Assessment of low-temperature PCM emulsions as TES

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Abstract

The increasing integration of renewable energies is driving research into phase change materials (PCMs) for efficient energy storage. PCM emulsions are a promising solution that combines latent storage with ease of fluid circulation. They facilitate integration into conventional tanks. This study evaluates two low-temperature PCM emulsions for cooling applications: a commercial emulsion (PCE18) containing 50 wt% PCM, and a novel, environmentally friendly Pickering PCM emulsion developed in-house with a 50 v/v% concentration. Their thermophysical (storage capacity, hysteresis, thermal conductivity) and rheological properties (viscosity, stability) have been characterized. The results show similar energy storage capacities, with a reduced level of hysteresis, but different operating temperature ranges. Both emulsions show promising behavior according to their use in the agitated tank concept and show physical stability. The final selection for practical applications will depend on the specific operational requirements and system design.

Keywords: Thermal Energy Storage; Phase Change Materials; PCM slurries; PCM emulsions

1. Introduction

Photovoltaic (PV) generation is inherently variable and often does not match the temporal profile of cooling demand. One promising strategy to address this mismatch is the use of chillers powered directly by PV electricity, where excess solar generation is converted into cooling and stored as thermal energy (e.g., in chilled-water tanks, ice storage, or phase-change materials). This approach may mitigate the need for costly and resource-intensive electrochemical batteries. By producing and storing cooling during periods of high solar irradiance, the system enables load shifting, allowing the stored cold to be used later in the afternoon or evening when cooling demand peaks and solar availability declines. Moreover, this strategy provides a pathway to utilize otherwise curtailed PV electricity, transforming surplus generation into a valuable resource that reduces grid dependence, alleviates peak demand stress, and contributes to the overall integration of renewable energy into the energy system.

Thermal energy storage and batteries are the most common devices for integration. Hao et al. (2022) compared the economic performance of ice storage and batteries for building with on-site PV by means of a numerical model predictive control algorithm. Ice storage had low investment and maintenance costs, but it can only shift electrical loads associated with building cooling requirements, in constrat to the ion-lithium battery. Kohole et al. (2024) presented a comparative analysis of differente energy storage technologies (batteries, pumped-hydro, hydrogen, and thermal enegy storage), integrated into twelve hybrid configurations based on wind and solar resources.The main objective is to optimize the size of the different technologies to meed the required demands in Kousseri, Camerron, in order to minimize economic cost and CO_2 emissions. The thermal energy storage (TES) system is the most economically viable option compared to the other technologies evaluated. The hybrid photovoltaic/wind system with TES proved to be the most cost-effective configuration to meet the demands. Pinto et al. (2022) carried out an optimization study to design the most cost-effective energy system for a residential building in Zaragoza, Spain, considered as a microgrid. Using a Mixed Integer Linear Programming

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(MILP) model, the study simultaneously analyzes electricity, heating, and cooling demands, evaluating various renewable (among them the solar thermal and photovoltaic energy) and conventional generation technologies. The main and most notable conclusion of this work is that, contrary to the current trend that prioritizes batteries, the optimal and most cost-effective solutions are achieved by replacing electrical energy storage with thermal energy storage (specifically for cooling). This clearly justifies and makes research into thermal energy storage systems of vital importance and relevance.

In recent years, research into PCM has gained significant momentum. Among the most promising strategies for incorporating PCMs into thermal storage systems are PCM slurries (Jurkowska and Szczygiel, 2016). Specifically, PCM emulsions are dispersions of a PCM in an immiscible liquid medium, usually water, using surfactants to ensure stability and functionality, which combine the advantages of latent storage with the ease of fluid circulation. These systems allow for enhanced thermal capacity and heat transfer without requiring specific containment structures or macro-encapsulation geometries. This facilitates their integration into conventional storage tanks, lowering costs and reducing system complexity. Recent research focuses on the development and optimization of these latent two-phase fluids, focusing on improving their stability and optimizing their thermophysical properties, such as latent heat, or suppressing phenomena such a supercooling or hysteresis. In addition, the aim is to understand and control its rheological behavior, in particular its viscosity, as it influences its pumpability and heat transfer (Abdeali and Bahramian, 2022). This study focuses on the evaluation of two low-temperature PCM emulsions as TES material. One of the emulsions is commercially available, while the other has been developed internally. Their operating temperature range makes them promising candidates for cooling purposes.

2. Materials

The commercial PCM emulsion evaluated for direct use as a TES material is PCE18 from Rurhtech (http://ruhrtech.com/es/index.php/pcms/), which according to its technical specifications has a PCM mass fraction of 50% and a phase change temperature between 12-18°C. No studies have been found in the literature that have carried out a sufficiently exhaustive analysis of this product.

The emulsion developed by the authors is a low-temperature, environmentally friendly Pickering PCM emulsion. A Pickering emulsion uses solid particles as emulsifying agents, instead of more traditional surfactants (like detergents), but by solid particles that adsorb onto the interface between the two immiscible liquids. These particles create a physical barrier that prevents the droplets from coalescing thereby stabilizing the emulsion, critical aspect in the development and viability of PCM emulsions. The stabilizing particles are typically in the nanometer and micrometer range. Common particle types include silica, clays, starch, proteins, or even specially designed nanoparticles. They are used in food, pharmaceutical and cosmetic field, particularly where low-toxicity of surfactant-free systems are desirable (Ming et al. 2023).

The vast majority of published works use molecular surfactants, such as Sodium Dodecyl Sulfate (SDS), Tween, Span, etc, to stabilize PCM droplets in water or other continuous media. This is the simplest and most widely used approach because surfactants effectively reduce interfacial tension and allow for relatively stable emulsions with controlled droplet sizes (Ji et al. 2024). In recent years, however, a growing number of studies have explored the development of Pickering-type PCM emulsions (Kaya et al., 2022; Lv et al., 2023; Zheng et al., 2022). To the best of our knowledge, the present work represents the first attempt to design a low-temperature, environmentally friendly PCM emulsion of this kind. In particular, n-tetradecane was selected as the PCM, and the emulsion was stabilized using a binary nanocomplex composed of the natural protein sodium caseinate (SCN) and the natural polysaccharide xanthan gum (XG), prepared by high-speed homogenization. The PCM content was approximately 50% (v/v). In addition, boron nitride (BN) particles were incorporated to enhance thermal conductivity and mitigate supercooling. The resulting PCM emulsion exhibited an average droplet size of approximately 15 μm.

3. Methodology

For the determination of their properties and the subsequent evaluation of the two PCM emulsions as a TES system, the storage capacity was assessed using a T-history method setup (Mazo et al., 2015). The sample volume was approximately 15 cm^3, ensuring that the chemical and physical composition was representative of the bulk material. The sample holder was designed to meet the requirements for a lumped capacitance system. The T-history setup was validated by calibrating the sensors, verifying the measurement temperature, and confirming the enthalpy measurements (Lázaro et al., 2006). Two pure substances with constant phase change temperatures and known enthalpies (gallium and hexadecane) were employed for validation. The difference in the determined enthalpy was below 12% in all cases. For the PCM emulsion measurements, particular attention was paid to the hysteresis between cooling and heating, the thermal operating window, and the comparison of storage capacity within this temperature range against the sensible heat storage of water.

The thermal conductivity was measured using a transient hot wire (THW) method, specifically with the Thermtest THW-L1. THW is an absolute technique based on an analytical solution to the heat transfer equation for an ideal linear heat source. The thermal conductivity is directly obtained from the fundamental measurements (power and temperature as a function of time) without requiring calibration with a reference material. As a transient method, each experiment lasts only a few seconds (typically 1–5 s), minimizing convective effects and ensuring that heat transfer occurs purely by conduction. Measurement uncertainties are below 1%.

The viscosity–shear rate curves used to analyze the rheological behavior of the PCM emulsions were obtained with a controlled-stress rheometer (TA Instruments, model AR-G2). Viscosity influences the heat transfer process and is necessary for estimating the pumping requirements when using the PCM emulsion as a heat transfer fluid. Peltier concentric cylinders were employed for both geometry and temperature control. During the tests, the samples were covered with a solvent trap to prevent evaporation of the continuous phase. Measurements were performed at X °C.

To assess and predict the physical stability, the methodology proposed by Delgado et al. (2013) was adopted. Structured fluids, such as PCM emulsions, generally exhibit similar qualitative behavior in frequency sweep tests. From the G′–ω and G″–ω curves obtained in oscillatory experiments, information on the microstructure of the PCM emulsion can be derived qualitatively. Specifically, the value of G′ at the frequency where G″ presents a minimum is related to the structural stability of the dispersed system, with higher G′ values indicating greater stability.

4. Results

4.1 Assessment of thermophysical properties

Figure 1 shows the enthalpy–temperature curves for both emulsions. An approximate operating temperature range of 10 °C can be defined for each PCM emulsion: from 2 °C to 12 °C for the own formulation, and from 13 °C to 23 °C for the commercial solution. Within these ranges, the enthalpy change is 132 kJ/kg and 124 kJ/kg, respectively. It is worth noting that the thermal hysteresis is lower in the commercial formulation—by approximately 1 °C—compared to the own developed emulsion. This difference can be attributed to the distinct interfacial stabilization mechanisms of the two emulsions. In the commercial formulation, molecular surfactants form a dynamic and flexible interfacial layer that facilitates heterogeneous nucleation at the droplet surface, leading to a smaller thermal hysteresis. In contrast, in the Pickering emulsion, the SCN–XG nanocomplex forms a rigid particle network at the oil–water interface, creating an energy barrier that suppresses heterogeneous nucleation and slows crystal growth during cooling. As a result, an increased thermal hysteresis is observed.

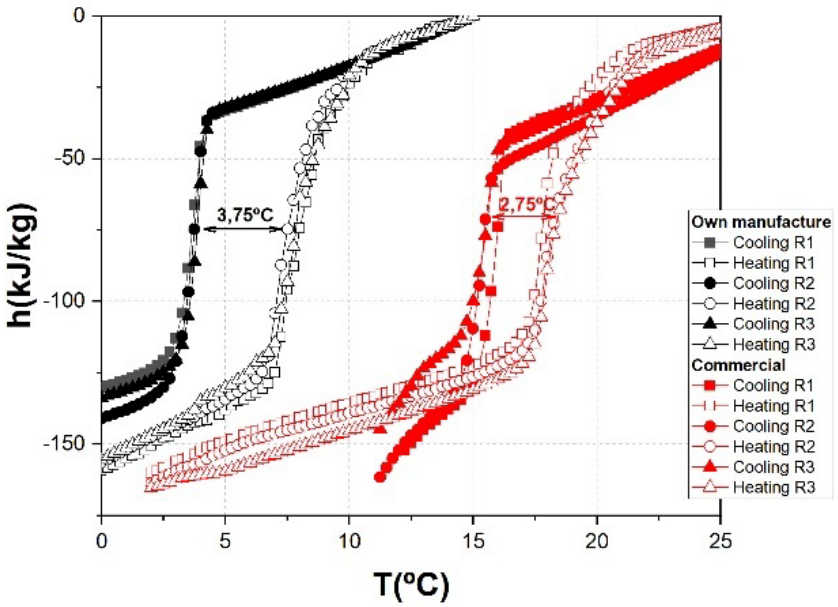

Figure 1. Enthalpy-temperatures curves obtained by the T-history setup. R: repetition

Regarding the thermal conductivity measurements, both emulsions exhibit values significantly lower than that of water, due to the inherent limitation imposed by the low thermal conductivity of the dispersed PCM. However, the own developed emulsion shows an improvement of approximately 15% compared to the commercial formulation. This enhancement is attributed to the incorporation of boron nitride (BN), a thermally conductive and chemically stable filler. In addition to improving thermal conductivity, the presence of BN also contributed to a slight reduction in thermal hysteresis.

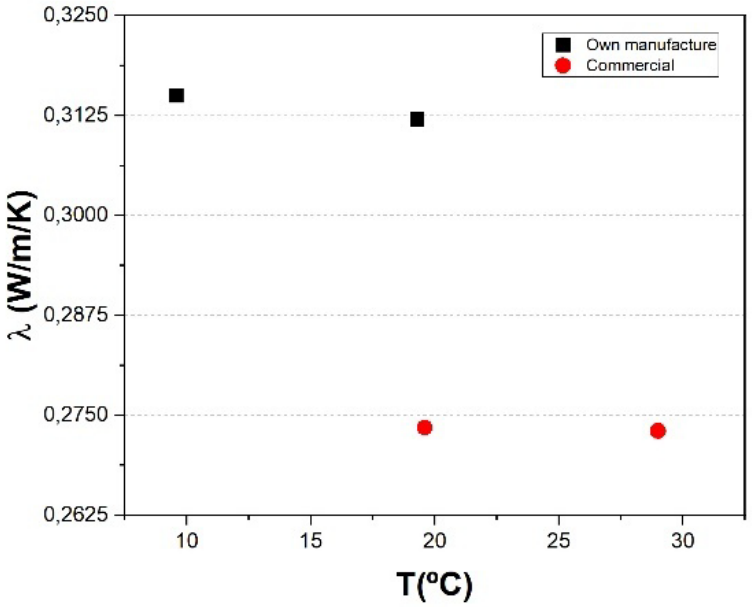

Figure 2. Thermal conductivity values for the liquid phase of the PCM by the THW

4.2 Assessment of the rheological properties

Figure 3 illustrates the thixotropic behavior of the commercial emulsion PCE18. Considering the concept of a stirred tank as a TES system (Garivalies et al. 2025), this behavior is advantageous in terms of both stability and operation. When the emulsion is pre-sheared for a specific duration (approximately 10 minutes), its internal structure breaks down, leading to a significant reduction in viscosity and the emergence of a Newtonian plateau, with minimum viscosity values around 0.1 Pa·s (see green curve in Figure 3). This suggests that even under low stirring conditions, heat transfer could be notably enhanced, due to the drastic reduction in viscosity.

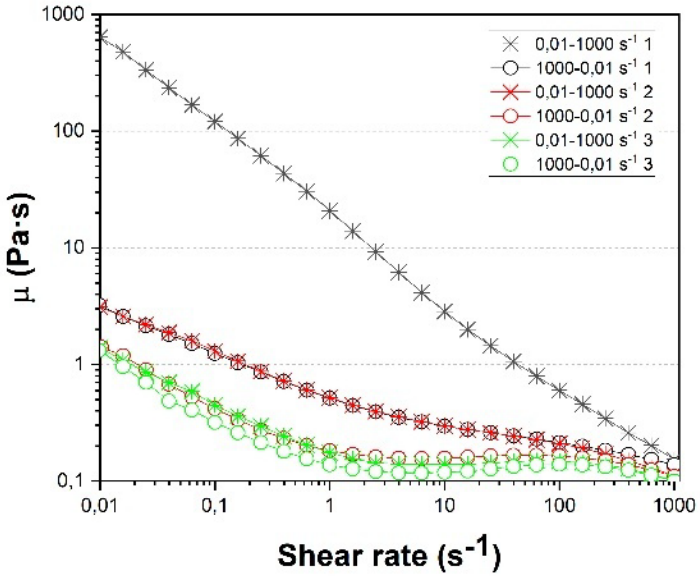

Figure 3. Viscosity-shear rate curves for commercial emulsion PCE18 at 30ºC

A recovery experiment was performed to observe if the fluid's structure recovered to its original resting viscosity. After applying a shear rate of 1000 s^{-1} during 15 minutes to simulate operation in a stirred tank or circulation in a pipe, a minimal shear rate ($0.001s^{-1}$) was applied to represent storage conditions. Thinking about the stirred tank concept, low viscosity is required during shearing for pumping efficiency and heat transfer; conversely, high viscosity is necessary at rest to ensure physical stability and prevent phase separation or sedimentation. Figure 4 shows the results of this recovery experiment. It is observed that the high shear applied makes the viscosity decrease because the internal structure (aggregates, interactions between droplets, etc) is broken and flows more easily. Lowering the shear rate allows the emulsion to slowly reorganize again, reaching a maximum viscosity value. The slight drop after this peak may be due to a balance between reconstruction and residual creep, not achieving the initial value of viscosit observed in figure 3.

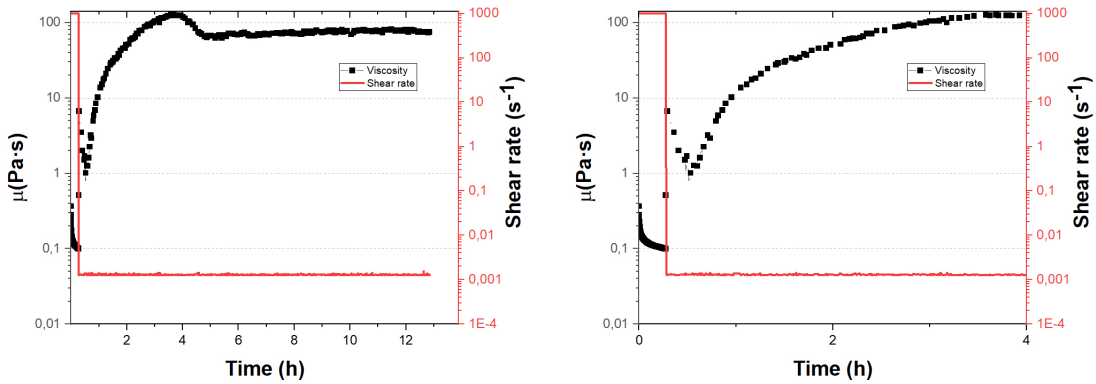

Figure 4. Rheological recovery experiment for the PCE18 commercial emulsion at 30ºC.

Note: *The right image is an enlarged view of the region of interest shown in the left image.*

In contrast, Figure 5 presents the more typical behavior of the own prepared PCM emulsion, which exhibits a pseudoplastic profile.

Sodium caseinate (SCN) adsorbs rapidly at the oil–water interface, forming a flexible protein film around the tetradecane droplets, which contributes to droplet stabilization and the formation of weak droplet networks. Xanthan gum (XG), a high-viscosity, shear-thinning polysaccharide, increases the viscosity of the continuous aqueous phase and, in combination with SCN, establishes a rigid interfacial network. This SCN–XG nanocomplex not only enhances the structural integrity of the emulsion, leading to higher resting viscosities, but also gives rise to pronounced pseudoplastic behavior under shear. During high shear, the network is disrupted, resulting in shear thinning, whereas at low shear, the network gradually reconstructs, partially restoring the viscosity. The combined effects of SCN and XG therefore account for the relatively high minimum viscosities.

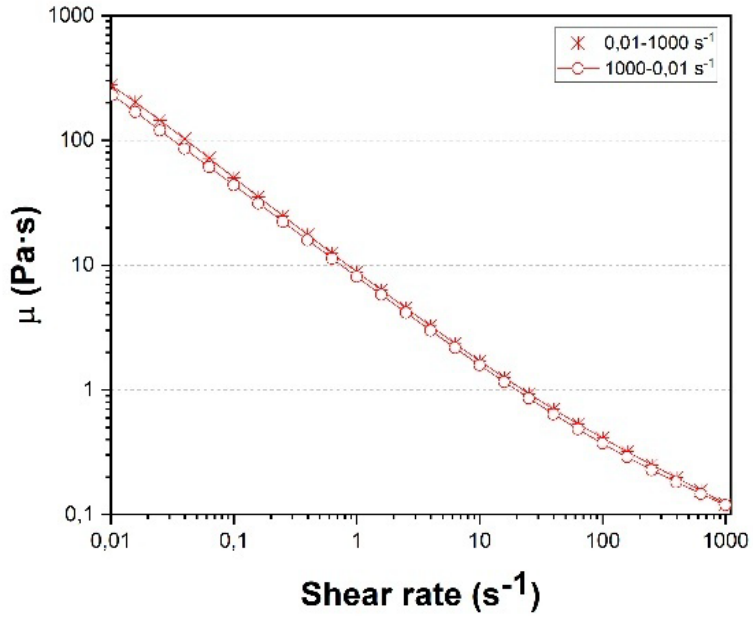

Figure 5. Viscosity-shear rate curve for own manufactured PCM emulsion at 15ºC

The oscillatory tests described in Section 3 were conducted to assess the physical stability of the emulsions. The analysis focuses on the Linear Viscoelastic Region (LVR), defined as the range of strain or stress within which the material's internal structure remains undisturbed and its response is independent of the deformation magnitude. Within the LVR, the material exhibits ideal elastic behavior: the measured properties (storage modulus, G′, and loss modulus, G″) are constant, indicating that the structural network between the emulsion droplets is merely stretched and compressed, allowing energy to be stored and recovered. When the limit of linearity is exceeded, the structure yields, as the applied forces overcome the cohesive strength of the droplet network. Therefore, the LVR is a direct indicator of the structural robustness of the emulsion at rest, with a wider LVR correlating to greater physical stability. As shown in Figure 6, both the commercial and the in-house manufactured PCM emulsions exhibit a very similar LVR, suggesting comparable physical stability under resting conditions.

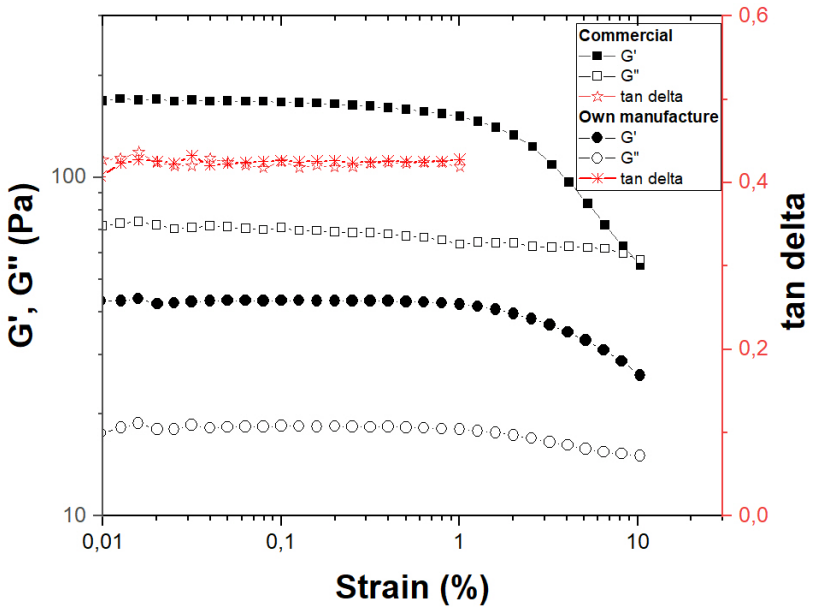

Figure 6. Strain sweep for the PCM emulsions, temperature: 20ºC for the own manufactured PCM emulsion and 30ºC for the commercial PCM emulsion, frequency = 1 Hz.

Figure 7 shows the frequency sweep executed within the LV. The value of G′ at the frequency where G″ presents a minimum is related to the structural stability of the dispersed system, with higher G′ values indicating greater stability. While the minimum of the G"-ω seems not to be definitively reached, the trend indicates that it has to be closely approached. Extending the frequency range further was deemed unnecessary, given the objective of the study and the consequent increase in total test duration. Therefore, observing the initial G' values confirms that the PCM emulsion exhibits greater physical stability under resting conditions. Also the value of tan $\delta = G''/G'$ has been taken, which also gives information about stability. Lower tan δ indicates greater stability due to the predominance of elastic behaviour, which is significantly higher in the own manufactured PCM emulsion. This suggests that, in terms of stability during storage at rest, it is less stable than the commercial formulation. All these parameters indicating physical stability have been collected in table 1. Based on the evaluated indicators, the commercial emulsion exhibits superior stability.

Tab. 1: Rheological parameters influencing physical stability of PCM emulsions. G': Elastic modulus; LVR: linear viscoelastic region

PCM emulsion	G'(Pa)	tan δ	LVR
Commercial emulsion PCE18	45,4	0,265	1,436
Own manufactured PCM emulsion	6,9	0,461	2,544

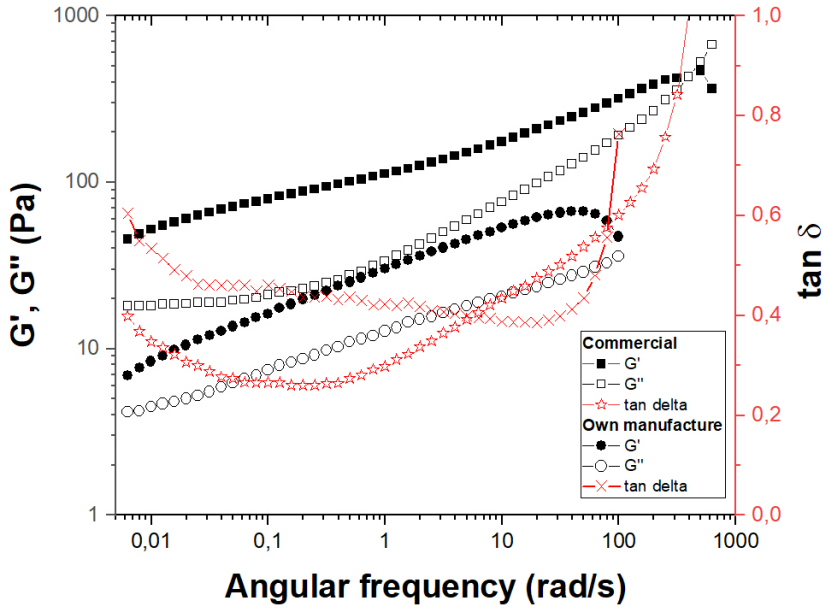

Figure 7. Frequency sweeps for the PCM emulsions within the LVR, temperature: 20ºC for the own manufactured PCM emulsion and 30ºC for the commercial PCM emulsion.

5. Discussion

Based on the results obtained for their main thermophysical properties, both PCM emulsions analyzed exhibit very similar characteristics. They show comparable phase change enthalpies and operating temperature ranges, with the Pickering PCM emulsion displaying slightly higher thermal conductivity. Regarding their rheological properties, the commercial emulsion appears advantageous due to its thixotropic behavior. Considering their potential application as an agitated TES system, it would be beneficial to stir the emulsion prior to thermal charging and discharging in order to reduce viscosity and enhance heat transfer processes. For instance, if applied in a stirred system, the effective shear rate experienced by the fluid in the tank would range from approximately 15 to 200 s^{-1} for agitation speeds between 100 and 1000 rpm, assuming a radial or pitched-blade turbine impeller (Metzner and Otto, 1957). In this scenario, the effective viscosity of the commercial PCE18 emulsion would remain around 0.12 Pa·s across the entire rpm range, whereas the Pickering PCM emulsion would exhibit values between 0.28 and 1.25 Pa·s. From a heat transfer perspective, this suggests that the commercial emulsion would likely achieve higher convective heat transfer coefficients, although its modulation during charging and discharging may be more challenging under varying operational requirements. Finally, based on the indicators used to assess physical stability, while both emulsions appear stable, the commercial emulsion shows a higher degree of stability.

6. Conclusions

The present study has evaluated two low-temperature PCM emulsions as TES materials, rather than exclusively as heat transfer fluids, which is their most common application. The emulsions assessed were a commercial product, PCE18, and a formulation developed using *n*-tetradecane. Both emulsions exhibit very similar thermophysical properties, (~132 kJ/kg and 124 kJ/kg), but in different operating temperature ranges (2-12 °C for the proprietary formulation and 13-23 °C for the commercial formulation), offering a threefold increase in storage capacity per kilogram compared to water, with a relatively low thermal hysteresis of approximately 3 °C. Regarding thermal conductivity, both solutions showed values 50% lower than that of water; however, the own developed emulsion exhibited a conductivity 15% higher than the commercial one. Significant differences were observed in their rheological behaviour. The commercial emulsion shows thixotropic properties, which is advantageous for TES systems using agitated tanks. In contrast, the own formulated

emulsion follows a pseudoplastic profile, lacking a clear Newtonian plateau and presenting minimum viscosities higher than the 0.1 Pa·s measured for the commercial emulsion. Oscillatory tests evaluating physical stability suggest that the own formulation is likely to be less stable during static storage phases.

In conclusion, there is no inherently superior emulsion, but the optimal choice depends on the application requirements. Commercial emulsion is the preferred candidate if heat transfer in stirred systems and long-term stability are a priority. On the other hand, the Pickering emulsion developed in-house is an innovative and promising alternative, with potential for further optimization.

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