. In order to demonstrate the benefits of such as this technology on the reduction of heating and cooling demand of buildings, a concentration of 50% in weight of nanoparticles was, then, embedded into a gypsum plasterboard and used for all indoor plastered surfaces of a reference residential buildings. A saving of respectively up to 4.3% and up to 1.1% of heating and cooling energy demand was predicted in comparison to the ones of a building without PCM. Finally, the material underwent a full toxicological characterization exposing human alveolar basal epithelial cells to nanoparticles. The results showed that there were no toxic effects on cell morphology.

Nomenclature

PCM	Phase Change Material
NP	Nanoparticle
USD	United States Dollars
PEG	Polyethylene glycol
SiO ₂	Silicon Dioxide

33	TEOS	Tetraethyl orthosilicate
34	NH ₄ OH	Ammonium hydroxide
35	SiO ₂ @PEG600	Nanoencapsulated PEG600 in SiO ₂ shells
36	TEM	Transmission Electron Microscopy
37	EDS	Energy Dispersive X-ray Spectroscopy
38	DLS	Dynamic Light Scattering
39	SEM	Scanning Electron Microscopy
40	IR	Infrared
41	FT-IR	Fourier-Transform IR Spectroscopy
42	DSC	Differential Scanning Calorimetry
43	T _m	Melting Temperature of a PCM (°C)
44	ΔH _m	Total Enthalpy of fusion (kJ)
45	Δh _m	Enthalpy of fusion per unit mass (kJ/kg)
46	U _f	Frame global heat transfer coefficient (W/m ² K)
47	U _g	Glazing global heat transfer coefficient (W/m ² K)
48	S	Superscript indicating the solid phase
49	L	Superscript indicating the liquid phase

50 **1. Introduction**

51 In the last decade, the potential integration of PCMs in building components, as suitable
52 latent thermal energy storage systems, has become a goal for several research activities.
53 PCMs can store large amounts of latent heat in their phase transitions [1], achieving
54 significant energy savings and comfort in buildings. If, on the one hand, sensible heat refers
55 to heat that can be sensed by means of a thermometer, latent heat storage refers to the
56 undetectable heat transfer, intrinsically associated with a phase transition [2]. PCMs can
57 utilise their high latent heat storage, corresponding to the number of chemical bonds to be
58 broken to activate the full isothermal phase transition at constant pressure. For this reason,
59 within the tight temperature range in which the phase transition occurs, PCMs show higher
60 efficiency than any other sensible heat storage material [3]. PCMs are classified in three
61 classes: organic, inorganic and eutectic [3]: organic PCMs are paraffins, fatty acids, esters,
62 and alcohols [4] while the most used inorganic PCMs are salt hydrates. Metallic PCMs, that
63 are classified as inorganic, are rarely used in buildings due to their weight and high melting
64 temperature. Generally, higher melting temperatures are reported for metals and inorganic
65 PCMs, whereas they are lower in organic, salt hydrate and eutectic PCMs [5]. The main

66 figures of merit affecting PCMs effectiveness are the melting temperature, the amount of
67 latent heat of transition per unit weight, thermal conductivity (λ) and the specific heat.
68 Shape-stabilized PCMs, by means of micro- and nano-encapsulation processes, avoid any
69 leakage risk in the liquid phase, but also maximize heat transfer due to larger available
70 surface area, compared to macrocapsules [6]. Micro-encapsulation is a technology to
71 encapsulate and shape-stabilize PCMs in spheres at microscale range ($> 1\mu\text{m}$); the current
72 research trend is aimed at reducing the encapsulation size within the nanoscale range, so
73 as to maximize size effects and surface area involved in heat transfer [7].

74 PCMs can help customizing the redistribution of thermal loads in buildings. A recent review
75 showed that generally PCMs are embedded in building elements and materials, especially
76 in walls and floor elements, because they can provide energy storage by means of latent
77 heat accumulation, resulting in higher heating storage with respect to typical sensible heat
78 processes of building materials [8]. The improvement observed in PCM-embodying
79 elements is due to this enhanced latent heating storage, even if no variation of specific heats
80 takes place. For instance, the application of PCM capsules with paraffinic wax in lime plaster
81 enhanced the apparent specific heat capacity, compared to the reference material [9]. PCM-
82 enhanced plasters have been investigated as a suitable chance in the refurbishment of
83 building envelopes, in the Mediterranean climate [10], in the hypothesis of adopting 3.0 cm
84 thick plaster on all exposures and in different climatic conditions. The heat storage capacity
85 of a special composite plaster was compared to a commercially produced lime-cement
86 mortar, reporting an increase from 0.4 kJ/(kg·K) to about 2.1 kJ/(kg·K) after the addition of
87 24% PCM [11]. Pavlick et al. [12], in 2014, reported the enhanced performance of a PCM-
88 modified plaster exhibiting specific heat capacity of 1.6 kJ/(kg·K) against 0.77 kJ/(kg·K)
89 observed in the reference plaster. The integration of PCMs in lightweight building
90 components was investigated by Fiorito [13], employing EnergyPlus for simulating the use
91 of PCMs in a naturally ventilated test room. In that study, higher benefits were obtained by
92 adding PCMs in walls or partitions, linearly with PCM thickness. Lee and Medina [14]
93 simulated a frame wall embodying hydrated salt (melting and solidification temperatures
94 between 27.6 °C–29.6 °C) macroencapsulated in containers larger than 1 mm. The aim was
95 to reduce the cooling on-peak demand in California. Total energy saving reached values of
96 9.21 kWh/(m²·yr) due to PCM-enhanced frame walls. Energy saving between 30% and 55%
97 in the HVAC system were registered by Navarro et al. [15], who used an internal slab as a
98 storage unit and as an active cooling supply in Spain. They used 52 kg of RT-21 paraffin
99 macro-encapsulated in 1456 aluminium tubes of 12 mm diameter. Kenisarin et al. observed

100 that further research activities on PCMs should, among the other objectives, achieve the
101 narrowest possible temperature range for the phase change process in PCMs and reduce
102 their costs [16]. Several research groups used paraffin, as reviewed by Zalba et al. [17] for
103 its melting temperature (for instance, paraffin wax has a melting temperature of 28 °C) and
104 its high latent heat (244 kJ/kg), highly compatible with uses in constructions.

105 Nanotechnologies can help enhancing PCMs performance, as a natural evolution, since
106 abrupt changes may occur, at nanoscale level, in thermophysical and physicochemical
107 properties. Then nano-enhanced features of PCM materials could be suitably exploited and
108 several research activities are currently working on this point, as reviewed by
109 Parameshwaran [18]. It has been observed that the inclusion of nanomaterials could
110 improve some PCMs figures of merit, overcoming some of their limitations, such as a low
111 value of thermal conductivity [19]. To this aim, several nano-enhanced PCMs have been
112 proposed, embodying, for instance, copper, titania, alumina, silica and zinc oxide
113 nanoparticles (NPs), thoroughly investigated by Teng et al. [20]: they showed that titania
114 NPs are more effective than other additives in order to enhance heat conduction and thermal
115 storage capacity in paraffins, also affecting both melting onset temperature and the
116 solidification temperature. A completely different route to nano-enhancement of PCMs
117 consists in their encapsulation within a nano-shell [21] or a nanofiber [22]. In addition, nano-
118 shells protect PCMs from the surrounding environment. Liu et al. [23] described the different
119 routes to synthesize different kinds of nano-PCMs (sol-gel, miniemulsion, emulsion and *in*
120 *situ* polymerization) and the respective advantages and disadvantages. Sari et al. [24]
121 synthesized polystyrene and n-heptadecane micro-/nanocapsules adopting the emulsion
122 polymerization route with capsule sizes ranging from 10 nm to 40 mm for a 1:2 ratio of
123 polystyrene and n-heptadecane. However, among different materials to be used for
124 encapsulation, amorphous silica shows high heat storage capacity and thermal conductivity
125 [25]. In addition, it is biocompatible, nontoxic for living organisms and the environment
126 [26,27], and in its core it is easy to confine active molecules acting as reservoir [28]. Zhang
127 et al. [29] synthesized silica spheres (7–16 µm) with *n*-octadecane core (melting temperature
128 range of 23–28 °C) using TEOS as an inorganic precursor by a sol–gel process, with
129 different steps. The obtained nanomaterials showed a good thermal conductivity. Similarly,
130 Belessiotis et al. [30] obtained silica spheres with paraffin core via sol gel method showing
131 a latent heat of ~ 156 kJ/kg. Latibari et al. [31] obtained nano-PCMs with palmitic acid core
132 and silica shell, using multistep sol-gel method and investigated their thermal figures. The
133 efficiency of encapsulation, defined as the percent ratio of the latent heat of the

134 encapsulated PCM and that of the pure PCM, ranged from 83.25% to 89.55% (with a particle
135 size between 183.7 nm and 722 nm) depending on pH of the chemical mix solution.
136 Nevertheless, since palmitic acid has a melting temperature of 61°C, the application in
137 buildings is quite difficult. The same limitation (high melting temperature ranging from 142.1
138 °C to 166.2 °C) concerned mannitol, chosen by Wu et al. [32] and Pethurajan et al. [33].

139 The cost-effectiveness of PCMs inclusion in building envelopes was investigated by Kosny
140 et al. [34], who found that the commercial cost of a PCM with a latent heat as high as 116
141 kJ/kg, while produced commercially, can be projected to be 4.4-6.6 USD/kg. On the other
142 hand, PCMs for building applications should be produced by means of environmental-
143 friendly processes and raw materials. Among the possible PCMs, paraffin is inflammable
144 and it is classified as a doubtful carcinogen (source: Sigma-Aldrich), while PEG is an inert
145 inexpensive and versatile polymer for customizing nanostructured materials due to its
146 intrinsic biocompatibility and water solubility [35]. It is also widely used in the biomedical field
147 and it has been approved by Food and Drug Administration for many applications [36]. In
148 addition, the range of melting temperature is between 17 and 22°C (Source: Sigma-Aldrich),
149 that is well within the range of comfortable indoor environment temperatures and, for this
150 reason, its application in buildings is preferable.

151 In this work, we obtained (300 ± 15) nm SiO₂@PEG600NP_s by means of a one step, easy
152 and reproducible synthetic route. The obtained nanostructures were then fully characterized,
153 before undergoing a toxicological assessment. The SiO₂@PEG600NP_s showed a good
154 thermal performance, with an enthalpy of fusion as high as 66.24 kJ/kg, in the tight melting
155 temperature range (20-21°C): such feature makes it a good candidate for thermal energy
156 storage in building applications, especially to reduce energy uses during winter season
157 HVAC. As will be seen hereafter, it is precisely during the winter season that the
158 incorporation of the PCM inside the plaster performs its effectiveness. On the contrary,
159 during the summer season, it shows no particular benefit, mainly because the temperature
160 of the internal surface of the vertical walls is almost always above the T_m of the PCM.
161 Following the experimental design and synthesis activities of the nanostructures
162 incorporating PCMs, we performed dynamic simulations able to show the possible extent of
163 energy savings obtained by integrating a certain percentage of SiO₂@PEG600NP_s (50%)
164 in building gypsum plasters, comparing a reference case, devoid of PCM, with another one,
165 containing the proposed material applied over all internal vertical plastered surfaces. It is
166 the case to specify that the choice of PEG600 as a suitable PCM was carried out following

167 a tight comparison aimed at identifying a material having, at the same time, different
168 specificities. Firstly, the compatibility with a low-cost synthesis mode of the hosting SiO₂
169 shell; secondly, it represented a biocompatible PCM and, finally, a series of preventive
170 simulation activities (not reported in the text) provided an ideal range of melting
171 temperatures to make the maximum contribution during the winter season, associated to the
172 maximum benefit in terms of energy saving. After all these considerations and activities, we
173 decided to adopt the PEG600 as a material able to guarantee a satisfactory compromise.

174 **2. Materials and Methods**

175 In this experimental activity we have reported the results of a cross-disciplinary design and
176 the full characterization of a novel nanostructured material, showing the advantage of
177 achieving full shape stabilization of a biocompatible PCM (PEG600) within the nanoscale,
178 inside a non-toxic amorphous SiO₂ shell. The main properties of this specially designed
179 material were fully characterized after the chemical synthesis. To this aim, at first microscopy
180 characterization was carried out to observe shape and size of nanoparticles; then, thermal
181 characterization was experienced in order to know the main figures of merit describing
182 PCMs behaviour. The last step was an in vitro toxicological assessment: this last
183 characterization activity was carried out in order to learn if the material presented significant
184 toxicity and, therefore, risk profiles for human health. Data thus obtained were used as an
185 input for the subsequent simulation activities.

186 **2.1 Synthesis and characterization of SiO₂@PEG600**

187 The synthesis was carried out adopting the so called Stöber method, following the procedure
188 described in Stöber et al. [37] with some modifications in order to encapsulate PCMs
189 materials. An amount of PEG600 was dissolved in 5 mL of ethanol to obtain a solution of
190 PEG600 concentrated at 1 mM in final volume of reaction. To ethanol-PEG600 solution was
191 added TEOS (100 µL), milliQ water (20 mL) and NH₄OH solution (28.0-30.0%, 10 mL) for 2
192 hours at 25°C (this temperature was optimal to maintain PEG600 in the liquid phase). Then,
193 the reaction was blocked with acetone and the solution is centrifuged at 4000 rpm for 20
194 minutes. The SiO₂@PEG600 NPs were rinsed with milliQ water and ethanol (1:1) 5 times
195 and successively dried under reduced pressure and then at 100 °C for 2 h in order to obtain
196 a white nano-powder. The yield for this synthesis was about 80%.

197 TEM characterization was carried out by means of a JEOL Jem 1011 microscope, operating
198 at an accelerating voltage of 100 kV (JEOL USA, Inc). TEM samples were prepared by

199 dropping a dilute solution of NPs in water on carbon-coated copper grids (Formvar/Carbon
200 300 Mesh Cu).

201 DLS and ζ -potential measurements were performed on a Zetasizer Nano-ZS equipped with
202 a 4.0 mW HeNe laser operating at 633 nm and an avalanche photodiode detector (Model
203 ZEN3600, Malvern Instruments Ltd., Malvern, UK).

204 SEM and EDS Measurements were recorded using a Phenom ProX microscope (Phenom-
205 World B. V., Eindhoven, Germany), at an accelerating voltage of 10 kV. The samples were
206 prepared by dropping a solution of NPs in water on monocrystalline silicon wafer.

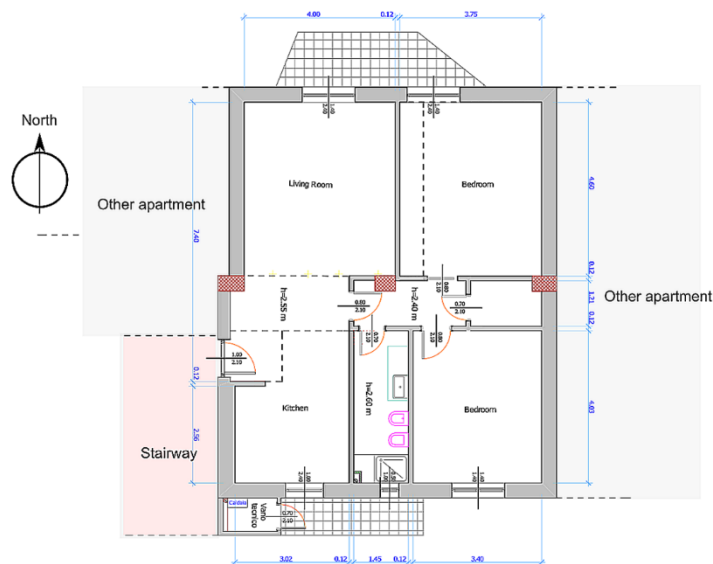
207 FT-IR analysis on SiO₂@PEG600 were recorded on a JASCO 660 plus infrared
208 spectrometer (Jasco, Gross-Umstadt, Germany). Spectral manipulations were performed
209 using the spectral analysis software provided by Jasco and spectra were acquired in the
210 number wave range of 4000-650 cm⁻¹ (resolution of 4 cm⁻¹) at room temperature on a square
211 micro aperture of 100 μ m, with the accumulation of 100 repeated scans in reflectance mode.
212 An isopropanol-treated silicon wafer was used, as background.

213 Thermal properties of SiO₂@PEG600, such as T_m, T_f and ΔH_m , were measured by means
214 of a DSC instrument (Mettler Toledo 822, Greifensee, Switzerland). The analysis was
215 performed on dried samples under a constant stream of nitrogen (60 mL \cdot min⁻¹) at
216 atmospheric pressure, applying a first isothermal step at -10 °C for 5 minutes, followed by a
217 heating scan between -10 °C and 90 °C at 1 °C \cdot min⁻¹. Then the samples were submitted
218 to a further isothermal step at 90°C for 5 minutes, followed by a cooling scan from 90 °C to
219 -10°C at 1°C \cdot min⁻¹. The phase change temperatures (melting and freezing points) were
220 evaluated as the intersection between the tangent to the maximum rising slope of the peak
221 and the sample baseline. The enthalpies related to the phase changes were determined by
222 integration of the area under the peaks *versus* time.

223 **2.2 Dynamic simulations in a case study**

224 In order to test the potential benefits resulting from the use of the proposed PCM, a typical
225 Italian dwelling, located in a multi-storey building, was modelled in EnergyPlus (Figure 1).
226 The overall floor surface is 78 m² and the internal height is 2.9 m. Its East and West walls
227 are shared with other apartments. The dividing walls are made of 20 cm thick tufa blocks,
228 with plaster on both faces ($U=0.622$ W/m²K). Internal walls are made of 10 cm thick tufa
229 blocks with plaster on both sides. Floor and ceiling are 30 cm thick and are made of hollow
230 clay blocks covered with concrete and plaster on the bottom face ($U_{\text{floor}}=0.819$ W/m²K,

231 $U_{\text{ceiling}}=0.857 \text{ W/m}^2\text{K}$). Heat exchange takes place through the North and South walls, made
232 of hollow clay blocks (30 cm thick), and through the west wall facing the stairway, which is
233 also made of clay blocks ($U=0.736 \text{ W/m}^2\text{K}$). Windows embody a 70 mm PVC frame ($U_f=1.2$
234 $\text{W/m}^2\text{K}$) and a glazing system made of two 4 mm panes, divided by a 20 mm air gap ($U_g=2.7$
235 $\text{W/m}^2\text{K}$). The values of global coefficient of heat exchange have been kept constant both in
236 the reference case and in the model embodying PCMs within the internal plasters of vertical
237 walls. This was done precisely in order to highlight the contribution of the PCMs on energy
238 consumption for HVAC. Moreover, ceiling and internal floor did not include PCMs and the
239 only non-adiabatic surfaces, therefore involved in the heat transmission mechanisms, were
240 the vertical walls respectively exposed to North and South, as shown in Figure 1.



241

242

Figure 1. Plan of the apartment used to create the EnergyPlus model

243 **2.2.1 The EnergyPlus model**

244 A 3D model of the case study was first made in SketchUp using the OpenStudio plugin,
245 and subsequently exported to EnergyPlus v. 8.8, a free simulation tool by the U.S.
246 Department of Energy's Building Technology Office, in order to perform the dynamic energy
247 analysis. To assess the heating and cooling energy uses in a simplified way, an
248 "IdealLoadAirSystem" with no outdoor air was considered. Adopting this approach,
249 EnergyPlus provides heating and cooling energy required to meet the temperature at the
250 selected setpoints (20.5 °C in winter, 26 °C in summer). This approach allows to calculate
251 the thermal energy strictly necessary to achieve the comfort objectives represented by the

252 temperature setpoints. In this way, we obtain the advantage of highlighting the free
253 contribution of the material, neglecting the optimization effects of real HVAC systems.

254 However, in order to better simulate the actual transients that typically occur in real
255 houses, the duty cycle of the heating thermostat was simulated by means of an Energy
256 Management System so that the heating was turned off when air temperature was above
257 $T_{\text{setpoint}}+0.5\text{ }^{\circ}\text{C}$, while it was turned on when air temperature fell below $T_{\text{setpoint}}-0.5\text{ }^{\circ}\text{C}$.

258 For ventilation, in order to simulate the actual opening cycles of windows in real conditions
259 of use, the "Wind and Stack Open Area" approach was adopted in EnergyPlus, which allows
260 to provide the effective opening surface on the respective exposures. Windows (having an
261 open area of 0.4 m^2 for both Northern and Southern façades) were supposed to be open
262 half an hour per day (from 7.30 to 8.00) during workdays, and one hour per day during
263 weekends. In addition, for fixed openings and windows cracks (summing up to 0.03 m^2 area)
264 an "always on" schedule was applied.

265 Simulations were carried out in three Italian cities belonging to different climatic zones:
266 Brindisi (climatic zone C, 1083 heating degree days), Rome (climatic zone D, 1415 heating
267 degree days), and Milan (climatic zone E, 2404 heating degree days). The heating schedule
268 was adapted to each location, according to the climatic zone they belonged to, depending
269 on national regulations (Figure 2). The definition of such climatic zones is carried out
270 according to the concept of heating degree day, i.e. the sum of the daily thermal excursions
271 extended to the winter heating period. The latter period is established by regulations in force.
272 According to the Italian standard, all municipalities with a number of degree days between
273 900 and 1400 are in zone C; the range of values for the D climatic zone is between 1400
274 and 2100 and between 2100 and 3000 for the E climatic zone.

275 Thus, in Brindisi heating worked from November 15th to March 31st, with up to 8 hours
276 per day. In Rome heating worked from November 1st to April 15th with a maximum of 10
277 hours per day, and in Milan from October 15th to April 15th with a maximum of 12 hour per
278 day. Cooling was considered to be turned on from July 1st to August 31st in all the locations.
279 Envelope thermal resistance was considered unvaried, although climate zones were
280 significantly different.

281 Among the different output variables that can be returned by the software, 60 seconds
282 timestep simulations (using conduction finite difference method ConFD, required for
283 simulations involving PCMs) and hourly values of surface temperature were considered as
284 more useful and instructive for the case under investigation. Overall values were employed
285 for heating energy.

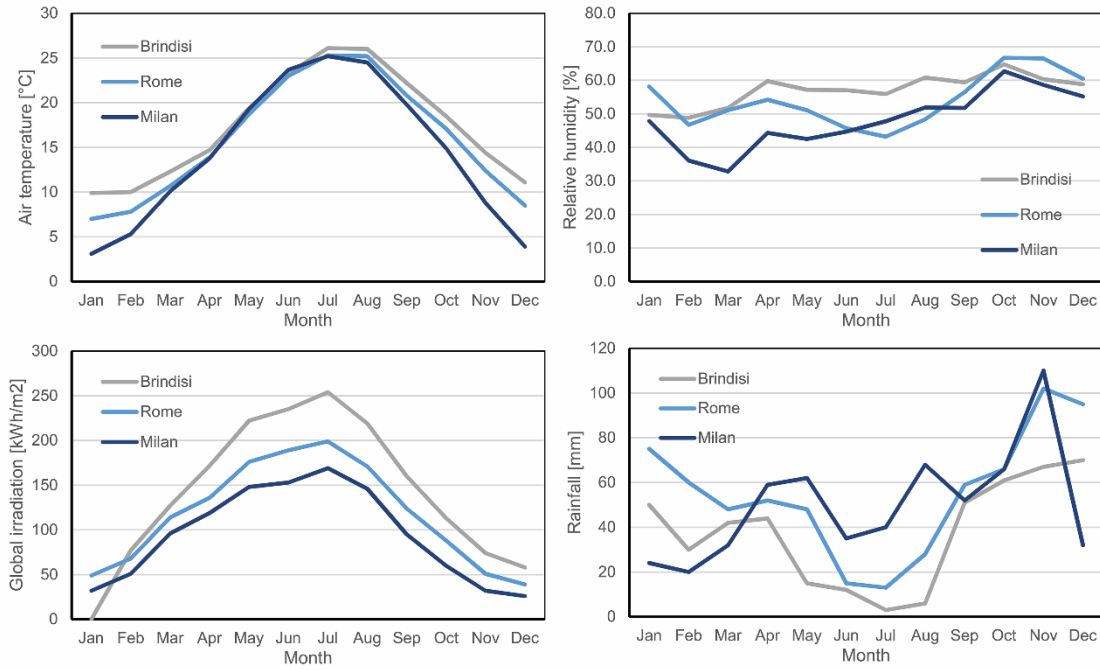


Figure 2. Monthly averages of climatic parameters for the three selected cities: a) Dry bulb outdoor temperature; b) Relative humidity; c) Global irradiation on horizontal surface; d) Rainfall. (Data source: Meteonorm 7.2)

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The two horizontal surfaces as well as the Eastern and Western walls were considered adiabatic, so that all the other surfaces were modelled to simulate a room laying in an intermediate floor. However, although not involved in heat exchange, their density, heat capacity and conductivity were provided, in order to take into account their contribution to internal mass and heat storage.

In order to evaluate the thermal and energy benefits attainable including nano-PCMs in building components and materials, a typical masonry in hollow clay blocks covered with plaster on both sides was used for modelling external walls. PCMs were included in the internal plaster layer (with a thickness of 5 cm) of vertical surfaces, also in partitions. The total enthalpy of fusion of nano-encapsulated PCMs embodied in plasters, used for the simulations, was calculated adding the sensitive and latent contributions of the specific enthalpy. The total enthalpy of nano-enhanced plaster was then calculated as follows:

$$\Delta H_{tot} = m (\Delta h_{mortar} + \Delta h_{PCM}) \quad [\text{kJ}] \quad (1)$$

where:

$$\Delta h_{mortar} = (1 - f) \int_{T_1}^{T_2} c \, dT \quad (2)$$

$$\Delta h_{PCM} = f \left[\int_{T_1}^{T_M} c^S \, dT + L + \int_{T_M}^{T_2} c^L \, dT \right] \quad (3)$$

307 with m being the plaster mass, f representing the mass fraction of PCMs in plaster, which
308 was 0.5 in our case study, and T_M the melting temperature of PCMs. No variation on plaster
309 conductivity with and without the PCM was considered in order to only take into account the
310 effect in terms of increased heat storage.

311 Finally, the effect of embodied PCM on thermal comfort was investigated by assuming the
312 presence of at least one occupant starting from 3 PM to 8 AM, and calculating occupants'
313 comfort conditions according to Fanger's model. In the specific "People" Energyplus object
314 both "work efficiency" and "air velocity" were assumed to be always zero, while clothing
315 insulation was assumed to be 1 clo during the heating season and in the two weeks before
316 and after, 0.5 clo during the cooling season and in the two weeks before and after, and 0.75
317 in the remaining periods. Results were finally analysed in terms of hours in which the
318 percentage of dissatisfied according to Fanger's model exceeded 15%.

319 **2.3 Toxicological assays**

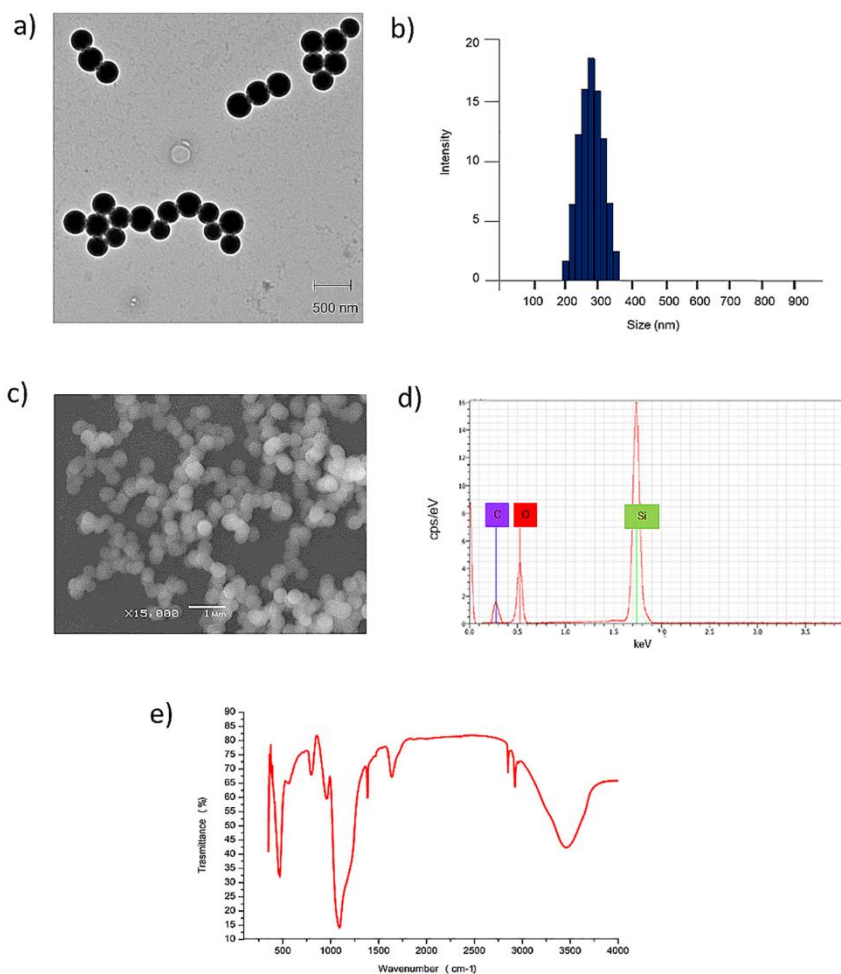
320 Human alveolar basal epithelial cells (A549, ATCC® CCL-185™) were maintained in
321 Dulbecco's Modified Eagle Medium supplemented with 10% FBS, 50 μ M glutamine,
322 supplemented 100 U/mL penicillin and 100 mg/mL streptomycin. Cells were incubated in a
323 humidified controlled atmosphere with a 95 % to 5 % ratio of air/CO₂, at 37 °C. For viability
324 assay, A549 cells were seeded in 96 well microplates (Corning) at concentration of $5 \cdot 10^3$
325 cells/well after 24 h of stabilization. The SiO₂@PEG600 NPs were added in order to obtain
326 a final concentration of 10 μ g/mL and 40 μ g/mL. The exposure was conducted for 24 h, 48
327 h, 72 h 96 h and the viability of cells expressed as percentage of living cells respect to control
328 was performed using the WST-8 assay (Sigma-Aldrich) following the procedure described
329 previously [38]. For confocal acquisitions, A549 cells were incubated with NPs at different
330 time points following the procedure described in Ref. [39]. All confocal images were acquired
331 using LSM700 (Zeiss, Germany) confocal microscope mounted on an Axio Observer Z1
332 (Zeiss, Germany) inverted microscope, by using the Alpha Plan-Apochromat (Zeiss) 100 x
333 oil-immersion with 1.46 NA.

334 **3. Results and Discussion**

335 **3.1 PCM properties**

336 SiO₂@PEG600 nano-particles were firstly characterized in water by TEM in order to analyze
337 their morphology, showing that NPs were spherical and monodispersed with a size of $(300$
338 $\pm 15)$ nm (Figure 3a). DLS measurements confirmed the size of NPs (Figure 3b) showing a

339 uniform size distribution. SEM-EDS analysis confirmed the morphology and smooth surface
340 of NPs and further corroborated the presence of confined PCM (PEG600) in the SiO₂ NPs
341 core. Indeed, the silicon, oxygen and carbon element peaks appeared in the graph (silicon
342 and oxygen for silica and carbon and oxygen for PEG600) (Figure 3c,d). FT-IR analysis was
343 conducted on the NPs samples in order to verify the presence of bonds corresponding to
344 PEG600 and SiO₂.



345

346 **Figure 3.** Characterization of SiO₂@PEG600 core/shell NPs. a. Representative image of NPs
347 acquired by Transmission Electron Microscopy (TEM) b. Dynamic Light Scattering (DLS)
348 measurement c. Representative image of NPs acquired by Scanning Electron Microscopy (SEM) d.
349 Energy Dispersive X-ray Spectrometry (EDS) curve e. Fourier Transform Infrared Spectroscopy
350 (FITR) analysis.

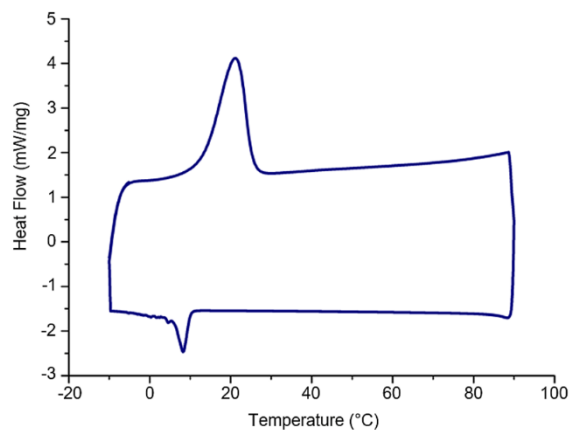
351 Figure 3e showed a broad band in the region of $\sim 3375\text{ cm}^{-1}$ that corresponds to -OH
352 stretching vibration. The vibrational bands observed at $\sim 2917\text{ cm}^{-1}$ and $\sim 2849\text{ cm}^{-1}$, related
353 to the stretching of -CH. The peak obtained at $\sim 1633\text{ cm}^{-1}$ was assigned to the stretching
354 of -OH band while the peak at $\sim 1403\text{ cm}^{-1}$ was attributed to the vibration of -CH. The very

355 strong and broad IR band at $\sim 1111\text{ cm}^{-1}$, with a shoulder at $\sim 1188\text{ cm}^{-1}$ represented the Si-
356 O-Si asymmetric stretching vibrations. The IR band at $\sim 800\text{ cm}^{-1}$ and 956 cm^{-1} can be
357 assigned to symmetric stretching vibrations of Si-O-Si and silanol groups respectively. The
358 peak at $\sim 474\text{ cm}^{-1}$ was due to O-Si-O bending vibrations.

359 Thermal performance of novel SiO₂@PEG600 was studied using a Differential Scanning
360 Calorimetry (DSC) testing, providing the thermogram showed in Figure 4. The melting
361 temperature (T_m) of the SiO₂@PEG600 NPs was found to be 21°C, with a smooth transition
362 starting from about 10 °C, which was similar to that of the pure PEG600 as described in a
363 previous work [40]. Moreover, the encapsulation efficiency (*R*) is an important index, which
364 was defined as follows [41,42]:

$$365 \quad R = \frac{\Delta h_m}{\Delta h_{mPCM}} * 100 [\%] \quad (4)$$

366 where Δh_m is the specific melting enthalpy of NPs and Δh_{mPCM} is the specific melting
367 enthalpy of the PCM in pure state. As the latter is 108.4 kJ/kg for PEG600 as measured by
368 DSC [43] and the melting enthalpy of core shell PCMs reaches a maximum of 66.24 kJ/kg
369 (using a concentration of 1M of PEG600) in the melting process, the resulting encapsulation
370 efficiency was 61%. Such result was in agreement with other works [44]. The resulting
371 enthalpy referred to core/shell NPs was used in the all the simulations that were carried out
372 subsequently.



373

374 **Figure 4.** Differential scanning calorimetry (DSC) curve.

375 **3.2 Energy saving potentials**

376 The heating energy consumption per unit area was calculated, on an annual basis, using
377 the results of the simulation process. This activity was carried out with reference to three

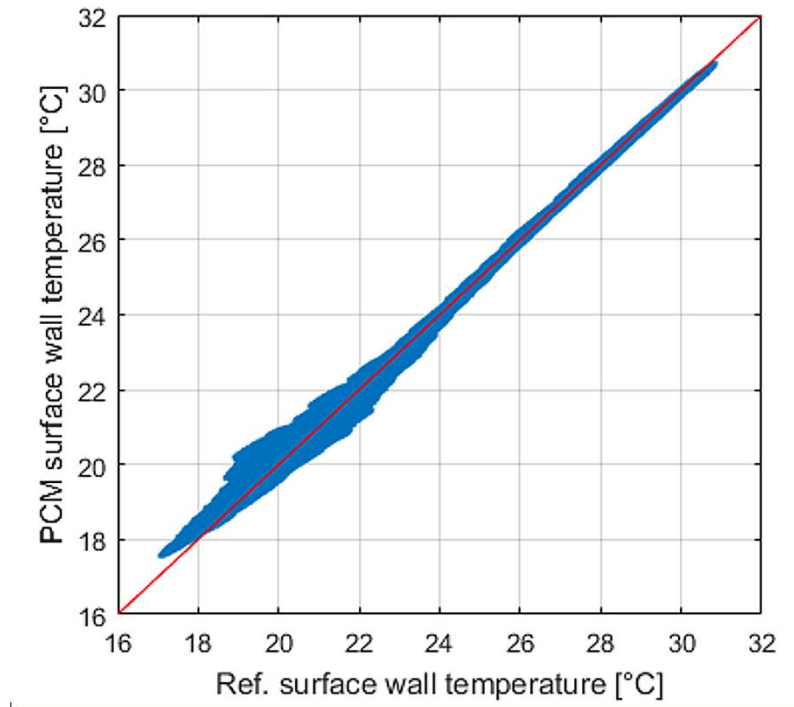
378 different climatic contexts, as mentioned previously (Brindisi, Rome, Milan). The outcome of
 379 performance comparisons among the plaster containing PCMs and the standard reference
 380 plaster demonstrated that energy savings for heating could be attained in all the cases
 381 although a strong dependence on climatic conditions appeared. In fact, in Brindisi savings
 382 were 4.3%, in Rome they reduced to 2.3%, and in Milan they dropped to 1.6%. Such climatic
 383 dependence is strongly related to the different profile of outdoor temperatures and radiation
 384 patterns which finally influence the rate interior surfaces get colder. A comparison of the
 385 absolute values of yearly energy demand per unit area, as shown in Table 1, showed that
 386 that in absolute terms the largest decrease was found in Milan (0.44 kWh/m²yr), while Rome
 387 (0.26 kWh/m²yr) and Brindisi (0.29 kWh/ m²yr) showed more similar results. This was due
 388 to the higher annual heating consumption in Milan and Rome as the first two cities belong
 389 to climate zones with a longer heating period, more heating hours, and lower outdoor
 390 temperatures.

391 **Table 1.** Specific energy use for heating on a yearly basis

	Brindisi		Rome		Milan	
	Ref.	PCM	Ref.	PCM	Ref.	PCM
Specific heating energy [kWh/m ² .yr]	6.92	6.63	11.64	11.38	26.80	26.36
Percent Variation [%]		-4.3%		-2.3%		-1.6%
Specific cooling energy [kWh/m ² .yr]	4.86	4.85	3.69	3.68	2.68	2.65
Percent variation [%]		-0.2%		-0.3%		-1.1%

392

393 The energy consumption for summer air-conditioning was barely affected by PCMs
 394 embodied in plaster, as shown by cooling energy comparisons (**Table 1**). In fact, results
 395 showed negligible effects due to PCMs because set-point temperatures of the cooling
 396 system was 26°C, well above the melting temperature of SiO₂@PEG600, taking place
 397 around 21 °C. Quite predictably, the same behavior was found in all the locations under
 398 investigation in this study. Figure 5 clearly shows this effect, by plotting a scatterplot of the
 399 surface temperatures (on the Southern wall, in Brindisi), of the wall with the reference
 400 treatment and the wall with PCM. Clearly, above 24 °C the temperatures converge, while
 401 they show significant variations (within a ±1°C range) between 18 and 23 °C.

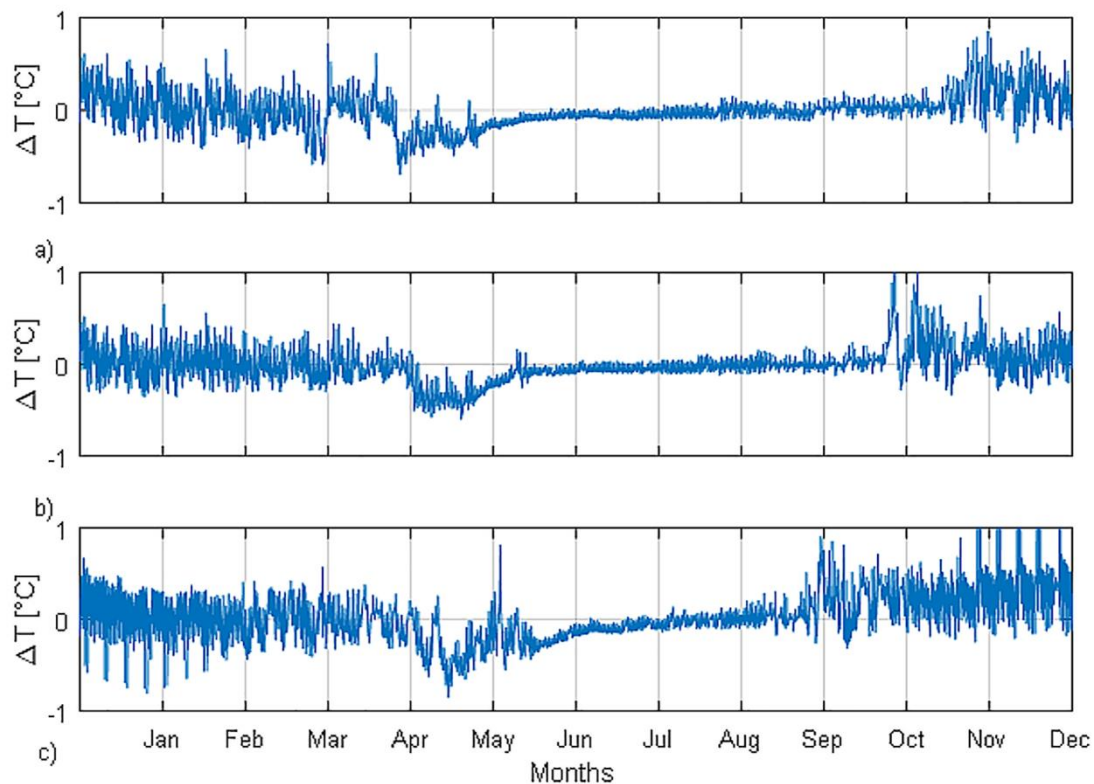


402

403 **Figure 5** Scatterplot of the interior surface temperature of the Southern wall of the reference
404 conditions vs. the same parameter on the wall treated with PCM.

405 In order to better understand how the surface temperature changes, depending on the
406 season, Figure 6 shows the variation of the internal surface temperature reported on
407 the South wall on a yearly basis for all three locations comparing the wall finished with
408 plaster embodying PCM with the reference one. The material is completely melted in
409 the summer season, while the difference in temperature shows a positive value in
410 winter and autumn, in all three locations. Average difference in temperature undergoes
411 a change of sign in spring (with a slight shift depending on the location) because the
412 presence of the PCM delays the heating of the interior surfaces, achieving a reduction
413 of temperatures on the wall surface, ranging around 0.5 °C in all the locations.

414 It can be observed that, in all cases, the main effect of the embodied PCMs consisted
415 in a positive variation of surface temperature, particularly evident in the Autumnal
416 period, meaning that the wall with PCM showed a higher temperature compared to the
417 reference wall, in concurrence with the heating system activation periods. Moreover,
418 the higher temperature of the surface of the plaster containing the PCM translated into
419 a benefit in terms of energy saving, as found in the analysis of the heating system
420 consumption, as well as in terms of indoor environment quality, as the mean radiant
421 temperature gets higher and more similar to air temperature.

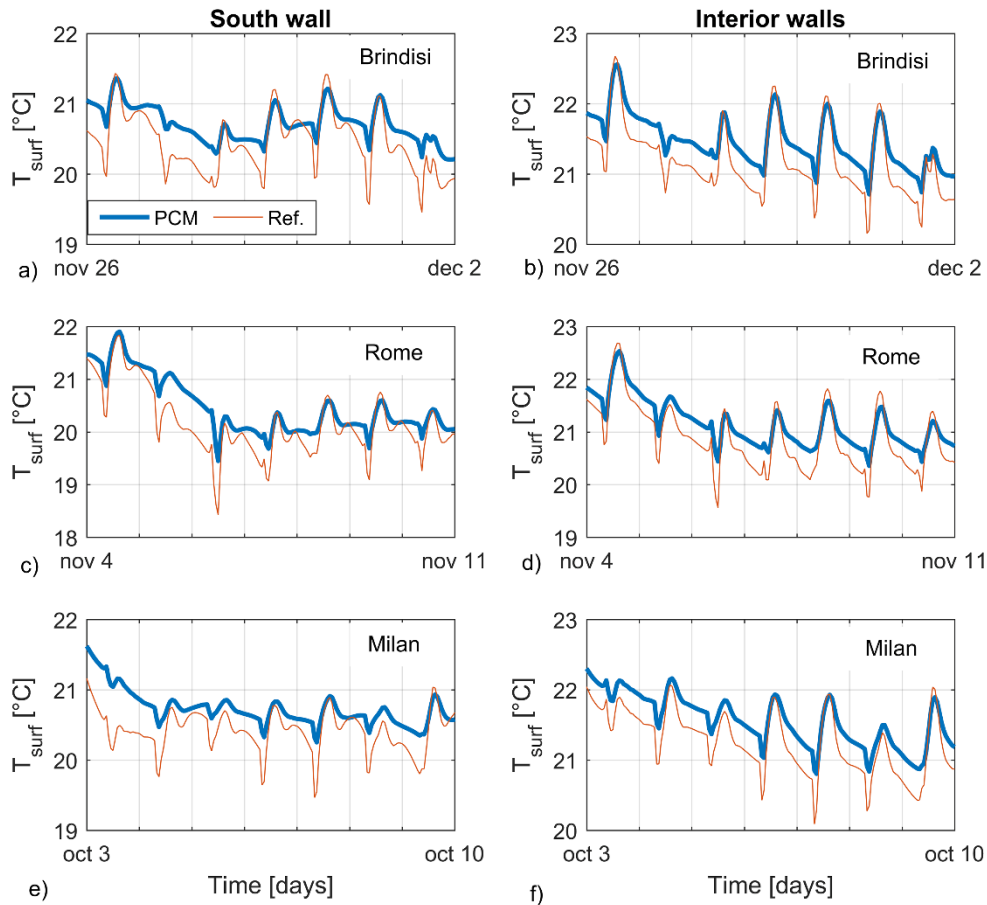


422

423 **Figure 6** Variation of internal surface temperature on the South wall calculated with and without PCM
424 in the plaster. a) Brindisi; b) Rome; c) Milan

425 In order to better investigate this aspect, Figure 7 shows the trends of the internal
426 surface temperature, with and without the PCMs, along one week for each location.
427 The week showing the highest differences between the two configurations (the
428 reference case and the one considering plasters embodying PCMs) was selected for
429 each location. In this way, the week with the largest temperature deviation in Brindisi
430 was found to be from November 26th to December 2nd, with maximum differences of
431 about 0.5°C (Figure 7a,b). Similar trends were observed for both exposed and
432 unexposed walls, with the first having lower temperatures and being clearly affected
433 by radiation effects. In all the cases, the PCM made the variations in temperature
434 smoother when compared to the reference plaster. Similar conditions were observed
435 in Rome, in the week from November 4th to November 11th (Figure 7c,d). On the other
436 hand, in Milan, the week reporting higher surface temperature deviations was the one
437 from October 3rd to October 10th, with temperature differences in the same range
438 observed in the other locations (Figure 7e,f). In all cases, it was observed that the
439 period of maximum effectiveness of the proposed phase change materials is the
440 Autumn, with shifts depending on the climatic conditions. This fact indeed confirmed

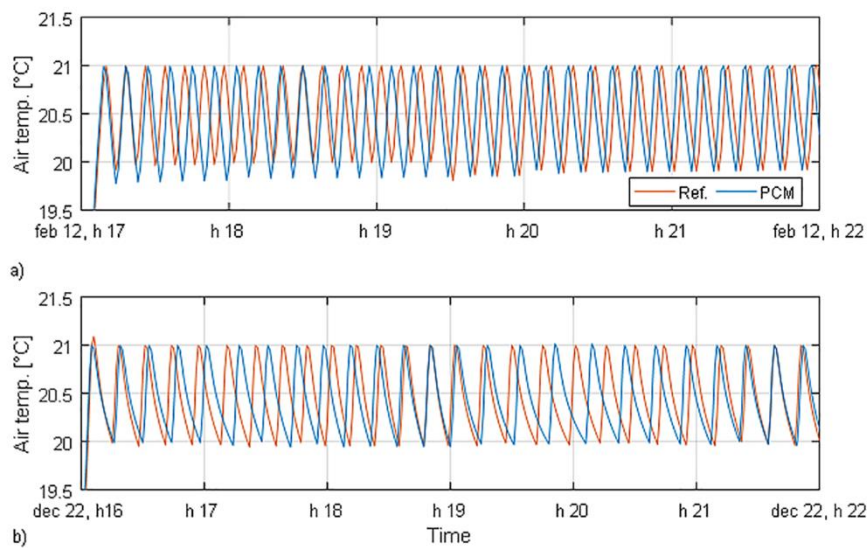
441 that the PCM performed best at lower latitudes and milder climates, where such
442 increased temperatures, combined with positive effects due to radiation, may lead to a
443 shift in the time at which the heating system becomes effective.



444

445 **Figure 7.** Graphs showing the difference in internal surface temperature of the plasters in the
446 reference case and the one containing the new $\text{SiO}_2\text{@PEG600}$ material. Southern wall exposed to
447 Sun radiation (a,c,e) and interior wall (b,d,f) were considered for the different locations: Brindisi
448 (a,b), Rome (c,d), and Milan (e,f). For each location the week showing the greatest deviations in
449 surface temperature was considered.

450 However, even in presence of the heating system, the addition of PCM to the interior walls
451 proved to induce positive effects, particularly at the beginning and at the end of the heating
452 season (when walls get warmer). As shown in Figure 8 in presence of a duty-cycle of the
453 heating system, the presence of the PCM may conveniently affect the time period of the
454 cycle, leading to a quantifiable reduction of the number of times the system is turned on. In
455 particular, at the beginning (and at the end) of the season the period is longer and the
456 contribution from the PCM is clearer. In February, in presence of more extreme climate
457 conditions, the difference between the case with reference wall and that treated with PCM
458 becomes much smaller.



459

460 **Figure 8.** Plot of the indoor air temperature in Brindisi at two different times of the year: a) February 12th, b)
461 December 22nd

462 Finally, the analysis of thermal comfort conditions showed (Table 2) that the addition of PCM
463 resulted in a generalized reduction of the number of hours in which discomfort conditions
464 are found. As expected, in Winter and Autumn a reduction of discomfort hours is observed,
465 and it is particularly evident in Rome and Milan. During the Spring the inclusion of PCM
466 determines a slight increase in the number of discomfort hours, as an obvious consequence
467 of the slower increase of the interior wall temperature compared to the reference case.
468 However, this increase is comparatively smaller than the benefits obtained during Autumn.
469 Finally, in Summer the smallest variations appeared, quite predictably considering that the
470 range of temperatures in which the PCM is effective is normally below room temperatures
471 in that season. Such results confirm the usefulness of the treatment with PCM, as even in
472 cities where their effect on energy saving is lower (like Milan), they nonetheless contribute
473 to improve indoor comfort conditions.

474 **Table 2.** Summary of the analysis of thermal comfort conditions expressed in terms of hour in which Fanger's
475 predicted percentage of dissatisfied (PPD) exceeds 15% as a function of season, for each of the locations
476 under analysis.

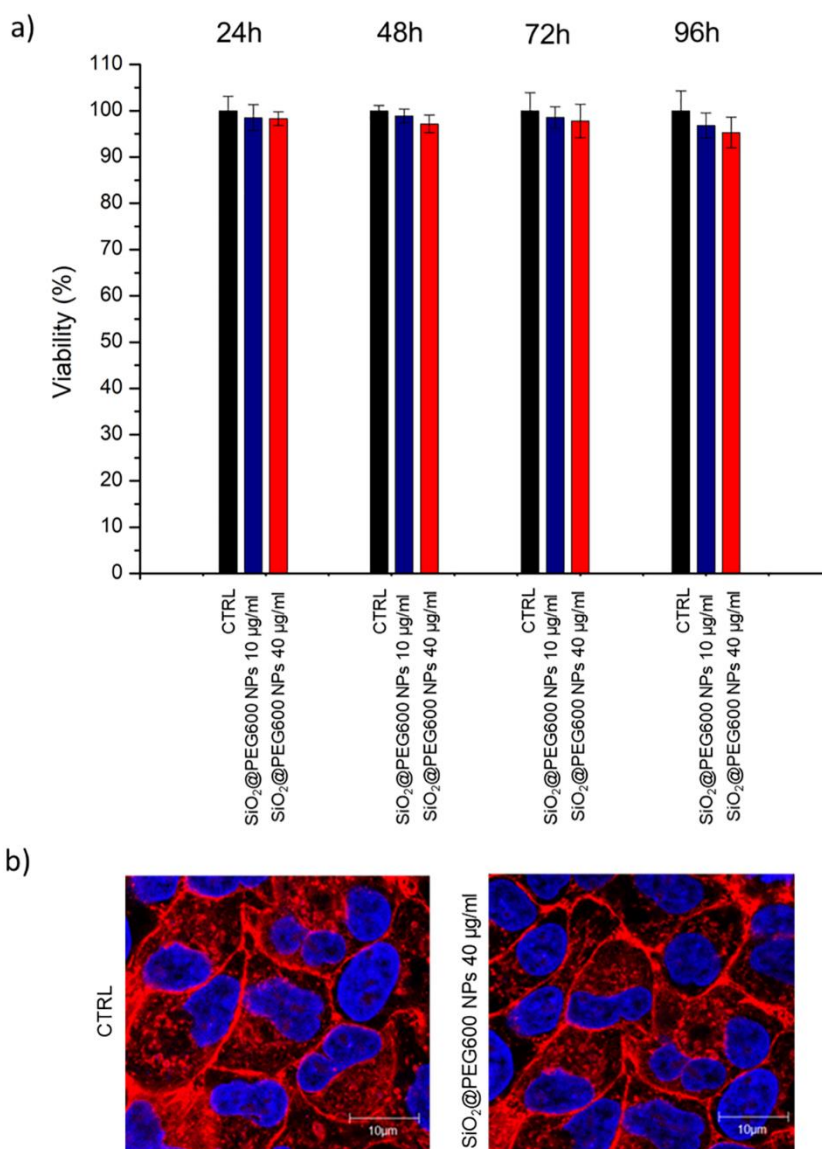
	BR_ref	BR_PCM	Var.	RM_ref	RM_PCM	Var.	MI_ref	MI_PCM	Var.
Overall	1389	1373	-14	781	745	-36	1529	1440	-89
Winter	12	3	-9	34	10	-24	466	441	-25
Spring	84	86	2	18	21	3	174	192	18
Summer	985	978	-7	567	563	-4	185	176	-9
Autumn	308	306	-2	162	151	-11	704	631	-73

477

478 This first round of simulations focused on the concise identification of the potential benefits
479 obtainable through the integration of the newly formulated PCM nanomaterial in building
480 plasters. Further activities will be aimed at demonstrating other possible uses of the
481 innovative material produced in this experimental activity; on the other hand, they will aim at
482 improving the efficiency of encapsulation and thermal performance. Moreover, it will be
483 possible to identify further PCMs suitable for uses related to constructions.

484 **3.3. Toxicological analysis**

485 In order to verify if the new synthesized nanomaterial were toxic, we exposed human alveolar
486 basal epithelial cells (A549) to NPs since they effectively mimic the inhalation exposure. Cell
487 viability was evaluated by means of the WST-8 assay. The treatment with SiO₂@PEG600
488 did not induce a dose-dependent reduction of cells viability after the treatment with 10 µg/mL
489 and 40 µg/mL of SiO₂@PEG600, for 24h, 48h, 72h, 96h. (Figure 9a). In addition, the
490 confocal analysis on A549 cells performed after incubation of cells with 40 µg/mL of
491 SiO₂@PEG600 for 72h, clearly showed that there were no toxic effects on cell morphology
492 (Figure 9b). The toxicological profile is a critical point to the use of these new nanomaterials
493 in buildings. In this way, our new synthesized nanomaterials have not only a great thermal
494 performance, but they are safe and can be exposed to living organisms.



495

496 **Figure 9. Toxicity assessment of SiO₂@PEG600 core/shell NPs on A549 cells.** Figure 9a.
497 Viability assay (WST-8) of A549 cells after 24 h, 48 h, 72 h and 96 h exposure to two doses (10
498 µg/mL and 40 µg/mL) SiO₂@PEG600 core/shell NPs. Viability of NPs-treated cells was normalized
499 to non-treated control cells. As positive control (P), cells were incubated with 5% DMSO (data not
500 shown). Data reported as mean ± SD from three independent experiments are considered
501 statistically significant compared with control (n= 8) for p value < 0.05 (<0.05 *, <0.01 ** and <0.005
502 ***). Figure 9b. A549 were treated with 10 µg/mL and 40 µg/mL of NPs for 72 h, fixed and then
503 stained with Phalloidin–ATTO 488 and DAPI. The 2D images of cortical actin were acquired by a
504 Zeiss LSM700 (Zeiss) confocal microscope equipped with an Axio Observer Z1 (Zeiss) inverted
505 microscope using a ×100, 1.46 numerical aperture oil immersion lens. All data were processed by
506 ZEN software (Zeiss).

507 4. Conclusions

508 The nano-encapsulation of a PCM for potential use in the construction sector was
509 investigated in this paper. In particular, in order to enhance the potential of the PCM to

510 contribute to energy saving and thermo-regulation of the indoor temperature in buildings
511 PEG600 was chosen because its melting temperature is close to 20°C. In addition, in order
512 to embody this material in plasters and other building mixtures, the PCM was nano-
513 encapsulated in a silica shell which may also contribute to enhance mechanical properties.
514 The resulting product was analyzed under different points of view.

515 Better results were obtained compared to commercial microencapsulated PCMs due to the
516 increased specific surface of silica nanoparticles, resulting in an increase of heat transfer
517 and due to the reduced thickness of silica shells, hosting higher amounts of PCM active
518 material in the nanoparticles core. Low-cost mass manufacturing techniques could take
519 advantage of the proposed low-cost, low temperature sol-gel approach, with further chances
520 to modify and improve nanoPCM performance, materials and morphology.

521 Further studies are under way in order to better understand the potential advantages
522 resulting from the use of this material, also including its influence on mechanical properties
523 of plasters.

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531 **Conflict of interest**

532 The authors declare that they have no conflict of interest.

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