ISIS@MACH ITALIA

Science and Technology Facilities Council
ISIS Neutron and Muon Source

Experiment Proposal

Experiment number GP2023010

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Experiment title	Phase Change Material Emulsions	
MRF Instrument	**Cryogenic Electron Microscopy**	**Days requested:** 1
Access Route	Direct Access	**Previous GP Number:** no
Science Areas	Energy, Materials	**DOI:** -
Sponsored Grant	Yes	**Sponsor:** CNR
Grant Title	Progetto@CNR "Phase change material nano-emulsions for energy efficient cooling" (PCM Cool)	**Grant Number:** -
Start Date	15/02/2022	**Finish Date:** 14/02/2024
Similar Submission?	-	
Industrial Links	-	

Non-Technical Abstract

Phase Change Materials (PCMs) such as paraffin waxes or fatty acids have attracted much attention due to the possibility of storing heat by changing phase. Phase change material emulsions (PCMEs) are colloidal dispersion of PCMs in fluids (typically water) and have risen interest in recent years as potential heat transfer and heat storage fluids for liquid cooling. The idea is to exploit the latent heat of melting of PCM to increase the thermal energy storage capacity of the base fluid. Applications include solar thermal storage, smart buildings, heat transfer and recently the cooling of lithium batteries. To develop these emulsions it is extremely important to understand how the preparation conditions and the materials used can influence the size and shape of the drops in the emulsions. To this end, typical techniques to analyze nanoparticle morphology as SEM and TEM are not suitable especially for PCM melting in the 20-40°C due to the melting of particles under electron radiation.

Publications

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IM@IT E-platform: No

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Sample record sheet

Principal contact Dr Simona Barison, CNR, ITALY
MRF Instrument **Cryogenic Electron Microscopy** **Days Requested:** 1
Special requirements:

SAMPLE

Material	water with <=1 wt% of a surfactant (typically sodium dodecyl sulphate) and 5wt% or 10wt% of a paraffin	-	-
Formula	-	-	-
Forms	Liquid		
Volume	20-30 cc		
Weight	mg		
Container or substrate	plastic bottle	-	-
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	- K	-	-
Pressure Range	- mbar	-	-
Magnetic field range	- T	-	-
Standard equipment	None	-	-
Special equipment	-	-	-

SAFETY

Prep lab needed	No	-	-
Sample Prep Hazards	-	-	-
Special equip. reqs	-	-	-
Sensitivity to air	No	-	-
Sensitivity to vapour	No	-	-
Experiment Hazards	-	-	-
Equipment Hazards	-	-	-
Biological hazards	no	-	-
Radioactive Hazards	no	-	-
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Returned to user by instrument scientist (when inactive)	-	-

Science Case

Phase Change Material Emulsions

1. Background and Context

Heating and cooling in European buildings and industry accounts for half of the EU's energy consumption and around 68% of all its gas imports. In this perspective, thermal management systems are crucial to improve performance and energy efficiency of buildings, devices and industrial plants in several applications. Liquid cooling was considered the most compelling due to its excellent cooling performance, good long-term reliability and good shape adaptability. Two widely used coolants are water and glycols. Since these refrigerants can only use sensible heat to transfer thermal energy, they suffer from a low energy storage density.
Phase Change Materials (PCMs) such as paraffin waxes or fatty acids have attracted much attention due to the possibility of harnessing their latent heat of melting/solidification for heat storage during heating or cooling, in addition to their chemical stability and tunable melting temperatures. Phase change material emulsions (PCMEs) or nano-encapsulated PCMs have risen interest in recent years as potential heat transfer and heat storage fluids for liquid cooling. These systems consist of a base fluid, a heat transfer fluid, and an emulsified PCM which should be immiscible with the base fluid. The idea is to exploit the latent heat of melting of PCM to increase the thermal energy storage capacity of the base fluid. Applications include solar thermal storage, smart buildings, heat transfer and recently the cooling of lithium batteries.
However, some issues currently hinder the application of PCMEs. One of the main issues is colloidal instability which is generally due to thermodynamic reasons (coalescence, creaming, flocculation, etc.). A further issue is the sub-cooling, i.e. the PCM cooling below its melting point without crystallization, that extends the operating temperature range of the systems, thus worsening energy efficiency and the coefficient of performance.
Recently the research group in CNR ICMATE received a grant from CNR (project@CNR) to develop PCMEs for cooling. Three main temperatures of interest will be considered in this project, one around 20-25°C (for cooling applications at room temperature), a range around 40-50°C for electronic cooling and one around 60-70°C, the working temperature of various devices.
Aim of the project is the achievement of 3 main objectives:
- Achieve long-term PCME stability under operating conditions
- Reduce the sub-cooling phenomenon typically observed in nano-PCMEs
- Increase the latent heat of emulsions.

However, to properly develop these emulsions it is extremely important to understand how the preparation conditions and the materials used can influence the size and shape of the drops in the emulsions. Furthermore, to improve the stability of these emulsions we want to develop micro and nano-encapsulation techniques and also for this activity it is extremely important to be able to observe the dimensions and coverage capacity of the drops.

2. Proposed experiment

As stated in Section 1, to properly develop PCM emulsions it is extremely important to understand how the preparation conditions and the materials used can influence the size and shape of the drops in the emulsions. The size of PCM droplets in emulsion can influence the stability, the subcooling effect as well as the heat stored in the droplets. Furthermore, a strategy to reduce the subcooling effect in PCMEs can be to add small quantities of some nucleating agents, some inert nanomaterials or PCM melting at higher temperatures that can induce heterogeneous nucleation thus reduce subcooling. However, nucleating agents can affect droplet size and shape depending on their nature. Despite the interest in understanding the shape of drops in emulsions, any attempt performed so far to characterize the PCM droplets by SEM and TEM techniques after emulsion drying resulted ineffective. In fact, especially for PCMs melting in the 20-50°C range, the PCM droplets melt under electron gun radiation under vacuum, thus making the morphology characterization impossible.

To this end, aim of this proposal is the application for some analyses with the **cryogenic electron microscopy** of ISIS@MACH Infrastructure. This technique would allow to "freeze" the PCM droplets in the solid state and avoid their melting during morphological analyses. To this end, some PCMEs will be prepared with at least 2 different PCMs, one in the 21-25°C range of melting temperature and one in the 40-50°C. Moreover, few nucleating agents will be tested in order to evaluate their influence on droplets morphology. In case more samples could be analyzed, the influence also of different emulsifying surfactants on the droplet size and morphology could be tested.

3. Summary of previous experimental proposals or characterisation

We have already performed some measurements with a SEM (Sigma ZEISS), but with no results due to the melting of the PCM droplets during the analysis. We did some Dynamic Light Scattering (DLS) measurements, which give us some indications regarding the mean hydrodynamic diameter of the drops. Below is a table with some examples of dimensions and polydispersity index in case of an emulsion in water of a commercial PCM, RT25HC, melting at 25°C, with various concentrations of a nucleating agent (a PCM melting at 65°C) and in the case of synthesis scale up (600 ml).

Tabella 1. Risultati dell'analisi DLS di campioni d RT25HC 10% in peso in acqua: diametro medio (Z-ave) e indice di polidispersità (pdi).

Campione	Z-ave (nm)	PDI
RT25HC10 10 wt%	237	0.38
RT25HC10 10 wt% + RT65 1wt%	260	0.27
RT25HC10 10 wt% + RT65 1.5wt%	270	0.26
RT25HC10 10 wt% + RT65 1.5wt% - 600 mL	369	0.42

We have measured various properties of emulsions produced: the stored heat by differential scanning calorimetry, the viscosities of the fluids, the thermal conductivities, the size of the drops by means of DLS and the stability over time. However, given that the DLS probably indicates the size of PCM+surfactant pair, we do not currently have the possibility of correlating the preparation method with size or shape, nor of correlating their functional properties.

4. Justification of experimental proposals request

Cryogenic electron microscopy analyses will be necessary in order to characterize size and shape of PCM droplets in different emulsions:

- 2 emulsions in water of a commercial PCM melting at 25°C (RT25HC) with 10 wt% of PCM and different quantities of RT65HC, a PCM melting at 65°C, as nucleating agent
- 2 emulsions in water of a commercial PCM melting at 44°C (RT44HC) with 5 wt% of PCM and 2 different nucleating agents

Other possible tests could be the measurement of the same PCM emulsified with 2 different surfactants and possibly an emulsion prepared with a fatty acid as PCM, in order to develop a method for the preparation of an emulsion with materials that could have natural origins.

Emulsions should be diluted and dried on the sample holder before analysis.