Graphene Nanoplatelets Dispersed In Isopropyl Palmitate for the Improvement of Cold Storage Applications

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Abstract - This study presents experimental results of temporary stability, thermal conductivity and phase change transitions of nano-enhanced phase change materials (NePCMs) based on isopropyl palmitate (IPP). Different concentrations from 0.10 to 1 wt.% of graphene nanoplatelets (GnP2) were dispersed into IPP and stabilized with cetyltrimethylammonium bromide (CTAB) surfactant with a CTAB:GnP2 mass ratio of 1:1. The samples were homogenized by means of an ultrasonic probe under the two step method. A diluted concentration of 0.1 wt.% GnP2/IPP (CTAB:GnP2 1:1) showed similar hydrodynamic sizes of the nanoadditives after two weeks revealing good temporary stability of the dispersion. An enhancement in thermal conductivity of 3.2% was evidenced for 1 wt.% GnP2/IPP (CTAB:GnP2 1:1). Additionally, a sub-cooling reduction of 10% was observed for the highest studied concentration.

Keywords: Graphene nanoplatelets, isopropyl palmitate, thermal conductivity, sub-cooling, temporal stability.

1. Introduction
There is currently a growing concern about the energy crisis that affects several problems of economic and social nature. There are more and more studies that focus on implementing certain technologies to minimize the reliance on fossil fuels and enhance the efficiency of processes, in order to cope with climate change and reduce energy consumption. Thus, it is important to invest efforts in boosting the use of renewable energies as well as improving the energy efficiency, which would strengthen energy independence. Moreover, energy consumption in the last fifty years has been higher than energy consumption in the previous two centuries [2,3]. Market coupling, interconnection and a common trading platform for electricity are important tools to increase the independence. Although Europe is a world leader on clean energy research and is at the forefront of green technology [1], coal, gas and oil constitute about 80% of the world's energy consumption. Phase change materials (PCMs) are latent heat storage media that attract particular attention due to the high energy storage density [4]. Isopropyl palmitate, an ester of isopropyl alcohol and palmitic acid, is an interesting proposal among the PCMs and is considered an eco-friendly material. Its phase transition temperature lies between 283 K and 286 K and the heat of fusion is ~113 J/g [5], so it is adequate to be used as a PCM in thermal energy storage applications.

2. Experimental, Results and Discussion
NePCMs from 0.10 wt% to 1 wt% were designed dispersing graphene nanoplatelets of 2 nm thickness (GnP2) in isopropyl palmitate (IPP). Due to the need to increase the temporary stability of the designed samples, they have been subjected to a treatment with the CTAB surfactant and the CTAB: GnP2 1:1 mass ratio has been selected in all cases.
Commercial graphene nanoplatelets were supplied by Avanzare (La Rioja, España), isopropyl palmitate was purchased from Thermo Fisher (Kandel, Germany), and the CTAB was supplied by Merck (Darmstadt, Germany).

2.1. Temporal stability

A Zetasizer Nano ZS (Malvern Instruments, UK) was used to study the temporal stability of the dispersion of the nanomaterials, observing the evolution of the hydrodynamic size by dynamic light scattering of the GnP2 over a period of three weeks. To carry out the study, and in accordance with the operating principle of the equipment, a sample with the most diluted concentration, 0.10 wt% GnP2/IPP, with CTAB:GnP2 1:1, was selected.

Fig. 1: a) Temporary evolution of hydrodynamic size for the 0.10 wt% GnP2/IPP (CTAB:GnP2 1:1) nanofluid. Solid lines: standard deviation; dashed lines: average value; b) Hydrodynamic size distribution by intensity of GnP2 nanoparticles just after preparation (−), and 14th day (---).

Fig. 1a shows that the mean hydrodynamic size of the studied sample remains around 549 nm, this value being very close to the values of the first and 14th days (498 and 513 nm, respectively) and the standard deviation of the hydrodynamic size measurements was lower than 6.4%. In addition, Fig. 1b shows that the hydrodynamic size distribution by intensity of GnP2 in dispersion remains almost stable after 14 days of study. Therefore, it can be considered that nanofluids showed very good stability for a reasonable period.

2.2. Thermal analysis

Solid-liquid phase changes have been observed using a Q2000 differential scanning heat flux calorimeter (DSC) (TA Instruments, New Castle, DE, USA). The modification of the onset temperature for cooling and freezing processes are observed in Fig. 2a. For the GnP2 (1.0 wt%)/IPP sample, recrystallization started around ~282.3 K while for IPP this transition is observed at ~281.7 K. In the same way, during the heating process, a slight decrease in the melting temperature was observed, as shown in the figure.
Fig. 2: a) DSC cooling and heating thermograms at scanning rates of 10 K·min⁻¹ for base fluid (solid line), and 1wt% GnP2/IPP (dotted lines); b) Mass fraction dependence on the melting and crystallization temperatures for base fluid (—), 0.25 wt% GnP2/IPP (—), 0.50 wt% GnP2/IPP (—), 0.50 wt% GnP2/IPP (—). (CTAB:GnP2 1:1). Droplines represent sub-cooling.

The melting and crystallization temperatures for the base IPP and the NePCMs were obtained from the thermograms and their evolution with the mass fraction is depicted in Fig. 2b. As can be seen, the dispersion of GnP2 within IPP leads to an increase in the crystallization temperature which does not depend on the mass fraction. On the other hand, the melting temperature slightly but continuously reduces with the increasing concentration of dispersed GnP2. These two combined effects induce reductions in the sub-cooling effect, as represented by the diminution of the droplines size in Fig. 2b. The maximum sub-cooling reduction was achieved for the 1.0 wt% GnP2/IPP (CTAB:GnP2 1:1) sample, accomplishing a diminution of 2.63 K with respect to the base IPP.

2.3. Thermal conductivity

The experimental determination of thermal conductivity was carried out by means of a THW-L2 device (Thermtest Inc., Hanwell, NB, Canada) following the procedure described in Prado et al. [6]. As can be seen in Fig. 3, the dispersion of graphene nanoplatelets improved the thermal conductivity of the isopropyl palmitate for all studied dispersions.

Fig. 3: Mass fraction dependence on the thermal conductivity enhancements at different temperatures.

The observed thermal conductivity enhancements increase with the loading of GnP2, reaching a 3.2% improvement for the maximum GnP2 concentration (1wt%) while it slightly decreases with increasing temperature. This last
temperature dependence is not always reported, for instance Renteria et al. [7] observed temperature independence of the thermal conductivity of some graphene/paraffin NePCM.

4. Conclusion

The temporal stability, thermal conductivity, and phase change transitions of different concentrations of GnP2 dispersed and stabilized in IPP have been studied. The dispersions of GnP2 in IPP show good stability with the addition of CTAB surfactant at 1:1 ratio. An increase in thermal conductivity of 3.2% for the highest concentration of GnP2 (1wt%), as well as a reduction in sub-cooling of 2.63 K, were observed.

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