

Universitat de Lleida

Document downloaded from:

<http://hdl.handle.net/10459.1/60228>

The final publication is available at:

<https://doi.org/10.1016/j.applthermaleng.2017.09.014>

Copyright

cc-by-nc-nd, (c) Elsevier, 2018



Està subjecte a una llicència de [Reconeixement-NoComercial-SenseObraDerivada 4.0 de Creative Commons](https://creativecommons.org/licenses/by-nc-nd/4.0/)

Influence of nanoparticle morphology and its dispersion ability regarding thermal properties of water used as Phase Change Material

Camila Barreneche¹, Rosa Mondragon^{2,*}, David Ventura-Espinosa³, Jose Mata³, Luisa F. Cabeza⁴, A. Inés Fernández¹, J. Enrique Julia²

¹Department of Materials Science and Physical Chemistry, Universitat de Barcelona, Martí i Franqués 1, 08028-Barcelona, Spain

²Departamento de Ingeniería Mecánica y Construcción, Universitat Jaume I, 12071-Castellón de la Plana, Spain

³Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, 12071-Castellón de la Plana, Spain

⁴GREC Innovació Concurrent, Universitat de Lleida, Edifici CREA, 25001-Lleida, Spain

*Corresponding author: mondrag@uji.es

Tel. +34 964 72 81 45 - Fax +34 964 72 81 06

Abstract

Nanoparticles with different morphologies were added to water to study if the morphology of the nanoparticles affects the main parameters of water used as phase change material (PCM). Considered morphologies were spherical, tubes and sheets in the form of spherical carbon black nanoparticles (CB), multiwalled carbon nanotubes (MWCNT), and graphene oxide nanosheets (GO). Results demonstrate that effectively the morphology of nanoparticles affect the thermophysical properties of the nano-enhanced PCM (NePCM). Depending on the morphology of the added nanoparticle, the final NePCM will have different subcooling and thermal conductivity, whereas its phase change enthalpy is not affected and, therefore, is the same for all produced NePCM.

Keywords: Phase Change Material; nanoparticles; morphology; dispersion; water.

1. Introduction

One of the conclusions reached in the 2010 United Nations Climate Change Conference was that Global Warming cannot be avoided, only mitigated [1]. To achieve this objective, efforts should focus on limiting the rise in global temperatures to 2 °C by 2100. In 2015, the Paris Agreement [2] it was established that the 2 °C reduction target was insufficient, and that a 1.5 °C target is required. To meet this goal, the emissions levels for 2030 are 55 GtCO₂e.

At the current pace of demography and with emerging economies consuming a steadily increasing amount of products and services [3,4], reducing CO₂ emissions relies undoubtedly on innovations in energy technologies to cover energy efficiency, energy harvesting, energy storage, and energy transmission and distribution [5]. These innovations depend on intensifying Research and Development (R&D) activities in forthcoming years to develop an innovative key that enables advanced heat transfer and energy storage materials with market uptake in the mid and long term.

Energy storage technologies can bridge temporal and geographical gaps between energy demand and supply [6]. Energy storage technologies can be implemented on large and small scales in distributed and centralized manners throughout the energy system. While some energy storage technologies are mature, most of them are still in the early stages of development and additional research efforts are needed. The development of affordable thermal energy storage (TES) technologies will improve the efficiency in the use of energy system resources, increase the use of variable renewable resources of energy, raise the self-consumption and self-production of energy, increase energy access (off-grid electrification), improve the electricity grid stability, reliability and resilience, and increase end-use sector of electrification (e.g. electrification of transport sector). Cold TES is an energy saving technology that reduces the electricity peak by storing cold during off peak hours and in seasonal storage [7,8].

TES technologies face some barriers to market entry and in this regard cost is a key issue [9,10]. Cost estimates of TES systems include storage media, system (containers, insulation, heat exchanger, and technical equipment for charging and discharging), and operation costs.

Phase change materials (PCM) can offer high storage capacity associated with the latent heat of the phase change [11,12]. PCM also enable a target-oriented discharging temperature that is set by the constant temperature of the phase change. In addition, in thermal energy storage applications PCM are static, so modular systems ranging from few kW to MW are feasible. However, PCM are not always stable and the boundary conditions of the final application must be controlled [12].

74 One of the most promising approaches to improve PCM properties/behaviour is the addition of well-
75 dispersed nanoparticles [13]. In this case, the PCMs are called nanostructured-enhanced phase change
76 materials (NePCM). Nanoparticles can reduce some of the above mentioned drawbacks, but the two
77 most promising to be reduced are low thermal conductivity and high subcooling, since the particles
78 added have higher thermal conductivity and they can act as nucleation points during the phase change.
79

80 Most NePCM studies have used water, ethylenglycol, paraffin wax, and cyclohexane as the base PCM
81 [13,14], most of them for cold storage. Different types of nanoparticles have been used including
82 carbon-based nanostructures (carbon nanofibres, graphite nanoplatelets, singlewalled nanotubes, and
83 multiwalled nanotubes, graphne), oxide-based nanoparticles (Al_2O_3 , MgO, TiO_2 , and CuO), and
84 metals (Cu, Al, and Ag) [13,15-17]. In some cases, additives were used to improve nanoparticle
85 dispersion and stability [13,18].
86

87 The last studies revealed that when grafted multi-walled nanotube (MWNT) are introduced in
88 paraffin-montmorillonite composite PCM, paraffin molecules are intercalated in the montmorillonite
89 layers and the grafted MWNTs are dispersed by decreasing the latent heat following the mixture rule
90 and increasing 34% the thermal conductivity [19]. Pissello et al. introduced nanoparticles in cement-
91 based composites encouraging results in terms of added functional properties as electrical conductivity
92 and self-sensing potential for a variety of field scopes, e.g. vibration measurements, damage detection,
93 structural health monitoring, electromagnetic shielding, self-heating pavements for deicing and more
94 [20]. In addition, Karaipekli et al. [21] used a perlite matrix where paraffin PCM was impregnated and
95 nanoparticles were added in order to improve the thermal conductivity and results show up to 25%
96 increment and proper durability and reliability.
97

98 As expected, in most cases, the latent heat of NePCM is lowered because of the presence of solid
99 nanoparticles. Although the rule of mixtures can be used to predict the latent heat in most cases [22],
100 some papers report a reduction in the latent heat even below than the one expected by the rules of
101 mixtures [23]. On the other hand, the addition of nanoparticles to PCM can show a strong influence on
102 the fusion temperature. In most of the studies published to date, a noticeable reduction in the fusion
103 temperature is observed. This reduction is due to a PCM-nanoparticle surface interaction [24].
104 However, some authors report no change in phase change temperature [25-26]. In all the studies, a
105 reduction in the degree of subcooling is observed in NePCM.
106

107 But one of the parameters to consider when adding nanoparticles to a PCM is which
108 material/nanoparticle to use and in which morphology, and this has not been clearly studied in the
109 literature so far. The aim of this paper is to investigate if the different morphology of nanoparticles
110 affects the main parameters of the nanofluid when added to a PCM, mainly its dispersion ability.

111 Therefore carbon based nanoparticles with different morphologies (nanoparticles, nanotubes and
112 nanosheets) were added into water to investigate the effect on this PCM. Other parameters that are
113 also influenced by the addition of nanoparticles in water as PCM were also tested, such as the
114 influence in the melting enthalpy, thermal conductivity and subcooling. The shape and size of the
115 nanostructures are important in a way that the surface to volume ratio of nanostructure alters the
116 thermo-physical properties of the PCM [27].

117

118 **2. Materials and methods**

119

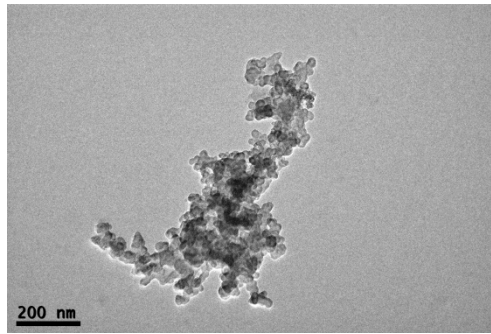
120 Water was doped with three different carbon-based nanoparticles:

- 121 - Spherical carbon black nanoparticles, CB, were supplied by Cabot Corporation. Commercial
122 nanoparticles ELFTEX 570 consist in amorphous carbon with a primary particle size (dp) of
123 10 nm.
- 124 - Multi-walled carbon nanotubes, MWCNT, were purchased from Nanocyl SA. Commercial
125 nanotubes NC7000 present a dp of 9.5 nm and a length of 1.5 μm .
- 126 - Graphene oxide nanosheets, GO, were prepared from graphite powder (natural, universal
127 grade, 200 mesh, 99.9995 %) by the Hummers method and were exfoliated using ultrasounds
128 [28]. Final achieved size was 2 nm in diameter and 1 μm in length.

129 In Figure 1 TEM images of the primary nanoparticles are shown.

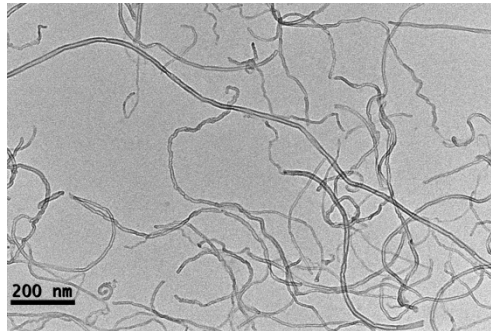
130

131
132



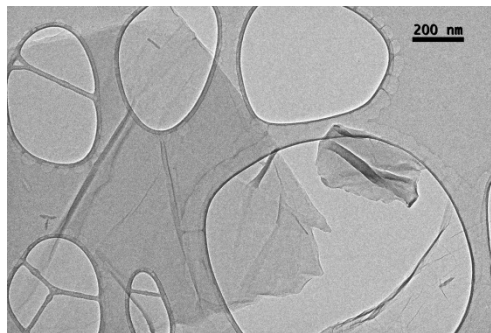
(a)

133
134



(b)

135
136



(c)

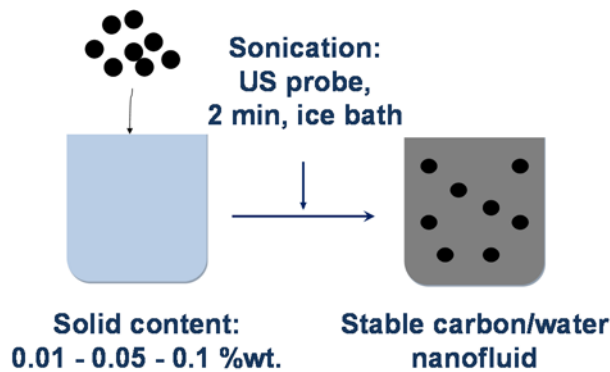
137

Figure 1. (a) Carbon black, (b) MWCNT, (c) graphene oxide nanosheets

138
139
140
141
142
143
144
145
146
147
148

Before the dispersion of the nanoparticles in water, both CB and MWCNT needed to be oxidized with hydrogen peroxide at 120 °C under magnetic stirring to ensure a good dispersion [29]. Finally, carbon-water NePCM were prepared by introducing the corresponding amount of solid into the water. Three solid mass content (0.01% wt., 0.05% wt., and 0.1% wt.) were tested. The breakage of the agglomerates and the dispersion was achieved by means of a sonication treatment with an ultrasound probe, for 2 minutes at low input energy (15%) in an ice bath to avoid heating of the sample (Figure 2). Ultrasound probes provide the highest degree of dispersion; however the breakage of the agglomerates into primary particles is not ensured. Therefore the final size is the lowest it can be obtained under this conditions but nanoparticles are still agglomerate as it can be observed in the results section. With the aim of comparing the different morphologies, it is important to ensure that all the samples are submitted to the same processing and that they were kept stable although there were

149 clusters of primary nanoparticles. In this case samples were checked to be stable and the clusters
150 present did not settle over time.
151



152

153

Figure 2. Preparation of the nanocomposite: nanoparticles + PCM

154

155 The nanoparticles dispersion was characterized by means of the Dynamic Light Scattering (DLS)
156 technique using a ZetaSizer Nano ZS (Malvern Instruments Ltd.). The size distribution of the
157 nanoparticles and agglomerates was obtained for all the samples.

158

159 The phase change enthalpy, temperature and the subcooling reduction were measured by Differential
160 Scanning Calorimetry (DSC) using a DSC2 (Mettler Toledo International Inc.). Approximately 20 mg
161 of sample were introduced in an aluminium crucible sealed in order to avoid loss of material. Samples
162 were submitted to the following cycle: isothermal stage 5 minutes at 20 °C, cooling from 20 °C to -25
163 °C at a cooling rate of 20 °C·min⁻¹, isothermal stage 5 minutes at -25 °C, and heating from -25 °C to 20
164 °C at a heating rate of 20 °C·min⁻¹. Three tests were run for each sample and a mean value was
165 obtained.

166

167 Moreover, the thermal conductivity differences between the samples under study were measured by a
168 hot-wire KD2 Pro thermal analyser device using a transient line heat source method [30] to measure
169 effective thermal conductivity. In this method, a thin metallic wire is embedded in the test liquid
170 acting both as heat source and temperature sensor. The transient hot wire technique works by
171 measuring the temperature/time response of the wire to an abrupt electrical pulse. The sample was
172 introduced in a sealed glass tube (20mL) where the sensor was inserted vertically. Measurements were
173 carried out in solid and liquid phase and the tube was immersed in a thermostatic bath with controlled
174 temperature. Eight measurements were performed for each sample, so the experimental error could be
175 determined at 95% of confidence level.

176

177

178

3. Results

Results related with particles size of nanoparticles and nanoparticles clusters are shown in Figure 3. Figure 3 shows the dispersion of the nanoparticles in the different NePCM measured by the DLS. The dispersion of nanoparticles provides information about the available surface area of the nanoparticles inside the PCM. The NePCM based on CB presented agglomeration, so the average size of the CB clusters, assuming spherical shape, is measured. CB nanoparticles dispersion showed almost no dependence with solid mass content and the cluster average values was similar to those found in other experiments [31]. In the case of NePCM based on GO and MWCNT, the results obtained by the DLS were not so conclusive since the primary nanoparticle morphology was not spherical, and the nanoparticle clusters, if present, neither. Consequently, DLS only provided a rough approximation of the nanoparticle dispersion in non-spherical morphologies. It is possible to observe that by using MWCNT better nanoparticle dispersion is achieved than by using GO nanosheets. This fact limits the available nanoparticle surface area in the case of GO-based nanofluids. Differences found in the agglomeration of nanoparticles of different morphologies depend also on the interparticle interactions due to the surface charges that appear in the nanoparticle surface when they are introduced in water. In the GO-based nanofluids attraction forces seem to be higher providing bigger agglomerates in water.

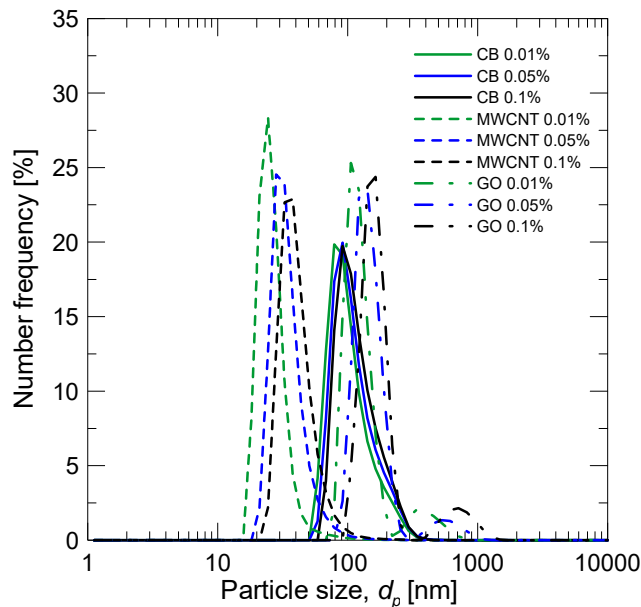
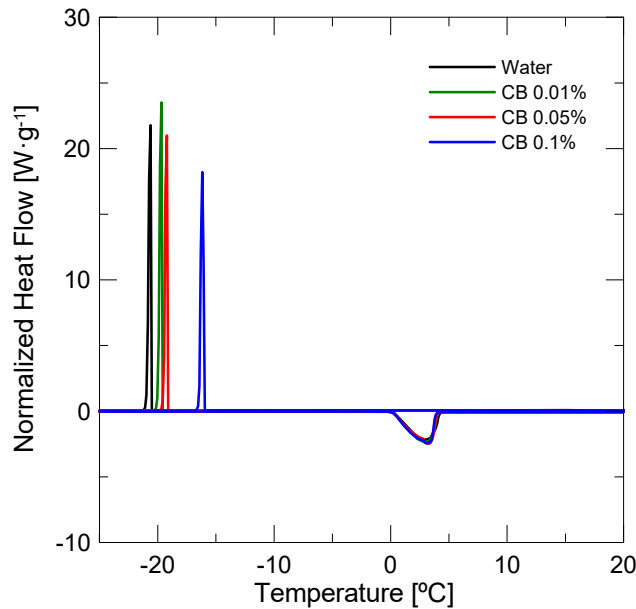


Figure 3. Nanoparticle dispersion degree measured by DLS.

Moreover, it is remarkable that after the same sonication process, the different morphologies studied provide also a different degree of agglomeration. All particle size averages obtained have higher values than those reported for the nanoparticles by themselves with cluster sizes bigger than the nano-scale range, depending on the sample. Differences obtained later in the thermal properties analyzed are mainly due to this cluster formation and the available surface area for each material.

205
206
207
208
209
210

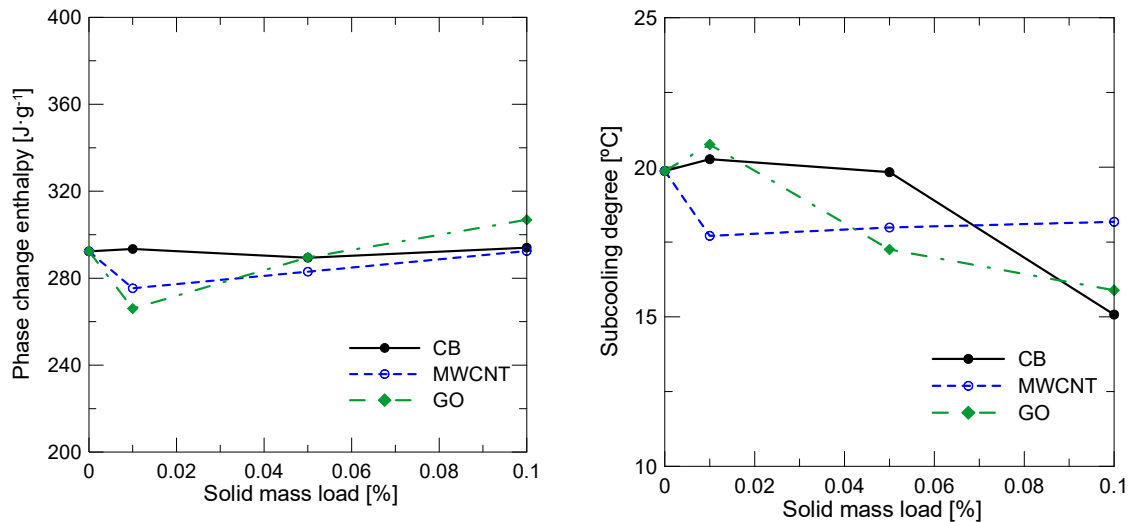
Otherwise, Figure 4 shows the DSC curves for the NePCM based on CB with different solid mass content. It is possible to observe that there was no noticeable dependence of the melting temperature and phase change enthalpy with the nanoparticle mass content. However, a drastic reduction in the subcooling degree of the NePCM when the nanoparticles content is incremented was observed.



211
212
213
214
215
216
217
218
219
220
221
222
223

Figure 4. DSC curves of NePCM based on CB

In order to compare the effect of the different nanoparticle morphologies, Figure 5 shows the phase change enthalpy and subcooling of all the NePCM tested. It is possible to observe that the phase change enthalpy value was almost constant for all the NePCM tested, with values close to the one obtained for the base fluid. However, the subcooling degree depends on the nanoparticle morphology. In the case of CB, it is necessary to use a minimum amount of 0.1% wt. of nanoparticles to get a measurable reduction of subcooling. The maximum reduction of the subcooling for CB is 5 °C. The maximum reduction of subcooling for MWCNT was only 2.5 °C, and it was obtained for low solid mass content (0.01% wt.). The reduction of the subcooling with the nanoparticle amount is almost linear for the GO nanosheets with a maximum decrement of 4 °C.



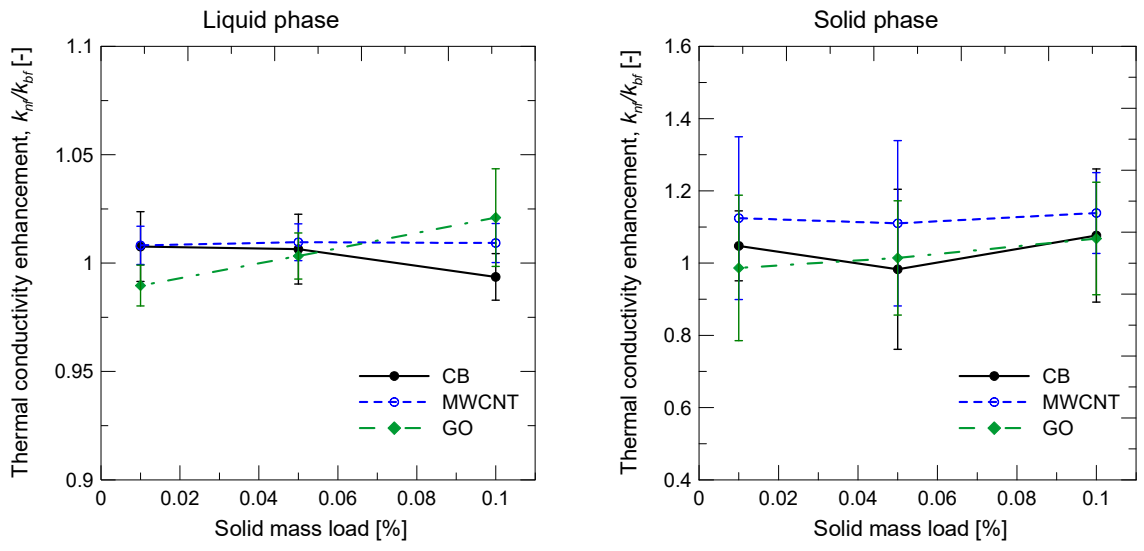
224 **Figure 5. Left: Phase change enthalpy dependence with nanoparticle morphology and solid mass**
 225 **content. Righth: Subcooling degree dependence with nanoparticle morphology and solid mass**
 226 **content.**
 227

228 The addition of solid particles with higher thermal conductivity than the base fluid results in a thermal
 229 conductivity enhancement that can be predicted by the Maxwell equation [32]. However, according to
 230 Gao et al. [33], the enhancement achieved also depends on the size and shape of the particles and
 231 clusters of particles in the nanofluid, and deviations from the Maxwell equation results can be found.
 232

233 The thermal conductivity enhancement measured for the samples under study and its error is shown in
 234 Figure 6. Although a general trend of thermal conductivity increment with solid content can be
 235 observed, it should be noticed that, as the nanofluids tested have a low particle concentration, the
 236 enhancement achieved in liquid phase is negligible for dilute samples. Moreover, for low viscosity
 237 fluids the experimental error increases, and the values obtained for thermal conductivity lie within the
 238 experimental uncertainty. Only for the highest concentration (0.1% wt.) a maximum enhancement of
 239 2.1% can be found for GO nanofluids. It can be also concluded that in liquid phase, the morphology of
 240 the nanoparticles influences the thermal conductivity. For 0.1% wt. solid mass content, nanosheets
 241 (GO) present higher conductivity than nanotubes (MWCNT), while the lower value corresponds to
 242 spherical nanoparticles (CB). The thermal conductivity enhancement and the morphology dependence
 243 measured is in agreement with well established equations [32-33].
 244

245 In solid state, after the phase change, crystallization of water produces a change in the nanoparticle
 246 cluster structure. Therefore, the thermal conductivity depends on the cluster size and its morphology,
 247 which is expected to be different from the primary particles. Consequently, the formation of clusters of
 248 nanoparticles also increases the conduction pathway providing higher enhancements than in liquid

249 phase. In this case, clusters of nanotubes (MWCNT) are the ones with the highest conductivity
 250 enhancement, 13.9%.
 251



252 **Figure 6. Thermal conductivity enhancement. Left: Liquid phase. Right: Solid phase.**

253
 254
 255 As a general rule the thermal properties depend always on the final size of the agglomerates of
 256 nanoparticles. However, for very dilute nanofluids where the interaction among clusters is reduced the
 257 influence of the presence of nanoparticles suspended in the base fluid is negligible and independent on
 258 the particle geometry. Therefore, only for nanofluids in liquid phase at 0.1% of solid mass load
 259 evidences of enhancement of the thermal behaviour can be observed. Otherwise, in solid phase where
 260 nanoparticles agglomerate even more during the phase change the influence of the morphology
 261 becomes important and nanotubes present the higher increase at any concentration due to the high
 262 aspect ratio and the better pathway provided for the transport of phonons responsible for the thermal
 263 conductivity enhancement. Moreover, some theoretical models found in the literature to predict this
 264 enhancement were modified to include the effect of the higher aspect ratio and are valid only for
 265 nanotubes [34].

266
 267 **4. Discussion**

268
 269 Comparing the results obtained in this paper, there are some important highlights detailed as follows:

- 270 - **CB** presented agglomeration, but **size** showed almost **no dependence with solid mass**
 271 **content**. It is possible to obtain a **better nanoparticle dispersion using MWCNT than GO**
 272 nanosheets.
- 273 - There is **no noticeable dependence of the melting temperature** and phase change enthalpy
 274 of the PCM with the nanoparticle mass content.
- 275 - **Subcooling** depends on the nanoparticle morphology:

- 276 • **CB:** it is necessary to use a minimum amount of 0.1% wt. nanoparticles to get a
- 277 measurable reduction of subcooling. The maximum reduction achieved is 5°C.
- 278 • **MWCNT:** The maximum reduction of subcooling is only 2.5°C, and it is obtained for
- 279 low solid mass content (0.01% wt.).
- 280 • **GO nanosheets:** The reduction of subcooling with the nanoparticle content is almost
- 281 linear with a maximum decrement of 4°C.
- 282 - The **phase change enthalpy** is **almost constant** for all the NePCM tested.
- 283 - The **thermal conductivity increment** in solid state is higher when MWCNT nanoparticles are
- 284 used.

285 Based on the results presented in this paper, Table 1 summarized the results obtained with NePCM
 286 containing 0.1% wt. nanoparticles.

287
 288 **Table 1. Summary of results obtained for 0.1% wt. NePCMs tested**

Nanoparticles type	Particle size [nm]	Phase change enthalpy [kJ·kg ⁻¹]	Subcooling reduction [°C]	Thermal conductivity increment (solid) [%]
CB	100	291	5	7.6
MWCNT	35	290	2.5	13.9
GO	110	308	4	6.8

289

290

291 5. Conclusions

292

293 Different morphologies of nanoparticles were used to study if this fact affects the main parameters of
 294 the NePCM when these nanoparticles (CB, MWCNT, and GO) are added to water used as PCM.

295 Results shows that:

- 296 - CB/H₂O NePCM agglomerated when it was put in contact with water, the water phase change
- 297 enthalpy decreased slightly and it had 5 °C of subcooling reduction (the highest obtained in
- 298 this study). The thermal conductivity in solid phase increased almost 8% in solid.
- 299 - MWCNT/H₂O presented the lowest degree of agglomeration when these nanoparticles were
- 300 put in contact with water, water phase change enthalpy remained almost equal and it had the
- 301 lowest subcooling reduction (2.5 °C). Finally, the thermal conductivity measured showed the
- 302 highest increment, around 14% in solid phase by the MWCNT addition.
- 303 - GO/H₂O presented agglomeration when GO nanoparticles were put in contact with water,
- 304 phase change enthalpy was almost not affected by the nanoparticles addition and the phase
- 305 change presented 4 °C of subcooling reduction. The thermal conductivity increased almost 7
- 306 % in solid phase.

307 Therefore, the morphology of the nanoparticles affects the NePCM thermophysical properties and this
308 fact must be taken into account when researchers are producing new NePCM.

309

310 To sum up, the nanoparticles type used will change the agglomerate sizes (notice that MWCNT and
311 GO are not spherical and this issue add an uncertainty to the obtained value); the larger the
312 agglomerate, the higher the subcooling reduction taking into account the subcooling decrement. In
313 addition thermal conductivity enhancement also depends on the morphology of the nanoparticles and
314 the clusters formed during the phase change, providing higher values in solid phase. Finally, the phase
315 change enthalpy for dilute nanofluids is fairly affected by the addition of nanoparticles and can be
316 considered to keep constant.

317

318 **Acknowledgements**

319

320 The research leading to these results has received funding from the European Commission Seventh
321 Framework Programme (FP/2007-2013) under grant agreement n° PIRSES-GA-2013-610692
322 (INNOSTORAGE) and from the European Union's Horizon 2020 research and innovation program
323 under grant agreement No 657466 (INPATH-TES). The authors would like to thank the Catalan
324 Government for the quality accreditation given to their research groups GREA (2014 SGR 123),
325 DIOPMA (2014 SGR 1543). This work has been partially funded by the Spanish government
326 (ENE2015-64117-C5-1-R (MINECO/FEDER) and ENE2015-64117-C5-2-R (MINECO/FEDER)).
327 Dr. Camila Barreneche would like to thank Ministerio de Economía y Competitividad de España for
328 Grant Juan de la Cierva FJCI-2014-22886. This work has been developed by participants of the COST
329 Action CA15119 Overcoming Barriers to Nanofluids Market Uptake (NANOUP TAKE).

330

331 **References**

332

- 333 1. CFR.org "The Global Climate Change Regime". Council on Foreign Relations, 21 July 2012.
334 Web. 16 Feb. 2016.
- 335 2. Sutter, John D.; Berlinger, Joshua (12 December 2015). "Final draft of climate deal formally
336 accepted in Paris". CNN. Cable News Network, Turner Broadcasting System, Inc. Retrieved 12
337 December 2015.
- 338 3. Cabeza, L.F., Urge-Vorsatz, D., McNeil, M.A., Barreneche, C., Serrano, S. Investigating
339 greenhouse challenge from growing trends of electricity consumption through home appliances in
340 buildings. 2014. Renewable and Sustainable Energy Reviews 36, 188-193.
- 341 4. Ürge-Vorsatz, D., Cabeza, L.F., Serrano, S., Barreneche, C., Petrichenko, K. Heating and cooling
342 energy trends and drivers in buildings. 2015. Renewable and Sustainable Energy Reviews 41, 85-
343 98.

- 344 5. EUROPEAN COMMISSION. 2015. A Framework Strategy for a Resilient Energy Union with a
345 Forward-Looking Climate Change Policy.
- 346 6. S. Kalaiselvam, R. Parameshwaran. Thermal Energy Storage Technologies for Sustainability:
347 Systems Design, Assessment and Applications. Elsevier, USA. ISBN: 978-0-12-417291-3. 2014.
- 348 7. Oró, E., de Gracia, A., Castell, A., Farid, M.M., Cabeza, L.F. Review on phase change materials
349 (PCMs) for cold thermal energy storage applications. 2012. Applied Energy 99, 513-533.
- 350 8. Veerakumar, C., Sreekumar, A. Phase change material based cold thermal energy storage:
351 Materials, techniques and applications - A review. 2016. International Journal of Refrigeration 67,
352 271-289.
- 353 9. IEA-ETSAP, IRENA. Thermal Energy Storage - Technology Brief E17. 2013. Available from:
354 [https://www.irena.org/DocumentDownloads/Publications/IRENA-](https://www.irena.org/DocumentDownloads/Publications/IRENA-ETSAP%20Tech%20Brief%20E17%20Thermal%20Energy%20Storage.pdf)
355 [ETSAP%20Tech%20Brief%20E17%20Thermal%20Energy%20Storage.pdf](https://www.irena.org/DocumentDownloads/Publications/IRENA-ETSAP%20Tech%20Brief%20E17%20Thermal%20Energy%20Storage.pdf) (16/02/2016)
- 356 10. SHC-Task 42, ECES-Annex 29. Compact Thermal Energy Storage IEA SHC Position Paper.
357 2015. Available from: [https://www.iea-shc.org/data/sites/1/publications/IEA-SHC-Compact-](https://www.iea-shc.org/data/sites/1/publications/IEA-SHC-Compact-Thermal-Storage-Position-Paper.pdf)
358 [Thermal-Storage-Position-Paper.pdf](https://www.iea-shc.org/data/sites/1/publications/IEA-SHC-Compact-Thermal-Storage-Position-Paper.pdf) (16/02/2016).
- 359 11. Farid, M.M., Khudhair, A.M., Razack, S.A.K., Al-Hallaj, S. A review on phase change energy
360 storage: Materials and applications. 2004. Energy Conversion and Management 45 (9-10), 1597-
361 1615.
- 362 12. Cabeza, L.F., Castell, A., Barreneche, C., De Gracia, A., Fernández, A.I. Materials used as PCM
363 in thermal energy storage in buildings: A review. 2011 Renewable and Sustainable Energy
364 Reviews 15 (3), 1675-1695.
- 365 13. Kaviarasu, C., Prakash, D. Review on phase change materials with nanoparticle in engineering
366 applications. 2016. Journal of Engineering Science and Technology Review 9 (4), 26-386.
- 367 14. Mondragón R., Martínez-Cuenca R., Hernández L., Andreu-Cabedo P., Cabedo L., Julià J.E.
368 Handbook of Clean Energy Systems, Volume 5 - Energy Storage: Thermal Energy Storage;
369 Chemical Storage; Mechanical Storage; Electrochemical Storage; Integrated Storage Systems.
370 Chapter 33 – Nanotechnology and Nanomaterials for thermal energy storage. Editor-in-chief:
371 Jinyue Yan. Wiley, UK, 2015. ISBN: 978-1-118-38858-7.
- 372 15. Li, Y., Zhou, J., Tung, S., Schneider, E., Xi, S. A review on development of nanofluid preparation
373 and characterization. 2009. Powder Technology 196 (2), 89-101.
- 374 16. Sidik, N.A.C., Mohammed, H.A., Alawi, O.A., Samion, S. A review on hybrid nanofluids: Recent
375 research, development and applications. 2014. International Communications in Heat and Mass
376 Transfer 54, 115-125.
- 377 17. Sathishkumar, A., Kumaresan, V., Velraj, R. Solidification characteristics of water based graphene
378 nanofluid PCM in a spherical capsule for cool thermal energy storage applications. 2016.
379 International Journal of Refrigeration 66, 73-83.

- 380 18. Wang, J., Xie, H., and Xin, Z. Thermal properties of heat storage composites containing
381 multiwalled carbon nanotubes. 2008. *Journal of Applied Physics* 104, 113537–113545.
- 382 19. Li, M., Guo, Q., Nutt, S. 2017. Carbon nanotube/paraffin/montmorillonite composite phase
383 change material for thermal energy storage. *Solar Energy* 146, 1–7.
- 384 20. Pisello, A.L., D’Alessandro, A., Sambuco, S., Rallinic, M., Ubertinia, F., Asdrubalia, F.,
385 Materazzic, A.L., Cotana F. 2017. Multipurpose experimental characterization of smart
386 nanocomposite cement-based materials for thermal-energy efficiency and strain-sensing
387 capability. *Solar Energy Materials & Solar Cells* 161, 77–88.
- 388 21. Karaipekli, A., Biçer, A., Sarı, A., Tyagi, V. 2017. Thermal characteristics of expanded
389 perlite/paraffin composite phase change material with enhanced thermal conductivity using carbon
390 nanotubes. *Energy Conversion and Management* 134, 373–381.
- 391 22. Zeng, J.L., Cao, Z., Yang, D.W., et al. Thermal conductivity enhancement of Ag nanowires on an
392 organic phase change material. 2010. *Journal of Thermal Analysis and Calorimetry* 101, 385–389.
- 393 23. Wu, S., Zhu, D., Zhang, X., and Huang, J. Preparation and melting/freezing characteristics of
394 Cu/paraffin nanofluid as phasechange material (PCM). 2010. *Energy and Fuels* 24, 1894–1898.
- 395 24. Hong, H., Wensel, J., Peterson, S., and Roy, W. Efficiently lowering the freezing point in heat
396 transfer coolants using carbon nanotubes. 2007. *Journal of Thermophysics and Heat Transfer* 21,
397 446–448.
- 398 25. Ho, C.J. and Gao, J.Y. Preparation and thermophysical properties of nanoparticle in paraffin
399 emulsion as phase change material. 2009. *International Communications in Heat and Mass*
400 *Transfer* 36, 467–470.
- 401 26. Kumaresan, V., Velraj, R., and Das, S.K. The effect of carbon nanotubes in enhancing the thermal
402 transport properties of PCM during solidification. 2012. *Heat and Mass Transfer* 48, 1345–1355.
- 403 27. Parameshwaran R., Kalaiselvam S.. Nanomaterial-embedded phase-change materials (PCMs) for
404 reducing building cooling needs. 2015. *Eco-efficient Materials for Mitigating Building Cooling*
405 *Needs* 401–443.
- 406 28. Hummers, W. S.; Offeman, R. E. 1958. Preparation of Graphitic Oxide. *Journal of the American*
407 *Chemical Society* 80, 1339-1339.
- 408 29. Han, D.X., Meng, Z.G., Wu, D.X., Zhang, C.Y., Zhu, H.T. Thermal properties of carbon black
409 aqueous nanofluids for solar absorption. 2011. *Nanoscale Research Letters* 6, 457, 1-7.
- 410 30. Mujumdar, A. S. *Handbook of Industrial Drying*. Third Edition 25 (6). CRC Press 2006.
- 411 31. Mondragon, R., Segarra, C., Martinez-Cuenca, R., Julià E, Jarque JC. Experimental
412 characterization and modeling of thermophysical properties of nanofluids at high temperature
413 conditions for heat transfer applications. 2013. *Powder Technology* 249, 516–529.
- 414 32. Maxwell J C. *A Treatise on Electricity and Magnetism* 1873, Clarendon Press Oxford
- 415 33. Gao J W, Zheng R T, Ohtani H, Zhu D S and Chen G. Experimental investigation of heat
416 conduction mechanisms in nanofluids. Clue on clustering. 2009. *Nano Letters* 9 (12) 4128-32.

417 34. Yang, L., Xu, J., Du, K., Zhang, X. 2017. Recent developments on viscosity and thermal
418 conductivity of nanofluids. *Powder Technology* 317, 348–369.