

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

Camila Barreneche<sup>1</sup>, Rosa Mondragon<sup>2\*</sup>, David Ventura-Espinosa<sup>3</sup>, Jose Mata<sup>3</sup>, Luisa F. Cabeza<sup>4</sup>, A. Inés Fernández<sup>1</sup>, J. Enrique Julia<sup>2</sup>

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

<sup>2</sup>Departamento de Ingeniería Mecánica y Construcción, Universitat Jaume I, 12071-Castellon de la Plana, Spain

<sup>3</sup>Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, 12071-Castellon de la Plana, Spain

<sup>4</sup>GREIA Innovació Concurrent, Universitat de Lleida, Edifici CREA, 25001-Lleida, Spain

\*Corresponding author: [mondrag@uji.es](mailto: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

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

42

43 At the current pace of demography and with emerging economies consuming a steadily increasing  
44 amount of products and services [3,4], reducing CO<sub>2</sub> emissions relies undoubtedly on innovations in  
45 energy technologies to cover energy efficiency, energy harvesting, energy storage, and energy  
46 transmission and distribution [5]. These innovations depend on intensifying Research and  
47 Development (R&D) activities in forthcoming years to develop an innovative key that enables  
48 advanced heat transfer and energy storage materials with market uptake in the mid and long term.

49

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

61

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

65

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

71

72 One of the most promising approaches to improve PCM properties/behaviour is the addition of well-  
73 dispersed nanoparticles [13]. In this case, the PCMs are called nanostructured-enhanced phase change

74 materials (NePCM). Nanoparticles can reduce some of the above mentioned drawbacks, but the two  
75 most promising to be reduced are low thermal conductivity and high subcooling, since the particles  
76 added have higher thermal conductivity and they can act as nucleation points during the phase change.

77

78 Most NePCM studies have used water, ethylenglycol, paraffin wax, and cyclohexane as the base PCM  
79 [13,14], most of them for cold storage. Different types of nanoparticles have been used including  
80 carbon-based nanostructures (carbon nanofibres, graphite nanoplatelets, singlewalled nanotubes, and  
81 multiwalled nanotubes, graphne), oxide-based nanoparticles ( $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ , and  $\text{CuO}$ ), and  
82 metals ( $\text{Cu}$ ,  $\text{Al}$ , and  $\text{Ag}$ ) [13,15-17]. In some cases, additives were used to improve nanoparticle  
83 dispersion and stability [13,18].

84

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

95

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

104

105 But one of the parameters to consider when adding nanoparticles to a PCM is which  
106 material/nanoparticle to use and in which morphology, and this has not been clearly studied in the  
107 literature so far. The aim of this paper is to investigate if the different morphology of nanoparticles  
108 affects the main parameters of the nanofluid when added to a PCM, mainly its dispersion ability.  
109 Therefore carbon based nanoparticles with different morphologies (nanoparticles, nanotubes and  
110 nanosheets) were added into water to investigate the effect on this PCM. Other parameters that are

111 also influenced by the addition of nanoparticles in water as PCM were also tested, such as the  
112 influence in the melting enthalpy, thermal conductivity and subcooling. The shape and size of the  
113 nanostructures are important in a way that the surface to volume ratio of nanostructure alters the  
114 thermo-physical properties of the PCM [27].

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## 116 **2. Materials and methods**

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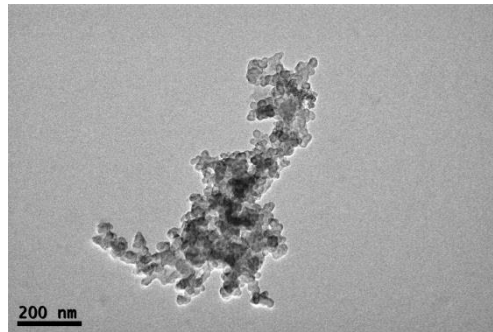
118 Water was doped with three different carbon-based nanoparticles:

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

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

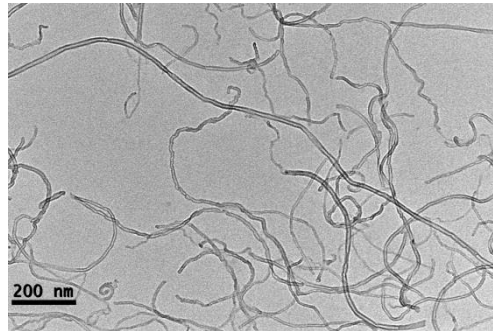
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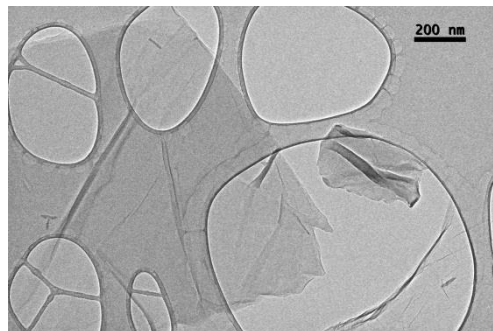
(a)

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(b)

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(c)

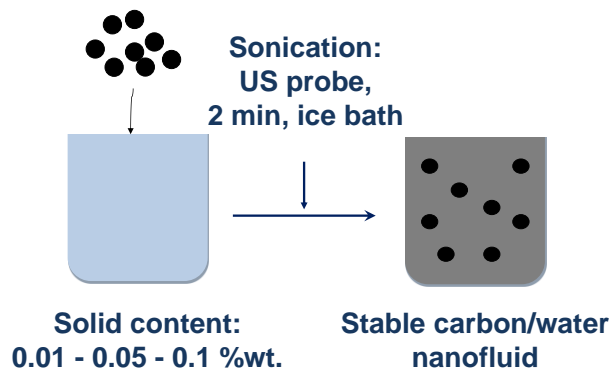
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**Figure 1. (a) Carbon black, (b) MWCNT, (c) graphene oxide nanosheets**

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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

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

**Figure 2. Preparation of the nanocomposite: nanoparticles + PCM**

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

156

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

164

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

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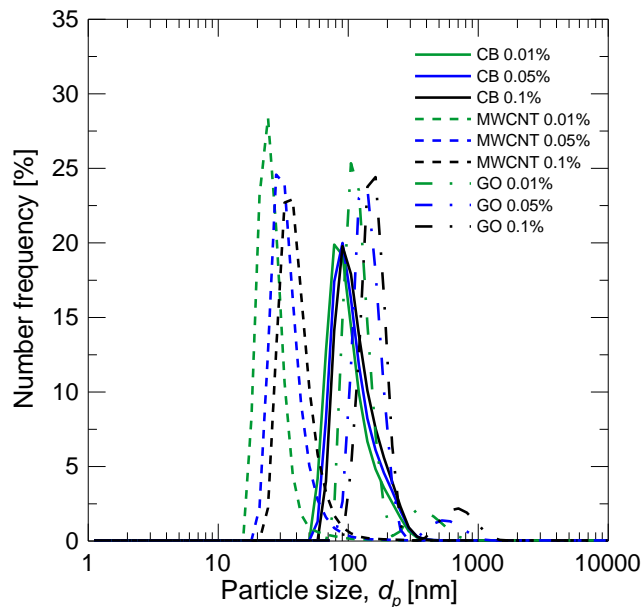
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177 **3. Results**

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

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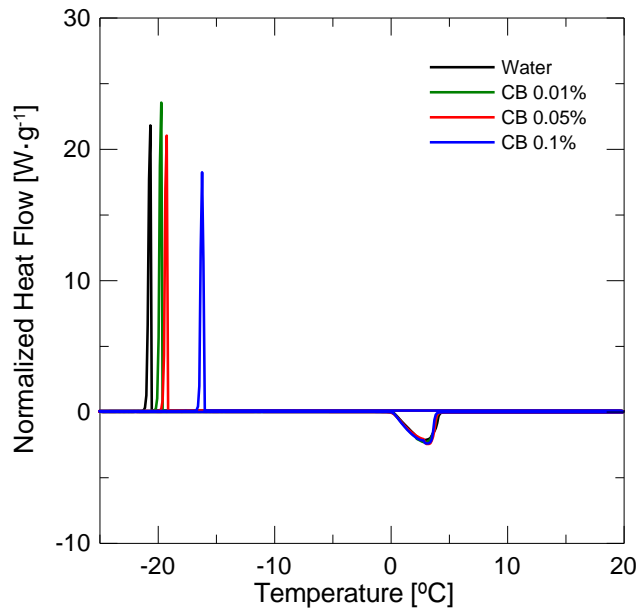
196 **Figure 3. Nanoparticle dispersion degree measured by DLS.**

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

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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.

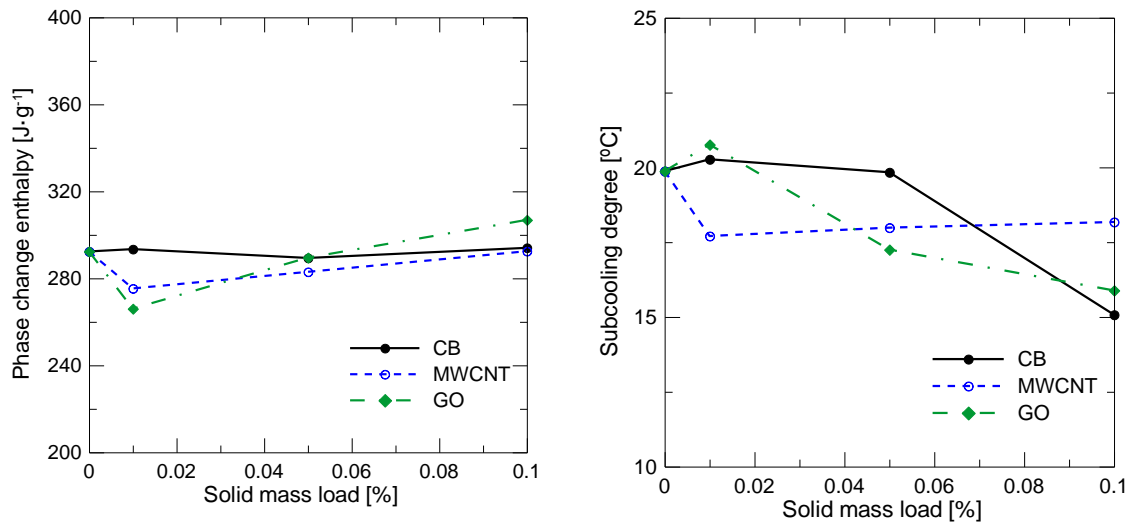


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**Figure 4. DSC curves of NePCM based on CB**

212 In order to compare the effect of the different nanoparticle morphologies, Figure 5 shows the phase  
213 change enthalpy and subcooling of all the NePCM tested. It is possible to observe that the phase  
214 change enthalpy value was almost constant for all the NePCM tested, with values close to the one  
215 obtained for the base fluid. However, the subcooling degree depends on the nanoparticle morphology.  
216 In the case of CB, it is necessary to use a minimum amount of 0.1% wt. of nanoparticles to get a  
217 measurable reduction of subcooling. The maximum reduction of the subcooling for CB is 5 °C. The  
218 maximum reduction of subcooling for MWCNT was only 2.5 °C, and it was obtained for low solid  
219 mass content (0.01% wt.). The reduction of the subcooling with the nanoparticle amount is almost  
220 linear for the GO nanosheets with a maximum decrement of 4 °C.  
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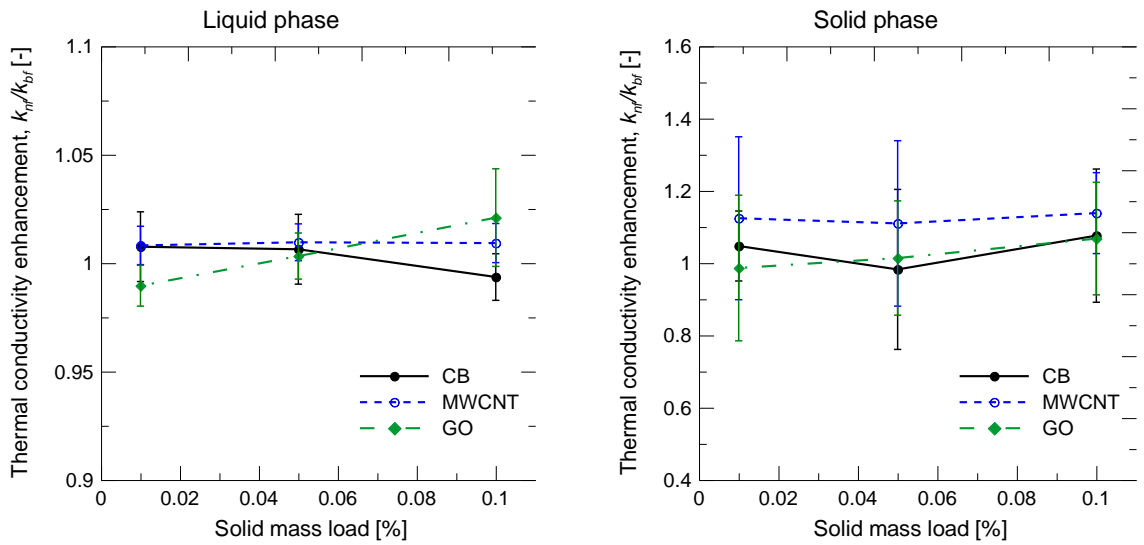
222 **Figure 5. Left: Phase change enthalpy dependence with nanoparticle morphology and solid mass**  
 223 **content. Righth: Subcooling degree dependence with nanoparticle morphology and solid mass**  
 224 **content.**  
 225

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

230  
 231 The thermal conductivity enhancement measured for the samples under study and its error is shown in  
 232 Figure 6. Although a general trend of thermal conductivity increment with solid content can be  
 233 observed, it should be noticed that, as the nanofluids tested have a low particle concentration, the  
 234 enhancement achieved in liquid phase is negligible for dilute samples. Moreover, for low viscosity  
 235 fluids the experimental error increases, and the values obtained for thermal conductivity lie within the  
 236 experimental uncertainty. Only for the highest concentration (0.1% wt.) a maximum enhancement of  
 237 2.1% can be found for GO nanofluids. It can be also concluded that in liquid phase, the morphology of  
 238 the nanoparticles influences the thermal conductivity. For 0.1% wt. solid mass content, nanosheets  
 239 (GO) present higher conductivity than nanotubes (MWCNT), while the lower value corresponds to  
 240 spherical nanoparticles (CB). The thermal conductivity enhancement and the morphology dependence  
 241 measured is in agreement with well established equations [32-33].

242  
 243 In solid state, after the phase change, crystallization of water produces a change in the nanoparticle  
 244 cluster structure. Therefore, the thermal conductivity depends on the cluster size and its morphology,  
 245 which is expected to be different from the primary particles. Consequently, the formation of clusters of  
 246 nanoparticles also increases the conduction pathway providing higher enhancements than in liquid

247 phase. In this case, clusters of nanotubes (MWCNT) are the ones with the highest conductivity  
 248 enhancement, 13.9%.  
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250  
 251 **Figure 6. Thermal conductivity enhancement. Left: Liquid phase. Right: Solid phase.**

252  
 253 As a general rule the thermal properties depend always on the final size of the agglomerates of  
 254 nanoparticles. However, for very dilute nanofluids where the interaction among clusters is reduced the  
 255 influence of the presence of nanoparticles suspended in the base fluid is negligible and independent on  
 256 the particle geometry. Therefore, only for nanofluids in liquid phase at 0.1% of solid mass load  
 257 evidences of enhancement of the thermal behaviour can be observed. Otherwise, in solid phase where  
 258 nanoparticles agglomerate even more during the phase change the influence of the morphology  
 259 becomes important and nanotubes present the higher increase at any concentration due to the high  
 260 aspect ratio and the better pathway provided for the transport of phonons responsible for the thermal  
 261 conductivity enhancement. Moreover, some theoretical models found in the literature to predict this  
 262 enhancement were modified to include the effect of the higher aspect ratio and are valid only for  
 263 nanotubes [34].

264  
 265 **4. Discussion**

266  
 267 Comparing the results obtained in this paper, there are some important highlights detailed as follows:

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

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

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

285  
 286 **Table 1. Summary of results obtained for 0.1% wt. NePCMs tested**

Nanoparticles type	Particle size [nm]	Phase change enthalpy [kJ·kg <sup>-1</sup> ]	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

287

288

## 289 5. Conclusions

290

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

293 Results shows that:

- 294 - CB/H<sub>2</sub>O NePCM agglomerated when it was put in contact with water, the water phase change
- 295 enthalpy decreased slightly and it had 5 °C of subcooling reduction (the highest obtained in
- 296 this study). The thermal conductivity in solid phase increased almost 8% in solid.
- 297 - MWCNT/H<sub>2</sub>O presented the lowest degree of agglomeration when these nanoparticles were
- 298 put in contact with water, water phase change enthalpy remained almost equal and it had the
- 299 lowest subcooling reduction (2.5 °C). Finally, the thermal conductivity measured showed the
- 300 highest increment, around 14% in solid phase by the MWCNT addition.
- 301 - GO/H<sub>2</sub>O presented agglomeration when GO nanoparticles were put in contact with water,
- 302 phase change enthalpy was almost not affected by the nanoparticles addition and the phase
- 303 change presented 4 °C of subcooling reduction. The thermal conductivity increased almost 7
- 304 % in solid phase.

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

307

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

315

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317

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