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## Gold nanoparticles dispersions in PEG 400 for thermal energy storage. Synthesis and physical characterization

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### Introduction

It is undeniable that the energy and the services that provides are a key issue in the development of the humanity and contribute directly to the well-being of people, among other things. Thus, more specifically, it is crucial to improve the thermal capacities of fluids, since there is a direct relationship between the heat transfer and storage abilities of working fluids and the thermal performance of most installations [1]. Additionally, the flexibility of thermal facilities or the correction of possible unforeseen mismatches between offer and demand can be improved by means of energy storage. A possibility to enhance the efficiency and optimize operating time of those thermal processes is the utilization of functional materials named Phase Change Materials, PCMs, which can storage and release large amounts of latent heat with a slight temperature change [1, 2]. In the last years, new materials with enhanced properties were developed by dispersing particles with high thermal conductivities and nanometric size into these PCMs [3]. Thermal conductivity is the key property in order to improve the charging and discharging mechanisms whereas heat capacity and melting enthalpy allow quantifying both sensible and latent heat storage capabilities.

In this work, oleylamine-coated gold nanoparticles were synthesized and dispersed in a polietilenglicol with a low molecular weight to formulate new nano-enhanced phase change materials, NePCMs. The thermal conductivity, heat capacity and enthalpy of these new NePCMs were experimentally determined and the temperature and nanoadditive concentration influences on these physical properties were analysed.

### Methods

~12nm oleylamine-coated gold nanoparticles were synthesized following a slightly modified procedure already present in the literature [4]. Namely, a solution of 3mL (6.4mmol) of oleylamine and 49mL of toluene was heated to reflux in a 100mL three-neck round-bottom flask and, subsequently, a solution containing 50mg (0.13mmol) of HAuCl<sub>4</sub>, 1.74mL (3.7mmol) of oleylamine and 1mL of toluene was quickly injected. The reaction mixture was magnetically stirred and refluxed for two hours. The as-synthesized gold nanoparticles were precipitated by adding 50mL of ethanol to the previous mixture and separated via centrifugation (5000rpm, 20min.). In order to remove any undispersed residue, the precipitate was washed three times with ethanol (40mL). Eventually, the black product was dried at 40°C overnight. All reagents, HAuCl<sub>4</sub> (trace metals basis, ≥99.9%), oleylamine (technical grade, 70%) and toluene (ACS reagent, ≥99.5%) were purchased from Sigma-Aldrich and used without further preparation or purification. Absolute ethanol was also used as received.

As base material it was used a pharmaceutical-grade polyethylene glycol with an average molecular weight of 400 g/mol, PEG400, supplied by Panreac AppliChem. Purity and molecular weight of PEG were determined through electrospray ionisation mass spectrometry. Thermal stabilities of both gold nanoparticles and PEG400 were studied through thermogravimetric analysis, TGA, with a Setsys 16 TG-DTA (Setaram Instrumentation). NePCMs were prepared following a two-step method by dispersing the dry nanoparticles in the PEG400 with an ultrasonic bath (Ultrasounds, JP Selecta S.A.) working at a frequency of 20 kHz and with a power of 200 W. Temporary stability of dispersions was evaluated by dynamic light scattering technique using a Zetasizer Nano ZS (Malvern Instruments). Thermal conductivity at temperatures from (283 to 323) K was measured using a KD2-Pro (Decagon) device which is based on the well-known transient hot wire technique [5]. Heat capacity was measured in the range between (193 and 313) K with a differential scanning calorimetry, DSC, Q2000 (TA Instruments) equipped with a RSC90 system of cooling and functioning in the quasi-isothermal

method (TMDSC) [6]. This last device was also used to analyse the characteristics of (solid - liquid) phase transitions in the temperature range between (193 and 313) K.

#### Results and conclusions

Thermal conductivities for both PEG400 and NePCMs decrease smoothly with temperature over the analysed temperature range. A perceptible increase in the thermal conductivity of gold nanoparticle dispersions is already appreciated in relation to base material even for low concentrations. In terms of heat capacity, we have found characteristic behavior in NePCMs in relation to the influence of nanoparticle loading. Figure 1 shows the thermograms obtained for PEG 400 and for the dispersion at 0.1 wt.%, using cooling rates between (1 and 10) K•min<sup>-1</sup> and a heating rate of 2 K/min. In this regard, we can underline that the addition of gold nanoparticles may play a role in an easier nucleation during solidification, reducing the temperature range in which fusion happens.

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**Primary author(s) :** Prof. LUGO LATAS, Luis (Departamento de Física Aplicada, Universidade de Vigo, E-36310, Vigo, Spain)

**Co-author(s) :** Dr. CABALEIRO ÁLVAREZ, David (Departamento de Física Aplicada, Universidade de Vigo, E-36310, Vigo, Spain); Sr. MASCOS MILLÁN, Marco Antonio (Departamento de Física Aplicada, Universidade de Vigo, E-36310, Vigo, Spain); Sr. TESTA ANTA, Martín (Departamento de Física Aplicada, Universidade de Vigo, E-36310, Vigo, Spain); Prof. SALGUEIRIÑO MACEIRA, Verónica (Departamento de Física Aplicada, Universidade de Vigo, E-36310, Vigo, Spain)

**Presenter(s) :** Sr. MASCOS MILLÁN, Marco Antonio (Departamento de Física Aplicada, Universidade de Vigo, E-36310, Vigo, Spain)

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