23rd International Conference on Renewable Energies and Power Quality (ICREPQ'25)
Tenerife (Spain), 25th to 27th June 2025
ISBN-13: 978-84-09-66511-2

Pickering Emulsions with Phase Change Materials: Advancing Thermal Energy Storage

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Abstract. Concerns about environmental issues and energy consumption have increased the need for efficient renewable energy utilization, with thermal energy storage (TES) systems playing a key role. TES systems using phase change materials (PCMs), which are able to store energy within narrow temperature ranges, show significant potential. One promising approach involves the use of phase change material emulsions, where PCMs are dispersed in heat transfer fluid and stabilized by emulsifying agents. Recently, Pickering emulsions, stabilized by solid particles, have gained interest for their enhanced long-term and thermal stability. This study focuses on oil-in-oil Pickering emulsions, using paraffin as the PCM and polyethylene glycol (PEG400) as the continuous phase, stabilized by solid silica nanoparticles. The thermal-mechanical properties of emulsions with different PCM concentrations were analyzed for energy storage applications.

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

1. Introduction

Global concerns about environmental sustainability, rising energy demands, and the urgent need to reduce greenhouse gas emissions have intensified the pursuit of cleaner and more efficient energy technologies. In this context, the efficient utilization of renewable energy sources such as solar and wind has become a central objective. However, the intermittent nature of many renewable sources presents significant challenges for ensuring a stable and reliable energy supply. To address this, thermal energy storage (TES) systems are emerging as a key technology that can bridge the gap between energy generation and demand.

TES allows excess thermal energy generated during periods of low demand or peak renewable availability to be captured and stored for later use. This strategy not only enhances energy efficiency but also contributes to grid stability by reducing reliance on conventional fossil fuel-based backup systems during periods of high demand or low renewable output. In real-world applications, such as solar thermal plants, district heating networks, industrial waste heat recovery, and building climate control, TES systems play a pivotal role in optimizing energy management and reducing operational costs [1].

Among TES technologies, latent heat storage systems that employ phase change materials (PCMs) are particularly promising. These materials store and release significant amounts of energy through phase transitions within narrow temperature ranges. Despite their advantages, the practical implementation of PCMs can be hindered by challenges related to stability, compatibility with heat transfer systems, and energy density.

To improve the performance and applicability of PCM-based TES systems, innovative strategies have been explored. One such approach involves formulating phase change material emulsions (PCMEs), in which the PCM is finely dispersed as droplets within an immiscible heat transfer fluid. These emulsions are stabilized using emulsifying agents that prevent droplet coalescence and phase separation, thereby enabling efficient and continuous thermal cycling. PCMEs offer several advantages, including improved thermal stability, better dispersion, and enhanced scalability for industrial and residential applications [2].

Recently, increasing attention has been directed toward Pickering emulsions for TES applications. Unlike traditional emulsions stabilized by surfactants, Pickering emulsions use solid particles to create a steric barrier at the droplet interface, significantly improving the thermal and long-term stability of the system. This stabilization mechanism may reduce degradation over repeated thermal cycles and eliminate issues such as emulsifier oxidation, which are common in surfactant-based systems [3]. Nevertheless, further research is needed to fully understand and optimize these systems for widespread use in TES.

This study investigates the formulation and characterization of oil-in-oil Pickering emulsions designed for thermal energy storage applications. Paraffin is selected as the dispersed phase due to its favorable phase change characteristics and widespread availability. As the continuous phase, polyethylene glycol (PEG400) is utilized for its efficient heat transfer properties. Hydrophobic silica nanoparticles are employed as stabilizing agents, forming a interfacial

barrier around the paraffin droplets to prevent coalescence and improve structural stability.

The thermal and rheological properties of the emulsions are examined across a range of PCM concentrations to evaluate their suitability for energy storage and mechanical performance. Key parameters analyzed include phase change enthalpies, crystallization behavior, morphological stability throughout thermal cycles, and flow characteristics. The findings offer insight into the potential of Pickering-stabilized PCM emulsions as a viable, efficient, and scalable solution for advanced thermal energy storage systems in real-world applications.

2. Materials and Methods

A series of Pickering emulsions were formulated using a selected paraffin with a nominal melting point of 58-60°C (PANREAC QUIMICA S.L.U., Spain) as the dispersed phase and polyethylene glycol with an average molecular mass 400 g/mol (PEG400, Merck Life Science S.L., Spain) as the continuous phase. Various dispersed phase concentrations were employed to investigate the influence of paraffin content on the emulsions' properties. Hydrophobically modified silica nanoparticles (Aerosil R-805, Evonik Operations GmbH, Germany) were selected as stabilizing agents due to their surface-modifying capabilities, enabling the formation of physically stable emulsions. These emulsions were carefully prepared and systematically characterized to evaluate their potential for thermal energy storage, focusing on both their physical and thermal behavior.

The enthalpies and thermal properties of the emulsions were assessed via modulated differential scanning calorimetry (MDSC) using a Q-250 calorimeter (TA Instruments, USA). This analysis provided detailed insights into their thermal behavior and phase transition characteristics. Additionally, morphological changes occurring during phase transitions were examined using an optical microscope (Olympus BX51, Japan), enabling the observation of structural stability under thermal cycling. To further assess the flow behavior and mechanical characteristics of the emulsions, rheological measurements were conducted with a controlled-stress Physica MCR 501 rheometer (Anton Paar GmbH, Graz, Austria), yielding comprehensive data on viscosity and shear stress response.

3. Results and Discussion

A. Rheological properties

Assessing the operational parameters of phase change material emulsions (PCMEs) is essential for evaluating their suitability and performance in real-world thermal energy storage and transfer systems. Among these parameters, rheological behavior plays a critical role, as it directly influences the efficiency of thermal fluid transport operations such as pumping, circulation, and heat exchange. In this context, flow curve tests (Fig. 1) were conducted to provide insight into the flow characteristics of the formulated emulsions under varying conditions.
The results revealed a continuous viscosity decrease with shear rate across all samples i.e. a shear-thinning behavior, followed by a tendency to reach the so-called infinite shear viscosity, which is a common trait in structured or complex fluids. Although typical shear rates in pumping operations vary depending on the type of pump, they are generally greater than 1 s^{-1}. Therefore, the high shear sensitivity of these emulsions enhances their suitability for industrial pumpability, thereby enhancing overall system efficiency.

Furthermore, flow tests demonstrated that viscosity was significantly influenced by both paraffin concentration and temperature. Specifically, emulsions with higher paraffin content exhibited increased viscosity, likely due to the greater volume fraction of the dispersed phase, which contributes to internal resistance to flow. Similarly, a decrease in temperature led to a marked rise in viscosity, which is attributed to the liquid to solid phase change of the dispersed paraffin. Following crystallization, the droplets solidify, becoming less deformable and exhibiting significantly reduced molecular mobility, which increases their resistance to deformation under applied stress **[4]**.

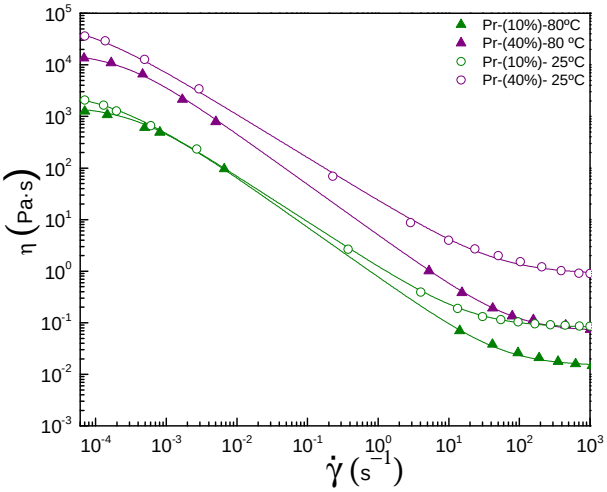

Fig. 1 Flow curves for PCM emulsions

B. Emulsions morphology

A key property of phase change material emulsions (PCMEs) is their thermal stability during phase transitions, which is critical for ensuring long-term performance and reliability in thermal energy storage applications [2]. Thermal stability in this context refers to the ability of the emulsion to retain its morphological structure through repeated heating and cooling cycles.

To evaluate this property, optical microscopy was employed to observe the emulsions during a complete thermal cycle consisting of heating, cooling, and reheating phases (Fig. 2). At 80 °C, corresponding to the molten state of the paraffin phase, the emulsions displayed well-defined spherical droplets that were

uniformly distributed within the continuous oil phase. This indicates effective dispersion and stabilization at elevated temperatures, which is essential for kinetic stability and consistent heat absorption and release**[5]**.

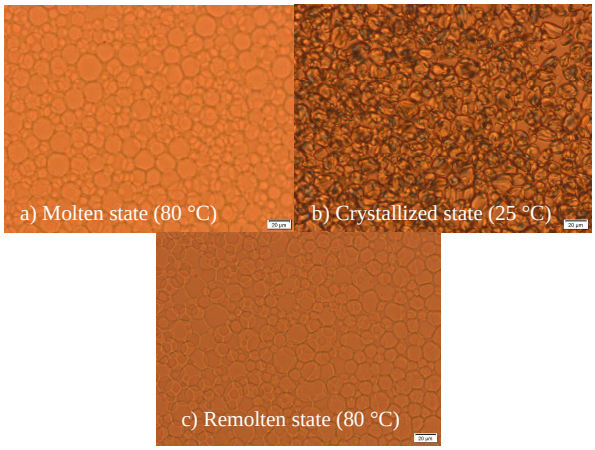

Fig. 2 Optical microscopy images of PCME (40%) emulsion at (a) 80 °C, (b) 25 °C, (c) 80 ºC

Upon controlled cooling to 25 °C, paraffin crystallization occurred. Notably, the droplets maintained their original size and distribution, suggesting that solidification did not compromise the internal structure of the emulsion. After the freezing of paraffin, only a minor deviation from its initial spherical shape is observed; however, this deviation is reversed upon remelting. The preservation of droplet morphology during crystallization indicates a kinetically stable system, supported by the presence of solid particles at the interface, which likely help prevent coalescence or deformation of the droplets.

Upon reheating the emulsions to 80 °C, the paraffin droplets remelted, and the emulsion regained its initial morphology with no droplet coalescence. The droplets reappeared with the same size and spatial arrangement as observed during the initial heating phase, without any droplet coalescence. Similar thermal behavior was observed in all the evaluated samples, highlighting the ability of nanoparticles to stabilize emulsions at various paraffin concentrations.

This reversible behavior suggests that no significant changes occurred in the structural integrity or thermal properties of the emulsion as a result of thermal cycling, which is crucial from an in-service perspective.

C. Thermal characterization

In certain instances, loss of energy storage capability may pose a considerable limitation for the practical implementation of phase change material emulsions (PCMEs) in thermal energy storage systems [2]. This challenge arises when the amount of latent heat stored and released during phase transitions is insufficient to meet the thermal requirements of specific applications **[6]**. Factors contributing to reduced energy density may include the dilution effect from the continuous phase, limited PCM content, or structural modifications resulting from the emulsification process. Therefore, it becomes essential to assess whether the formulation of PCMEs compromises their energy storage capabilities compared to the pure PCM.

To address this concern, the thermal properties and enthalpic behavior of both pure paraffin and the formulated PCM emulsions were systematically evaluated using modulated differential scanning calorimetry (MDSC). This technique provides data on heat flow associated with thermal events, such as melting and crystallization, and allows for the precise determination of phase transition temperatures and enthalpy values.

The main results obtained from these analyses are summarized in Table 1. By comparing the enthalpy values of emulsions to those of pure paraffin, it is possible to quantify the impact of the emulsification and stabilization mechanisms on latent heat storage. This comparison also helps determine whether the presence of the continuous phase and the introduction of nanoparticles for stabilization significantly affect the PCM's ability to undergo efficient phase transitions

Table 1. Normalized enthalpy values and phase transitions temperatures for emulsions.

Sample	Crystallization		Melting	
	Tc Peak (°C)	$\Delta H_c \left(\frac{J}{gpf}\right)$	Tc Peak (°C)	$\Delta H_m \left(\frac{J}{gpf}\right)$
Pr –(10%)	**56.55**	**177.92**	**57.50**	**132.51**
Pr –(40%)	**56.59**	**182.09**	**57.70**	**180.89**
Parafin bulk	**56.86**	**192.61**	**58.23**	**193.60**

The normalized enthalpies of emulsion transitions i.e., per gram of paraffin, showed only a slight difference compared to bulk paraffin. This suggests that the thermal performance of the paraffin remains largely unaffected by the presence of other emulsion components or by the emulsification process itself. In other words, the latent heat storage capacity of paraffin is preserved even when it is dispersed within a complex emulsion system, indicating that neither the interfacial interactions nor the structural confinement imposed by the emulsion significantly hinder the phase change behavior.

Moreover, an increase in the concentration of the dispersed phase was correlated with higher overall enthalpy values. This outcome is expected, as a greater proportion of phase change material within the emulsion leads to an increased amount of latent heat storage per unit mass of emulsion. These findings further support the potential of tailoring emulsion formulations to enhance energy storage capacity while maintaining the favorable thermal characteristics of the base PCM. This adaptability is particularly valuable for optimizing

PCMEs for specific thermal management applications where both efficiency and stability are required.

For thermal energy storage systems to be viable in industrial settings, phase change material emulsions (PCMEs) must exhibit long-term thermal stability and maintain their performance after undergoing numerous phase change cycles **[1]**. This includes the ability to resist degradation or morphological changes resulting from repeated melting and crystallization. In this context, a thermal cycling test was performed to evaluate the thermal reliability of the formulated Pickering emulsions. The test involved subjecting a paraffin emulsion to 20 controlled heating and cooling cycles.

Fig. 3 presents the differential scanning calorimetry (DSC) curves obtained after thermal cycling. The results demonstrate minimal shifts in the melting and crystallization peaks, indicating that the thermal behavior of the emulsion remains largely unchanged, even after repeated heating and cooling cycles. This suggests that the emulsions are able to retain their phase change properties over repeated use, without significant loss of energy storage capacity. This ability positions the emulsions as a promising alternative for scalable and efficient thermal energy storage systems, offering both operational reliability and long-term performance sustainability.

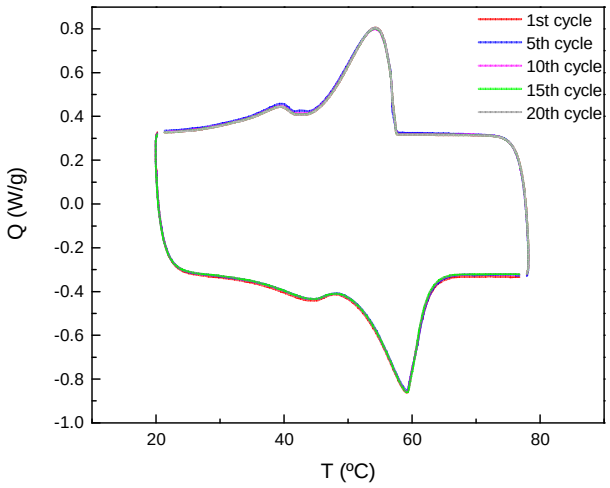

Fig. 3 MSDC curves for emulsions after thermal cycling

4. Conclusions

Paraffin-based emulsions stabilized with hydrophobic solid silica nanoparticles were successfully formulated and thoroughly characterized to assess their suitability for thermal energy storage applications. Rheological analysis revealed that the emulsions exhibited non-Newtonian, shear-thinning behavior, with viscosity increasing as a function of paraffin concentration. This behavior suggests the formation of an internal microstructure influenced by the dispersed phase volume and the presence of stabilizing particles, which can impact flow dynamics and processability.

Thermal characterization using differential scanning calorimetry (DSC) showed that the latent heat storage capacity, as indicated by enthalpy values, increased proportionally with the paraffin content. Importantly, the melting and crystallization peaks of the emulsions closely aligned with those of bulk paraffin, suggesting that the inclusion of silica nanoparticles and the emulsification process did not significantly alter the inherent thermal properties of the PCM. Nevertheless, the pronounced shear-thinning behavior enhances the pumpability required for industrial applications.

The long-term thermal reliability of the emulsions was further supported by results from thermal cycling tests. After 20 heating and cooling cycles, the DSC curves showed negligible shifts in phase transition temperatures and enthalpy values, indicating excellent thermal stability and resistance to degradation over repeated use.

Complementary optical microscopy confirmed the structural integrity of the emulsions throughout the thermal cycle. Spherical paraffin droplets remained uniformly dispersed during melting and solidification, and their morphology was preserved even after repeated cycling, reflecting high morphological and thermal resilience.

These findings underscore the potential of Pickering-stabilized PCM emulsions as durable and tunable thermal energy storage materials. The ability to tailor their composition and maintain performance over multiple thermal cycles positions them as promising candidates for integration into real-world systems, such as solar energy storage, industrial heat recovery, and building temperature regulation

Acknowledgement

This work is part of the projects PID2023-151306OB-I00 and PID2020-116905RB-I00 funded by MCIN/AEI/10.13039/501100011033 (Spanish Ministry of Science, Innovation and Universities) and ERDF "A way of making Europe". C. Delgado-Sánchez acknowledges Junta de Andalucía-post-doctoral Grants DC 01228, co-funded by the EU.

References

[1] B. Zalba, J. M. Marín, L. F. Cabeza, y H. Mehling, «Review on thermal energy storage with phase change: materials, heat transfer analysis and applications», *Applied Thermal Engineering*, vol. 23, n.º 3, Art. n.º 3, feb. 2003, doi: 10.1016/S1359-4311(02)00192-8.

[2] F. Wang, W. Lin, Z. Ling, y X. Fang, «A comprehensive review on phase change material emulsions: Fabrication, characteristics, and heat transfer performance», *Solar Energy Materials and Solar Cells*, vol. 191, pp. 218-234, mar. 2019, doi: 10.1016/j.solmat.2018.11.016.

[3] L. E. Low, S. P. Siva, Y. K. Ho, E. S. Chan, y B. T. Tey, «Recent advances of characterization techniques for the formation, physical properties and stability of Pickering emulsion», *Advances in Colloid and Interface Science*, vol. 277, p. 102117, mar. 2020, doi: 10.1016/j.cis.2020.102117.

[4] J. Giermanska, F. Thivilliers, R. Backov, V. Schmitt, N. Drelon, y F. Leal-Calderon, «Gelling of Oil-in-Water Emulsions Comprising Crystallized Droplets», *Langmuir*, vol. 23, n.º 9, pp. 4792-4799, abr. 2007, doi: 10.1021/la070071c.
[5] H. Inaba, «New challenge in advanced thermal energy transportation using functionally thermal fluids», *International Journal of Thermal Sciences*, vol. 39, n.º 9, pp. 991-1003, oct. 2000, doi: 10.1016/S1290-0729(00)01191-1.
[6] M. M. Farid, A. M. Khudhair, S. A. K. Razack, y S. Al-Hallaj, «A review on phase change energy storage: materials and applications», *Energy Conversion and Management*, vol. 45, n.º 9, pp. 1597-1615, jun. 2004, doi: 10.1016/j.enconman.2003.09.015.