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1 **Recent advances in thermophysical properties enhancement of phase**
2 **change materials for thermal energy storage**

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17 Phase change materials (PCM) are promising technology to store thermal energy at a constant
18 temperature. A large amount of energy can be stored or released in latent heat form during
19 the transition of material from one phase to another. Despite the great benefits, most PCMs
20 have their own limitations i.e., low phase change enthalpy, poor specific heat and thermal
21 conductivity, supercooling, volume change, phase segregation, etc. Consequently, efficient
22 thermal energy storage requires improving the thermophysical properties of PCMs. The
23 present study is a comprehensive review of existing techniques for PCMs thermophysical
24 properties enhancement. The research progresses on adding zero, one, two, and three-
25 dimensionally structured additives to PCM is assessed to improve the thermal transport by
26 enhancing the PCM effective thermal conductivity. The enhancement of latent heat of fusion
27 and specific heat using various additives is also discussed. Further, the latest techniques on
28 supercooling and phase segregation reduction are also presented. Last, the modelling of the
29 novel composite materials formed by combining a PCM with other materials is presented.
30 Despite the fact that the majority of these methods are still in the research and development
31 stage, some of them have the potential to be commercialized in the near future. Reliable and
32 efficient PCMs are exceptionally useful for storing solar energy and industrial waste heat,
33 especially for constant temperature applications.

34 **Keywords:** PCM; Thermo-physical properties enhancement; composite PCM; Thermal
35 energy storage; Supercooling

36 **1. Introduction**

37 The demand for energy and its utilization is increasing rapidly due to population growth and
38 improved living standards [1–3]. The supply of energy still mainly depends on traditional
39 energy sources such as coal and fossil fuel. However, traditional energy sources have several
40 disadvantages such as their unbalanced geographical distribution in the different countries,
41 which increases investment costs in transport and security for countries with low resources,
42 and their direct impact on the environment signified by global warming and its impacts on the
43 ecosystem. Moreover, these resources are limited and severe consumption leads to its
44 unavoidable deficiency [3]. To overcome the above-mentioned challenges, the need for clean,
45 cheap, and sustainable energy sources becomes a priority. The use of renewable energy
46 sources (solar, wind, and hydro, etc.) decreases the demand for traditional resources of
47 energy and serves in decentralizing the energy supply. Renewable energy sources are
48 abundantly available, however intermittent in nature [4]. For example, the productivity of
49 photovoltaic panels depends on the presence of light, which in turn is dependent on time and
50 season (day or night, position of the sun). Due to intermittency in the energy supply, energy
51 storage devices are required to reduce the gap between energy demand and supply. The
52 energy storage systems store excess energy to be used later in deficiency periods. Phase
53 change materials (PCM) are materials that can store solar thermal energy to enhance the
54 performance of solar thermal systems. PCM change phase at a constant temperature by
55 absorbing or releasing heat energy in the form of latent heat. PCM can be utilized for several
56 applications such as concentrating solar power (CSP) plants [5], thermal management of
57 photovoltaic [6,7], buildings [8], electronics cooling [9], etc. However, the thermophysical
58 properties of PCM are responsible for several limitations. These limitations are associated
59 with the PCM's ability to store and transport heat. In other words, the behavior of any PCM
60 depends on its thermophysical properties such as thermal conductivity, heat capacity, latent
61 heat, degree of supercooling, phase segregation, etc. The low thermal conductivity imposes a
62 prolonged time to release and store the thermal energy, which reduces the performance of the
63 energy storage device. The low specific heat and latent heat of fusion result in a larger
64 volume of the thermal energy storage device to store the thermal energy. Supercooling may
65 delay the start of thermal energy release while phase segregation may eventually lead to
66 material degradation. These phenomena are undesired and may dramatically change the
67 behavior of the system by causing severe problems to its efficiency.

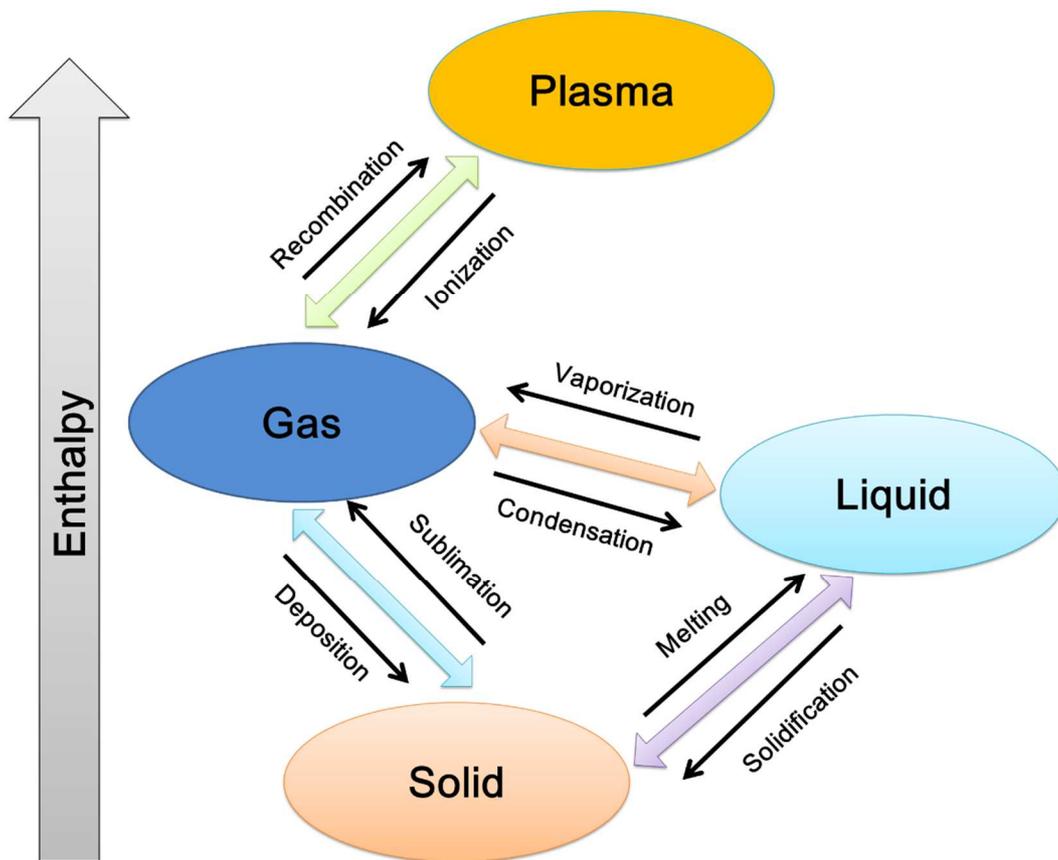
68 During the past decade, significant efforts have been made to improve the properties of the
69 PCM in order to make them more efficient and cost-effective. The current study delves into
70 the specific methods for improving PCM thermophysical properties. Despite the fact that the
71 majority of these methods are only in the research and development stage, some of them have
72 the potential to be commercialized in the near future. In the first part of this paper, thermal
73 energy storage using PCM is described. Next, a detailed discussion on enhancing thermal
74 conductivity, latent heat of fusion, and specific heat capacity by different methods is
75 presented. The following section presents the main reasons that cause supercooling and phase
76 segregation as well as the applied techniques to suppress these phenomena. Further, the
77 different modeling techniques to model the newly developed composite PCM are outlined.
78 Finally, future developments are discussed.

79 **2. Thermal energy storage using PCM**

80 Thermal energy storage using PCM is based on the heat absorption or release when a storage
81 material undergoes a reversible phase change from solid to liquid, liquid to gas, solid to gas,
82 solid to gas, or solid to solid, as shown in Figure 1 [10]. The most commonly used latent heat
83 storage systems undergo solid-liquid phase transitions due to large heat storage capacity and
84 small volume change between phases [11,12]. When the temperature exceeds a certain
85 threshold (i.e., the phase transition temperature), solid-liquid PCMs shift their internal
86 molecular arrangement from an ordered crystalline structure to a disordered amorphous form.
87 An increase in vibrational energy breaks the supramolecular connections that hold individual
88 molecules together, causing the crystalline arrangement to degrade into a randomly oriented
89 liquid state (Figure 2) [13]. In reverse, when temperatures fall below the phase transition
90 temperature, a nucleation process begins, in which molecules reorganize into a crystalline
91 lattice. Many factors influence the shape and number of crystals that form during
92 crystallization, including cooling rate, molecule type, and the presence of impurities that can
93 act as nucleating agents. The advantages offered by solid-liquid PCMs lead to their
94 contribution in different applications such as greenhouses [14–16], photovoltaic systems [17–
95 19], buildings [20–23], cooling systems [24], heat sinks [25–27], and other applications.

96 The solid-liquid phase changes are accompanied by a volume change, with volume typically
97 increases when the material becomes liquid. Organic PCMs (e.g., paraffin) and inorganic
98 PCMs (e.g., salt hydrates), as well as various mixtures of these (e.g., eutectics), are common
99 solid-liquid PCMs utilized for thermal energy storage [28]. Various strategies can be used to

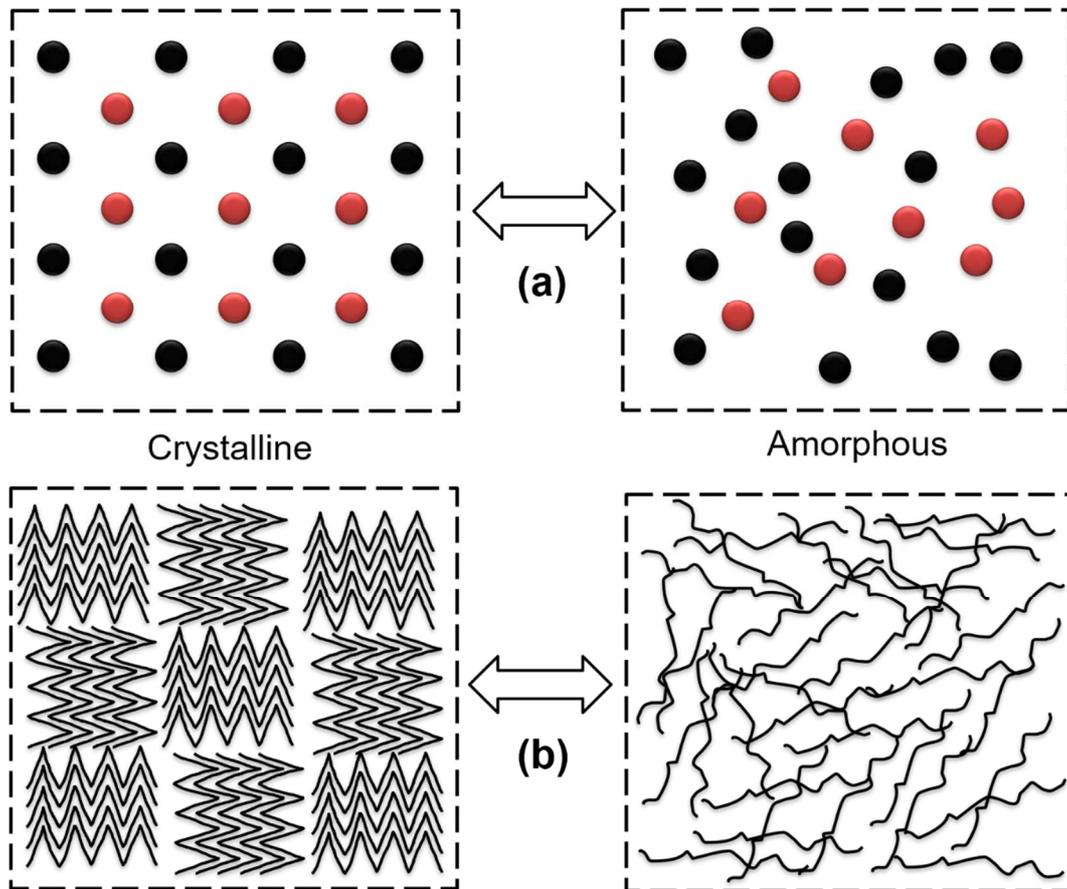
100 enhance the performance of solid-liquid PCMs for thermal storage applications by addressing
101 their inherent drawbacks. For example, the phase transition temperature of paraffin can be
102 tailored by changing the length of the carbohydrate chain. The low thermal conductivity of
103 most solid-liquid PCMs is among the main barriers for many thermal energy storage (TES)
104 applications [29] because of the reduced heat transfer rate. Some other practical challenges of
105 using solid-liquid PCMs include the need for containment or encapsulation when in the liquid
106 state to avoid leakage, the occurrence of phase segregation in mixed systems when going
107 through multiple phase change cycles, material degradation, supercooling, and hysteresis
108 occurring between cooling and heating cycles. The following paragraphs discuss the
109 enhancement of PCM thermophysical properties, to increase the performance of thermal
110 storage systems.



111

112

Figure 1 Possible phase transitions of materials [10]



113

114 Figure 2 Schematic representation of solid-liquid PCM's phase change processes for (a) A
 115 salt-hydrate system transitioning from an ordered crystalline to a disordered non-crystalline
 116 phase, and (b) transition of a paraffin-type system from a lamellar crystal phase to a random
 117 disordered phase [13].

118 3. Enhancement of thermal conductivity

119 One of the main issues for PCM in latent heat storage applications is thermal conductivity
 120 enhancement. Several theoretical and practical investigations were conducted to examine the
 121 heat transmission process of various latent heat storage systems [30]. Currently, the major
 122 ways for increasing the thermal conductivity of PCM are to add a high thermal conductivity
 123 matrix and chemically modify the additive's surface. These include surface and grafted
 124 functional group modification, as well as the inclusion of porous three-dimensional (3D),
 125 two-dimensional (2D), one-dimensional (1D), and zero-dimensional (0D) structural additives.
 126 Although modification and grafted functional groups can increase material compatibility and
 127 reduce interfacial heat resistance, the success rate of modification is lower and the operation
 128 is more intricate. The inclusion of a thermal conduction matrix can result in the formation of
 129 a thermally conductive chain, which reduces phonon scattering and speeds up heat
 130 transmission. Higher additive mass content, on the other hand, will considerably limit PCM's
 131 heat storage capability. As a result, while selecting techniques to increase the thermal
 132 conductivity of PCM, the appropriate additional amount and experimental conditions should
 133 be taken into account.

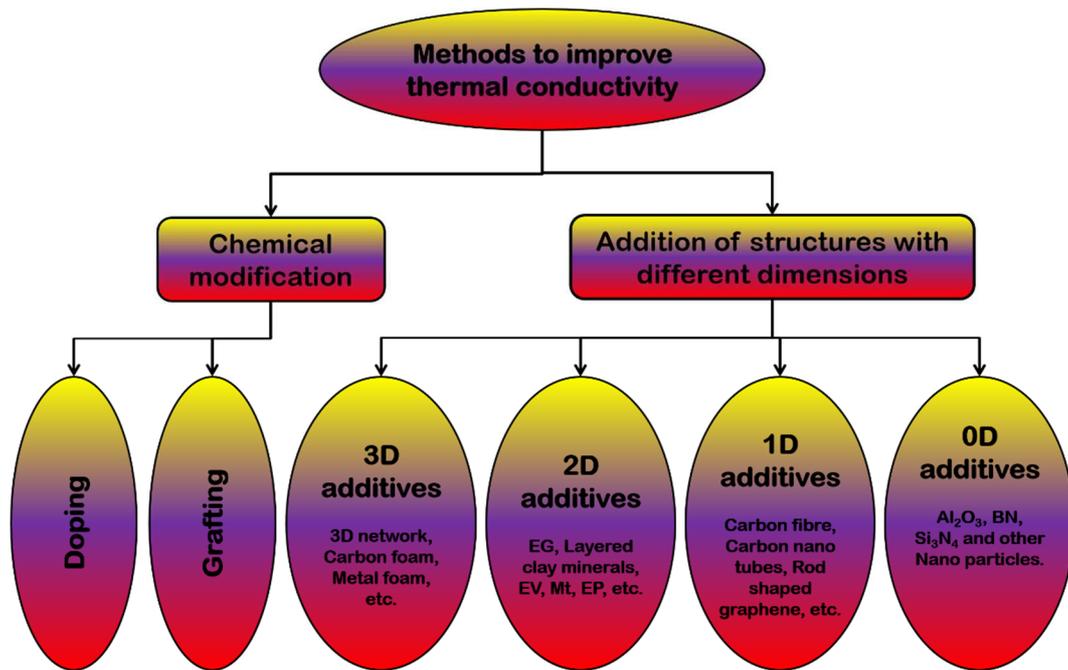
134 **3.1. Mechanism of thermal conductivity**

135 The low thermal conductivity of PCMs is a major drawback. The development of
136 composite materials with high thermal conductivity matrices can solve this problem. Thermal
137 conductivity enhancement of PCMs using composites is still a prominent research subject
138 [28,31–35]. A variety of factors influence the thermal conductivity of PCMs, and phonon
139 scattering is one of the most important factors that limit the thermal conductivity of
140 composite PCMs. The phonon is the most fundamental description of thermal transfer at the
141 microscopic level, as well as a moving force that transports heat from one end to the other.
142 The factors that govern phonon transmission in composites are basic heat power, phonon
143 velocity, and mean free path. Heat transport in PCM and interfacial phonons are not
144 constrained to each of these parameters since they are influenced directly or indirectly by a
145 number of other factors such as atomic weight, temperature, mass, and binding energy.
146 Various studies have discussed heat transmission in the materials by lattice vibration and
147 phonon transmission [34–39].

148 **3.2. Methods to increase PCM thermal conductivity**

149 By analyzing the microscopic structure of the materials, the thermal conductivity of the
150 PCM can be enhanced. The heat transfer mechanism is affected by the morphological
151 structure of the PCM. Figure 3 depicts various pathways for improving a PCM thermal
152 conductivity. This section presents PCM thermal conductivity enhancement by chemical
153 modification, as well as the morphological characterization, preparation methods, and
154 microscopic level description of composite PCM.

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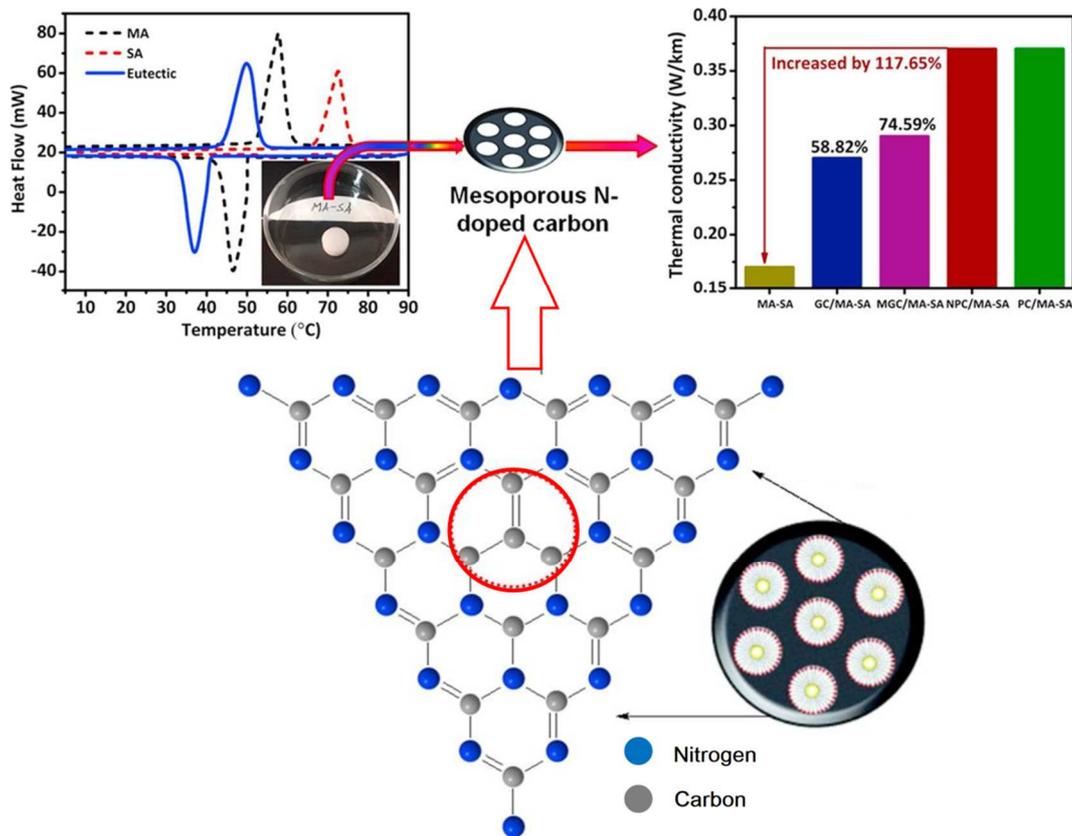
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Figure 3 Methods for improving PCM thermal conductivity

158 3.2.1. Chemical modification

159 3.2.1.1. Doping

160 The impact of macroscopic doping on the micromorphology of the composite is primarily
 161 expressed in the matrix's pore quantity and size. Doping causes significant changes in the
 162 thermal conductive matrix's surface phase composition and structure. It reduces phonon
 163 scattering and increases the number of thermal conduction channels. Porous materials
 164 obtained with a doped element will improve PCM cyclic stability and thermal conductivity
 165 while also improving its microstructure and surface compatibility. Significant research has
 166 been done on the doping of the components of the additive substrate. In this regard, Atinafu
 167 *et al.* [40] used two synthesis strategies to create mesoporous N-doped carbons/myristic acid-
 168 stearic acid (MA-SA) form shape stabilized PCM. Various synthesis techniques and N
 169 species present in porous carbons were used to examine the microstructure and thermal
 170 energy storage characteristics of the composite PCM. From the obtained results, it was found
 171 that the N-doped porous carbons derived from *in situ* (NPC/MA-SA) have a remarkable heat
 172 storage capacity of 164.33 kJ/kg with a limit of up to 88 wt% PCM loading. The resulting
 173 melting temperature of NPC/MA-SA PCM is 49.45 °C, which is lower than that of the pure
 174 PCM, while the thermal increases up to 117.65%, as shown in Figure 4.

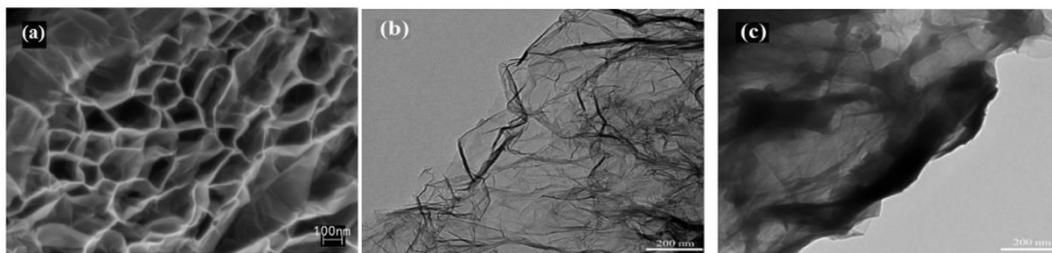


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176 *Figure 4 Porous carbon matrix/MA-SA composite PCM thermal conductivity and heat flow.*
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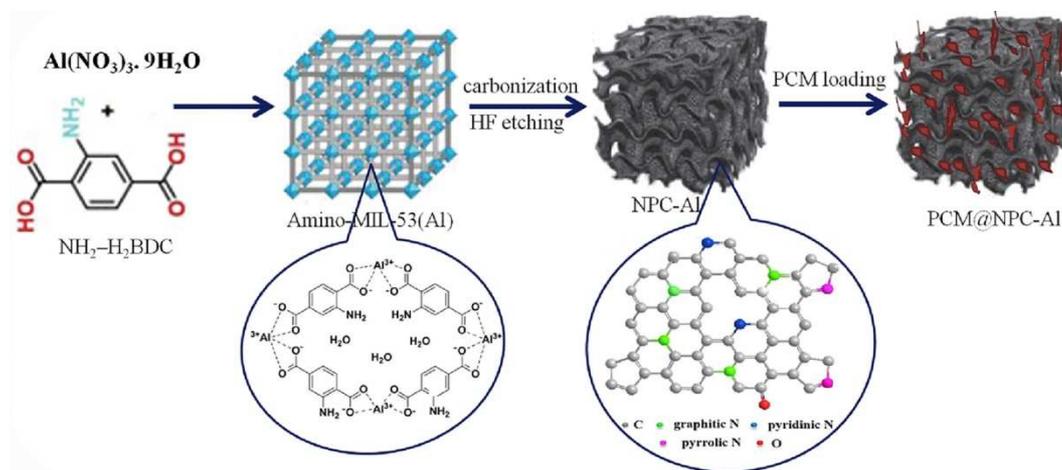
178 Mehrali *et al.* [41] developed a shape-stabilized NDG/palmitic acid (PA) composite PCM
 179 with improved thermal conductivity. The TEM and field emission SEM images of the NDG
 180 with the PA/NDG composite PCM are presented in Figure 5, revealing the porous structure
 181 and randomly stacked nanosheets of NDG, while the adsorption of PA causes a denser
 182 structure. NDG was dispersed at different mass fractions (varying from 1% to 5%) in liquid
 183 PA using high-power ultrasonication. To quantify the thermal stability and thermophysical
 184 properties of the composite, a thermogravimetric analyzer (TGA) and a differential scanning
 185 calorimeter (DSC) were used. The thermal conductivity of NDG/PA composite is tested
 186 using the laser flash method at 35 °C, and the results show that with the maximum 5%
 187 loading of NDG, the thermal conductivity is increased by 500%. The established composite
 188 was submitted to thermal cycle tests up to 1000 cycles, with the results suggesting that the
 189 NDG/PA composite has good thermal and chemical stabilities. Chen *et al.* [42] investigated
 190 the thermal behavior of organic PCMs with N-doped hierarchical carbon. Their study sheds
 191 light on how small molecular organic PCM are confined within a sequestered nanoscale N-
 192 doped hierarchical carbon structure. The composite PCM has a superior heat transfer rate as

193 compared to pure PCM and maximum crystallinity of 90.71%. To produce polyethylene
 194 glycol (PEG)-based composite PCM, Atinafu *et al.* [43] synthesized N-doped porous carbon
 195 (NPC-Al) applying a one-step NH₂-MIL-53(Al) metal-organic structure. A schematic of the
 196 synthesis process is presented in Figure 6. NPC-Al demonstrated homogeneous PEG packing
 197 potential (up to 90 wt%), enhanced thermal conductivity (up to 52%), and thermal storage
 198 capability (up to 100.3%). Furthermore, the composites demonstrated superior reliability,
 199 with 99.5 % retention after 50 heating and cooling cycles without leakage, as well as higher
 200 thermal effusivity and specific heat power than pure PEG.



201

202 *Figure 5 (a) NDG field emission SEM images, (b) NDG TEM images, (c) PA/NDG composite*
 203 *PCM TEM images. Reproduced with permission from ref. [41], Copyright (2014) with*
 204 *permission from Elsevier.*



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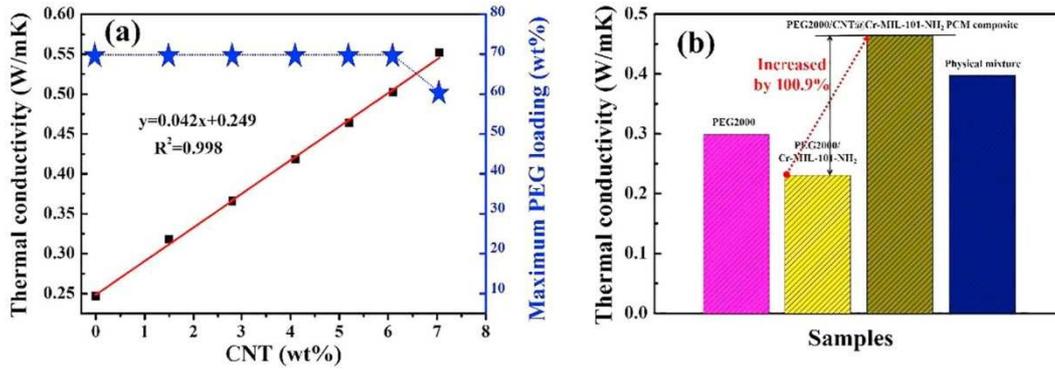
206 *Figure 6 PEG@NPC-Al composite syntheses schematic illustration. Reproduced with*
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208 3.2.1.2. Functional groups grafting

209 Grafting, also referred to as post-synthesis, is a chemical reaction in which organic groups
 210 are introduced onto the surface of mesoporous channels. Following grafting, additional

211 reactions are carried out to generate new active centers. The newly formed active centers
212 have no impact on the matrix material's mesoporous structure in any of the organic functional
213 groups. However, it reduces pore volume by blocking mesoporous channels due to unevenly
214 spaced organic functional groups on the orifice and exterior surface. The following are the
215 characteristics of grafting organic functional groups into composite materials: (i) the pore size
216 of the matrix steadily decreases as the number of organic groups increases, (ii) the
217 mesoporous structure of the matrix material remains unchanged (iii) the form of the organic
218 group may be changed to control the thermal conductivity of composite materials.

219 The supporting materials are grafted to improve the thermophysical properties of the PCM
220 based on the characteristics discussed above. In this regard, Wang *et al.* [44] used
221 heterogeneous ribbons to develop Cr-MIL-101-NH₂ metal-organic frameworks (MOFs)
222 nanoparticles network structures on the surfaces of carbon nanotubes (CNTs). PCMs were
223 stabilized by MOF nanoparticles, which were absorbed by the capillary force of the porous
224 structure and anchored by the hydrogen bond interaction of amino groups. As seen in Figure
225 7, the thermal conductivity of the PEG2000/CNT@Cr-MIL-101-NH₂ shape-stabilized PCM
226 composite was 100.9 % higher than that of the PEG2000/Cr-MIL-101-NH₂ PCM composite.
227 The energy storage capability and thermal stability of PEG2000/CNT@Cr-MIL-101-NH₂
228 over PEG2000/Cr-MIL-101-NH₂ PCM were also increased, according to the findings. Li *et*
229 *al.* [45] grafted various polyhydric alcohols onto carbon nanotubes (alcohols octanol,
230 tetradecyl alcohol, and stearyl alcohol). CNTs-C8, CNTs-C14, and CNTs-C18 had graft ratio
231 values of 11 %, 32 %, and 38 %, respectively, and CNTs were shortened and evenly
232 distributed after the grafting procedure. The agglomeration of CNTs was minimized [46].
233 Grafted CNTs/paraffin have significantly higher thermal conductivities than CNTs/paraffin
234 as shown in Figure 8.



235

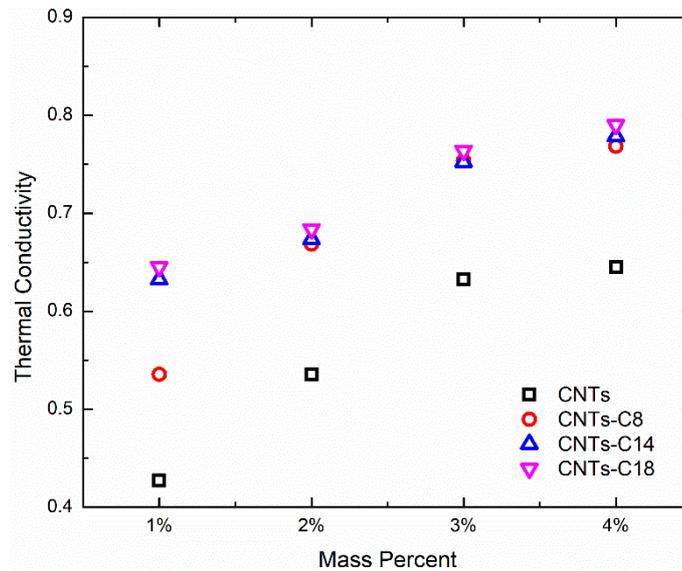
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Figure 7 (a) Thermal conductivity of composites containing different CNT mass percentages; (b) A comparison of the prepared composites' thermal conductivity improvement. Reproduced with permission from ref. [44], Copyright (2018) with permission from Elsevier.



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Figure 8 Thermal conductivity of CNTs /paraffin composite PCM. Reproduced with permission from ref. [46], Copyright (2019) with permission from Elsevier.

243

3.2.2. Addition of structures with different dimensions

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There are two modes for adding high thermal conductivity materials to PCM. The first approach involves creating a form-stable composite PCM in which the PCM is absorbed in the pores accessible inside the supporting materials, completely preventing leakage as the PCM undergoes a phase change. To minimize phonon scattering and increase thermal conductivity, these PCMs are primarily formed by heat-conducting chains inside the composite, using 3D or 2D organized additives. The resulting materials from this mode are

250 generally referred to as passive composite PCM. The second approach entails a limited
251 volume of extremely thermally conductive materials being added, to simply improve thermal
252 conductivity. Since liquid PCM leakage cannot be prevented, the formed mixture of PCM
253 and thermally conductive materials is called an initiative composite PCM. Following the
254 addition of the PCM to a 1D or 0D structure, this process creates a heat conduction path.

255 3.2.2.1. 3D additives for composite PCMs

256 Many morphological structures exist in 3D structured additives, such as graphite foams
257 (GF), heavily graphitized network carbon and metallic foams, etc. [47]. The additives easily
258 form an integrated pore network and have a conductive pathway for enhancing heat transfer
259 in the PCM due to their composition. The 3D additives are the ideal choice as they increase
260 the thermal conductivity as well as reduce the degree of supercooling [48]. Different studies
261 have been carried out in the recent past to improve the thermal conductivity of PCM using 3D
262 structures. Ji *et al.* [49] added ultra-thin graphite to improve the effective thermal
263 conductivity of a PCM without changing its melting temperature and energy storage capacity.
264 The graphite has high porosity, low density, the high thermal conductivity of up to 200 W/(m
265 K), high thermal stability, corrosion resistance, properties that are compatible with most PCM
266 [50–56]. A highly graphitized 3D carbon network is an attractive matrix with a high thermal
267 conductivity that increases phonon transmission routes. As a result, adding a heavily
268 graphitized 3D carbon network to the PCMs effectively improves the composite PCM
269 thermal conductivity [57–62]. Zhang *et al.* [54] proposed a three-dimensional diamond foam
270 (DF) on Cr-modified Cu foam by template-directed chemical vapor deposition (CVD) as a
271 highly conductive filler for paraffin-based PCM. The thermal conductivity of pure paraffin,
272 diamond particle (DP)/paraffin, copper foam (CF)/paraffin, and diamond foam (DF)/paraffin
273 were 0.25 W/m K, 0.45 W/m K, 2.56 W/m K and 6.70 W/m K, respectively. Even at a very
274 low volume fraction of diamond (1.3 vol%), the thermal conductivity of DF/paraffin was
275 162% higher than that of CF/paraffin and 2580% higher than that of pure paraffin. Chen *et al.*
276 [57] prepared 3D highly graphitic compact carbon network for providing a superior
277 interconnected path for phonon propagation in the composite PCM. Carbon quantum dots
278 (CQDs) derived from acetone and divinyl benzene (DVB) provide a simple, low-cost, and
279 controlled method for constructing a compactly linked 3D celosia-like highly graphitized
280 thermally conductive network carbon. The novel function of CQDs is first developed for
281 enhanced thermal energy harvesting, thereby expanding their conventional fluorescence and

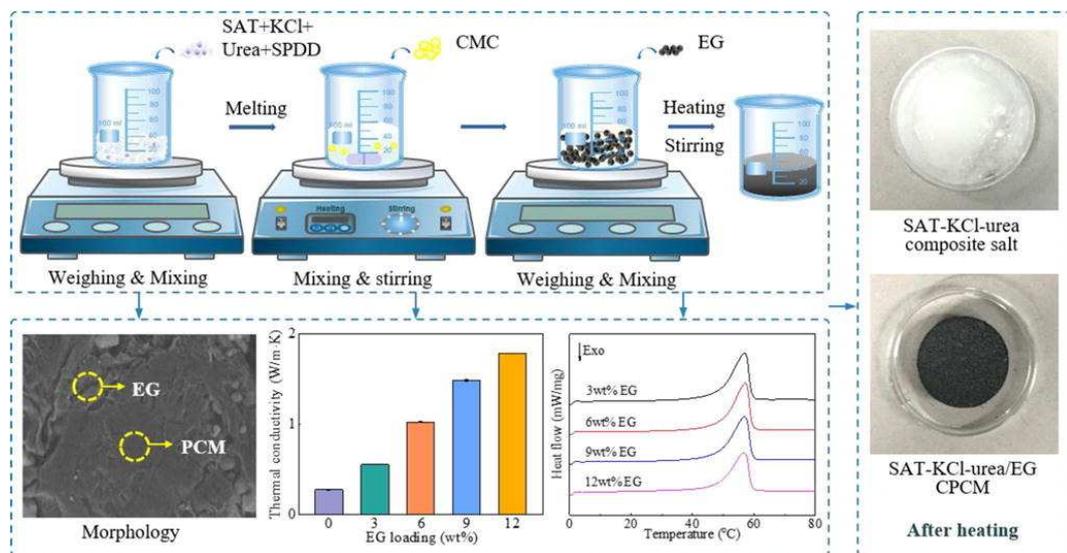
282 catalysis field to innovative thermal energy storage. This solution incorporates adequate
283 power capacity as well as the additional thermal conductivity of the PCMs (increased by 236
284 %). Hu *et al.* [60] enhanced the thermal conductivity of a paraffin phase change material from
285 0.105 W/(m K) to 9.72 W/(m K) by introducing diamond-carbon nanotube foams,
286 representing one of the highest enhancements ever reported.

287 The addition of PCM to the metal foam's extremely porous continuous skeleton structure
288 will significantly increase the thermal conductivity of the composite PCM while reducing its
289 heat storage ability to some degree. Copper [63–65], aluminum [66,67], titanium dioxide [68]
290 and nickel [69–71] are the most widely examined metal foams. Abdulmunem *et al.* [72]
291 dispersed nanoparticles within a combination of PCM and copper foam matrix (CFM). The
292 results demonstrate the effect of the bundles of tangled tubes of the multi-walled carbon
293 nanotubes (MWCNTs) additives. With a 0.2% concentration ratio within the PCM/CFM, the
294 effective thermal conductivity was increased from 2.90 W/(m K) to 2.95 W/(m K).

295 3.2.2.2. 2D additives for composite PCM

296 Because of its 2D lamellar form which is identical to clay mineral, expanded graphite
297 (EG) is compatible with PCM and avoids leakage. It also features a wide surface area and
298 pore network, which means it has numerous active sites and heat conduction chains, which in
299 turn will enhance the thermal conductivity of the composite PCM [73–75]. The clay network
300 structures result in quicker absorption of PCM into the pore system to form solid PCM.
301 However, because of the small pore openings and the short distance between clay layers,
302 PCM absorption may be reduced in certain situations. The interaction between clay and PCM
303 mainly depends on surface tension, van der Waals forces, capillary force, and hydrogen bond.
304 SiO₂ is used as a supporting material to resist PCM outflow, owing to its three-layer
305 reticulated crystal structure [76–81]. Sepiolite, extended perlite, attapulgite, and expanded
306 vermiculite provide broad unique surface areas [82,83,92–97,84–91]. Jin *et al.* [98]
307 developed a novel sodium acetate trihydrate (SAT)–potassium chloride (KCl)–urea/expanded
308 graphite (EG) composite PCM. EG was infused into the source composite salt to get ready
309 SAT–KCl–urea/EG. The SAT–KCl–urea/EG CPCM, which contains 9 wt% EG, was found
310 to be the best for improving thermal energy storage efficiency without losing phase shift
311 properties. The preparation method of (SAT)–(KCl)–urea/EG CPCM, the enhanced thermal
312 conductivities and the DSC curves at different EG loading are presented in Figure 9. From
313 Figure 9, it can be observed that the thermal conductivity of pure PCM is increased with an

314 increase in EG loading. Ma *et al.* [99] prepared a series of stearic acid (SA)/benzamide (BA)
 315 binary mixtures and EG was impregnated to enhance the thermal conductivity because of its
 316 good compatibility. As compared to the eutectic mixture, the thermal conductivity of the
 317 composite with 12 wt% EG was improved by 12.30 times. Rathore *et al.* [100] used
 318 PCM/expanded vermiculite/expanded graphite shape stabilized composite PCM for building
 319 energy applications. The thermal conductivity of the composite PCM was significantly
 320 affected by the presence of EG and increased with the increase in mass content of EG. The
 321 maximum value of thermal conductivity of 0.311 W/(mK) was obtained with an increment of
 322 114.4% in comparison to the pure PCM.



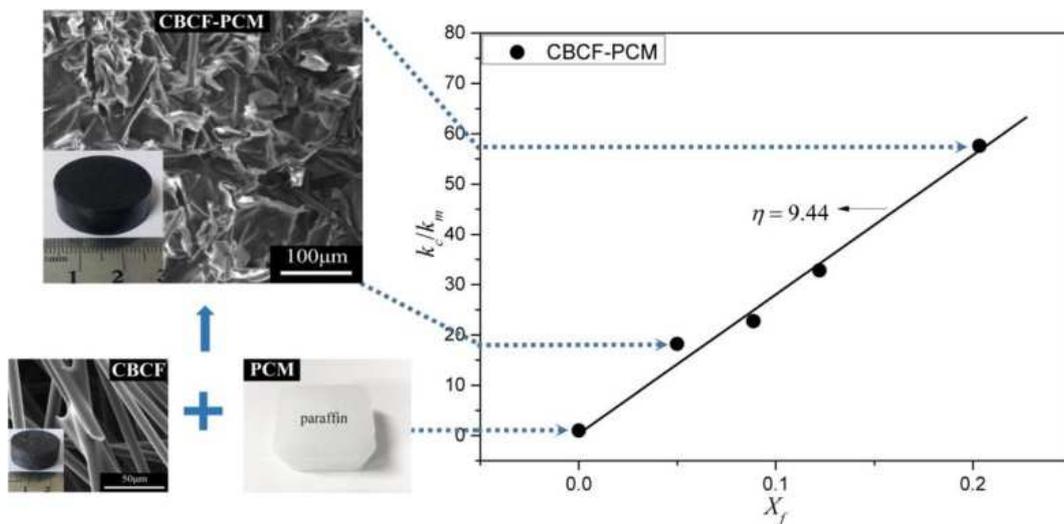
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324 *Figure 9 Preparation method of (SAT)-(KCl)-urea/EG CPCM, enhanced thermal*
 325 *conductivities and DSC curves at different EG loading. Reproduced with permission from ref.*
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327 3.2.2.3. Initiative composite PCM using 1D additives

328 Carbon nanotubes (CNTs), carbon fiber (CF), and cylindrical type graphene are only a few
 329 of the morphological structures used in 1D form additives. Because of the 1D structure's
 330 excellent thermal conductivity, even a limited amount of additives will greatly improve the
 331 thermal conductivity. Furthermore, 1D structure additives are lighter than metal additives and
 332 minimize supercooling, making them an excellent alternative for a high-performance PCM.
 333 High-temperature corrosion resistance, low density, and high thermal conductivity are
 334 benefits of CF [101]. It can also absorb almost all organic PCM, making it one of the
 335 strongest materials for increasing organic PCM thermal conductivity [102]. To improve

336 thermal transport and stabilize the form of the PCM, Jiang *et al.* [103] prepared carbon
 337 bonded carbon fiber (CBCF) monoliths from graphite fibers. CBCF density ranged from 0.09
 338 to 0.39 g/cm³, and PCM was filled into the pore of the CBCF. Due to anisotropy in the CBCF
 339 material, the thermal conductivity of the composite PCM was directional dependent.
 340 According to the findings, the in-plane thermal conductivity of the composite PCM was
 341 improved by 18 to 57 times over pure wax, while the out-of-plane thermal conductivity was
 342 also increased by 3.7 to 5.5 times. Furthermore, as seen in Figure 10 the thermal conductivity
 343 of CPCM increases linearly as the volume fraction of CF increases. In Figure 10, k_c and k_m
 344 are composite PCM and pure paraffin wax thermal conductivities respectively, while X_f is the
 345 volume fraction of carbon fiber. Qian *et al.* [104] used an impregnation approach to make
 346 PEG/SWCNTs nano-composite PCM to increase the thermal conductivity of polyethylene
 347 glycol. The measurements revealed that a small amount of SWCNT (4%) significantly
 348 increases thermal conductivities of the solid (375%) and liquid states (121 %).



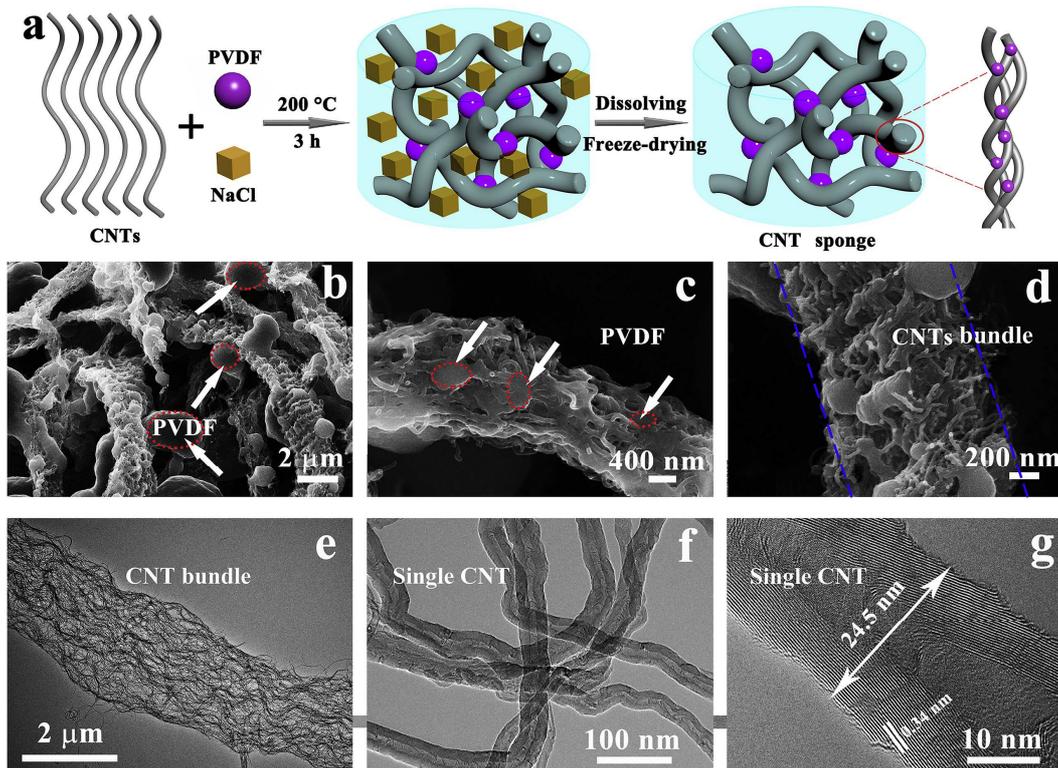
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350 *Figure 10 CBCF composite PCM and linearly increase in its thermal conductivity.*

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 352 *Elsevier.*

353 Chen *et al.* [105] designed advanced CNT bundles assembled in a flexible hierarchical
 354 framework based on PCM composites, for high-performance thermotherapy of allergic
 355 rhinitis. Figure 11 illustrates the organic solvent-free self-assembly procedure of a 3D
 356 flexible CNT sponge. The bulk product was manufactured by heating a mixture of CNTs,
 357 PVDF and NaCl in a specific mold for 3 h in an oven, in which NaCl served as a sacrificial
 358 template and PVDF served as a binder. The resulting hierarchical CNT sponge was used as a
 359 compatible supporting host and polyethylene glycol (PEG) served as the thermal energy

360 guest. The constructed flexible CNT sponge-involved composite PCMs assisted by
 361 polyvinylidene fluoride (PVDF) yielded high-performance thermotherapy (~33 min of the
 362 plateau at ~43.5 °C). Cheng *et al.* [106] developed flexible monolithic PCM based on CNT,
 363 chitosan (CS) and poly vinyl alcohol (PVA) using a directional freezing method. The
 364 CS/PVA/CNTs (CPC) scaffold was infiltrated with polyethylene glycol (PEG) to prepare
 365 PEG@CPC composite PCM. The resulting flexible composite PCM displayed excellent
 366 mechanical properties, such as high tensile strength of 2.42 MPa and high bending resistance
 367 after 100 cycles. Moreover, it showed very good thermal properties, such as high crystallinity
 368 close to 100% and encapsulation ratio of 92.6 wt%.

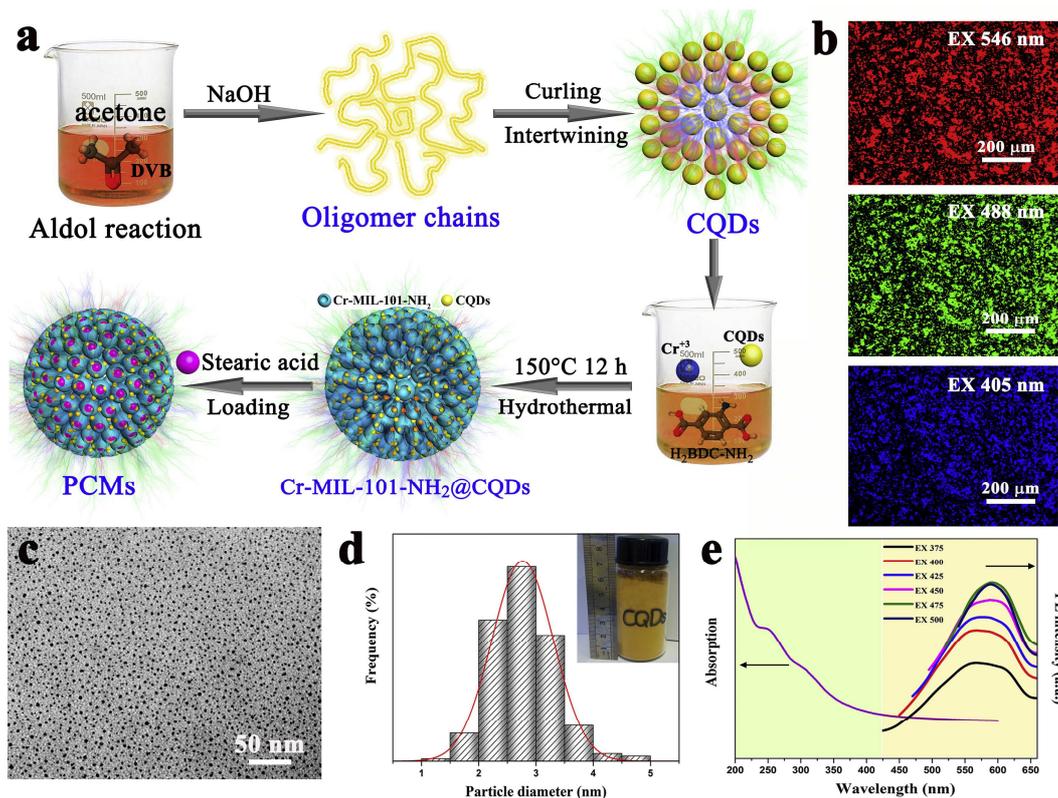


369
 370 *Figure 11 Preparation schematic illustration, (b–d) SEM images, (e–g) TEM images of CNT sponge.*
 371 *Reproduced with permission from ref. [106], Copyright (2020) with permission from*
 372 *Elsevier.*

373 3.2.2.4. Initiative composite PCMs using 0D additives

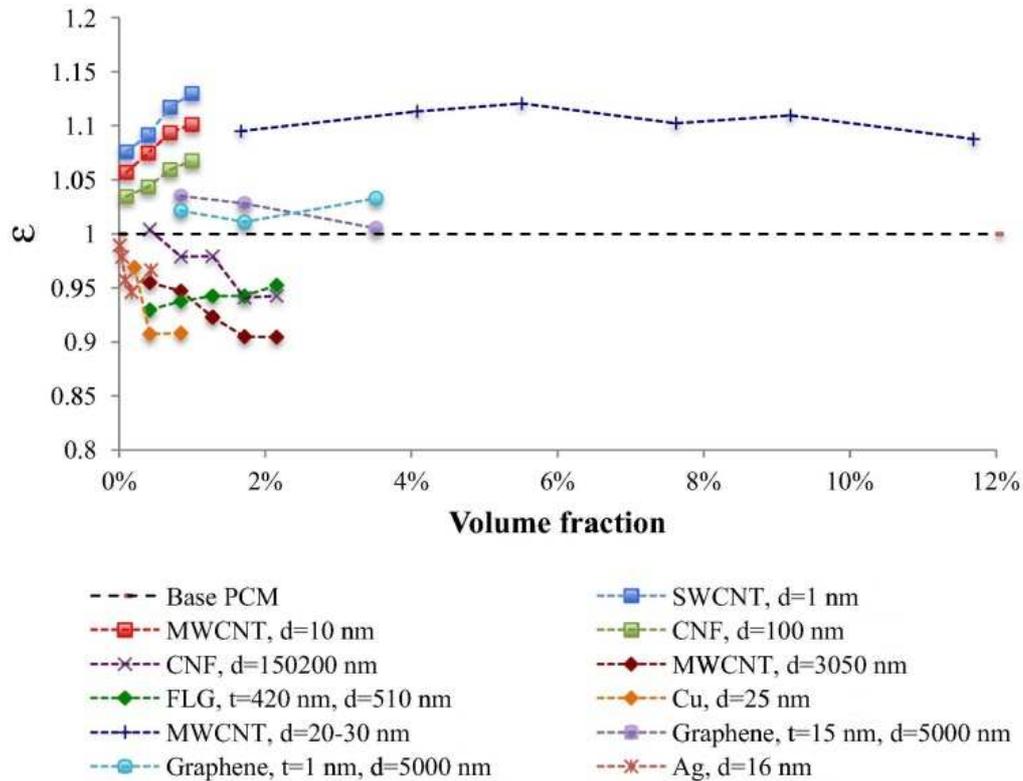
374 In the preparation of composite PCM, 0D structure additives have gained a lot of interest.
 375 These nanoparticles are ceramic-based and nanoscale-based. Powerful interface interaction,
 376 large specific surface region, suitable homogeneity, and good dispersion are all
 377 characteristics of 0D standardized additives. Due to their high thermal conductivity, a limited
 378 amount of 0D structure additives can greatly increase the thermal conductivity of initiative
 379 composite PCMs [107]. Furthermore, inserting nanoparticles in a specific way and proportion
 380 improves heat transfer in the composite PCM. Due to the absence of free electrons, heat is

381 mostly transported by phonons. Several metal oxide additives, such as titanium dioxide
 382 (TiO_2), are used in addition to beryllium oxide (BeO) [108–110], aluminum oxide (Al_2O_3)
 383 [7], and copper oxide (CuO) [7,111] to give elevated thermal conductivities. Non-oxide
 384 additives such as silicon nitride (Si_3N_4) [112], boron nitride (BN) [113–118], silicon carbide
 385 (SiC) [96,119], and MOFs [120] have strong interatomic bond energy and crystal structure,
 386 which reduces phonon scattering while still providing for high thermal conductivity. Chen *et*
 387 *al.* [121] developed a novel type of MOFs based photoluminescence-functionalized (PL)
 388 PCMs for superior thermal energy and fluorescence harvesting using a facile synthetic
 389 strategy. The Stearic acid (SA) and carbon quantum dot (CQD) molecules were
 390 synchronously incorporated into the Cr-MIL-101- NH_2 framework (Figure 12), in which the
 391 MOF framework serves as the support host, CQD as the fluorescent guest, and stearic acid as
 392 the thermal energy guest. The fabricated composite PCMs exhibit thermal conductivity of
 393 0.42 W/mK and very good thermal stability, durability, and shape-stabilized ability. Thermal
 394 conductivity was enhanced around 1.6 times compared to the pure PCM.



395

396 *Figure 12 (a) Schematic illustration of photoluminescence-functionalized composite PCM;*
 397 *(b) fluorescent images of pure CQDs at different excitation wavelengths, (c) HRTEM image*
 398 *of pure CQDs, (d) diameter distribution of pure CQDs, the insert is CQDs production, (e)*
 399 *UV-vis absorption spectrum and excitation-independent PL spectra of pure CQDs.*

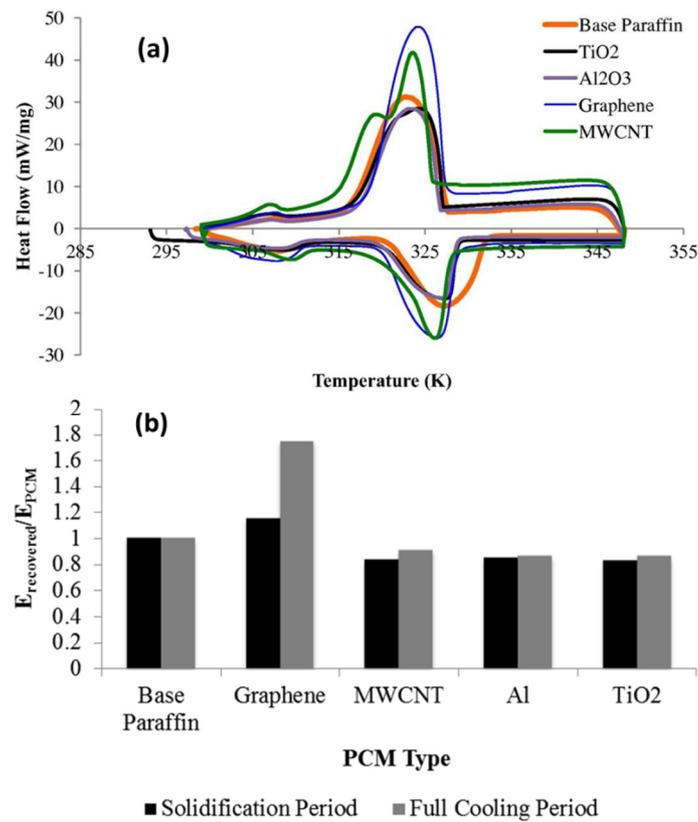


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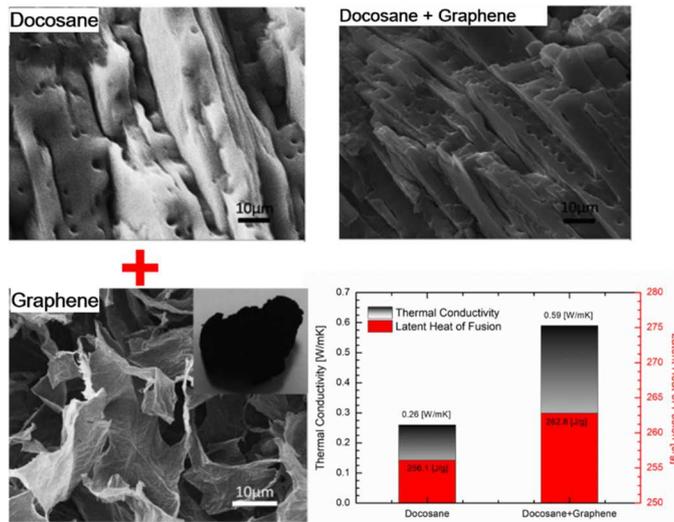
427 *Figure 13 Ratio of absolute phase change enthalpy of nanocomposite paraffin PCMs to the*
 428 *phase change enthalpy of base paraffin PCMs (ϵ). Reproduced with permission from ref.*
 429 *[124], Copyright (2014) with permission from Elsevier*

430 Experimental work was performed by Warzoha *et al.* [124] to harness thermal energy from
 431 the composite PCM using a heat exchanger. The thermal energy extracted during the
 432 solidification of MWCNT-paraffin, Al-paraffin, or TiO₂ composite PCM at 20% volume
 433 loading is about 15-17% lower than that of the base paraffin. The thermal energy extracted by
 434 graphene nanoparticle networks (15 nm thickness, 5 μ m diameter, 20 v. %) is about 11%
 435 higher than for base paraffin (Figure 14). Sun *et al.* [125] used ultra-flyweight, synergistically
 436 assembled carbon aerogels and paraffin to create composite PCM. According to the data, the
 437 melting and freezing latent heat of the fabricated composite PCM were respectively 7.8% and
 438 28.7% higher than that of paraffin. It was explained by the relationship between paraffin and
 439 the hydrophobic surfaces of graphene and CNTs. Li *et al.* [127] looked into the impact of
 440 spongy graphene on the latent heat of fusion of a PCM made up of docosane and spongy
 441 graphene (G22). The graphene sheets serve as a nucleating agent, increasing the crystallinity
 442 of the docosane and thereby increasing the thermal energy storage potential. In a lower
 443 graphene concentration of 3 mg/cm³, the latent heat increased from 256.1 J/g to 262.8 J/g,
 444 and the thermal conductivity was more than doubled, as seen in Figure 15. By doping wax

445 with single-wall carbon nanotubes (SWCNTs), multiwall carbon nanotubes (MWCNTs), and
 446 carbon nanofibers, Shaikh *et al.* [130] produced three types of carbon nanoparticles doped
 447 PCM. The prepared samples exhibit strong latent heat enhancement as compared to pure shell
 448 wax, with a maximum enhancement of 13% for the wax/SWCNT composite equivalent to 1%
 449 SWCNT filling. The enhancement of latent heat for the different samples is presented in
 450 Figure 16. Lin *et al.* [133] used the solution blending approach to create a new form-stable
 451 PCM. The best CPCM sample had a thermal conductivity approximately 4.2 times that of
 452 pure PCM and a higher latent heat storage capacity.



453
 454 *Figure 14(a) DSC heating and cooling curves normalized against PCM mass, (b) the ratio of*
 455 *heat extracted from composite PCM to base paraffin for the solidification time (black bars)*
 456 *and the full cooling cycle (gray bars). Reproduced with permission from ref. [124],*
 457 *Copyright (2014) with permission from Elsevier*



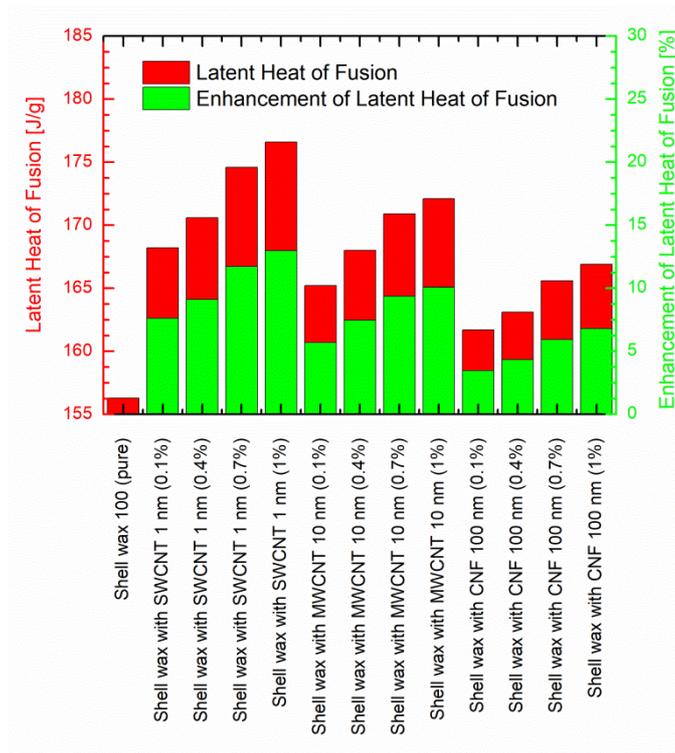
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Figure 15 Simultaneous enhancement of latent heat and thermal conductivity of docosane/graphene composite, Reproduced with permission from ref. [127], Copyright (2014) with permission from Elsevier



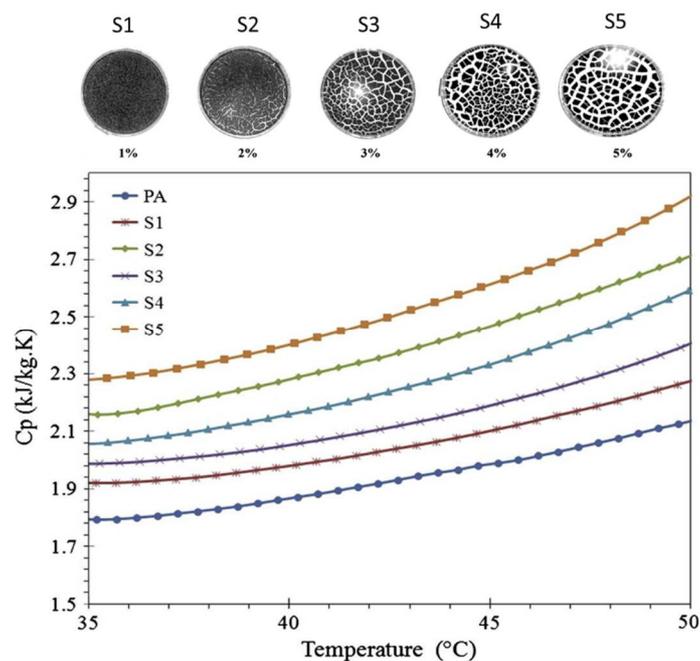
462

463

Figure 16 DSC values of latent heat of wax and nanoparticle doped composites [130].

464 4.2. Enhancement of specific heat capacity

465 Mehrali *et al.* [41] used nitrogen-doped graphene (NDG) as a supporting medium to create
466 novel form-stable PCM. Based on the additives used, shape stabilization of the PCM
467 addressed leakage problems and changed the thermal conductivity. Figure 17 illustrates the
468 various configurations of PA/NDG composite PCM after drying, with the PA being fully
469 absorbed by NDG particles for the higher NDG mass percentages. The PA had a constant
470 stable form in the mass percentages of 1% and 2%, but this shape was completely modified in
471 other samples due to the absorption of the PA by NDG particles. In temperatures ranging
472 from 35 to 50 °C, the specific heat of pure PA and PA/NDG composite PCM was calculated
473 using the multiple curves method. As seen in Figure 17, the addition of NDG raised the
474 individual temperatures, with the increase becoming more significant for higher NDG
475 loadings.



476

477 *Figure 17 Dried PA/NDG composite PCMs and corresponding specific heat. Reproduced*
478 *with permission from ref. [41], Copyright (2014) with permission from Elsevier*

479 Shin *et al.* [134] stated that doping silica nanoparticles at 1% mass concentration improves
480 the specific heat capacity of high-temperature nano fluids (alkali metal chloride salt
481 eutectics). The observed 14.5% increase in nanofluid's heat capacity can be explained by
482 three independent competing transport mechanisms: (i) higher specific heat capacity of

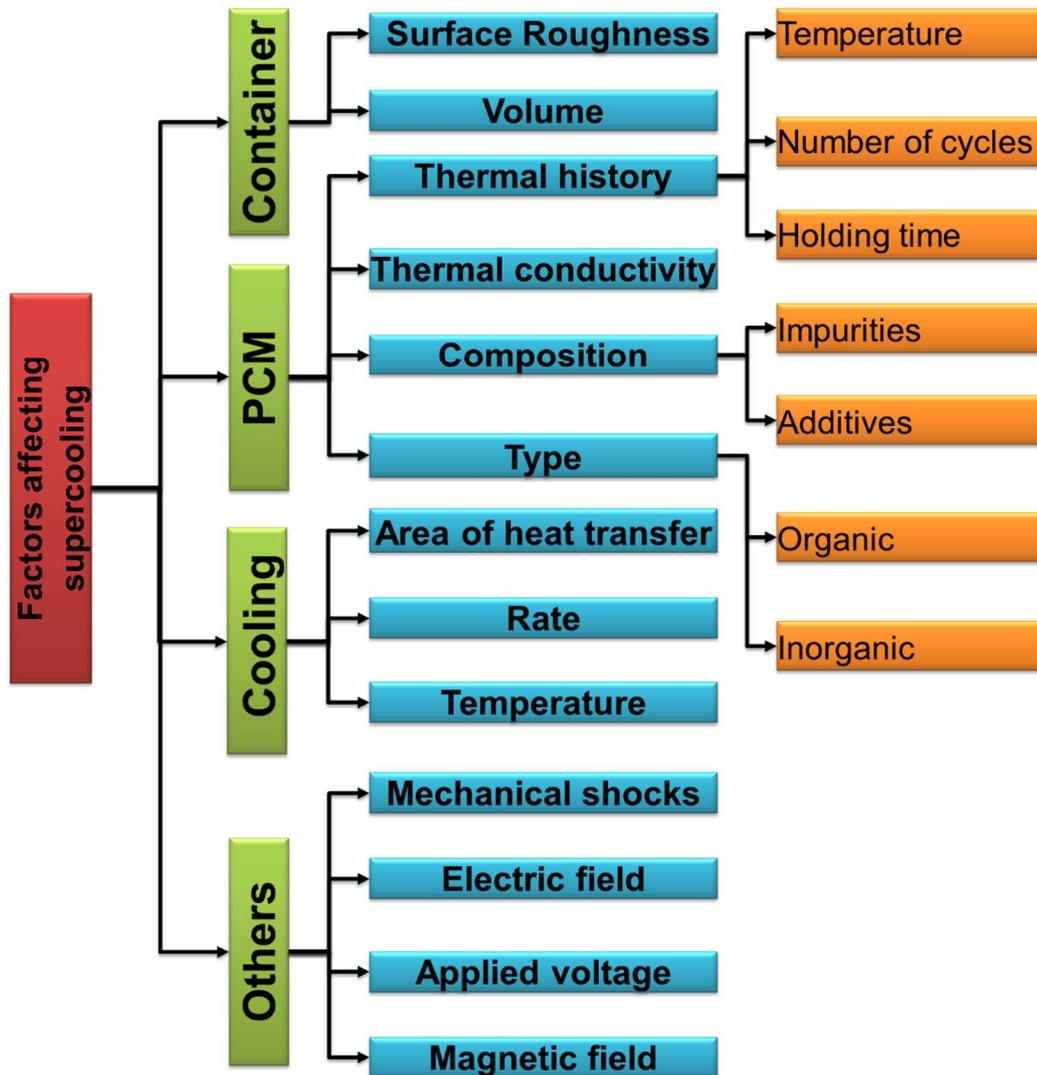
483 nanoparticles than that of bulk silica, (ii) high interfacial thermal resistance between the
484 nanoparticles and fluid, (iii) semi-solid behavior of liquid molecules adhering on the surface
485 of the nanoparticles. Chieruzzi *et al.* [135] developed nano-fluids by direct synthesis of nano-
486 particles and molten salt. A $\text{NaNO}_3\text{-KNO}_3$ (60:40 ratio) binary salt and silica dioxide (SiO_2),
487 alumina (Al_2O_3), titanium dioxide (TiO_2) and a mix of silica-alumina ($\text{SiO}_2\text{-Al}_2\text{O}_3$)
488 nanoparticles were used to prepare the nanofluids. According to the results, applying 1.0 %
489 nanoparticles to the base salt increases the specific heat by 15% and 57 % in the solid stage
490 and of 1% and 22% in the liquid state.

491 The above sections show that a significant amount of research has been devoted to the
492 enhancement of the thermal conductivity, specific heat and latent heat of fusion. However,
493 the efficiency of the energy storage devices also depends on the supercooling and phase
494 segregation behavior of the PCM. The following sections present methods to reduce these
495 drawbacks.

496 **5. Reduction of supercooling**

497 **5.1. Mechanism of supercooling**

498 Supercooling refers to a solidification impediment. The material remains in a liquid state
499 even after being cooled below its melting temperature. The presence of supercooling and its
500 amplitude (degree of supercooling) depends on several factors. The most important factors
501 are summarized in Figure 18 and will be detailed hereafter. They are all connected to one
502 major reason for supercooling presence, which is the absence of nucleation sites. Indeed, the
503 initiation of solidification requires a solid particle referred to as a nucleus, which may be too
504 small and even not present at the liquid state. This nucleus is formed and grows by the
505 solidification of the liquid on the solid surface. In this case, the liquid releases its heat to
506 reach minimum energy. The heat release and solid formation depend on the radius r of the
507 nucleus. The released heat is the function of the volume (proportional to r^3) while the solid
508 formation depends on the surface area of the nucleus (proportional to r^2). An energetic barrier
509 is formed for small values of r , which means that the gained surface energy is larger than the
510 heat released by solidification [136]. Liquids enter the supercooled state when energy release
511 from the nucleus necessary to form the solid-liquid interface is not sufficient [137]. In this
512 case, solidification is prevented and the liquid enters into the supercooling state.
513 Solidification initiates when the radius of the nucleus is sufficiently large.



514

515

Figure 18 Factors affecting the supercooling degree

516

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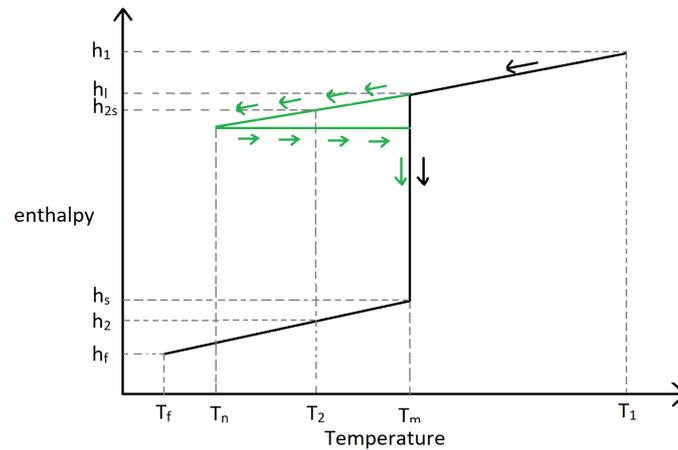
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525

In PCM based thermal energy storage systems, interruptions in PCM solidification avoid the release of latent heat, causing a problem in the system's engineered solidification-melting period. A PCM is cooled from a temperature T_2 to temperature T_1 or heated from T_1 to T_2 exchanges the same quantity of heat. Figure 19 shows the enthalpy change in the cases of the presence or nonappearance of supercooling. In the case of no supercooling, the enthalpy changes according to the black line as temperature drops from T_1 to T_f . As shown in green color, the presence of supercooling prevents solidification and the liquid PCM temperature decreases to the nucleation temperature T_n , where the solidification initiates. Considering the case where a PCM of melting temperature T_m is designed to operate between T_1 to T_2 , the PCM will remain in supercooled state upon cooling rather than changing phase. In the case of

526 supercooling, the released heat will be $(h_1 - h_{2s})$ rather than $(h_1 - h_l) + (h_l - h_s) + (h_s -$
 527 $h_2)$, where $(h_l - h_s)$ is the latent heat. Supercooling is therefore undesirable in most thermal
 528 energy storage systems. The difference between the melting point and the temperature at
 529 which nucleation begins is the degree of supercooling $(T_m - T_n)$. Supercooling depends on
 530 many factors which effects are usually correlated and non-linear. The following sections
 531 describe the effects of such factors.



532

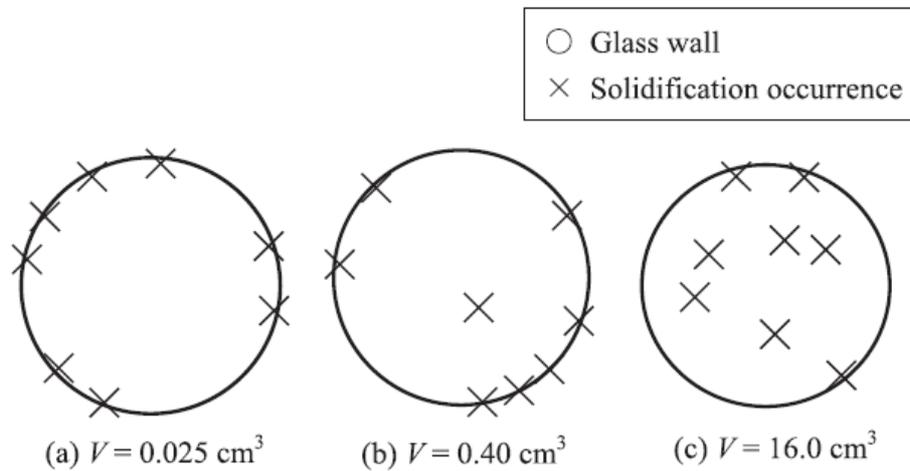
533 *Figure 19 Variation of enthalpy as a function of temperature for the case of no supercooling*
 534 *(in black) and the case of supercooling (in green)*

535 5.2. Methods to reduce supercooling

536 5.2.1. Effect of the PCM container volume

537 The container in which the PCM is added can affect the degree of supercooling by its surface
 538 roughness and volume. As the surface roughness and the volume increase, the degree of
 539 supercooling decreases. The rough surface provides a surface of crystallization. As reported
 540 by several studies, the solidification of PCM initiates from the scratched (rough) surfaces of
 541 the container and any other rough surface introduced in the PCM rather than smooth surfaces
 542 [138–142]. The increase in container volume increases the probability of nucleation by
 543 increasing the germination sites inside the PCM. Several experiments were held on different
 544 PCM, and by changing the volume from cm^3 to mm^3 or from mm^3 to μm^3 , the degree of
 545 supercooling increased [143–145]. Figure 20 shows the position of nucleation sites of the
 546 same PCM encapsulated in different volumes [143]. By increasing the volume from 0.025
 547 cm^3 to 0.4 cm^3 and 16 cm^3 , the degree of supercooling decreased from $88 \text{ }^\circ\text{C}$ to $58 \text{ }^\circ\text{C}$ and 48
 548 $^\circ\text{C}$ respectively. However, the applied techniques to reduce supercooling should not affect the

549 performance of the PCM based thermal energy storage system. In thermal storage systems, it
 550 is better to store PCM in a confined volume. Confining the PCM in many reduced volumes,
 551 as it is the case in encapsulation, increases the surface of heat exchange, which in turn
 552 enhances the heat transfer rate. Besides, the solidification of the large volume of supercooled
 553 liquid leads to the release of a large amount of energy in a short time.



554

555 *Figure 20 Different solidification site positions for an encapsulated PCM [143]*

556 **5.2.2. Effect of the cooling rate**

557 The cooling technique also affects the supercooling of PCM. As mentioned before, increasing
 558 the exchange surface area increases the cooling rate. Using a cooling fluid with a temperature
 559 higher than the nucleation temperature may lead to the PCM entering supercooling for an
 560 undermined time. Increasing the cooling rate for example by further reducing the temperature
 561 of the cooling fluid may increase the degree of supercooling but decreases the time spent at
 562 the supercooled state because the PCM reaches its nucleation temperature faster. On the other
 563 hand, using a low cooling rate (low-temperature difference between cooling fluid and PCM)
 564 increases the supercooling time but decreases the supercooling degree.

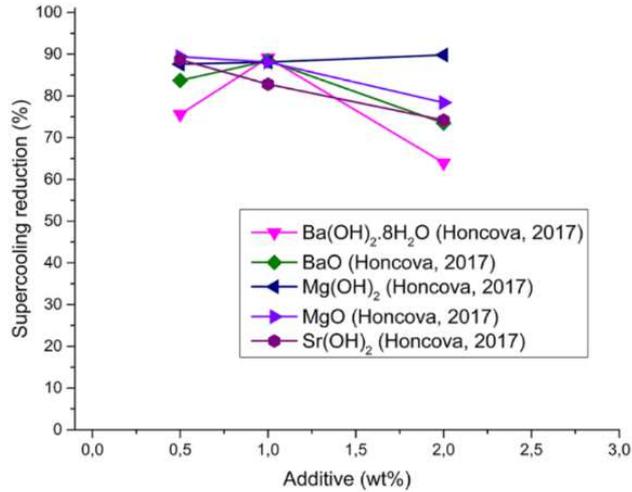
565 **5.2.3. Crystallization inducing methods**

566 Two methods are generally used to induce crystallization. The first is called manual seeding
 567 and is considered very effective [146]. Manual seeding is the addition of seed particles to the
 568 supercooled liquid, which triggers crystallization immediately. When crystallization initiates,
 569 the temperature increases due to the release of latent heat. As long as the temperature of the

570 liquid is lower than the melting temperature, the crystalline structure continues to spread in
571 the supercooled liquid [147]. The second method is called dynamic stimulation. The
572 supercooled liquid is in an unstable state. Mechanical shocks, ultrasonic vibrations [148],
573 friction [149], agitation [150], magnetic fields [151] etc. can trigger solidification [152,153].

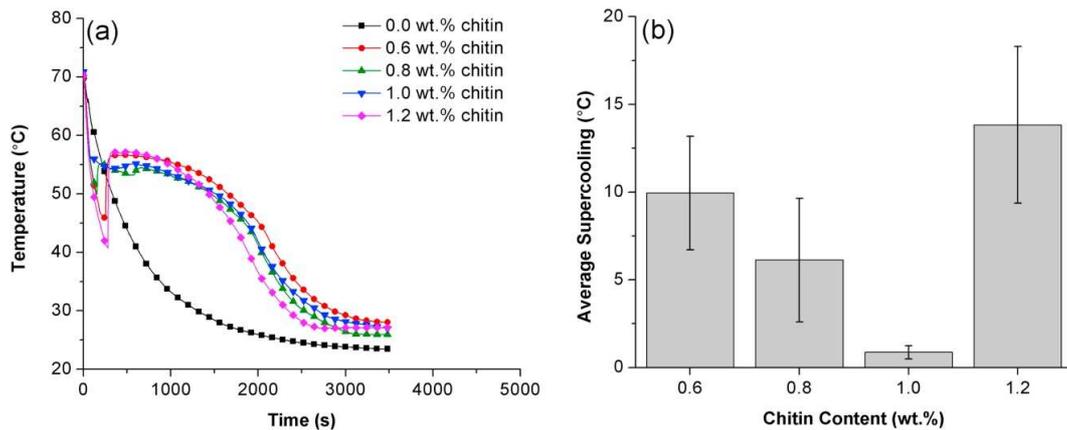
574 5.2.4. *Change in the PCM formulation: effect of additives*

575 The PCM composition and characteristics also have a direct effect on the degree of
576 supercooling. Nucleation can be homogeneous or heterogeneous. In heterogeneous
577 nucleation, the first nuclei of nucleation initiate from a rough surface, impurities, or additives
578 [154]. On the contrary, homogeneous nucleation occurs suddenly from the liquid with no
579 solid surface aid. Additives serve in decreasing the degree of supercooling to very low values,
580 as found by different experiments [155–158]. However, after a certain percentage, the degree
581 of supercooling increases again, as shown in Figure 21. This is due to the gathering of
582 additives molecules, which reduce their contact surface with PCM molecules. The exact
583 percentage of loading cannot be calculated because of the lack of data on the degree of
584 supercooling for pure materials. The presented values in Figure 21 and Figure 22 are for a
585 given initial value of supercooling. Figure 22(a) shows that for 0 % additive used nucleation
586 cannot occur and the PCM enters in the supercooling state. On the contrary, using 1 %
587 additive almost prevents supercooling. The thermophysical properties of nucleating agents
588 present in additives are very different from that of PCM and modify their chemical
589 composition. The use of these agents should not prevent the PCM from correctly performing
590 its role in the energy storage system [159].



591

592 *Figure 21 Percentage of reduction of supercooling as a function of different additive*
 593 *percentages. Reproduced with permission from ref. [159], Copyright (2018) with permission*
 594 *from Elsevier*



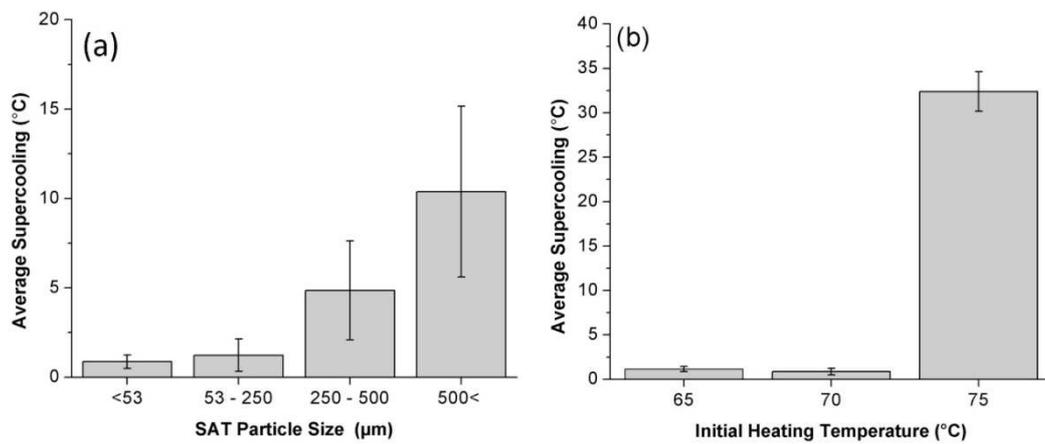
595

596 *Figure 22 Average degree of supercooling for different percentages of additive. Reproduced*
 597 *with permission from ref. [155], Copyright (2018) with permission from Elsevier*

598 **5.2.5. Other factors affecting supercooling**

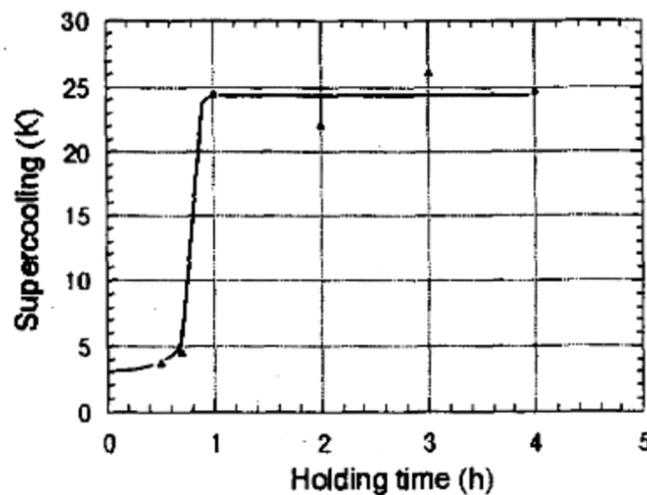
599 The PCM particle size and the PCM thermal history also affect the degree of supercooling.
 600 For PCM initially in powder form, the degree of supercooling increases with the size of the
 601 particle. Fashandi and Leung [155] measured the supercooling degree of a series of sodium
 602 acetate trihydrate (SAT) PCM, with SAT powder particle size ranging from less than 53 μm
 603 to more than 500 μm . As shown in Figure 23a, the supercooling degree increased along, from
 604 1 $^{\circ}\text{C}$ to 10 $^{\circ}\text{C}$. Regarding the thermal history of the PCM, heating a PCM over a certain limit
 605 may cause an increase in the degree of supercooling [160]. Figure 23b shows the sudden

606 increase of the degree of supercooling after heating the PCM over 70 °C [155]. In addition to
 607 the heating temperature value, Figure 24 shows that the time held at this temperature also
 608 affects the degree of supercooling [161]. Therefore, when integrating PCM in an application,
 609 attention should be given to the PCM overheating problem. All other PCM thermophysical
 610 characteristics such as latent heat, melting temperature, thermal conductivity, thermal
 611 expansion coefficient, etc. are likely in a way or another to change the degree of
 612 supercooling.



613

614 *Figure 23 Variation of degree of supercooling as a function of (a) particle size and (b)*
 615 *overheating. Reproduced with permission from ref. [155], Copyright (2018) with permission*
 616 *from Elsevier*



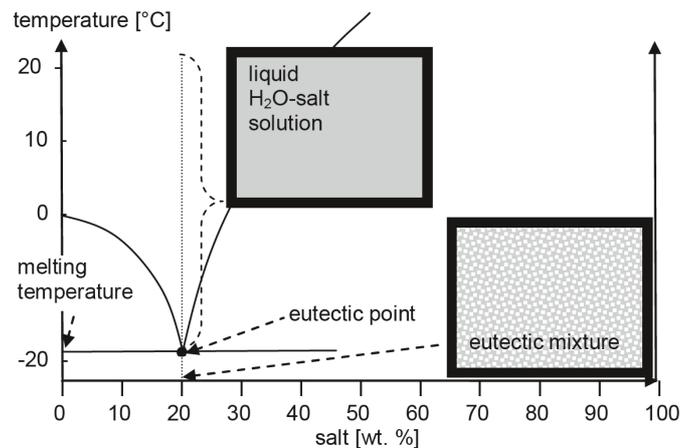
617

618 *Figure 24 Increase in the degree of supercooling as a function of holding time. Reproduced*
 619 *with permission from ref. [161], Copyright (1996) with permission from Elsevier*

6. Reduction of phase segregation

6.1. Mechanism of phase segregation

622 Heating a pure solid material i.e. a homogeneous material composed of only one type of
623 atom, molecule, or compound, above its melting temperature gives a homogeneous liquid.
624 Solidifying the obtained liquid again yields a solid with the same homogeneous composition,
625 the same phase change temperature and the same phase change enthalpy. In this case, the
626 material is congruently melting. A mixture of two or more materials does not necessarily
627 keep the same behavior under successive heating/cooling processes. Not every multiple
628 component material undergoes phase segregation. Eutectic mixtures solidify simultaneously
629 at the eutectic point and give different solid-phase compositions having the same
630 characteristics as the homogeneous mixture. The eutectic point depends on the concentration
631 of the components in the mixture and on the melting temperature as shown in Figure 25. For
632 that reason, a PCM undergoing supercooling risks having phase segregation. In this case, the
633 eutectic mixture is not a congruent melting mixture.

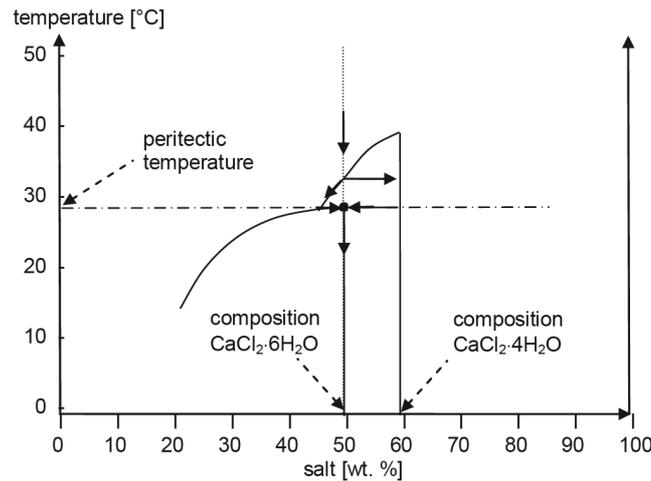


634

635 *Figure 25 Congruent melting of the eutectic mixture having 20 wt % salt. Reproduced with*
636 *permission from ref. [136], Copyright (2008) with permission from Elsevier*

637 The behavior of salt hydrates is more complicated than the before mentioned. Using
638 $\text{Salt} \cdot n\text{H}_2\text{O}$ with different values of n yields different phase diagrams. For example, the
639 cooling of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ does not directly form solid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Instead, a solid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
640 and a liquid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ are formed first, due to the low concentration of salt $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
641 which gives a similar phase change temperature as the solid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, as shown in Figure
642 26. At this temperature, the solid and liquid phases react to give a single solid solution. The

643 transformation is known as a *peritectic* transformation which is the transformation of a solid
644 and a liquid to a solid. Above the *peritectic* temperature, a homogenous liquid mixture is
645 obtained. The thermophysical properties of the PCM change during the phase change, which
646 is a disadvantage in regard to phase segregation. If the cooling rate is low, phase segregation
647 of the liquid and solid phases may happen due to density differences. This type of melting is
648 called semi-congruent melting.



649

650 *Figure 26 incongruent melting of hydrated calcium chloride. Reproduced with permission*
651 *from ref. [136], Copyright (2008) with permission from Elsevier*

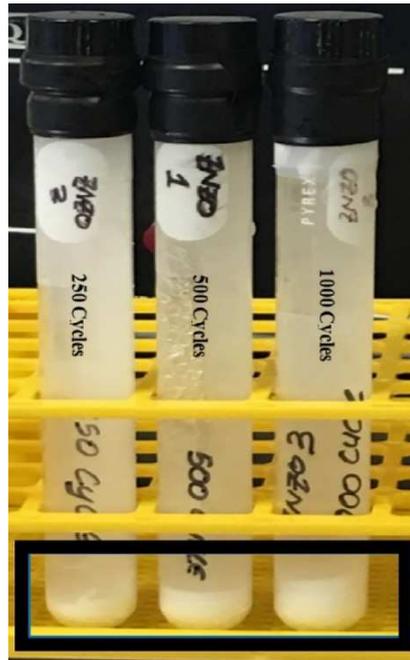
652 **6.2. Methods to reduce phase segregation**

653 **6.2.1. Effect of the mixture homogeneity**

654 Phase segregation causes a change in thermophysical properties of the PCM that can ruin the
655 system. Several solutions exist to reduce phase segregation. In the preparation of a composite
656 PCM, reducing the density difference among the used compounds may reduce the risk of
657 phase segregation. Indeed, one basic cause for phase segregation is the difference in gravity
658 forces applied within a nonhomogeneous PCM [162,163]. In mixtures of PCM, another cause
659 for phase segregation is the difference in melting temperatures of the used PCM, which leads
660 to incongruent melting [162]. For a given PCM, one solution to insure the homogeneity of a
661 mixture is to use a rotating container [163].

662 6.2.2. *Effect of thickening agents*

663 Thickening agents increase the viscosity of the mixture without changing its properties. The
664 experiment held by Ryu *et al.* [164] shows that using 3 to 5 wt% thickening agent on an
665 inorganic PCM was able to remove phase segregation. Zinc nitrate hexahydrate was tested by
666 Kumar *et al.* [165] as a PCM with a high degree of supercooling. By adding 5 wt% zinc oxide
667 nucleating additives, the PCM displayed phase segregation as shown in Figure 27.



668

669 *Figure 27 Phase segregation after 250, 500 and 1000 thermal cycles of repeated melting and*
670 *solidification from left to right respectively. Reproduced with permission from ref. [165],*
671 *Copyright (2018) with permission from Elsevier*

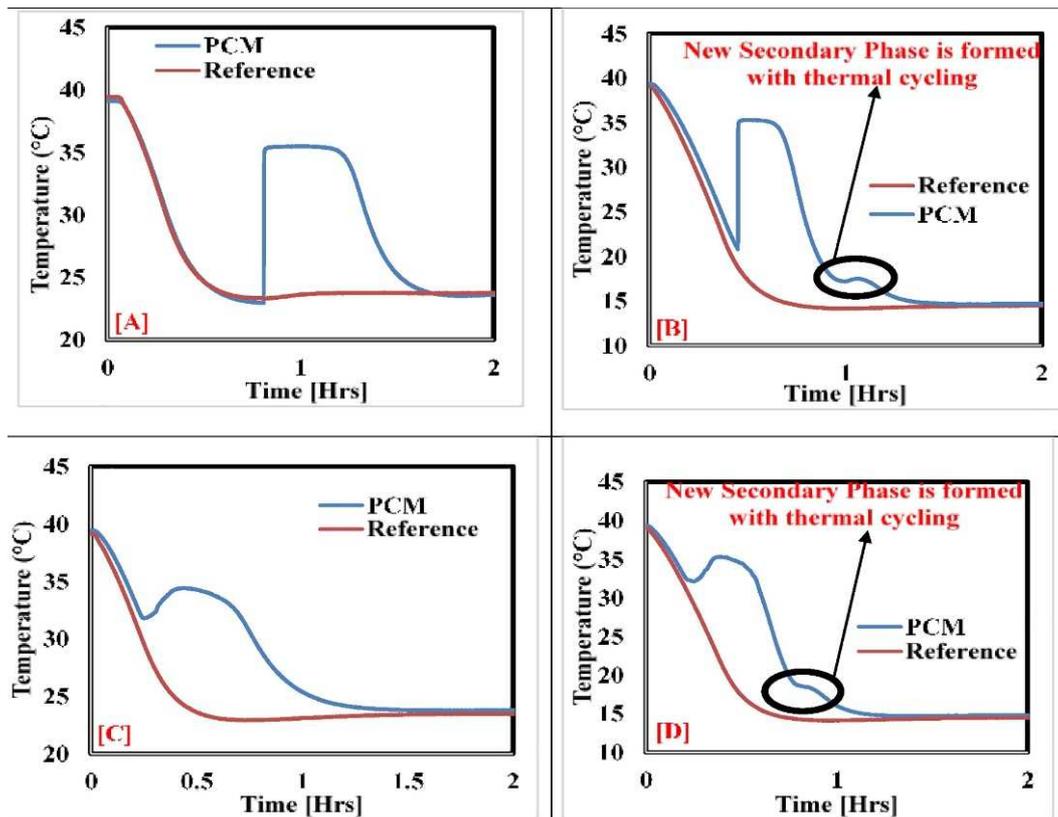
672 In the same experiment [165], using additives (zinc hydroxyl nitrate) allowed to decrease the
673 supercooling degree and the energy loss, but not to eliminate phase segregation after 750
674 cycles of melting/solidification.

675 6.2.3. *Effect of the cooling rate*

676 The cooling rate has a direct effect on the presence of phase segregation. Reducing the
677 cooling rate may reduce phase segregation. Figure 28 shows no phase segregation when
678 cooling a zinc nitrate hexahydrate PCM at 24 °C (cases A and C). However, phase
679 segregation appears when using a cooling fluid of temperature 15 °C, regardless of the

680 presence of additives (cases B and D). An average value of energy loss due to phase
 681 segregation after 750 cycles was estimated at 30kJ/kg.

682 Other methods to reduce phase segregation include gelling and adding water to the PCM
 683 mixture. Table 1 summarizes the most used methods to overcome phase segregation. For
 684 each method used, there are several advantages and disadvantages.



685
 686 *Figure 28 Cooling curves of zinc nitrate hexahydrate after 750 cycles for the cases with*
 687 *additives (C and D) and without additives (A and B) upon cooling at 24 °C (case A and C)*
 688 *and 15 °C (case B and D). Reproduced with permission from ref. [165], Copyright (2018)*
 689 *with permission from Elsevier*

690 Table 1 Advantages and disadvantages of different methods to reduce phase segregation

| Method | Advantages | Disadvantages |
|--------|---|---|
| Mixing | Fast process | Needed equipment to perform this method |
| | No need to wait for diffusion to obtain a homogeneous mixture | |

| | | |
|-------------------------------|--|---|
| Add water (for salt hydrates) | Faster homogenization by diffusion of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ | Decrease storage density Increase phase change range |
| Diffusion process | Natural process | Efficient for small scale |
| Gelling | Forms a network that holds the different phases together at the microscopic scale | |
| Thickening agents | Increase viscosity of the liquid Segregation is prevented until solidification ends | |
| Adding other materials | Modify phase diagram to obtain congruent melting No restrictions Enhance behavior of PCM | |

691 7. Mathematical modelling of pure and composite PCM

692 7.1. Modelling of pure PCM

693 7.1.1. *Stefan problem*

694 Numerous studies deal with the numerical modelling of a PCM in the melting and
695 solidification processes. They show that convection heat transfer significantly affects the
696 melting process, while the conduction heat transfer is dominant in the solidification of the
697 material. Phase change systems characteristics are difficult to predict due to their non-linear
698 nature and the presence of moving interfaces. This problem is known as the Stefan problem,
699 which assumes the presence of two main domains, the liquid and the solid region, separated
700 by a moving interface [166].

701 One-dimensional mathematical models can be formulated using assumptions such as a
702 constant latent heat, fixed melting temperature, without mushy zone and without super-
703 cooling phenomena [167].

704 Heat transfer problem in the solid part is expressed through the heat diffusion equation:

705
$$\rho C_S \frac{\partial T_S}{\partial t} = \nabla \cdot (\lambda_S \nabla T_S) + \dot{q}_{v,S} \quad \forall \mathbf{x} \in D_S \quad (1)$$

706 which also applies in the liquid part:

707
$$\rho C_L \frac{\partial T_L}{\partial t} = \nabla \cdot (\lambda_L \nabla T_L) + \dot{q}_{v,L} \quad \forall \mathbf{x} \in D_L \quad (2)$$

708 Heat balance at the sharp front interface, namely the Stefan condition, reads:

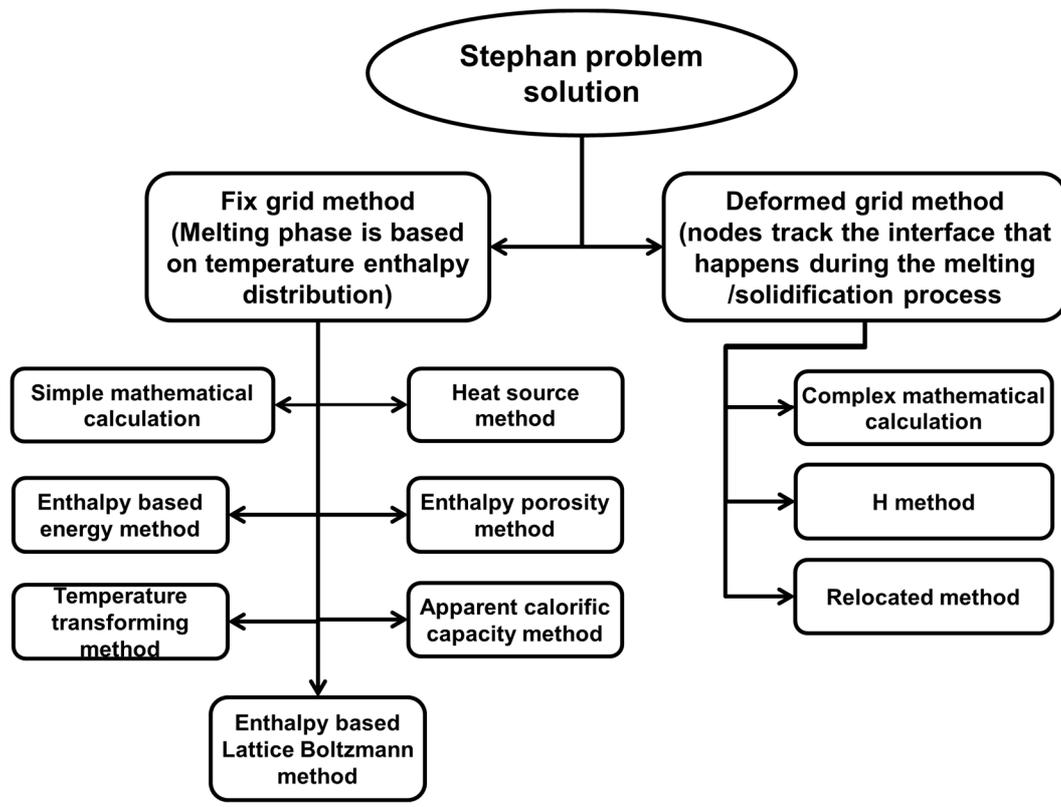
709
$$\lambda_S \nabla T_S \cdot \mathbf{n} - \lambda_L \nabla T_L \cdot \mathbf{n} = \rho L \frac{d\bar{X}}{dt} \cdot \mathbf{n} \quad \forall \bar{X} \in D_{interface} \quad (3)$$

710 where ρ is the density, T_S and T_L are the temperatures of the PCM in solid and liquid phase
 711 respectively and $\lambda_S = \lambda_S(T_S, \mathbf{x})$ and $\lambda_L = \lambda_L(T_L, \mathbf{x})$ are the thermal conductivities of the solid
 712 and liquid phase respectively. $C_S = C_S(T_S, \mathbf{x})$ and $C_L = C_L(T_L, \mathbf{x})$ are the heat capacities of the
 713 solid and liquid phase respectively and $\dot{q}_{v,S}$ and $\dot{q}_{v,L}$ are source terms. Besides, t stands for
 714 the time, \mathbf{n} for the unit normal vector on the interface, $\frac{d\bar{X}}{dt}$ for its velocity and L for the latent
 715 heat.

716 Research has overcome the Stefan problem by assuming a simplified 1D model to determine
 717 the temperature range in the liquid, solid and interface zones [168–170]. Further research
 718 [171] studied the three distinct regions in a PCM (solid, liquid and mushy zone) by using
 719 computational fluid dynamics. Sciacovelli *et al.* [172] showed the importance of taking into
 720 account both the conduction and convection heat transfer modes since they can both affect
 721 the phase change process of the material.

722 In general, two separate methods, the fixed grid method and the deforming grid method, can
 723 be used to numerically implement the set of partial differential equations governing the phase
 724 change. The first one leads to straightforward mathematical calculations and determines the
 725 melting front by the temperature or the enthalpy distribution. In this approach, fixed grid
 726 nodes can help to track the liquid-solid interface. These models were first described in [173–
 727 175] and are now very popular among researchers, due to their easy and straightforward
 728 implementation. The second method yields a more complex implementation since the grid
 729 must deform to track the solid-liquid interface. Besides, it requires the existence of a liquid
 730 layer at the start of the simulation. Two main approaches are used within the deforming grid
 731 method, namely the h -approach and the r -approach. The h -approach starts with a uniform

732 grid and adds or removes mesh points to improve accuracy with each iteration, necessitating
 733 the use of data structures [176]. The r-approach also begins with a uniform grid, but it shifts
 734 the mesh at each iteration while maintaining the number and topology of the mesh fixed
 735 [177,178],[179,180]. In the context of the fixed grid method, many models can be found in
 736 the literature, including the enthalpy-porosity formulation, the temperature-transforming
 737 model (TTM), the analogous thermal capacity method, the Lattice Boltzmann Method
 738 (LBM), which are described in the following sections. Figure 29 summarizes the most
 739 common methods used to solve the Stephan problem.



740

741 *Figure 29 Diagram resuming the different methods used to model the phase change process*

742 **7.1.2. Enthalpy-based energy method**

743 Eyres *et al.* [175] proposed the enthalpy-based energy method to solve diffusion phase
 744 change problems. The equations of this method are based on the basic equations of heat
 745 conduction. The enthalpy $f(T)$ of a PCM can be calculated by applying equations (4) and (5)
 746 respectively for an isothermal and a non-isothermal phase change, assuming a constant heat
 747 capacity and a linear expression for $f(T)$ in each phase:

748
$$f(T) = \begin{cases} \rho C_s T & \text{if } T \leq T_m \\ \rho(C_s T_m + L + C_L(T - T_m)) & \text{if } T > T_m \end{cases} \quad (4)$$

749
$$f(T) = \begin{cases} \rho C_s T & \text{if } T \leq T_S \\ \rho \left(C_s T_S + L \frac{T - T_S}{T_L - T_S} \right) & \text{if } T_S < T \leq T_L \\ \rho(C_s T_S + L + C_L(T - T_L)) & \text{if } T > T_L \end{cases} \quad (5)$$

750 Voller *et al.* [181–183] used this method while solving a 1D problem with an isothermal
 751 phase change. Costa *et al.* [184] also validated the method in presence of conduction and
 752 convection by using the finite difference method. Stephan's problem was also solved by the
 753 enthalpy method by using Neumann-type boundary conditions and the finite difference
 754 method [185]. Vyshak and Jilani [186] modified this method by decoupling the temperature
 755 from the liquid fraction.

756 **7.1.3. Temperature transforming model (TTM)**

757 Cao and Faghri [187] suggested the TTM include the natural convection effect while
 758 modeling the phase-change problem. Except for the energy equations, which are different
 759 from the enthalpy-based energy equations, the equations are similar to that the fluid flow
 760 models. The governing equations are as follows:

761 Continuity equation:

762
$$\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0 \quad (6)$$

763 Momentum equation:

764
$$\frac{\partial(\rho u)}{\partial t} + \frac{\partial(\rho u u)}{\partial x} + \frac{\partial(\rho v u)}{\partial y} = -\frac{\partial p}{\partial x} + \frac{\partial}{\partial x} \left(\mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad (7)$$

765
$$\frac{\partial(\rho v)}{\partial t} + \frac{\partial(\rho u v)}{\partial x} + \frac{\partial(\rho v v)}{\partial y} = -\frac{\partial p}{\partial y} + \frac{\partial}{\partial x} \left(\mu \frac{\partial v}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial v}{\partial y} \right) + \rho g [\beta(T^*) - 1] \quad (8)$$

766 Energy equation:

767
$$\partial \frac{\rho C T^*}{\partial t} + \partial \frac{\rho u C T^*}{\partial x} + \partial \frac{\rho v C T^*}{\partial y} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T^*}{\partial x} \right) + \frac{\partial}{\partial y} \left(\lambda \frac{\partial T^*}{\partial y} \right) - \partial \frac{\rho C s}{\partial t} - \partial \frac{\rho u C s}{\partial x} - \partial \frac{\rho v C s}{\partial y} \quad (9)$$

$$768 \quad \begin{cases} c = C_S & \text{if } T^* < -\Delta T \\ c = \frac{(C_S+C_L)}{2} + \frac{h}{2\Delta T} & \text{if } -\Delta T \leq T^* \leq \Delta T \\ c = C_L & \text{if } T^* > \Delta T \end{cases} \quad (10)$$

$$769 \quad \begin{cases} s = \Delta T & \text{if } T^* < -\Delta T \\ s = \Delta T & \text{if } -\Delta T \leq T^* \leq \Delta T \\ s = \left(\frac{C_S}{C_L}\right) \Delta T + \frac{h}{c_L} & \text{if } T^* > \Delta T \end{cases} \quad (11)$$

$$770 \quad \begin{cases} \lambda = \lambda_S & \text{if } T^* < -\Delta T \\ \lambda = \lambda_S + \frac{(\lambda_L-\lambda_S)(T^*+\Delta T)}{2\Delta T} & \text{if } -\Delta T \leq T^* \leq \Delta T \\ \lambda = \lambda_L & \text{if } T^* > \Delta T \end{cases} \quad (12)$$

771 with u the velocity in x-direction, v the velocity in the y-direction, T^* the scaled temperature
 772 defined as $T^* = T - T_m$, β the thermal expansion coefficient, h is the latent heat, ΔT the half
 773 range of temperatures in the mushy zone, and C the specific heat. $T^* < -\Delta T$ gives the
 774 temperature of the solid zone, $-\Delta T \leq T^* \leq \Delta T$ the temperature of the mushy zone, and
 775 $T^* > \Delta T$ the temperature of the liquid zone.

776 This method was used by Wang et al [188] to study the melting process in a 2D square
 777 geometry in presence of natural convection. Different researchers [188–190] proposed a
 778 velocity correction in the solid medium and used a consistent update technique (CUT)
 779 algorithm to solve the velocity-pressure coupling. Corrections were proposed to obtain zero
 780 velocity in the solid zone and were referred to as switch-off, ramped switch-off, variable
 781 viscosity and Darcy source term techniques.

782 7.1.4. **Enthalpy-Porosity method**

783 The enthalpy-porosity method is one of the most widely used approaches for modeling phase-
 784 change problems in presence of natural convection [191]. In this method, the liquid fraction is
 785 determined at each iteration. It is 1 in the liquid phase and 0 in the solid phase. Liquid
 786 Fractions between 0 and 1 are obtained for the mushy zone in quasi-porous mediums [192].
 787 The momentum equations are the same as in the TTM method but the method adds two
 788 porosity functions named Darcy terms A_u and A_v that allow reducing the velocities gradually
 789 in the solid phase. The energy and the total enthalpy in this method can be expressed by:

790 Energy equation:

$$791 \quad \partial \frac{\rho h}{\partial t} + \partial \frac{\rho u h}{\partial x} + \partial \frac{\rho v h}{\partial y} = \frac{\partial}{\partial x} \left(\alpha \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(\alpha \frac{\partial h}{\partial y} \right) - \partial \frac{\rho \Delta H}{\partial t} - \partial \frac{\rho \Delta H}{\partial x} - \partial \frac{\rho \Delta H}{\partial y} \quad (13)$$

792 Total enthalpy:

$$793 \quad H = h + f_L \cdot L \quad (14)$$

794 where h is the sensible enthalpy, f_L is the liquid fraction and L is the latent heat. The change
 795 in density value between the solid and liquid phases is calculated by $\rho = \rho_L f_L + (1 - f_L) \rho_S$,
 796 the thermal conductivity by $\lambda = \lambda_L f_L + (1 - f_L) \lambda_S$ and the specific heat by $C = C_L f_L +$
 797 $(1 - f_L) C_S$.

798 7.1.5. *Enthalpy based -Lattice Boltzmann Method*

799 Lattice Boltzmann method (LBM) was used to analyze the melting process in porous
 800 materials that includes natural convection [193–195]. This method offers numerical stability
 801 and high accuracy. It can be set up for complex geometries. The LBM is advantageous since
 802 it has a high parallel implementation of the algorithm [196]. The energy-based method is
 803 applied to model the phase change problem and then the LBM comes to solve the fluid flow
 804 equations. The Boltzmann equation reads:

$$805 \quad \frac{\partial f}{\partial t} + \frac{d\bar{x}}{dt} \cdot \nabla f = \Omega \quad (15)$$

806 where f is the one-particle distribution function at time t , and Ω is an integrodifferential
 807 component that relates to the collision operation. Collisions are responsible for making the
 808 distribution function close to the equilibrium distribution. Gross *et al.* [197] introduced a new
 809 model that approaches closer to the equilibrium by adding a constant relaxation time τ_f that
 810 concerns the viscosity of the fluid. The equation (15) becomes:

$$811 \quad \frac{\partial f}{\partial t} + e \cdot \nabla f = \frac{1}{\tau_f} (f^{eq} - f) \quad (16)$$

812 where f^{eq} is an equilibrium distribution function and e the velocity at time t . The LBM offers
 813 solutions for complex problems by using the morphological development of complex
 814 boundaries [198]. In this method, both micro and mesoscale physics are incorporated and the
 815 explicit calculation, leading to time-efficient simulations. Besides, large-scale computational
 816 problems can be addressed by LBM.

817 The mathematical description of microscopic and mesoscopic phenomena in PCM can face
818 many challenges as described by Chatterje [198]. The accuracy of the performance of LBM
819 simulations is influenced by the determination of the thermophysical properties of the
820 substance and the uncertainty of the boundary between the two phases.

821 **7.2. Modelling of enhanced PCM**

822 **7.2.1. PCM with metallic nanoparticles foams and structures**

823 As shown in Sections 3 and 4, the metallic additives in a PCM are likely to enhance its
824 thermal conductivity and its melting enthalpy. These two parameters can affect the
825 performance of the material since the heat storage rate and the heat storage density are
826 determined respectively by the thermal conductivity and the melting enthalpy. Metallic
827 nanoparticles, foams and structures are known for their strong ability to blend into the host
828 material. In order to study the PCM melting enthalpy reduction produced by the use of
829 nanoparticles, Zhao *et al.* [199] adopted the molecular dynamics method to reveal and
830 analyze the behavior of the material. The first model contained one CuO nanoparticle with
831 different dimensions and 200 n-octadecane paraffin molecules. The interaction between
832 molecules was studied based on CHARMM (Chemistry at HARvard Macromolecular
833 Mechanics) equations [200]. The NPT, or isothermal-isobaric ensemble, and the NVE, or
834 micro-canonical ensemble, were used in the simulation. The results showed that the melting
835 enthalpy quickly decreased with the increase of nanoparticle mass fractions. For 19.72 wt%
836 nanoparticles, the melting enthalpy of the nanoparticle/paraffin decreased by around 51.5 %.
837 As the mass fraction increased, the influence of molecule interactions decreased. It was found
838 that the melting enthalpy reduction was caused by the presence of a dense phase surrounding
839 the nanoparticle [199].

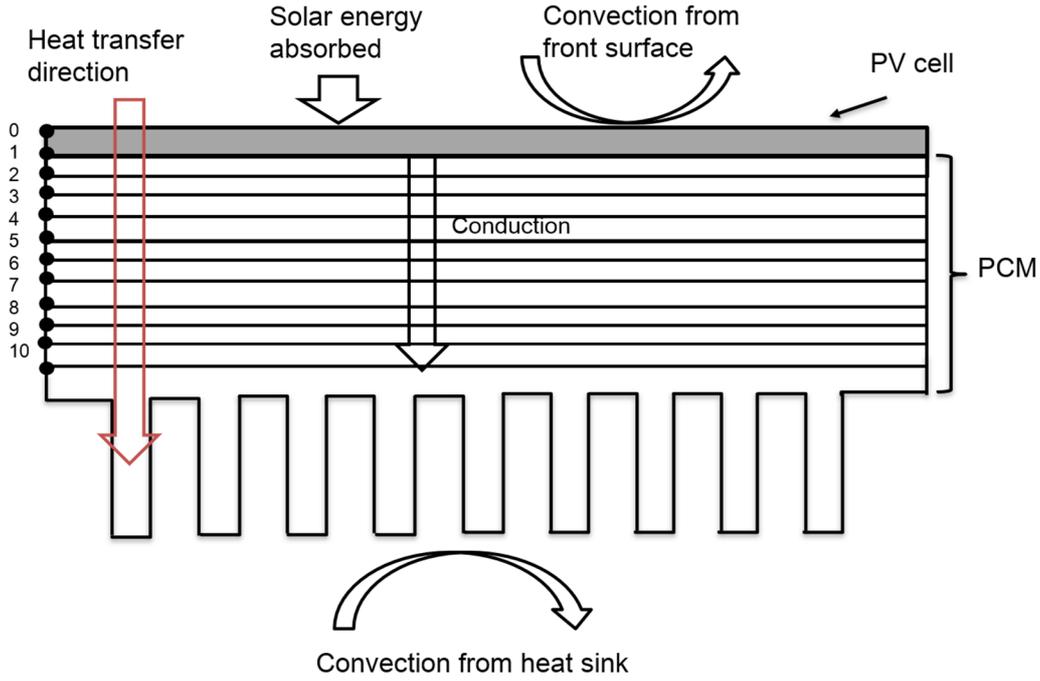
840 Sciacovelli *et al.* [172] also investigated the thermal properties enhancement of a PCM by
841 nanoparticles (copper powder) dispersion. The simulations were done using a CFD model
842 using the enthalpy method. Results presented an increase in the thermal performance of the
843 material. The melting time was decreased by 15% when the heat flux increased by 16% with
844 4% of particle volume fraction. Besides, the nanoparticles affected the phase change process
845 since it was noticed a melting time reduction when the mass flow rate was increased. Similar
846 simulations were carried out by Sheikholeslami *et al.* [201] to model the melting process with
847 nanoparticles using the enthalpy-porosity method implemented in ANSYS FLUENT

848 software. The properties of the nanoparticle-enhanced PCM (NEPCM) were calculated by
849 using the single-phase model equations. This study confirmed the influence of nanoparticles
850 on the thermal behavior of the material. The NEPCM melted faster than the PCM. It was
851 clear that the nanoparticles increased the heat transfer and the melting time was shorter than
852 in the PCM.

853 Di Giorgio *et al.* [202] developed a mathematical model to study the phase change process
854 and characterize a metallic foam/PCM composite. The model was created using both the
855 volume of fluid (VOF) approach and the volume average technique (VAT). The liquid PCM
856 was assumed incompressible, Newtonian, and depending on the Boussinesq approximation.
857 Besides, the density of the paraffin was supposed constant during melting. The volume-
858 averaged equations used the continuity equation, the averaged momentum balance equation,
859 and the energy balance equation. The heat transfer coefficient for the model without
860 convection was calculated by:

$$861 \quad U = \frac{1}{t_f} \int_0^{t_f} \frac{\dot{q}_{p-f}(t)}{T_f(t) - T_{PCM}(t)} dt \quad (17)$$

862 where $\dot{q}_{p-f}(t)$ is the heat flux between the PCM and the metal additive, $T_f(t)$ and $T_{PCM}(t)$
863 are the temperatures of the foam and the PCM, respectively. For the same model but with
864 convection, the heat transfer coefficient was found by calculating the velocity in the first
865 iteration and using it as an input condition for the simulation with atmospheric pressure at the
866 outlet. Moreover, the researcher considered a uniform temperature for the energy equations.
867 This system was solved by using COMSOL software. The numerical model findings were
868 compared to the experimental results and showed good agreement. Atkin and Farid [203]
869 estimated the thermal performance and the viability of using an external finned heat sink
870 through a MATLAB model. One of the studied cases was that of a photovoltaic cell
871 combined with about 30 mm thick PCM infused graphite and aluminum heat sink as shown
872 in Figure 30. The finned heat sink increased the effective area from 0.052 to 0.238 m²,
873 resulting in a surface ratio of 4.58.



874

875 *Figure 30 The energy flow scheme of a PV with a finned heat sink. Reproduced with*
 876 *permission from ref. [203], Copyright (2015) with permission from Elsevier*

877 The equations used to model the temperatures at all points and the effective specific heat
 878 capacity were as follow:

879
$$\eta Q_{in} = UA(T_0^P - T_\infty) + \rho_{al} V_{al} C_{al} \frac{T_0^{P+\Delta t} - T_0^P}{\Delta t} + \lambda_{al} A \frac{T_0^P - T_1^P}{\Delta x} \quad \text{at point 0} \quad (18)$$

880
$$\lambda_{al} A \frac{T_0^P - T_1^P}{\Delta x} = \rho_{PCM} V_1 C_{PCM} \frac{T_1^{P+\Delta t} - T_1^P}{\Delta t} + \lambda_{PCM} A \frac{T_1^P - T_2^P}{\Delta x} \quad \text{at point 1} \quad (19)$$

881
$$\lambda_{PCM} A \frac{T_{n-1}^P - T_n^P}{\Delta x_{(n-1)-n}} = \rho_{PCM} V_n C_{PCM} \frac{T_n^{P+\Delta t} - T_n^P}{\Delta t} + \lambda_{PCM} A \frac{T_n^P - T_{n+1}^P}{\Delta x_{n-(n+1)}} \quad \text{for points 2 to 9} \quad (20)$$

882
$$\lambda_{PCM} A \frac{T_9^P - T_{10}^P}{\Delta x_{9-10}} = \rho_{PCM} V_n C_{PCM} \frac{T_n^{P+\Delta t} - T_n^P}{\Delta t} + UA_f \eta_f (T_{10}^P - T_\infty) \quad \text{at point 10} \quad (21)$$

883
$$\begin{cases} C = C_{p0} & \text{if } T \leq T_{m1} \text{ and } T > T_{m2} \\ C = C_{p0} + \frac{4\Delta H - 4C_{p0}(T_{m1} - T_{m2})}{(T_{m1} - T_{m2})^2} (T - T_{m1}) & \text{if } T_{m1} < T \leq \frac{T_{m1} + T_{m2}}{2} \\ C = C_{p0} + \frac{4\Delta H - 4C_{p0}(T_{m2} - T_{m1})}{(T_{m1} - T_{m2})^2} (T_{m2} - T) & \text{if } \frac{T_{m1} + T_{m2}}{2} < T \leq T_{m2} \end{cases} \quad (22)$$

884 where Q_{in} stands for the solar radiation, η is the solar absorptance, A and A_f are the cross-
885 section area and the surface area of fins, respectively, η_f is the fin efficiency, T_n^P and T_∞ are
886 respectively the solar panel temperature and the environment temperature. T_{m1} and T_{m2} are
887 respectively the temperature at the beginning of the melting process and the end of the
888 process. Equation (18) was used to calculate the temperature at point 0, equation (19) at
889 point 1, equation (20) at points 2 to 9 and equation (21) at point 10. The researcher assumed
890 that the heat transfer is unidirectional, the thermal conductivity and the density are constant
891 and the heat sink is in perfect contact with the solar panel and the PCM. A similar study was
892 done by Zhang *et al.* [203]. They proposed a combination of heat pipes with fins and copper
893 foam to investigate its performance by using the effective heat capacity method and the
894 thermal resistance network. In the same way, Hu *et al.* [204] simulated numerically the
895 thermal behavior of a PCM infiltrated with metallic foam having low porosity. The researcher
896 solved the continuity, energy and momentum equations by using CFD Fluent 18.0 package.
897 The metal-based additives revealed excellent thermal conductivity enhancement. It was
898 noticed by comparing the types of metal additives that the foam could improve the
899 conductivity better than the other types owing to its high porosity and low density.

900 7.2.2. *PCM with carbon-based additives*

901 Carbon-based additives such as graphite, graphene, carbon fiber and carbon nanotube, with
902 their different morphology and microscopic structure, have been used owing to their high
903 thermal conductivity, their low density and their chemical stability [205]. Ling *et al.* [206]
904 studied an organic PCM by using expanded graphite. The thermal conductivity of the
905 composite was predicted by applying a simple equation based on the bulk density and the
906 expanded graphite mass fraction at the ambient temperature. The final equation for the
907 effective thermal conductivity used in the model reads as follow:

$$908 \quad \lambda_{eff} = \frac{\lambda_G \rho_C \varphi}{\rho_G} \quad (23)$$

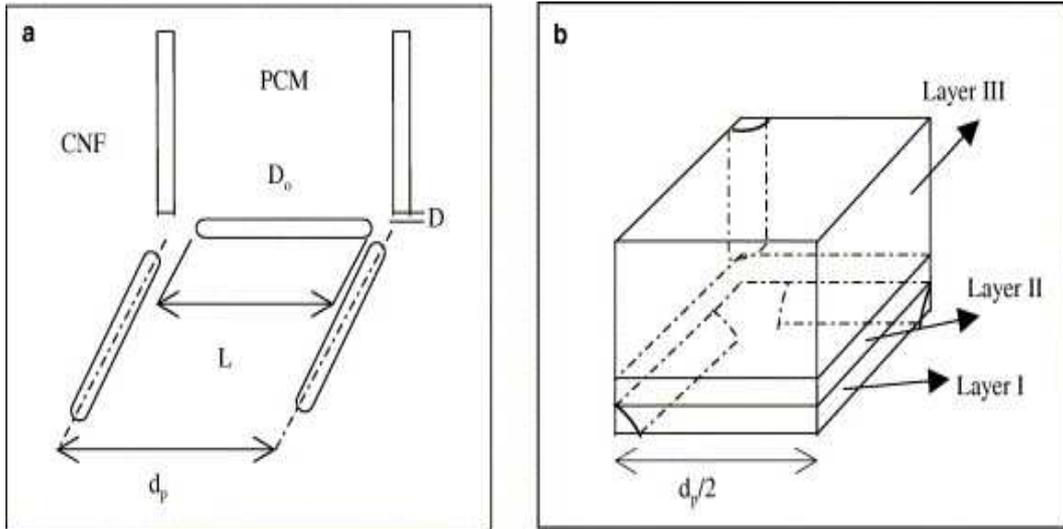
909 where λ_G is the thermal conductivity of the graphite, φ is the mass fraction of the graphite,
910 ρ_C and ρ_G are the bulk density of the composite and the graphite, respectively. Besides,
911 experimental work was achieved to characterize the material with 25% and 35% content of
912 graphite and to validate the numerical model. Results showed that the thermal conductivity of
913 the composite with 35% of graphite is greater by 30% than the composite with 25% of

914 graphite. This model can be applied to low thermal conductivity PCM with expanded
 915 composites.

916 Elgafi *et al.* [102] also numerically estimated the thermal conductivity of a carbon nanofibers
 917 PCM composite and validated the results with an experiment. The analytical model was
 918 based on a one-dimensional heat conduction process for a material with low conductivity.
 919 Several assumptions were considered such as the uniform distribution of the fibers in the
 920 PCM (Figure 31a). The unit cell with symmetry consideration consists of three layers as
 921 shown in Figure 31b. The first (I) was composed of PCM and two carbon nanofibers. The
 922 second (II) was composed of pure PCM and the third (III) was filled with one carbon
 923 nanofiber and PCM. The CNFs are cylinders that have an average outer diameter, D_o , inner
 924 diameter, D_i , and length L . Also, it is assumed that $D_i = D_o/4$ and the inner space of the CNFs
 925 is filled with air. the CNFs are perpendicular to each other and separated by a distance $D =$
 926 $D_o/4$ from their perpendicular ends and by a distance $d_p = (L + 3D_o/2)$ between their axial
 927 axis. The effective thermal conductivity of the material was estimated as the resultant of the
 928 thermal conductivities of the three layers. The final equation of the model is as follow:

929
$$\lambda_{eff} = \frac{2 \lambda_I \lambda_{II} \lambda_{III}}{2 \frac{D_o}{d_p} \lambda_{II} \lambda_{III} + \frac{D_o}{d_p} \lambda_I \lambda_{III} + (2 - 3 \frac{D_o}{d_p}) \lambda_I \lambda_{II}} \quad (24)$$

930 The model's findings were in strong agreement with the results of the experiments. During
 931 the study, it was noticed that the thermal conductivity of the tested composite was enhanced
 932 since the cooling rate was increased.



933

934 *Figure 31 (a) Carbon nanofibers distribution of the composite cell (b) and model of the unit*
 935 *cell. Reproduced with permission from ref. [102], Copyright (2015) with permission from*
 936 *Elsevier*

937 Shaikh *et al.* [130] formulated a mathematical model as presented in equation (25), to
 938 calculate the latent energy of the carbon nanotubes, multiwall CNT and carbon nanofibers
 939 composites. As a first step, the researchers calculated the interaction between the PCM
 940 molecules and the carbon nanoparticles by using Matlab software as an equation solver.
 941 Then, a study was carried out to estimate the latent energy of the composite material as a
 942 function of the volume fraction of its components.

943
$$Q = m_{PCM}L + m_{carbon}\Delta H_{max} \quad (25)$$

944 where Q is the total latent energy, L is the latent heat of the PCM, m_{PCM} and m_{carbon} are the
 945 mass of the PCM and the carbon nanoparticles, respectively, and ΔH_{max} is maximum heat
 946 capacity. The findings concerning the latent energy determined by using the analytical model
 947 agreed well with the experimental results. This theoretical study proves the theory of
 948 interaction between particles that can affect the latent heat of the PCM composite. The model
 949 can be used for all types of carbon nanoparticle additives. Kant *et al.* [31] investigated the
 950 melting of graphene dispersed PCM in an aluminum cavity. Three distinct volume fractions
 951 of graphene 1%, 3%, and 5% were considered. The effective thermal conductivity was
 952 believed to be the sum of thermal conductivity due to the Brownian motion of nanoparticles
 953 and thermal conductivity due to stagnation. The considered equations were solved by using
 954 the heat transfer and fluid flow module of COMSOL software. The thermal conductivity of

955 the graphene/PCM hybrid was increased with the three different volume fractions, resulting
 956 in improved heat flow in the cavity. Li *et al.* [207] used the T-history method [208] to
 957 determine the thermophysical properties of a paraffin-based composite PCM with different
 958 concentrations of graphite. The model is expressed by the following equations that can give
 959 the effective specific heat, thermal conductivity, and latent heat:

$$960 \quad C_S = \left(\frac{m_0 C_0 + m_w C_w}{m_{PCM}} \right) \times \left(\frac{A_3}{A_2} \right) - \frac{m_0}{m_{PCM}} C_0 \quad (26)$$

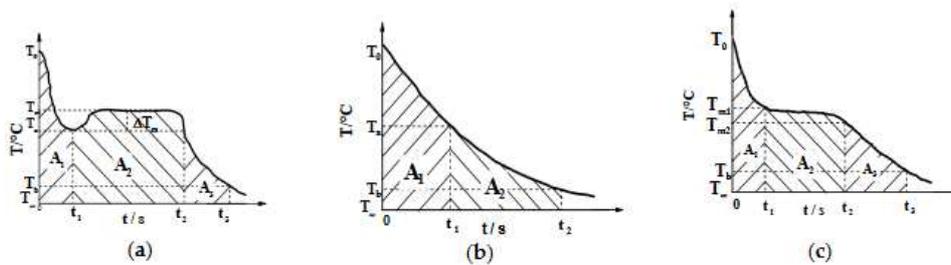
$$961 \quad C_L = \left(\frac{m_0 C_0 + m_w C_w}{m_{PCM}} \right) \times \left(\frac{A_1}{A_0} \right) - \frac{m_0}{m_{PCM}} C_0 \quad (27)$$

$$962 \quad \lambda_s = \frac{1}{1 + \frac{C_S(T_m - T_\infty)}{L}} \times \frac{0.25}{\frac{t_f(T_m - T_\infty)}{\rho R^2 L} + \frac{1}{2hR}} \quad (28)$$

$$963 \quad L = \left(\frac{m_0 C_0 + m_w C_w}{m_{PCM}} \right) \times \left(\frac{A_2}{A_0} \right) \times (T_0 - T_{m1}) - \frac{m_0 C_0 (T_{m1} - T_{m2})}{m_{PCM}} \quad (29)$$

964 where T_0 is the initial temperature, m_0 and m_w are respectively, the mass of the tube filled
 965 with the composite PCM and the water mass. R is the radius of the tube, t_f is the time of the
 966 solidification. A is the area of the different regions surrounded by the cooling curve as shown
 967 in Figure 32. The findings of the numerical model were in agreement with the experimental
 968 results.

969 From the recent studies, it is clear that carbon-based additives can improve the conductivity
 970 of the PCM. However, studies showed that the thermal properties of the carbon additives
 971 depend on their aspect ratio. Moreover, the carbon-based additives geometry, density and the
 972 method of preparation of the carbon-based composites can also affect the thermal properties
 973 of the ensemble.



974

975 *Figure 32 Surrounding region areas A of three PCM cooling curves with (a) supercooling,*
 976 *(b) water and (c) without supercooling. Permission not required [207].*

977 **8. Outlook**

978 To date, extensive research has been conducted worldwide to improve the thermophysical
979 properties of PCM in order to promote its use as an efficient thermal energy storage medium.
980 Overall, the findings of the literature review revealed that improving the thermophysical
981 properties of PCM improves the thermal performance of energy storage devices. Several
982 critical issues, however, were identified, including the selection of appropriate additives and
983 concentrations that could meet all of the desired properties. According to the findings, when
984 non-carbon-based additives are added to improve the thermal conductivity of composite
985 PCM, the latent heat of fusion decreases for the same volume of PCM. This improves heat
986 transfer for faster PCM charging and discharging, but decreases the amount of thermal energy
987 stored during the melting of the composite PCM, resulting in a larger container volume for
988 the same amount of thermal energy storage. As a result, using graphene and other carbon-
989 based additives, new ways to develop PCM with improved thermal conductivity and thermal
990 energy storage capacity and minimum supercooling and phase segregation have recently been
991 investigated. Preparing a composite PCM with graphene, for example, is one of the novel
992 concepts to continue to investigate. The advantages of using this additive are the thermal
993 conductivity increase and the latent heat of fusion expansion. Composite PCM are produced
994 and tested for different on-ground applications like electronics cooling, buildings envelop,
995 energy storage reservoirs, heat exchangers, PV panels, etc., and underground geo-structures
996 like heaps, retaining walls, raft foundations, etc. Besides, Repeated cycles of PCM melting
997 and solidification may cause mechanical fatigue on the metallic or carbon-based structures
998 integrated with composite PCM due to the repeated thermal stresses. New research should
999 provide insight into the fluid-structure interactions within such materials.

1000

1001 **9. Conclusion**

1002 The efficiency of a phase change thermal energy storage device is directly related to its
1003 thermophysical properties. The present paper provides a detailed description of PCM
1004 thermophysical properties enhancement. The enhancement of thermal conductivity, specific
1005 heat and latent heat of fusion, as well as the reduction in the supercooling and phase
1006 segregation are discussed. Based on the literature the following conclusions has been drawn:

- 1007 1. To obtain PCM with high thermal conductivity, thermally conductive nano additives can
1008 be used. Nano additive dimension (including pore size, morphology and structure), as
1009 well as the loading, determine the thermal conductivity of the resulting composite PCM.
1010 Besides, the use of nano additives with anisotropic thermal conductivity or the poor
1011 mixing of the composite formulation can result in a PCM with anisotropic thermal
1012 conductivity. When nano additives establish phonon channels and minimize interfacial
1013 thermal resistance, high thermal conductivity may be reached at large nano additive
1014 loadings. Because the pore size influences the heat conductivity and form stability of the
1015 final composite PCM, the pore size and structure should be optimized further.
- 1016 2. Limited studies are focused on the heat storage capacity enhancement of PCM. The heat
1017 storage capacity of PCM can be improved by using suitable additives in an appropriate
1018 proportion. The addition of single and multiwall carbon nanotubes with specific
1019 diameters and appropriate proportions enhances the heat storage capacity of PCM.
1020 However, inappropriate concentration may lead to the reduction of the heat storage
1021 capacity.
- 1022 3. The degree of supercooling depends on the container shape and size, PCM composition,
1023 heating and cooling rate, heat transfer area, etc. The supercooling can be reduced by
1024 adding additives that promote PCM nucleation, by increasing the volume of the PCM
1025 container and by avoiding the overheating of the PCM. Reducing the cooling rate may
1026 decrease the supercooling degree but increase the time spent in a supercooled state.
- 1027 4. Phase segregation is bound to happen in PC mixture with different thermophysical
1028 properties (density, melting temperature, etc.) Phase segregation may be reduced by
1029 increasing the homogeneity of the PCM mixture, by using thickening agents, and by
1030 reducing the PCM cooling rate.
- 1031 5. Various mathematical modelling methods for pure and composite PCM are proposed that
1032 can be applied to numerically investigate their thermal behavior and energy storage
1033 performance.

1034 Over the past few decades, a great deal of experimental and analytical work has been
1035 undertaken, resulting in significant improvements towards reliable and cost-effective PCM.
1036 Doping, grafting, or incorporating uniquely structured materials improves the thermal
1037 conductivity, sensible heat, and latent heat of fusion of pure PCM. The thermal and chemical
1038 stability of such engineered composites must be further assessed before practical use. Novel
1039 blends of pure PCM and additives are being developed for the use of thermal energy storage.

1040 This is a very fascinating and important research area currently. The majority of methods for
1041 improving PCM properties, production, and cost-effectiveness are still in the testing stage,
1042 even though the findings suggest that they are very promising for the thermal energy storage
1043 industry.

1044 ***Nomenclature***

| | | |
|------|--------------------|---|
| 1045 | A | Cross-sectional area [m ²] |
| 1046 | A_f | The cross-sectional area of the fins [m ²] |
| 1047 | C_0 | Thermal capacity of the tube [J/(kg.K)] |
| 1048 | C_w | The thermal capacity of the water [J/(kg.K)] |
| 1049 | C_S | The heat capacity in solid-phase [J/(kg.K)] |
| 1050 | C_L | The heat capacity in the liquid phase [J/(kg.K)] |
| 1051 | C_{al} | The thermal capacity of the aluminum [J/(kg.K)] |
| 1052 | f | Number of molecules |
| 1053 | f^{eq} | Equilibrium distribution function |
| 1054 | f_L | The liquid fraction (%) |
| 1055 | h | Enthalpy [J] |
| 1056 | $H(T)$ | The total enthalpy function [J] |
| 1057 | L | The Latent heat (J/kg) |
| 1058 | m_{PCM} | Mass of the PCM material [kg] |
| 1059 | m_{carbon} | Mass of the carbon nanoparticles [kg] |
| 1060 | m_0 | The tube mass [kg] |
| 1061 | m_w | The water mass [kg] |
| 1062 | n | The unit normal vector on the interface |
| 1063 | $\dot{q}_{p-f}(t)$ | Heat flux on the paraffin cell boundary [W/m ²] |
| 1064 | $\dot{q}_{v,s}$ | The source term in solid-phase [W/m] |
| 1065 | $\dot{q}_{v,L}$ | The source term in solid-phase [W/m] |

| | | |
|------|-----------------------|---|
| 1066 | Q | Total latent energy [J] |
| 1067 | Q_{in} | Solar energy [J] |
| 1068 | R | Radius of the tube [m] |
| 1069 | T_S | PCM temperature in solid-phase [K] |
| 1070 | T_L | PCM temperature in the liquid phase [K] |
| 1071 | T_m | Melting temperature [K] |
| 1072 | T^* | Scaled temperature [K] |
| 1073 | T_f | Foam temperature [K] |
| 1074 | T_{m1} | The temperature at the beginning of the melting phase [K] |
| 1075 | T_{m2} | The temperature at the end of the melting phase [K] |
| 1076 | T_{PCM} | PCM temperature [K] |
| 1077 | T_n^P | Solar panel temperature [K] |
| 1078 | T_∞ | Environment temperature [K] |
| 1079 | T_0 | Initial temperature [K] |
| 1080 | t_f | Time of solidification [s] |
| 1081 | u | Velocity in x direction [m/s] |
| 1082 | U | Heat transfer coefficient [W/(K.m ²)] |
| 1083 | v | Velocity in y-direction [m/s] |
| 1084 | V_{al} | The volume of the aluminum [m ³] |
| 1085 | η | Solar Absorptance |
| 1086 | η_f | The fin efficiency [%] |
| 1087 | $\frac{d\bar{X}}{dt}$ | The velocity [m/s] |

| | | |
|------|-----------------|--|
| 1088 | ρ | The density [kg/m ³] |
| 1089 | ρ_{al} | The density of the aluminum [kg/m ³] |
| 1090 | ρ_C | Composite density [kg/m ³] |
| 1091 | ρ_G | Graphite density [kg/m ³] |
| 1092 | λ_{eff} | Effective thermal conductivity [W/(K.m)] |
| 1093 | λ_{al} | Thermal conductivity of the aluminum [W/(K.m)] |
| 1094 | λ_L | The thermal conductivity in the liquid phase [W/(K.m)] |
| 1095 | λ_S | The thermal conductivity in solid-phase [W/(K.m)] |
| 1096 | β | The thermal expansion coefficient [1/K] |
| 1097 | μ | Dynamic viscosity [kg/(m.s)] |
| 1098 | Ω | Integrodifferential factor |
| 1099 | CF | Carbon fiber |
| 1100 | CNF | Carbon nanofiber |
| 1101 | CNT | Carbon nanotubes |
| 1102 | MWCNT | Multiwall carbon nanotubes |
| 1103 | NDG | Nitrogen-doped graphene |
| 1104 | SWCNT | Single-wall carbon nanotubes |
| 1105 | | |
| 1106 | | |

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