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Enhancing the Thermal Performance of a Stearate Phase Change Material with Graphene Nanoplatelets and MgO Nanoparticles

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## Enhancing the Thermal Performance of a Stearate Phase Change Material with Graphene Nanoplatelets and MgO Nanoparticles

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**KEYWORDS:**

Phase change material, thermal performance, stearate, graphene nanoplatelets, MgO, NePCMs.

**ABSTRACT**

The effectiveness of dispersed nanomaterials to improve the thermal performance of phase change materials (PCMs) is well-proven in the literature. The proposal of new engineered nanoenhanced phase change materials (NePCMs) with customized characteristics may lead to more efficient thermal energy storage (TES) systems. This work is focused on the development of new NePCMs based on dispersions of graphene nanoplatelets (GnPs) or MgO nanoparticles in a stearate PCM. The new proposed materials were developed using the two-step method and acetic acid was selected as surfactant to improve the stability of the dispersions. An extensive characterization of the constitutive materials and the developed dispersions through different spectroscopy techniques is reported. Also, the GnPs nanopowder was explored by using the XPS technique with the aim to characterized the used carbon nanomaterial. The obtained spectra were discussed in terms of the chemical bonds related to the found peaks. The thermophysical profile (density, thermal conductivity, isobaric heat capacity and thermal diffusivity) was experimentally determined once the main components of the NePCMs were characterized and dispersions were designed and developed. The differentiated and distinguished effect of the dispersed GnPs and MgO in the properties of the NePCMs have focused the discussion. A comprehensive analysis of the measurements to elucidate the mechanism that promoted higher improvements using GnPs instead of MgO was performed.

## 1. INTRODUCTION

Nanostructured materials have been proving their capability to create a huge number of new opportunities in a wide variety of fields, such as energy,<sup>1, 2</sup> biomedical,<sup>3</sup> electronic,<sup>4</sup> or environmental<sup>5</sup> applications. An assortment of nanomaterials can be synthesized with tailored properties, including thermophysical, optical, chemical, or magnetic, among many other characteristics.<sup>2, 6-8</sup> Nowadays, a research area with high growing potential is the use of phase change materials (PCMs) in thermal energy storage (TES). The high latent heats of these materials allow large amounts of stored and released thermal energies.<sup>9</sup> However, their thermophysical profile could be tuned to improve the heat transfer performance despite of the extended use of coolants and PCMs in cold storage applications as air conditioning in domestic systems.<sup>9, 10</sup> In such a way, a huge number of publications have demonstrated that the dispersion of nanomaterials into a PCM enhance its thermal behavior.<sup>11, 12</sup> These kind of nanomaterials comprised of a dispersion of any nanoadditive into a base PCM are termed nanoenhanced phase change materials (NePCMs).

The key parameter in the design of a TES system that uses latent heat materials is the selection of PCMs whose melting point matches with the temperature range of the application.<sup>13</sup> Cold TES used in home applications usually operates in the temperature range of 277-285 K. Another important characteristic is the chemical nature of the selected PCM which has impact on the final thermal performance of the TES.<sup>13</sup> Among the different families of PCMs, organic materials have better phase change performance, i.e., congruent melting, low or negligible subcooling, and physicochemical stability. Nonetheless, the main drawback of organic PCMs is their poor thermal conductivity that leads to low heat transfer rates.<sup>11</sup> Fatty acids, whether pure compounds or their eutectic mixtures, have a noticeable interest within the group of the organic PCMs due to their low

cost and relatively high latent heat.<sup>13</sup> In addition, they are synthesized from natural renewable sources such as vegetable oils and animal fats instead of another organic compounds like paraffins which come from crude oils.<sup>14</sup> The most extended fatty acids are capric acid (CA), lauric acid (LA), myristic acid (MA), palmitic acid (PA), stearic acid (SA), and their esters produced by transesterification reaction from alcohols, either linear or branched.<sup>15</sup> Beeswax is another widely used ester obtained from fatty acids, which consists of palmitate, palmitoleate, hydroxypalmitate, and oleate esters of long chain aliphatic alcohols.<sup>16</sup> Along the initial lines of this work, these materials could be substantially improved with the use of nanotechnology.

In the literature, different nanomaterials based on carbon structures have been dispersed on fatty acids. Thereby, NePCMs based on graphene nanoplatelets (GnPs), expanded graphite (microscale), multi-walled carbon nanotubes (MWCNT), and activated carbon (AC) were studied and no significant changes in latent heat were reported.<sup>17, 18</sup> However, there are some studies which use beeswax as base PCM and different carbon based nanomaterials that reported some variations on the latent heat.<sup>16, 19</sup> Also, large thermal conductivity enhancements were found by using GnPs, such as in the work by Harish et al.<sup>20</sup> They argued that this high improvement was due to the huge thermal interface conductance (around  $100 \text{ MW m}^{-2} \text{ K}^{-1}$ ) of the nanomaterial within the base PCM.

PCMs derived from SA, i.e., SA itself and its esters, have been used in the literature to produce a variety of latent heat materials, such as nano and micro encapsulated PCMs, composites, and eutectic PCMs.<sup>21</sup> A thorough study on stearate esters was performed by Yi et al.<sup>22</sup> These authors investigated the thermal properties of octyl, decyl, dodecyl, and tetradecyl stearates, concluding that these materials have a great potential for the use in domestic applications.

To the best of our knowledge, regarding to the preparation and characterization of NePCMs based on a stearate PCM only the article by Hashempour and Vakili<sup>23</sup> should be highlighted. They

utilized carbon nanotube structures -single walled (SWCNTs), multi walled (MWCNTs), and modified MWCNTs- with the aim of increase the thermal conductivity of butyl stearate. Also, different surfactants and mass fractions of CNTs were considered, 17 times higher thermal conductivity being obtained without a significant change in the melting point when 3 wt% of modified MWCNTs are dispersed.

In the present work, two different nanomaterials, namely graphene nanoplatelets (GnPs) and MgO nanoparticles, were dispersed into a stearate base PCM, obtaining new NePCMs with potential use in cold TES applications. Base PCM, both nanoadditives and designed NePCMs were characterized *via* different spectroscopy techniques. Then, we focused on the understanding of how the chemical nature of dispersed nanomaterials influences their thermal performance through thermophysical properties, such as density, thermal conductivity, heat capacity, and thermal diffusivity. Furthermore, we performed a comprehensive analysis of these results to figure out the optimum and main parameters in the design of new NePCMs.

## 2. MATERIALS AND METHODS

### 2.1. Materials

PureTemp® 8 (PT8) was provided by Entropy Solutions (Plymouth, USA). It is a commercial PCM, with declared latent heat of  $178 \text{ J g}^{-1}$  and melting point of 281 K. Graphene nanoplatelets, GnP, and MgO nanoparticles were purchased from IoLiTec (Heilbronn, Germany) with a mass purity of 99.5% and 99%, and declared sizes of 11-15 nm (thickness) and 35 nm (diameter), respectively. Acetic acid, provided by Sigma-Aldric (St. Louis, USA) with a mass purity of 99.7% and a declared density of  $1.049 \text{ kg} \cdot \text{m}^{-3}$ , was used as a surfactant to stabilize the samples. Samples

were weighted by using a Sartorius CPA225 analytical balance (Göttingen, Germany) whose accuracy is  $1 \cdot 10^{-5}$  g. No additional purification was performed in the products.

## 2.2. Experimental methods

In this work, a set of experimental techniques were used for both characterization of the nanomaterials, base PCM, and designed NePCMs and study of their thermal performance. Figure 1 enclosed a schematic summary of the employed methods.

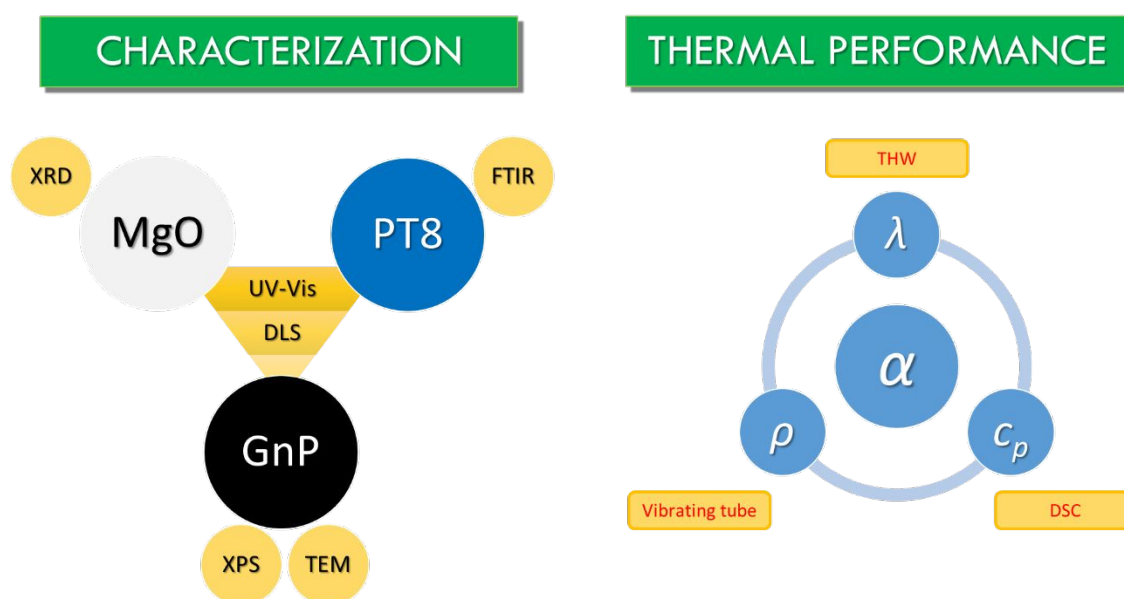


Figure 1. Schematic diagram of the experimental techniques used in this work, classified in two main groups: characterization and thermal performance.

Structural analysis of PT8 was performed through Fourier-Transform Infrared Spectroscopy (FTIR) technique by using a Thermo Scientific Nicolet 6700 FTIR spectrometer (Waltham, USA) equipped with an Attenuated Total Reflection (ATR) attachment. Thus, spectrum of the sample was recorded within the wavenumber range between  $4000$  and  $400\text{ cm}^{-1}$ , performing 34 scans with a resolution of  $4\text{ cm}^{-1}$ . Also, background spectrum of ambient air was collected after each

measurement and subtracted to the measured spectra with the software OMNIC (Thermo Scientific, v7.3).

In the literature, there is a wide variety of GnPs taking into account aspect ratio, number of layers, and type of functionalization. An X-ray photoelectron spectroscopy (XPS) technique was used to investigate the chemical state and composition of the graphene sheets. Tests were performed on a Thermo Scientific K-Alpha ESCA instrument with Al-K $\alpha$  monochromatic radiation at 1486.6 eV. Neutralization of the surface charge was achieved by using both a low energy flood gun and a low energy Argon ions gun, due to the no-conductive nature of GnP samples. A small quantity of the nanopowder was pressed onto a conductive double side adhesive tape and placed on the standard sample holder. Binding energies (BE) for all photopeaks were referenced to the C1s photopeak position for C-C and C-H species at 285.0 eV.

Also, images of the GnPs were obtained by using a transmission electron microscope (TEM) JEM 1010 (JEOL, Japan) with an accelerating voltage of 100 kV to assess the potential impact of the ultrasonication process in the GnPs. Nanopowder was dispersed in analytical grade 1-butanol and then deposited on the top of a 400-mesh copper grid covered with a Formvar film coated with a conductive carbon layer.

The phase and crystallinity of MgO nanoparticles were studied *via* X-ray diffraction (XRD) tests carried out on a PANalytical X'Pert PRO diffractometer (Malvern, UK) with Cu-K $\alpha$  monochromatic radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 30 mA and operational voltage of 40 kV. The crystallites size of MgO was estimated by the Debye-Scherrer formula:<sup>24</sup>

$$D = \frac{K \lambda}{\beta \cos(\theta)} \quad (1)$$

where  $K$  is a constant related to the shape of the crystals, typically 0.94 for spherical nanoparticles,<sup>25</sup>  $\lambda$  is the wavelength of the incident X-ray beam, and  $\beta$  is the full width at half maximum (FWHM) of the diffraction peak corresponding to Bragg angle.

Firstly, UV-Vis spectroscopy characterization was carried out to assess the developed NePCMs by using a Fisher Scientific Helios Omega UV-VIS spectrophotometer (Hampton, USA). Useful information about the molecular bonds and chemical structure of the base fluid and nanoparticles can be extracted from this characterization since UV-Vis absorption is related to the electronic structure of the sample.<sup>26</sup>

Moreover, stability of the developed NePCMs was examined by means of the Dynamic Light Scattering (DLS) technique using a Malvern Instruments Zetasizer Nano ZS (Malvern, United Kingdom) with a scattering angle of 173°. Aliquots of diluted samples of both nanoadditives based dispersions using 0.75:1, 1:1, and 1.5:1 rates were deposited in standard cuvettes and rested for several days, the size distribution being measured once per day. The optimum surfactant:nanomaterial rate was elucidated by studying the evolution of the apparent size over time.

Densities of the designed NePCMs were measured on samples of approximately 1 ml using the vibrating tube technique.<sup>27</sup> These measurements were performed on an Anton Paar DMA 500 (Graz, Austria) within the temperature range from 288.15 K to 313.15 K. The instrument works using the widespread vibrating tube technique whose measurement principle can be found elsewhere. The expanded uncertainty of the results is better than 0.1%.<sup>28</sup> Thermal conductivity was measured with a Decagon KD2 Pro Thermal Properties Analyser (Pullman, USA) coupled with a KS-1 stainless steel sensor (length of 60 mm and diameter of 1.3 mm) over the temperature range from 283.15 K to 333.15 K. Samples were completely soaked on a thermostatic bath

Polyscience 9510 (Illinois, USA) to achieve thermal stability. The expanded uncertainty of the device for values below  $0.200 \text{ W m}^{-1} \text{ K}^{-1}$  is better than  $0.010 \text{ W m}^{-1} \text{ K}^{-1}$ .<sup>29</sup> Heat capacities were determined using a TA Instruments Q2000 (New Castle, USA) heat-flux Differential Scanning Calorimeter (DSC) equipped with a refrigerated cooling system RSC90 and by using a quasi-isothermal temperature-modulated method. Tests were performed in the temperature range from 243.15 K to 313.15 K. Samples were placed in aluminium cells hermetically sealed using thin lids. The estimated expanded uncertainty for these experiments was settled as 3% in the entire temperature range.<sup>30</sup>

In the performance of PCMs and/or NePCMs in cold energy applications, the two relevant characteristics are the capability to store thermal energy along with the efficiency of the heat transfer process when the stored energy is required. Thermal diffusivity is the thermophysical property that accounts the ability to propagate the energy stored in any material. Its definition comes from the simplified energy equation in transient conditions, without considering convection and heat generation effects:

$$\nabla^2 T = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (2)$$

where  $T$  is the absolute temperature and  $\alpha$  is the thermal diffusivity. From Eq. (2) it is possible to figure out the physical interpretation of the thermal diffusivity by rearranging the equation as following:

$$\alpha = \frac{\frac{\partial T}{\partial t}}{\nabla^2 T} \quad (3)$$

Therefore, it is possible to derive it from the thermal conductivity, density and heat capacity by means of the following equation:

$$\alpha = \frac{\lambda}{\rho c_p} \quad (4)$$

where  $\lambda$ ,  $\rho$ , and  $c_p$  refer to thermal conductivity, density and isobaric heat capacity, respectively.

In such a way, it is clear to observe that thermal diffusivity assesses the ability to balance the temperature within the material by rating its heat transfer rate and its heat storage capacity.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization

##### 3.1.1. Base PCM characterization

Certainly, an examination of the FTIR spectrum of PT8 (Figure 2) provides information about functional groups in this PCM. The intense peak observed at  $1737\text{ cm}^{-1}$  indicates stretching of the C=O group referred to a saturated aliphatic ester. The peaks that represented C-O stretching of C-O-H and C-O-C groups were found at  $1169\text{ cm}^{-1}$  and  $1112\text{ cm}^{-1}$ , respectively. As usual for C-O stretching, the band at higher wavenumber is stronger and broader than the other one. The peaks corresponding to  $\text{sp}^3$  C-H stretching of the  $\text{CH}_3$  and  $\text{CH}_2$  groups were observed at  $2954\text{ cm}^{-1}$  (asymmetric stretching) and at  $2922$  and  $2853\text{ cm}^{-1}$  (symmetric stretching), while  $\text{sp}^3$  C-H bending vibration bands of the saturated aliphatic groups were observed at  $1466$  and  $1377$  (scissoring) and at  $722\text{ cm}^{-1}$  (rocking).

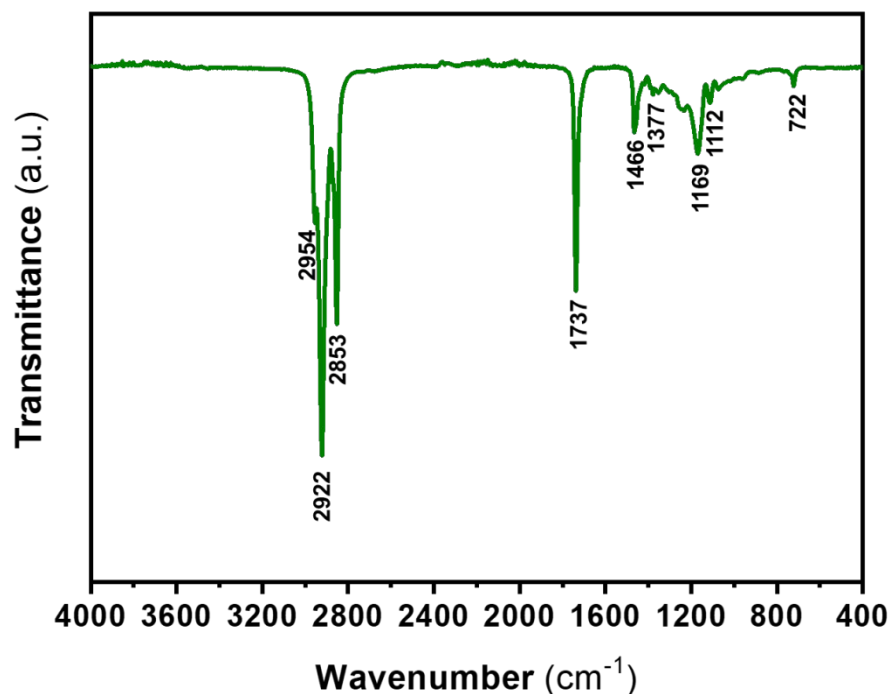


Figure 2. FTIR spectrum of PT8.

Hence, these findings pointed out that PT8 fits with a saturated aliphatic ester. Taking also into account the melting point along with the IR results, among the different possible esters, sample spectrum matches within a 97.16% agreement with isooctyl stearate spectrum.

### 3.1.2. Nanomaterial characterization

Figure 3a depicts the survey XPS spectrum of GnPs in which two main peaks were identified at 284.19 eV and 532.02 eV due to carbon (C1s) and oxygen (O1s) regions, respectively. It should be noted that binding energies extracted from the survey spectrum are not energy referenced since this spectrum is only intended for quantitative elemental analysis. Also, a smaller peak was found at 163.27 eV, corresponding to sulphur (S2p). From the analysis of this survey spectrum, the elemental composition of the sample was obtained and summarized in Table 1.

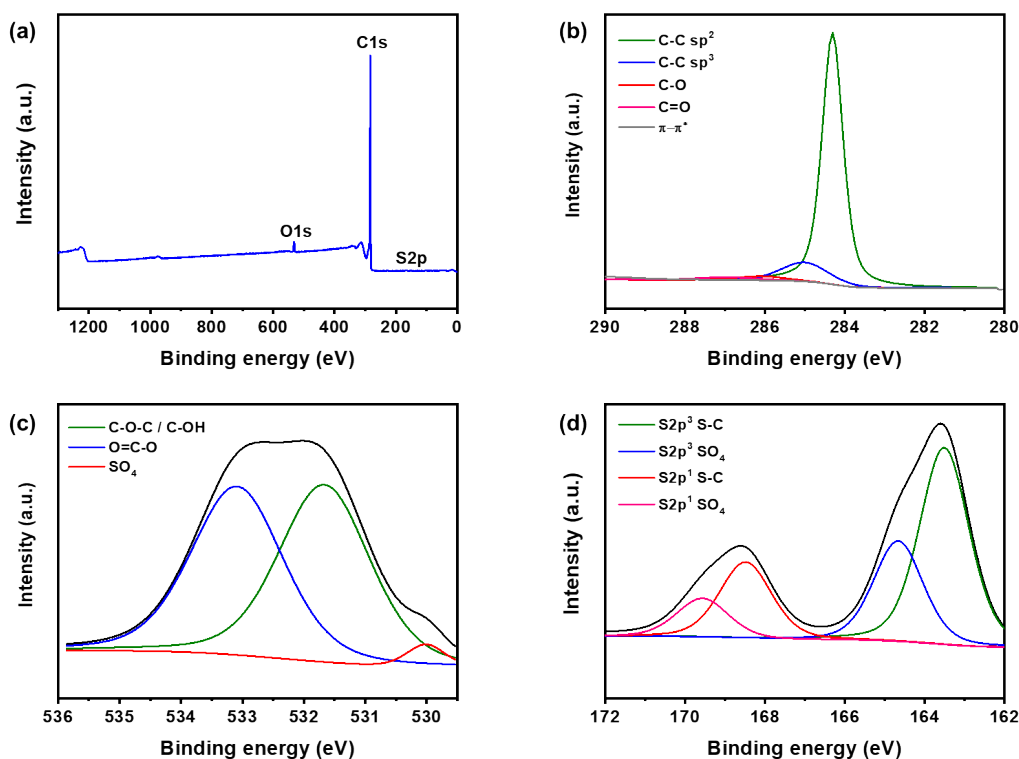


Figure 3. (a) Survey XPS spectrum of GnPs; (b) High resolution XPS spectrum of C1s; (c) High resolution XPS spectrum of O1s; (d) High resolution XPS spectrum of S2p.

Table 1. Elemental composition of the main species found in GnPs.

| Species       | Atomic ratio (%) |
|---------------|------------------|
| Carbon (C1s)  | 96.70            |
| Oxygen (O1s)  | 3.18             |
| Sulphur (S2p) | 0.11             |

High resolution spectra of C1s, O1s and S2p regions (Figure 3b-d) were deconvoluted and analysed to ascertain the chemical state of these elements in the GnPs. Table 2 sums up the chemical state, binding energies and found relative composition in each component. The intensive

C1s contribution (Figure 3b) shows an asymmetric and broad peak for carbon, a complex bonding scheme being suggested and deconvoluted into 5 peaks. The elemental oxygen contribution (Figure 3c) was fitted in three components. Two of them are related to single and double Carbon-Oxygen bonds and are the most intensive components with similar abundance in the sample. In addition, there is a small contribution at lower binding energy related to the oxidized sulphur bonds. The smallest elemental, S2p (Figure 3d), was fitted in 2 components, one associated with C-S bonds and the other at higher BE with the oxidized sulphur bonds. From the analysis of XPS spectra, it is possible to conclude that GnPs used in these work were functionalized with carboxylic groups. Sulphur species may probably come from the functionalization process accomplished by the manufacturer.

Table 2. Relative composition of each species obtained from the deconvolution of C1s, O1s and S2p spectra in Figure 3, respectively.

| Species | Chemical state       | Peak (eV) | Relative composition (%) |
|---------|----------------------|-----------|--------------------------|
| C1s     | sp <sup>2</sup>      | 284.30    | 78.15                    |
|         | sp <sup>3</sup>      | 285.00    | 12.28                    |
|         | C-O                  | 286.09    | 2.91                     |
|         | C=O                  | 286.96    | 2.45                     |
|         | $\pi$ - $\pi^*$      | 290.44    | 4.20                     |
| O1s     | C-O-C / C-OH         | 531.67    | 49.71                    |
|         | O=C-O                | 533.09    | 47.56                    |
|         | SO <sub>4</sub>      | 530.01    | 2.73                     |
| S2p     | S2p <sup>3</sup> S-C | 163.51    | 70.90                    |

|  |                                  |        |       |
|--|----------------------------------|--------|-------|
|  | S2p <sup>1</sup> S-C             | 164.66 |       |
|  | S2p <sup>3</sup> SO <sub>4</sub> | 168.48 | 29.10 |
|  | S2p <sup>1</sup> SO <sub>4</sub> | 169.56 |       |

A previous work showed other structural information of these particles. Particularly, atomic force microscopy (AFM) analyses were conducted to determine the surface topography and morphology of these GnPs. This nanomaterial is made of multiple groups of stacked graphene layers with a mean height per layer of 2-6 nm.<sup>31</sup>

MgO nanoparticles were analysed in terms of crystallinity by means of XRD technique. The obtained diffraction pattern (Figure 4) shows Bragg reflections with  $2\theta$  values of 36.87°, 42.89°, 62.24°, 74.60°, and 78.53° corresponding to the (111), (200), (220), (311), and (222) planes (JCPDS No. 87-0653) for the primitive cubic MgO structure ( $a = 4.211 \text{ \AA}$ ), respectively.<sup>32</sup> The crystallites size was found to be 39.01 nm, calculated from (200) reflection by using the equation (1).

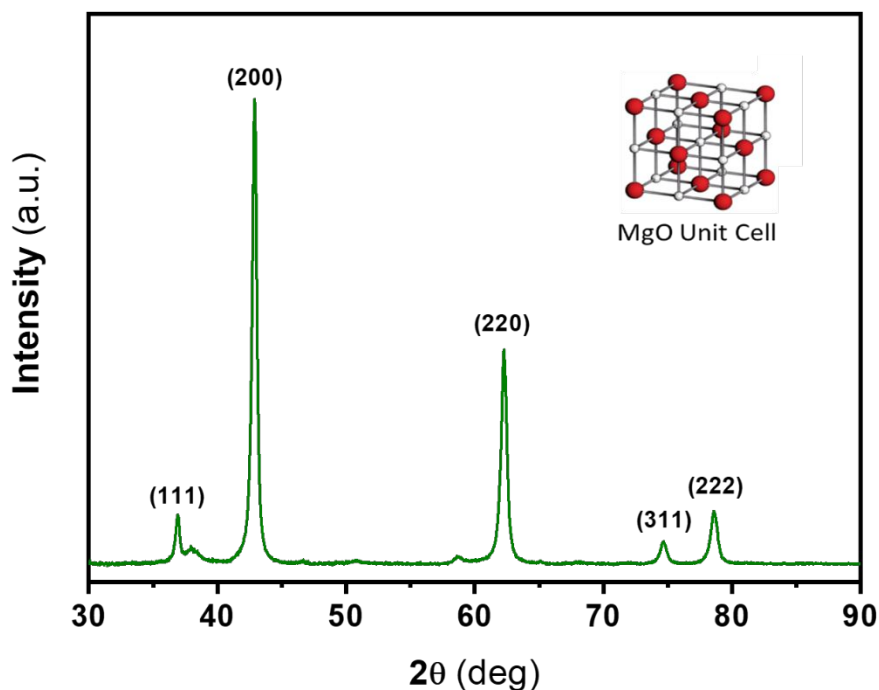


Figure 4. XRD spectrum of MgO nanoparticles with the main crystalline planes identified.

### 3.1.3. NePCM preparation and characterization

NePCMs were produced following the two-step method.<sup>33</sup> Accordingly, calculated GnPs and MgO nanoparticles amounts were dispersed into the base fluid to obtain NePCMs with different desired mass fractions. In this study, we considered mass fractions within the ranges (0.25-2)% for GnP-based NePCMs, named as GnP/PT8, and (1-15)% for MgO-based NePCMs, named as MgO/PT8. A surfactant was selected to create a layer that engulf the nanomaterials by means of a noncovalent interaction with the aim of achieve a proper stability of the NePCMs. In order to guarantee an appropriate dispersion of the nanomaterials in the base fluid, samples were prepared using an ultrasonic homogenizer Bandelin Sonopuls HD 2200 (Berlin, Germany) with an operating frequency of 20 kHz for about 30 min. Samples were soaked in an ice bath during sonication to

avoid the degradation of the surfactant. Furthermore, the application of low-temperature during sonication guarantees that the fluid keeps a high viscosity, preventing the breakage of the GnPs. This effect was checked by comparing TEM images before and after the process (Figure 5), the morphology and length of the GnPs being kept.

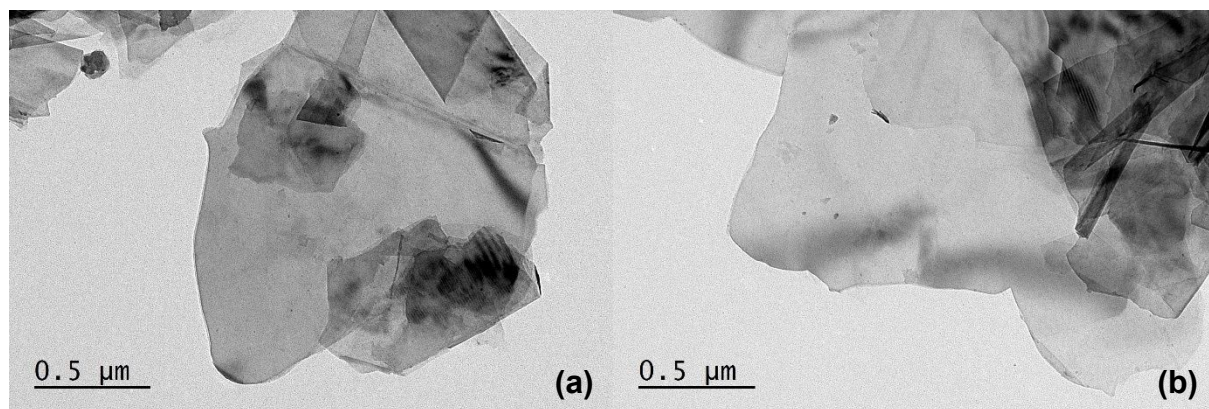


Figure 5. TEM images of the GnPs (a) before and (b) after ultrasonication process.

In Figure 6a, the UV-Vis spectrum of a diluted GnP/PT8 dispersion shows a peak at a wavelength value of 223 nm. This obtained result agrees with the study concerning graphene oxide nanofluids reported by Paredes et al.,<sup>34</sup> who identified a peak around 230 nm with the  $\pi$ - $\pi^*$  electronic transition due to the aromatic C=C bonds of the graphene structure.

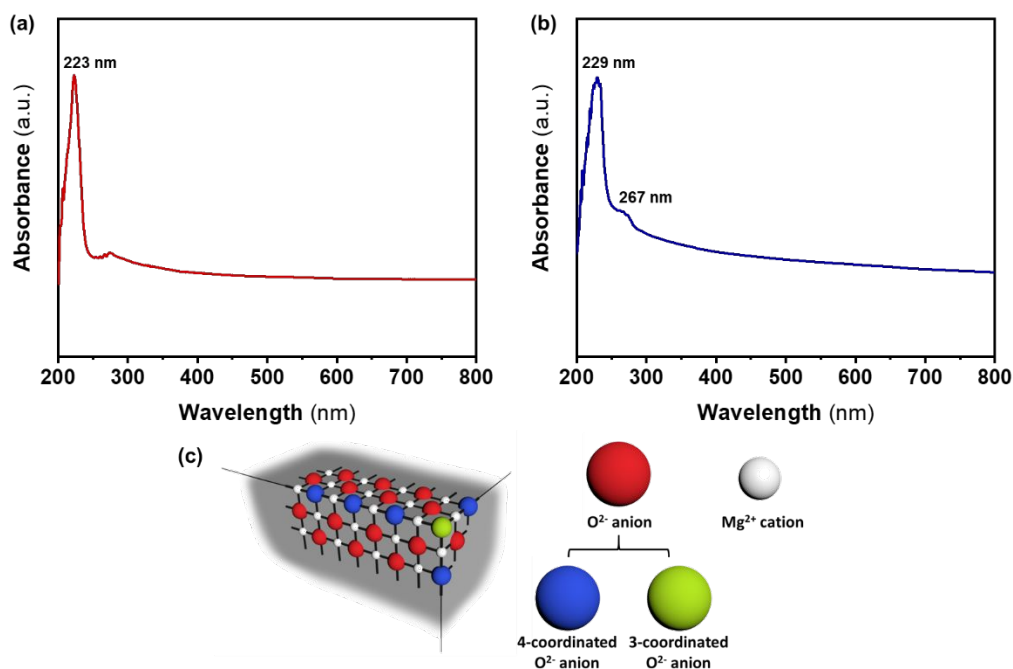


Figure 6. (a) UV-Vis spectrum of GnP/PT8; (b) UV-Vis spectrum of MgO/PT8; (c) crystalline structure of MgO nanoparticles indicating the two coordination numbers of O<sup>2-</sup> anions.

UV-Vis spectrum of a diluted MgO/PT8 dispersion in Figure 6b has two notable peaks, at 229 nm and 267 nm. Sterrer et al.<sup>35</sup> theoretically stated that both peaks are produced by the excitation of O<sup>2-</sup> anions placed on the surface of MgO nanoparticles. The peak around 229 nm is produced by the excitation of 4-coordinated O<sup>2-</sup> anions and the peak at 267 nm is produced by the excitation of 3-coordinated O<sup>2-</sup> anions. For a more understandable description of this effect, Figure 6c depicts a scheme of MgO crystalline structure, where the 4-coordinated O<sup>2-</sup> anions are placed in the edges and the 3-coordinated O<sup>2-</sup> anions are placed in the corner of the crystalline structure.

In order to assess the stability of the NePCMs and also to determine the optimum surfactant:nanomaterial rate, DLS tests were performed during several days. Three different diluted samples using surfactant:nanomaterial rates at 0.75:1, 1:1, and 1.5:1 were prepared for both nanomaterials. A stable dispersion should be non-time dependence in terms of size distribution

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3 and unimodal size distributions with a single narrow peak may contribute to this issue. Likewise,  
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5 controlled decreases in the polydispersity index and in the average apparent size may lead also to  
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7 stable NePCMs.<sup>36</sup>  
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10 As it can be observed in Figure 7, after several days less polydisperse samples were obtained  
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12 and the shown initial bimodal size distributions evolved to narrower single peaks with a tiny size  
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14 shift between the first and the last measured day. It entails the existence of some disaggregation  
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16 phenomena of the initial clusters which it may lead to the improvement of the stability.<sup>36</sup> Among  
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18 the three studied surfactant:nanomaterial rates, 0.75:1 corresponded to the proportion that optimise  
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20 the stability of the samples for both nanoadditives.  
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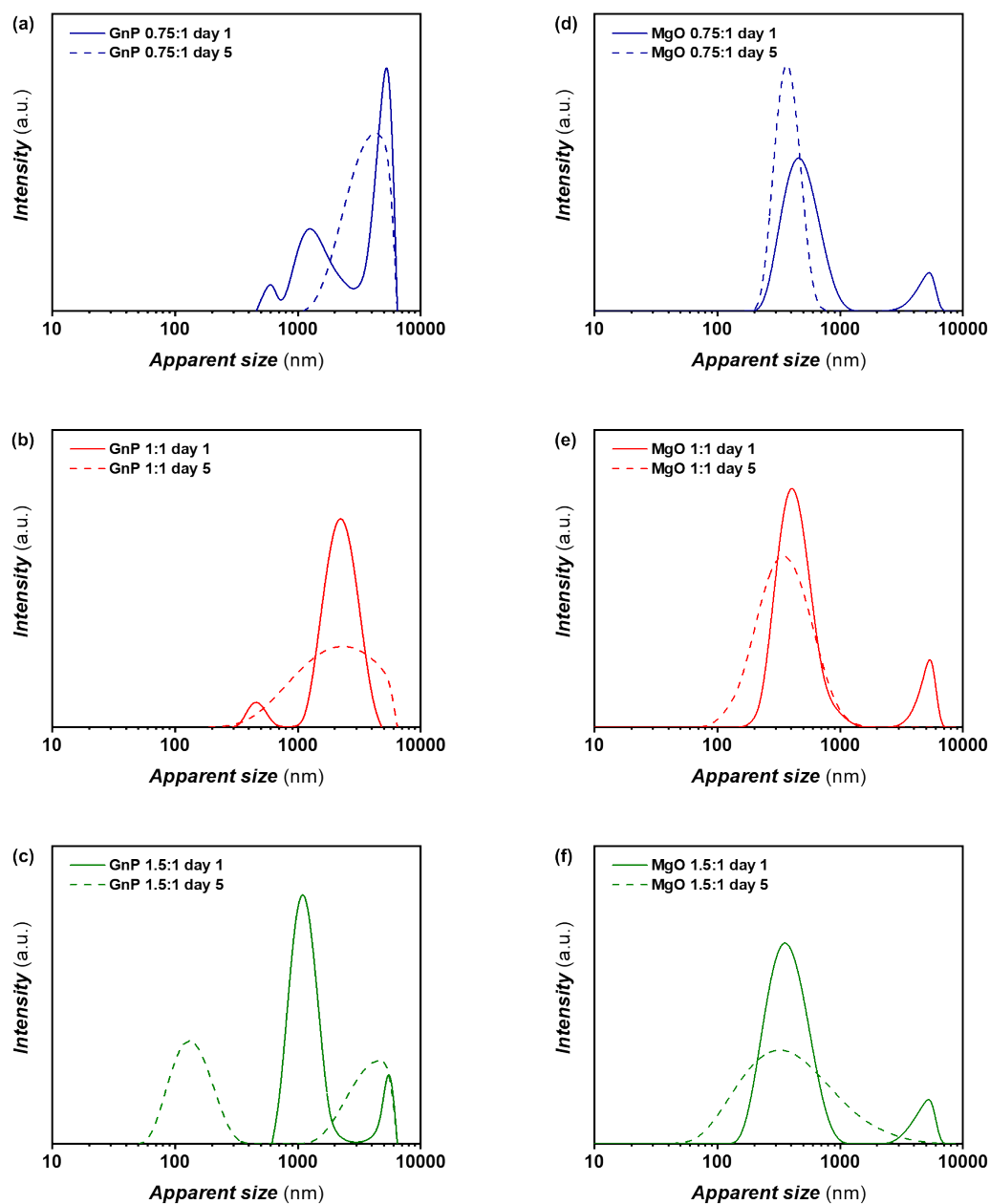


Figure 7. Apparent size distribution in terms of intensity for the first and the fifth day after preparation at different surfactant:nanomaterial rates: GnP/PT8 at (a) 0.75:1; (b) 1:1; and (c) 1.5:1 and MgO/PT8 at (d) 0.75:1; (e) 1:1; and (f) 1.5:1.

3.2. Thermal performance

3.2.1. Density

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3 Firstly, the performance of the device had been checked using water and toluene as reference  
4 materials.<sup>28</sup> As expected, density of the NePCMs has the same temperature dependence as density  
5 of the base fluid (Table S1, Supporting Information) beyond of the dispersed nanomaterial on the  
6 base PCM (MgO or GnPs), as displayed in Figure 8a.  
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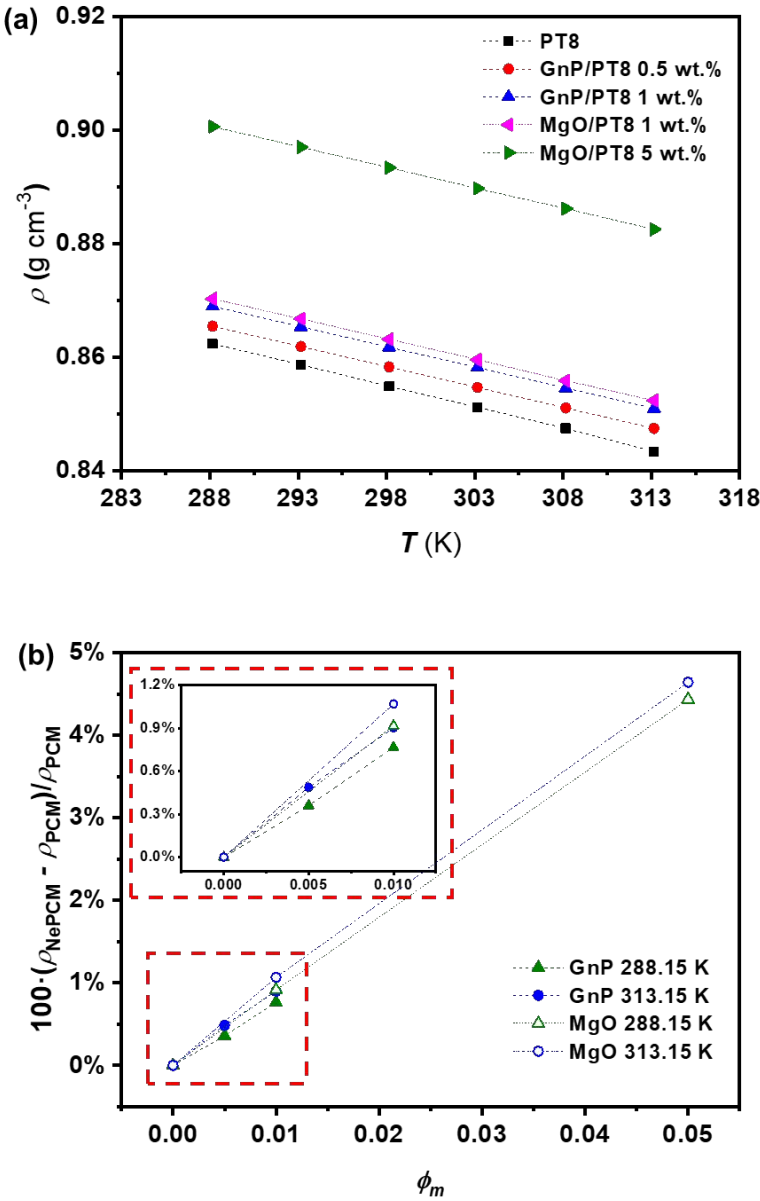


Figure 8. (a) Density as a function of the temperature for PT8, GnP/PT8 (0.5 wt%, 1 wt%), and MgO/PT8 (1 wt%, 5 wt%); (b) density increase as a function of the mass fraction for GnP/PT8 and MgO/PT8 at 288.15 K and 313.15 K.

Seemingly, the higher the mass fraction, the higher the density (Figure 8b) and this increment is larger when MgO nanoparticles are employed instead of GnP. As an example, density increases of

0.8% and 1.0% over the base PCM are obtained for GnP/PT8 and MgO/PT8 at 1 wt%, respectively. This effect is observed in the inset in Figure 8b where the surpass of MgO tendency is noticeable. Besides, this outcome may be attributed to the lower density of GnPs<sup>27</sup> in comparison with MgO nanoparticles.<sup>37</sup> Even so, the outcome caused in the density by the dispersion of GnPs or MgO in the base PCM is lower than 5% for all designed NePCMs and, consequently, these minor changes favour their heat transfer behaviour.

### 3.2.2. Thermal conductivity

Thermal conductivity results of the base fluid (Table S2, Supporting Information) and the developed NePCMs are presented and discussed in the temperature range from 283.15 K to 333.15 K with steps of 10 K and mass fractions of 0.5 wt%, 1 wt%, and 2 wt% for GnP/PT8 and 1 wt% and 5 wt% for MgO/PT8. Accordingly, Figure 9 clearly evidences the effect of nanoparticle content and temperature on the thermal conductivity and on the thermal conductivity enhancement of NePCMs.

It is well-known that properly dispersed nanomaterials enhance thermal conductivity of NePCMs and the higher the load of nanomaterial, the higher the enhancement,<sup>28</sup> as it is clearly observed in Figure 9a. In addition, this thermal conductivity enhancement depends on the mass fraction of dispersed nanomaterials, but it remains constant with the temperature (Figure 9b). All these general remarks are valid for both GnPs and MgO nanoparticles dispersed into the base PCM.

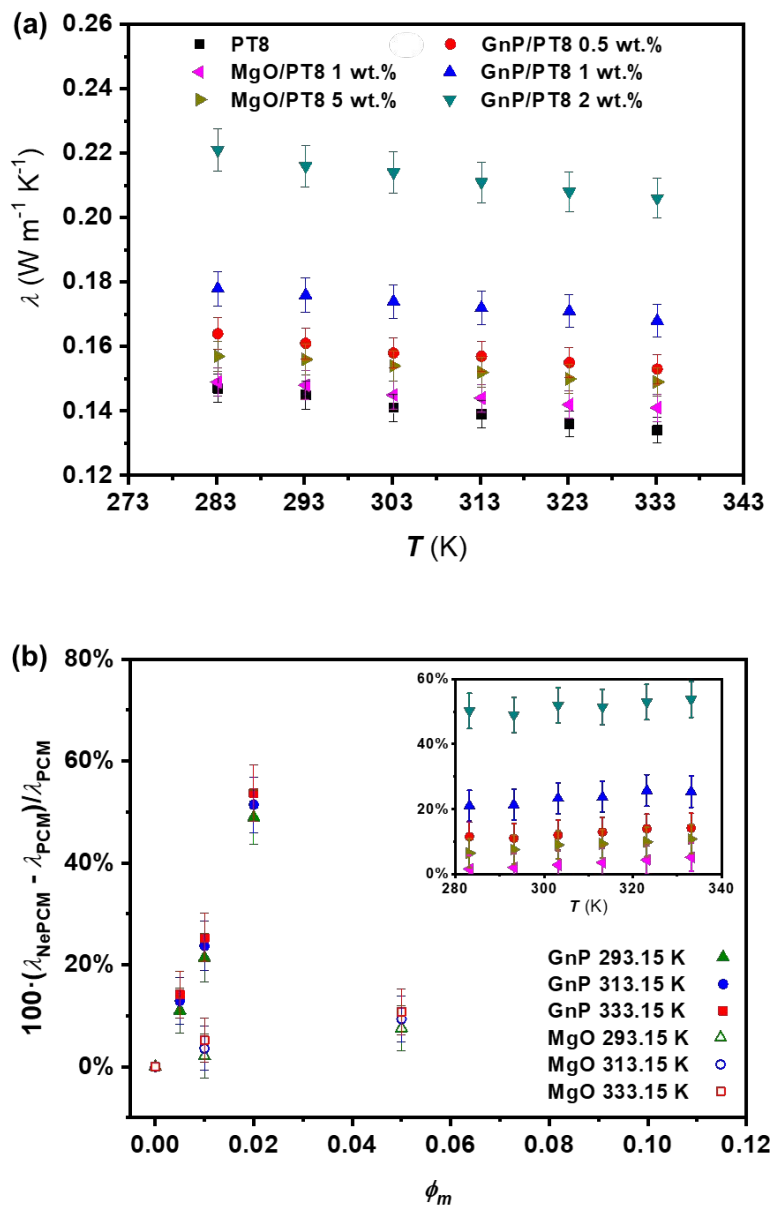


Figure 9. (a) Thermal conductivity as a function of the temperature for PT8, GnP/PT8 (0.5 wt%, 1 wt%, 2 wt%), and MgO/PT8 (1 wt%, 5 wt%); (b) Thermal conductivity enhancement as a function of the mass fraction of GnP/PT8 and MgO/PT8 at 293.15 K, 313.15 K and 333.15 K. The inset shows the thermal conductivity enhancement as a function of the temperature for GnP/PT8 (0.5 wt%, 1 wt%, 2 wt%) and MgO/PT8 (1 wt%, 5 wt%).

The concentration dependence of the thermal conductivity enhancement is linear for both nanomaterials within a low-concentration range, as can be observed in Figure 9b. As an example, when dispersing 1 wt% of GnPs into the base PCM, an enhancement around 24% is achieved; instead 3% of enhancement is accomplished when using MgO nanoparticles. Thus, noteworthy higher enhancements in the thermal conductivity are achieved when same mass amounts of GnPs are used in comparison with those employing MgO nanoparticles.

As can be elucidated, the higher the thermal conductivity of the dispersed nanomaterial, the better the effective thermal conductivity of the NePCM. Therefore, based on this premise, enhancements obtained with GnPs are larger than those obtained with MgO since thermal conductivity of graphene is about  $3000 \text{ W m}^{-1} \text{ K}^{-1}$  while thermal conductivity of MgO nanoparticles is about  $48 \text{ W m}^{-1} \text{ K}^{-1}$ .<sup>2, 38</sup>

Furthermore, the sheet-like configuration of the GnPs leads to higher thermal conductivity of the NePCMs than the spherical shape of MgO nanoparticles. This configuration favours the heat transfer mechanism within the NePCMs caused by the percolation network established by the nanoparticles in which thermal conductivity is higher than in the base PCM. When the number of interfaces between nanoparticles is high, the thermal conductivity enhancement is limited because of the low-frequency phonons transfer at the interface. Inasmuch as the structure of the GnPs is thick but long, the density of interfaces is low and the thermal conductivity enhancement is less limited than in the case of MgO nanoparticles.<sup>39</sup> In addition, there is a threshold for the nanoparticles concerning the mutual interlinkage needed to establish the percolating network<sup>40</sup> and this threshold is highly dependent on the aspect ratio of the nanomaterials.<sup>39</sup> Since the aspect ratio of the GnPs is much longer than the MgO nanoparticles, a lower mass fraction is required using

GnPs instead of MgO to form the percolating network and hence, to accomplish an expected level of thermal conductivity enhancement.<sup>40</sup>

Anyway, there are several effects related with the thermal conductivity enhancement in nanostructured fluids and it is still on discussion in the literature. Herein, above we have presented a tentative explanation of the differentiated behaviour which we observed by using GnPs or MgO.

### 3.2.3. Isobaric heat capacity

Isobaric heat capacities of the base fluid (Table S3, Supporting Information) and the designed NePCMs were experimentally determined within the solid (243 K to 263 K) and liquid phases (283 K to 313 K). Measurements on the boundaries of the solid-liquid phase change transition were avoided to avert instabilities that could lead to inaccuracies. Figure 10a depicts these results over the above mentioned temperature range. As usually in organic materials like, isobaric heat capacity in the solid phase is lower than in the liquid range.<sup>41</sup> Hereabouts, the increase in the isobaric heat capacity is around 4% for base PT8 once the melting occurs in the material, comparing the values obtained in solid and liquid phases on the boundary of the transition. Very similar increments referred to the values close to the transition were also observed for all designed NePCMs, regardless of the mass fraction and the kind of nanomaterial. Additionally, the trend of the isobaric heat capacity curve over temperature (Figure 10a) is different in both sides of the phase change transition: quadratic in the solid region and linear in the liquid region.

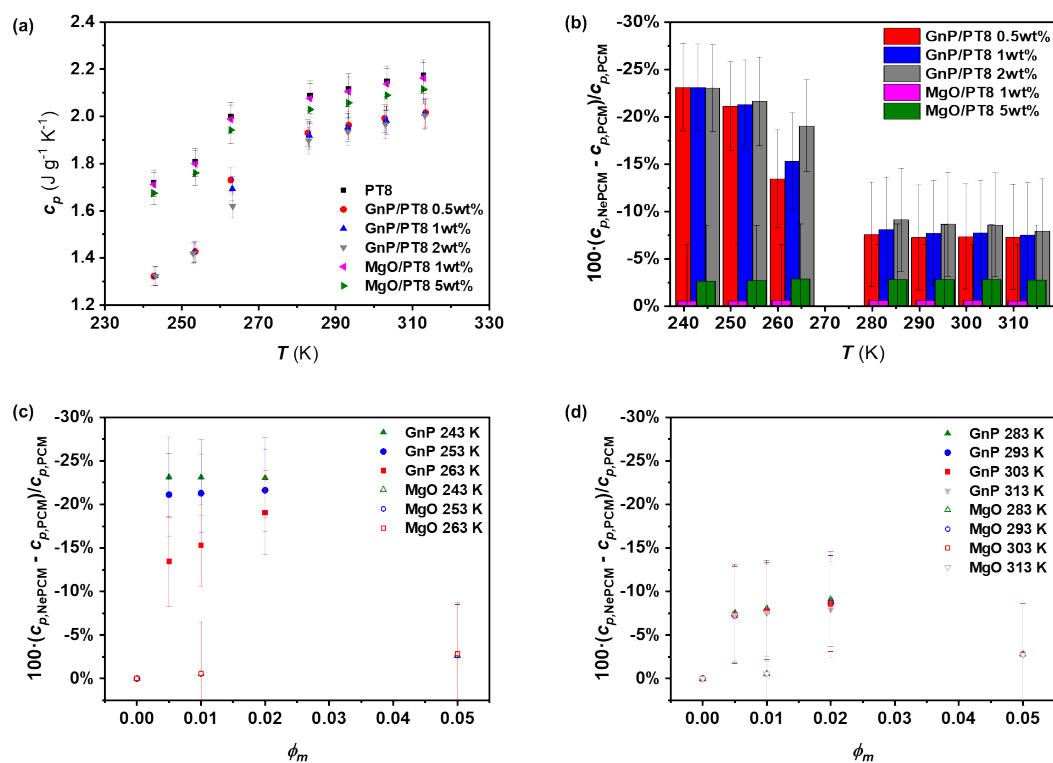


Figure 10. (a)  $c_p$  as a function of the temperature for PT8, GnP/PT8 (0.5 wt%, 1 wt%, 2 wt%), and MgO/PT8 (1 wt%, 5 wt%); (b) Percentage decreases in the  $c_p$  for the studied NePCMs vs. temperature; (c) Percentage decreases in the  $c_p$  vs. mass fraction of nanoparticles in the solid phase; (d) Percentage decreases in the  $c_p$  vs. mass fraction of nanoparticles in the liquid phase.

Another clearly observed effect is the reduction of isobaric heat capacity caused by the dispersed nanomaterials in the base PCM. In order to account this effect, Figure 10b-d enclose the percentage variation of the isobaric heat capacity in relation to PT8. MgO-based NePCMs account lower diminutions comparing with GnP/PT8 dispersions. This agrees with the order of the reported isobaric heat capacities of MgO nanoparticles and graphene nanoplatelets, i.e.  $c_{p, \text{MgO}} > c_{p, \text{GnP}}$ .<sup>30, 42</sup> As well, there is a decreasing in these reductions as temperature rises especially for GnP/PT8 NePCMs, in the same way as in the study performed by Marcos et al.<sup>43</sup> These decreases for GnP/PT8 dispersions in the solid phase are lower than 23% (Figure 10c) while within the liquid

range are lower than 9% (Figure 10d). On the contrary, small and similar  $c_p$  decreases about 2% are obtained over the entire temperature range in the isobaric heat capacity for MgO/PT8 dispersions for both solid and liquid phases (Figure 10c-d).

#### 3.2.4. Thermal diffusivity

In this work, thermal diffusivity was computed for the base fluid (Table S4, Supporting Information) and the prepared NePCMs from our  $\lambda$ ,  $\rho$ , and  $c_p$  values and the resulting data have been plotted in Figure 11a. The tendencies of thermal diffusivity with temperature and mass fractions reproduce in some way those observed for thermal conductivity: it decreases with temperature and rises with mass fraction of dispersed nanomaterial.

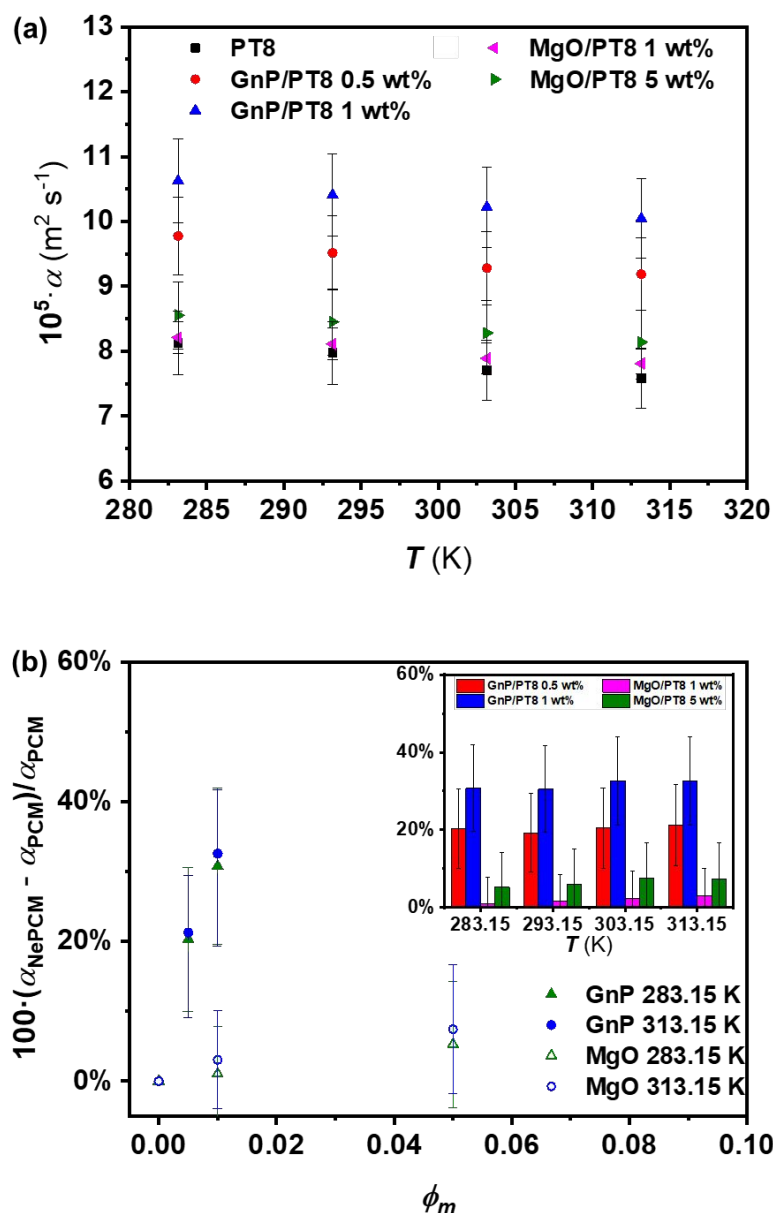


Figure 11. (a) Thermal diffusivity as a function of the temperature for PT8, GnP/PT8 (0.5 wt%, 1 wt%), and MgO/PT8 (1 wt%, 5 wt%); (b) Thermal diffusivity enhancement as a function of the mass fraction. The inset shows the thermal diffusivity enhancement as a function of the temperature.

Figure 11b encloses the thermal diffusivity enhancements achieved when MgO and GnP are dispersed in the base PCM. On the one hand, enhancements were found for all designed NePCMs independently of the dispersed nanomaterial, reaching a maximum enhancement around 33% for GnP/PT8 NePCM (at 1 wt%). This value is higher than those reported by Cheng et al.<sup>44</sup> and Marcos et al.<sup>43</sup> which had used graphene as nanoadditive in their correspondingly works on NePCMs. On the other hand, comparing the enhancements achieved with MgO and GnPs, GnP/PT8 dispersions reached higher values for the same mass fraction. As an example, when 1 wt% of nanoadditives are dispersed, thermal diffusivity enhanced ~13 times using GnP than MgO.

It is possible to figure out that there is a valued improvement in the heat transfer performance of the developed NePCMs, either by using GnPs or MgO, comparing with the base PCM when considering all studied thermophysical properties. Interestingly, despite the fact that the isobaric heat capacity of NePCMs are lower than the base PCM, this diminutions are not a handicap for the enhancement of thermal diffusivity, as can be observed in Figure 11. Thus, the higher impact on the increment in thermal diffusivity comes from the thermal conductivity enhancement along with a tiny effect from the density increments that lead to a better contact between nanoparticles, allowing the formation of the percolation network, which brings several benefits.

#### 4. CONCLUSIONS

A comprehensive comparative study of the effect of two different nanostructured materials dispersed in a stearate PCM to produce new NePCMs is presented. A commercial PCM for cold TES applications, named as PT8, was used as base material in which GnPs and MgO nanoparticles were conveniently dispersed. FTIR revealed the presence of C=O, C-O, C-O-H, and C-O-C groups along with saturated aliphatic saturated which confirmed that the main chemical component of the

base PCM is isooctyl stearate. Chemical state and composition of the GnPs were investigated by using XPS technique and we could conclude that they are functionalized with carboxyl groups. Crystallinity of MgO nanoparticles was determined *via* XRD characterization. The acquired diffraction pattern matched with the primitive cubic MgO structure. In addition, a crystallites size of 39.01 nm was determined using Debye-Scherrer formula.

Obtained GnP/PT8 and MgO/PT8 dispersions were assessed by means of UV-Vis spectroscopy analysis, studying the chemical state of GnPs and MgO nanoparticles in that dispersions, respectively. Also, DLS results clarified that the optimum amount of surfactant for both GnPs and MgO based NePCMs is 0.75:1. We observed densities for MgO/PT8 higher than for GnP/PT8 according to the density of MgO nanoparticles is larger than that of GnPs. As well, thermal conductivity enhancements of up to 52% and 9% were accomplished for GnP/PT8 and MgO/PT8 NePCMs, respectively. We figured out that the different percolation network formed by GnPs and MgO plays a pivotal role, determining the capability of these nanostructured systems to improve their thermal conductivity. Regarding the isobaric heat capacity results, a divergent influence when compared with the thermal conductivity was found: the higher the mass fraction of nanoadditive, the lower the heat capacity, more remarkable being this effect in the presence of GnPs. Finally, thermal diffusivity was computed to obtain a property assessment of the heat transfer capability of these new NePCMs for the use in a TES. Notwithstanding the diminution in isobaric heat capacity, thermal diffusivity of the NePCMs is higher (up to 32% for GnP/PT8 at 1 wt%) than in the base PCM due to the huge influence of thermal conductivity enhancements. These mean very promising results, which indicated that the proposed NePCMs could increase the global heat transfer performance of a TES in domestic and/or industrial applications, leading to more efficient and sustainable exploitation of the energy sources.

This paper reports an initial work on stearate based NePCMs comparing the distinctive effect of dispersing GnPs and/or MgO nanoparticles. Further studies should be accomplished to achieve a stage in which these new NePCMs could be employed in cold TES applications. Therefore, a complete calorimetric analysis determining their phase change properties (latent heat, melting point, subcooling...) together with a rheological study should be performed in the future. Moreover, the performance of a pilot TES plant operating with these NePCMs, in an encapsulated form or not, should be desirable once these new materials are completely characterized.

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### Notes

The authors declare no competing financial interest.

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