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

**Camila Barreneche[1], Rosa Mondragon[2,*], David Ventura-Espinosa[3], Jose Mata[3], Luisa F. Cabeza[4], A. Inés Fernández[1], J. Enrique Julia[2]**

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

[2]Departamento de Ingenieria Mecanica y Construccion, Universitat Jaume I, 12071-Castellon de la Plana, Spain

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

[4]GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, 25001-Lleida, Spain

[*]*Corresponding author: mondragn@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 ºC by 2100. In 2015, the Paris Agreement [2] it was stablished that the 2 ºC reduction target was insufficient, and that a 1.5 ºC target is required. To meet this goal, the emissions levels for 2030 are 55 $GtCO_2e$.

At the current pace of demography and with emerging economies consuming a steadily increasing amount of products and services [3,4], reducing $CO_2$ 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].

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

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

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

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

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

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

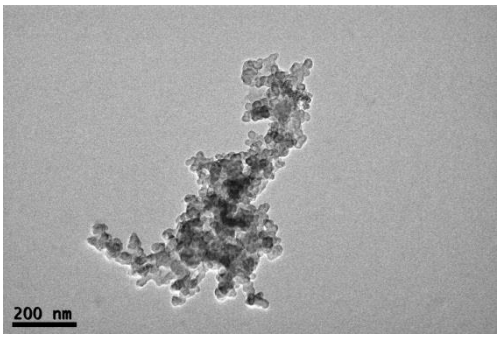
also influenced by the addition of nanoparticles in water as PCM were also tested, such as the influence in the melting enthalpy, thermal conductivity and subcooling. The shape and size of the nanostructures are important in a way that the surface to volume ratio of nanostructure alters the thermo-physical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

## 2. Materials and methods

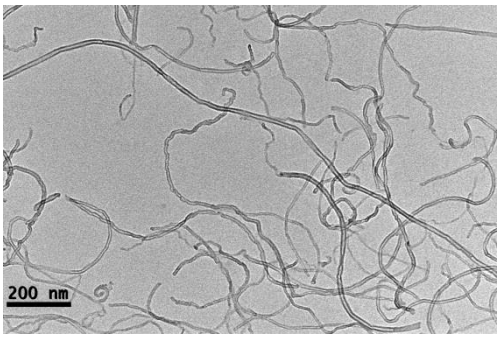
Water was doped with three different carbon-based nanoparticles:

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

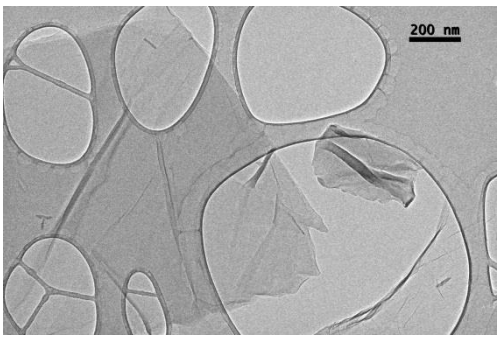
In Figure 1 TEM images of the primary nanoparticles are shown.




(a)




(b)




**(c)**

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

Before the dispersion of the nanoparticles in water, both CB and MWCNT needed to be oxidized with hydrogen peroxide at 120 ºC 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

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

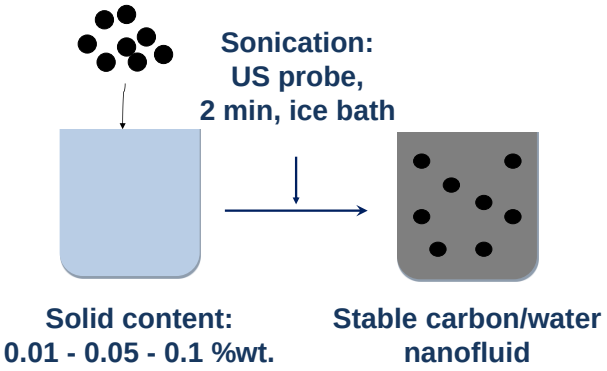



**Figure 2. Preparation of the nanocomposite: nanoparticles + PCM**

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

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

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

## 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.

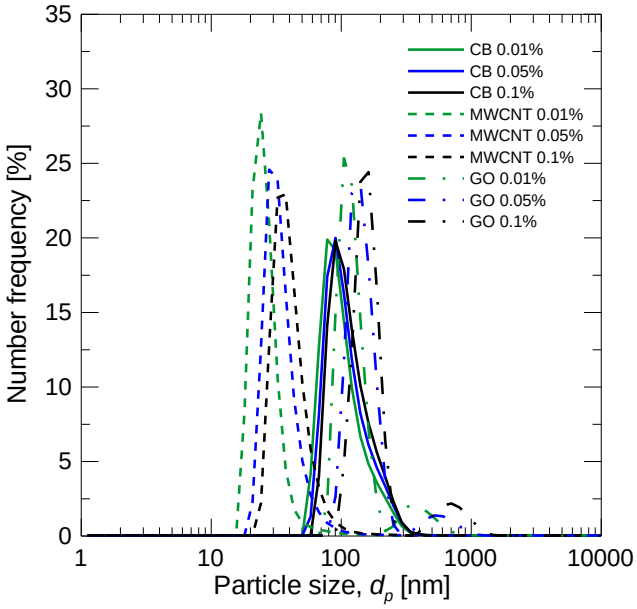



**Figure 3. Nanoparticle dispersion degree measured by DLS.**

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.

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.

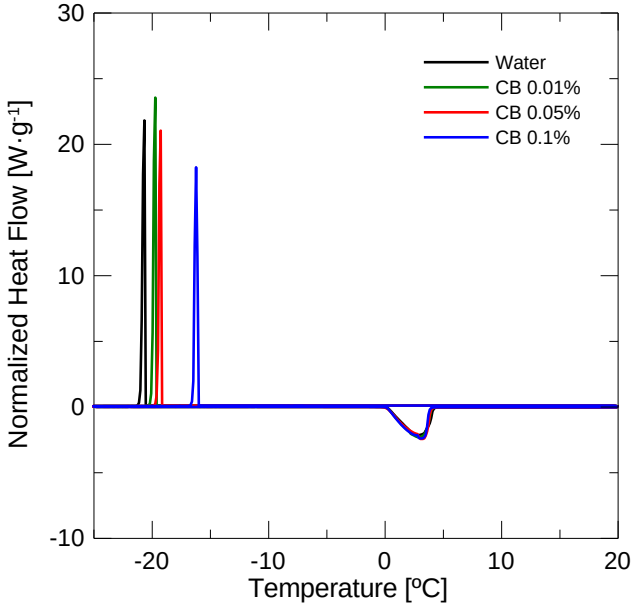



**Figure 4.** ***DSC curves of NePCM based on CB***

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 ºC. The maximum reduction of subcooling for MWCNT was only 2.5 ºC, 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 ºC.

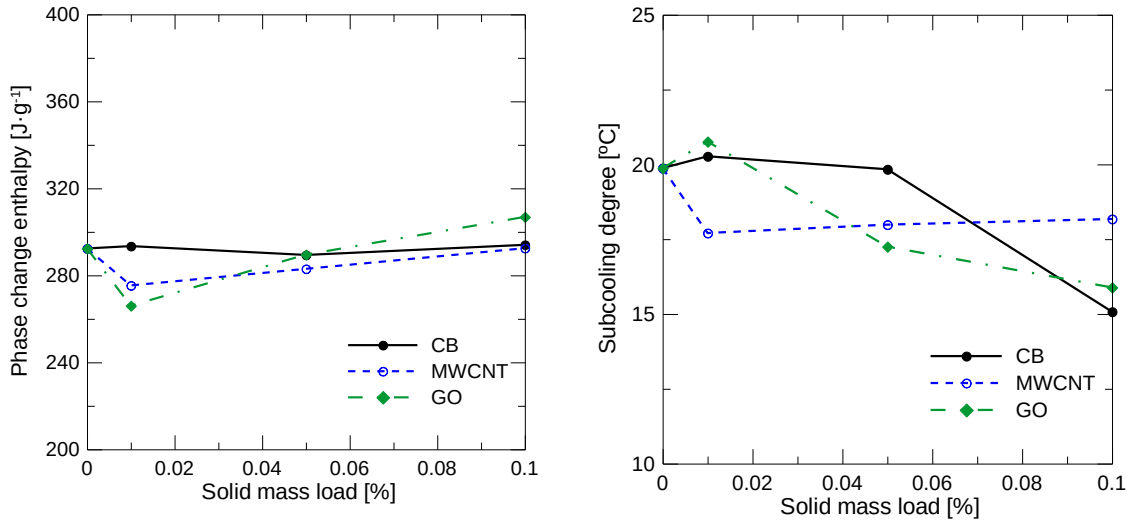



**Figure 5.** ***Left*: *Phase change enthalpy dependence with nanoparticle morphology and solid mass content. Rigth: Subcooling degree dependence with nanoparticle morphology and solid mass content.***

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

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

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

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

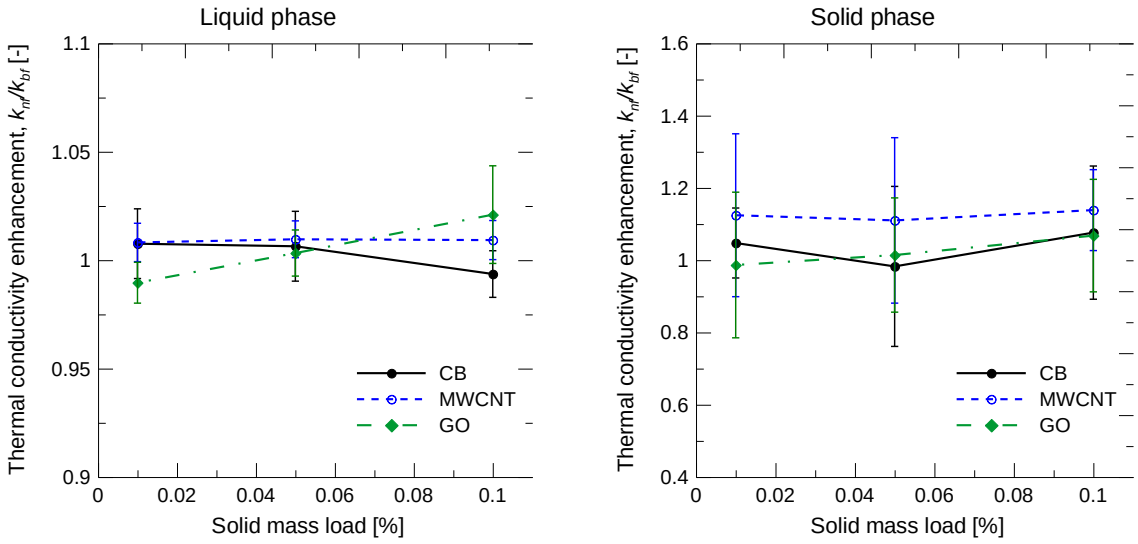



**Figure 6.** ***Thermal conductivity enhancement. Left: Liquid phase. Rigth: Solid phase.***

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

## 4. Discussion

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

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

- **CB**: it is necessary to use a minimum amount of 0.1% wt. nanoparticles to get a measurable reduction of subcooling. The maximum reduction achieved is **5ºC**.
- **MWCNT**: The maximum reduction of subcooling is only **2.5ºC**, and it is obtained for low solid mass content (0.01% wt.).
- **GO nanosheets:** The reduction of subcooling with the nanoparticle content is almost linear with a maximum decrement of **4ºC**.

- The **phase change enthalpy** is **almost constant** for all the NePCM tested.
- The **thermal conductivity increment** in solid state is higher when MWCNT nanoparticles are used.

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

**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 [ºC] | Thermal conductivity increment (solid) [%] |
|---|---|---|---|---|
| CB | 100 | 291 | 5 | 7.6 |
| MWCNT | 35 | 290 | 2.5 | 13.9 |
| GO | 110 | 308 | 4 | 6.8 |

## 5. Conclusions

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

- CB/$H_2O$ NePCM agglomerated when it was put in contact with water, the water phase change enthalpy decreased slightly and it had 5 ºC of subcooling reduction (the highest obtained in this study). The thermal conductivity in solid phase increased almost 8% in solid.
- MWCNT/$H_2O$ presented the lowest degree of agglomeration when these nanoparticles were put in contact with water, water phase change enthalpy remained almost equal and it had the lowest subcooling reduction (2.5 ºC). Finally, the thermal conductivity measured showed the highest increment, around 14% in solid phase by the MWCNT addition.
- GO/$H_2O$ presented agglomeration when GO nanoparticles were put in contact with water, phase change enthalpy was almost not affected by the nanoparticles addition and the phase change presented 4 ºC of subcooling reduction. The thermal conductivity increased almost 7 % in solid phase.

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

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

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