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Towards Sustainable Energy Storage: The Potential of anhydrous Pickering Emulsions

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Abstract. As the global demand for renewable energy accelerates, finding reliable and efficient energy storage solutions becomes increasingly essential to address the challenge of intermittency on energy generation, as in the case of solar and wind energy (1). One promising approach involves the use of emulsions containing phase change materials (PCMs), systems that can effectively store and release thermal energy during phase transitions (2). Despite their potential, PCM-based emulsions face key challenges, such as long-term stability and ensuring processability in practical applications. Our study introduces an innovative approach by developing and characterizing water-free Pickering emulsions, in which paraffin (with a melting point of 58-60°C) acts as the PCM dispersed as droplets, while PEG serves as the continuous phase, and are stabilized using solid silica nanoparticles.

Key words. Thermal energy storing, Phase change materials, Pickering emulsions.

1. Introduction

The increasing global energy demand, driven by population growth and technological advancements reliant on fossil fuels, has intensified concerns about climate change and greenhouse gas emissions. Promoting renewable sources like solar and wind offers a sustainable alternative, but their fluctuating sources creates a challenge in balancing energy generation and consumption. Thermal energy storage (TES) systems, which involve the temporary accumulation of thermal energy for later use, stand out as an efficient solution to bridge this gap and enhance the reliability of renewable energy **[1]**.

Phase change materials (PCMs) are a promising medium for thermal energy storage, as they can absorb and release a significant amount of latent heat when undergoing a phase change, typically between solid and liquid states. Additionally, a strategy for incorporating PCMs into thermal systems is the use of phase change material emulsions (PCME). PCMEs are two-phase fluids composed of a carrier fluid and well-dispersed PCM characterized by high latent heat. In these systems, the PCM and heat transfer fluid (HTF) can exchange thermal energy directly through the large surface that enhance heat transfer efficiency. Furthermore, as PCM slurries remain pumpable throughout the phase change process, they serve not only as energy storage materials but also as effective heat transfer media **[2]**.

A promising approach to improving the stability of these emulsions involves the use of nanoparticles instead of traditional emulsifiers. These nanoparticles are placed in the interface, where they function as a physical barrier to boost stability. One of the main advantages of stabilization using solid particles is their strong resistance to coalescence and higher thermal stability. Referred to as Pickering emulsions, they have been explored for a variety of applications **[3]**; however, there is a significant gap in the literature regarding their characterization for thermal energy storage applications.

PCM-based anhydrous emulsions could represent a promising alternative for thermal energy storage. They would help overcome the typical temperature and pressure limitations of water-based systems. Additionally, they might improve the stability and thermal storage capacity of conventional technologies. These properties could lead to a more efficient heat and mass transfer, potentially expanding their range of applications.

However, PCMEs are often affected by supercooling, a phenomenon in which droplets must be cooled below their melting point to trigger the freezing process. This is generally regarded as a drawback, as it leads to the release of stored energy at lower temperatures or over a wider temperature range, potentially reducing system efficiency and limiting the practical applicability of PCMEs.

This study focused on the formulation and characterization of anhydrous Pickering emulsions for energy storage applications. Paraffin, a phase change material (PCM) with a melting point of 58-60°C, was chosen as the dispersed phase, while polyethylene glycol, a heat transfer fluid, served as the continuous phase. The emulsions were stabilized with hydrophobized pyrogenic silica nanoparticles. The research examined how varying nanoparticle concentrations affected the emulsions thermo-physical properties.

2. Materials and Methods

A. Materials

The dispersed phase of the PCM consisted of paraffin with a melting point of 58-60°C, supplied by PANREAC QUIMICA S.L.U. (Spain), while the continuous phase was comprised polyethylene glycol (PEG400), having a mean molecular weight of 400 g/mol, obtained from Merck Life Science S.L. (Spain). To stabilize the emulsion, hydrophobic surface-modified pyrogenic silica nanoparticles (Aerosil R-805) were employed, sourced from Evonik Operations GmbH (Germany).

B. Methods

A set of Pickering emulsions of paraffin in PEG 400 were formulated with a constant dispersed phase concentration (20% w/w) and nanoparticles of Aerosil as the stabilizing agent. Samples with various nanoparticle amounts (0.50, 1.00, and 3.00 wt. %) were prepared and characterized to study the PCM emulsions properties related to thermal energy storing.

Enthalpies and thermal properties were measured by modulated differential scanning calorimetry (MDSC), carried out using a Q-250 DSC calorimeter (TA Instruments, USA).

Changes in the morphology of the emulsion during the phase transition were observed by means of optical microscope (Olympus BX51, Japan). Rheological characterization was also carried out, using a controlled-stress Physica MCR 501 rheometer (Anton Paar GmbH, Graz, Austria).

3. Results and Discussion

A. Energy performance and thermo-physical properties

In order to ensure their functionality in thermal energy storage applications, it is essential for PCMEs to effectively release the thermal energy stored during phase transitions. To assess this capability, the thermal properties and crystallization enthalpies of both pure paraffin and the PCMEs were analyzed using modulated differential scanning calorimetry (MDSC). The resulting MDSC curves are presented in Fig. 1.

The MDSC analysis of pure paraffin exhibits two broad, merged peaks centered at 42.75 and 56.86 °C with a total associated enthalpy value of 191.2 J/g. Although total enthalpy is a key parameter for thermal storage and heat transport performance, it is worth noting some structural considerations. Thus, the maximum at the lower temperature has been extensively associated with solid-to-solid transitions while the second peak, which accounts for the majority of enthalpy, corresponds to the crystallization of the paraffin wax from the melted state.

Furthermore, the characteristic crystallization peaks identified in the pure paraffin sample were also present in all MDSC thermograms of the emulsions. This confirms that neither the incorporation of emulsion components nor the emulsification process negatively impacted the thermal behavior of the paraffin.

By integrating the area under the curve, the enthalpy of the crystallization process can be calculated and further normalized in the case of emulsions, i.e., presented as energy per gram of paraffin in the emulsion for comparison. The selected paraffin wax displays a crystallization enthalpy of 190.9 J/g, which is only slightly reduced to 172.7, 168.6, and 157.2 J/(g of paraffin) for phase change emulsions containing 0.5, 1, and 3 wt.% of nanoparticles.

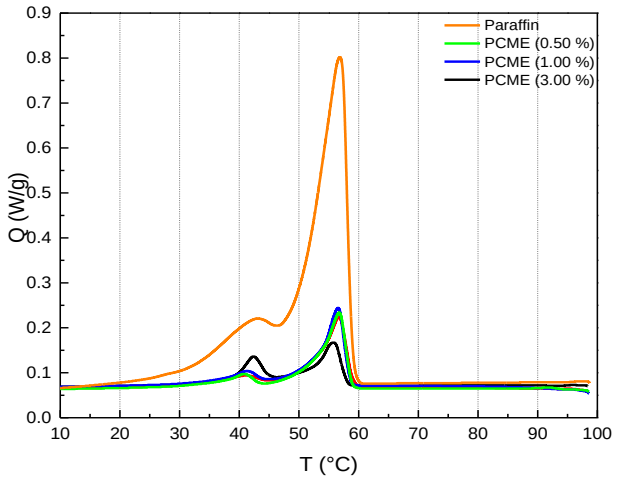

Fig. 1 MDSC crystallization curves for paraffin and PCME samples, with various nanoparticle amounts (0.50, 1.00, and 3.00 wt. %)

These findings suggest that the emulsification process preserves the intrinsic phase change properties of the paraffin, thereby validating the potential of PCMEs as efficient thermal energy storage systems without compromising latent heat performance.

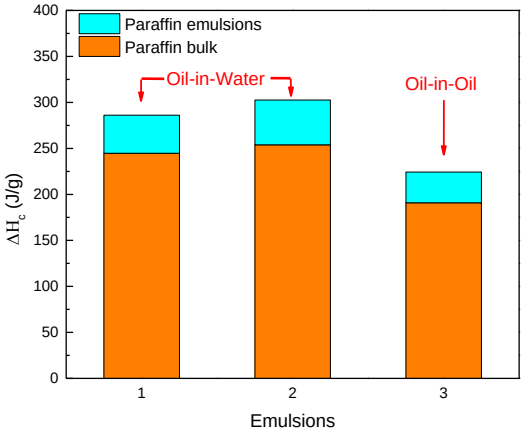

Fig. 2 Crystallization enthalpies for different paraffin-based emulsions and paraffin bulks.

Fig. 2 shows the mean melting enthalpy values of the presented Pickering emulsions, without normalization,

compared to some aqueous and paraffin-based emulsions reported in the literature, along with their respective paraffin bulks. Thus, the phase change enthalpy may vary depending on the emulsion formulation and the specific type of paraffin used. For the sake of comparison and to evaluate the thermal performance of the emulsions stabilized by solid particles, a quantitative analysis was conducted between the thermal storage efficiency of two surfactant-stabilized aqueous emulsions and the Pickering emulsions. This efficiency, denoted as H, was defined as (1):

$$H = \frac{\Delta H_c \text{ bulk paraffin}}{\Delta H_c \text{ emulsions}} \quad (1)$$

Where ΔH_c represents the crystallization enthalpy per gram of sample for both neat paraffin and the resulting emulsions. The results presented in table 1 reveal that all evaluated systems exhibit relatively similar thermal storage efficiency values, indicating that the thermal storage capacity of the developed oil-in-oil Pickering emulsions is comparable to that of conventional surfactant-stabilized aqueous emulsions. The similarity in H values suggests that the Pickering emulsion formulation effectively does not disturb the energy storage potential characteristic of PCM systems, despite employing a different stabilization approach based on solid particles rather than surfactants.

Table 1. Comparison between thermal storage capacity of different paraffin-based emulsions (20% w/w paraffin)

Sample	Continuous phase	Stabilizer	H
1 [4]	Water	Surfactant polysorbate	5.92
2 [5]	Water	surfactant polysorbate	5.22
3	Oil	Solid nanoparticles	5.72

This preservation of latent heat storage capacity is particularly significant, as it demonstrates that the change in stabilization mechanism and the presence of solid nanoparticles (at least at concentrations up to 3.00%) do not compromise the primary functional property of the PCM i.e. the ability to store and release thermal energy during phase transitions. Collectively, these findings underscore the potential of Pickering emulsions as a competitive alternative in the field of thermal energy storage, with promising implications for both stationary and mobile energy systems.

B. *Optical microscopy*

The morphology of emulsions in both their liquid and solid phases is a key parameter for evaluating thermal and kinetic stability, as it directly influences the system's structural integrity and long-term performance. To investigate this, optical microscopy images were obtained for emulsions with the dispersed phase in both the molten state (80 °C) and the crystallized state (25 °C). In the molten state, the emulsions display well-defined, fully spherical paraffin droplets that are homogeneously dispersed throughout the continuous phase, as illustrated in Fig. 2-A.

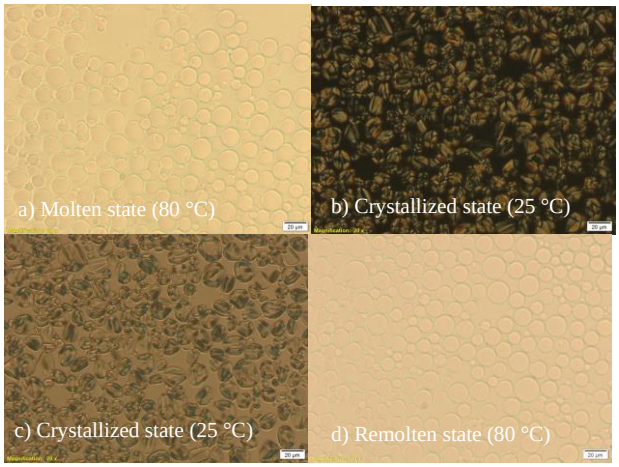

Fig. 3 . Optical microscopy images of PCME (0.5%) emulsion during a heal-cold cycle at (a) 80 °C, (b) 25 °C at cross-polarized light, (c) 25 ºC and again at (d) 80 ºC

Following controlled cooling, these droplets undergo the liquid-to-solid phase change, forming semi-spherical paraffin crystals while retaining their original size and spatial distribution (Fig. 2-B, C). This preservation of droplet structure suggests minimal coalescence or aggregation during the phase transition. Notably, after reheating the emulsions, the original droplet morphology is fully recovered (Fig. 2-D), indicating that the emulsions can withstand multiple heating and cooling cycles without undergoing structural degradation or phase separation. These findings were also observed in all the evaluated samples, highlighting the ability of nanoparticles to stabilize emulsions even at low concentrations as 0.5 wt.%.

Such reversible morphological behavior points to a high degree of thermal stability, a critical requirement for materials intended for repeated use in thermal energy storage applications. This stability not only ensures consistent thermal performance over time but also contributes to the reliability and efficiency of the system under practical operating conditions.

C. *Rheological characterization*

The rheological properties of emulsions are crucial for various practical applications, particularly in terms of pumping energy consumption and heat transfer performance. These properties are influenced by processing conditions, including the concentration of stabilizing agents such as nanoparticles.

Steady-state flow tests on the emulsions demonstrated shear-thinning behavior (data not shown for brevity), where the viscosity decreases with an increasing shear rate, indicating a non-Newtonian flow characteristic. It was observed that viscosity increased at lower temperatures and with higher concentrations of silica nanoparticles.

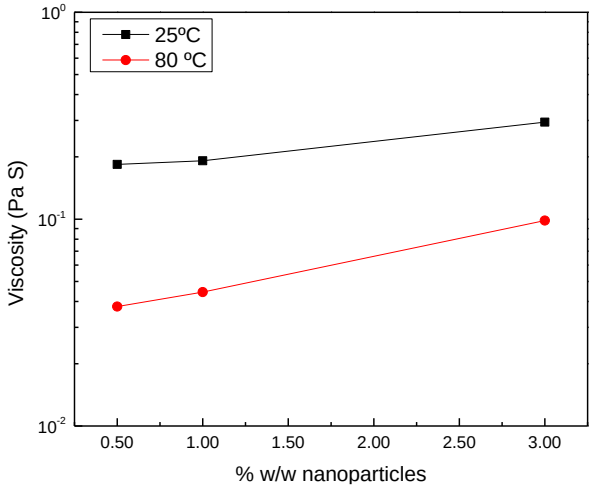

Fig. 4 Effect of nanoparticles on the apparent viscosity of emulsion samples at 1E-4 s^{-1}

To further explore the impact of nanoparticle concentration on the rheological behavior, apparent viscosity values are presented at two different temperatures, using a shear rate of 500 s^{-1}, since industrial processing and pumping operations typically occur within the intermediate to high shear rate range (1-1000 s^{-1}) **[6]**. The results indicated that higher concentrations of nanoparticles were directly associated with a rise in viscosity. This suggests that the incorporation of silica nanoparticles played a role in the formation of a structured network within the emulsion, which likely enhanced its overall viscosity. While this increase in viscosity could be viewed as a challenge for the pumping and transportation of emulsions, it is important to note that such behavior can be controlled by accurately adjusting the nanoparticle concentration. In that sense, a controlled increase in viscosity can offer several advantages. Higher viscosity improves the stability of the emulsion, reducing the risk of phase separation and ensuring more consistent performance during thermal cycling.

Furthermore, the ability to fine-tune the viscosity by adjusting the concentration of silica nanoparticles provides flexibility in optimizing the emulsion's properties for specific applications. This adaptability can be particularly beneficial for tailoring the system to meet the requirements of different thermal energy storage scenarios, where variations in viscosity might be needed to optimize heat transfer or system flow.

Additionally, small amplitude oscillatory shear tests revealed a clear elastic response and the development of a gel structure throughout the emulsions at both paraffin phases. These findings provide insight into high kinetic stabilizations **[7]**.

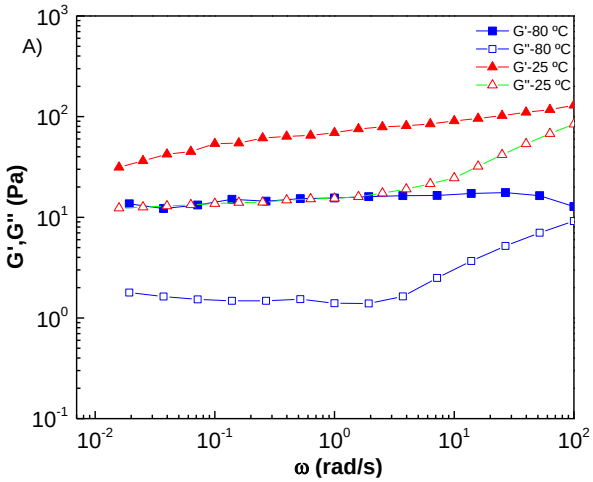

Fig. 5 Storage and loss modules as a function of frequency of the emulsion at 80ºC and 25ºC.

4. Conclusions

A set of anhydrous Pickering emulsions was successfully formulated and characterized, demonstrating favorable properties for thermal energy storage applications. The thermal analysis, including measurements of enthalpy and related thermal transitions, indicated that the incorporation of silica nanoparticles for emulsification did not significantly alter the energy storage capacity of the paraffin phase. This suggests that the latent heat characteristics essential to PCM functionality were preserved despite the change in stabilization mechanism.

Microscopic observations further supported the emulsions' structural resilience, showing that droplet morphology remained stable throughout at least one complete thermal cycle (heating–cooling–reheating). This reversible behavior reflects a high degree of thermal stability and indicates the system's ability to withstand phase changes without degradation or coalescence, which is critical for long-term application.

Rheological measurements revealed that the emulsions exhibit non-Newtonian, shear-thinning behavior with gel-like characteristics, suggesting the presence of a structured internal network. Such rheological properties may enhance system stability and minimize phase separation, while also providing opportunities for tunable flow behavior in practical applications.

Taken together, these results highlight the promise of the developed oil-in-oil Pickering emulsions as robust, efficient, and thermally stable phase change material emulsions (PCMEs). Their ability to maintain thermal performance, resist morphological changes during cycling, and exhibit controllable rheological properties position them as competitive and versatile alternative for future thermal energy storage technologies.

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