Research Paper

Influence of nanoparticle morphology and its dispersion ability regarding thermal properties of water used as phase change material

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HIGHLIGHTS

- Addition of carbon nanoparticles to water used as phase change material.
- Reduction of subcooling degree and increase of thermal conductivity.
- Influence of nanoparticle morphology: use of spheres, nanotubes and nanosheets.

ARTICLE INFO

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.

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1. Introduction

One of the conclusions reached in the 2010 United Nations Climate Change Conference was that Global Warming cannot be avoided, only mitigated [1]. To achieve this objective, efforts should focus on limiting the rise in global temperatures to 2 °C by 2100. In 2015, the Paris Agreement [2] it was stablished that the 2 °C reduction target was insufficient, and that a 1.5 °C target is required. To meet this goal, the emissions levels for 2030 are 55 $GtCO_2e$.

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 electrifica-

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tion), 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 nano-

fluid 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 Fig. 1 TEM images of the primary nanoparticles are shown.

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 min at low input energy (15%) in an ice bath to avoid heating of the sample (Fig. 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.

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 min at 20 °C, cooling from 20 °C to −25 °C at a cooling rate of 20 °C·min^{-1}, isothermal stage 5 min at −25 °C, and heating from −25 °C to 20 °C at a heating rate of 20 °C·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