



Pickering anhydrous emulsions as heat transfer fluids with cold energy storage characteristics for refrigeration and freezing

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ABSTRACT

The study presents a new class of Phase Change Emulsions (PCE) formulated with polyethylene glycol 400 as the disperse phase, D-limonene as the continuous phase, and hydrophobic fumed silica nanoparticles (Aerosil® R805) as Pickering stabilisers. Model emulsions containing ~10 wt.% Phase Change Material (PCM) were characterised through calorimetry, thermogravimetry, thermal conductivity measurements, rheology, laser diffraction, and optical microscopy to evaluate their energy-storage capacity, thermal stability, microstructure, and flow behaviour. The emulsions exhibited homogeneous droplet dispersions and stable sub-zero phase-change transitions, with a minimum nanoparticle content of ~0.05 wt.% required to prevent crystallisation-induced coalescence. Increasing silica concentration reduced droplet size and enhanced interfacial stabilisation but also promoted viscosity growth and shear-thinning behaviour. Compared with commercial secondary refrigerants, the PCEs offered a markedly broader operational window (−85 °C to +20 °C) and up to 2.4-fold higher cumulative volumetric enthalpy change. Forced-convection analysis further showed that lightly stabilised formulations achieve favourable heat-transfer effectiveness and pumping-power balance, positioning these emulsions as promising candidates for ultra-low-temperature refrigeration and thermal-buffering applications.

1. Introduction

The rapid technological development of modern society has led to a significant increase in global energy demand, which can barely be fulfilled with the conventional dwindling fossil fuel resources (Chen and Zhang, 2017). This situation has accelerated the shift toward renewable energy sources such as solar, wind, and tidal power (Holecck et al., 2022). However, the intermittent and weather-dependent nature of these resources limits their ability to provide a stable energy supply (Li et al., 2022).

To address this mismatch between fluctuating energy generation and consumption, Thermal Energy Storage (TES) technology emerges as an effective strategy to ensure a reliable and continuous energy supply (Chen and Zhang, 2017; Lu and Tassou, 2012). Among all TES systems, Latent Heat Storage (LHS) stands out due to its high energy density and the quasi-isothermal phase transitions of Phase Change Materials (PCMs) (Huang et al., 2009). PCMs store and release heat through phase

transitions, with solid–liquid PCMs being the most widely used because of their high efficiency, small volume change, and ease of operation (Huang and Petermann, 2015; Oró et al., 2012). Their phase transition temperatures can be tailored to specific applications, making them suitable for both heating and cooling processes. As a result, PCMs have gained increasing attention in recent decades for applications requiring controlled thermal management (Delgado et al., 2012).

Conventional cold-storage materials such as water, brine, salt hydrates, and eutectics are widely used due to their low cost (Wang et al., 2017). However, they suffer from limitations including restricted sensible heat capacity, supercooling, phase instability, and fixed melting points. In contrast, PCMs offer superior thermal storage density, low supercooling, adjustable melting temperatures, and non-corrosive behaviour (Huang et al., 2009; Oró et al., 2012). These advantages have expanded their use in diverse fields such as air-conditioning (Said and Hassan, 2018), energy-efficient building design (Rodríguez-Ubinas et al., 2012), food preservation (Liu et al., 2022), refrigerated transport

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(Zhang et al., 2022), and biomedical and pharmaceutical logistics (Huang and Piontek, 2017).

Despite their benefits, the direct use of bulk PCMs presents challenges such as leakage during melting, low thermal conductivity, limited surface area, and poor flowability (Lu and Tassou, 2012; Huang et al., 2009; Huang and Petermann, 2015; Zhang et al., 2016). One effective strategy to overcome these drawbacks is the dispersion of PCMs into heat-transfer fluids, producing multiphase systems with enhanced heat transfer, improved pumpability, and high energy storage ability (Wang et al., 2017; Wang et al., 2019; Wang et al., 2018). Phase Change Emulsions (PCEs) are particularly attractive because they can be prepared through simple emulsification processes, offer good stability, and require lower pumping energy compared to other PCM-based fluids (Chen and Zhang, 2017; Huang and Petermann, 2015).

PCEs consist of PCM droplets dispersed within a continuous carrier fluid and stabilised by agents that reduce interfacial tension (Wang et al., 2019; Barros et al., 2022). Pickering PCEs—stabilised by solid particles—have gained considerable interest due to their enhanced stability, tunable interfacial properties, and environmentally friendly nature (Wang et al., 2019). Silica nanoparticles, in particular, are widely used as stabilisers because of their low cost, biocompatibility, antimicrobial activity, and low toxicity (Heidari et al., 2022). They have been successfully employed in both their unmodified form (Linke and Drusch, 2018) and after surface functionalisation (Griffith and Daigle, 2018) to improve their affinity for specific phases.

Most Pickering emulsions reported in the literature involve water as either the continuous (Wang et al., 2020) or disperse (Wu et al., 2018) phase, which restricts their applicability in low-temperature environments (Delgado-Sánchez et al., 2022). Furthermore, studies specifically addressing the development of Pickering emulsions for cold energy storage remain scarce, what highlights the need for new anhydrous Pickering systems capable of operating efficiently at sub-zero temperatures (Yan et al., 2023; Wang et al., 2018).

In this context, the present work develops anhydrous Pickering PCEs by dispersing polyethylene glycol 400 as the PCM, stabilised with surface-modified fumed silica nanoparticles (Aerosil® 805), using high-shear homogenisation. *D*-limonene, a major component of citrus essential oils, is selected as the continuous phase due to its low viscosity, environmental friendliness, antimicrobial properties, and wide availability (Andriotis et al., 2021). The influence of the nanoparticle-to-PCM weight ratio on the thermal, rheological, and morphological properties of the resulting emulsions is systematically investigated to assess their suitability for cold energy storage applications.

2. Experimental

2.1. Materials

In this study, *D*-limonene (0.842 g·cm⁻³, refractive index 0.14743 20/D), was supplied by PanReac AppliChem ITW Reagents (Barcelona, Spain). Polyethylene glycol 400 (PEG400, <−14 °C freezing point at 973.5 hPa), was provided by Sigma-Aldrich (Merck KGaA, Darmstadt, Germany). Furthermore, hydrophobic fumed SiO₂ treated with octyltrimethoxysilane (Aerosil® R805, 1.99 g·cm⁻³, 125–175 m²·g⁻¹, ≥99.8% SiO₂ content) (Fambri et al., 2020), purchased from Evonik Operations GmbH (Essen, Germany), was used as the emulsion stabilising agent. All these materials were utilized as received without further purification processes.

2.2. Pickering emulsions manufacture

In this research, PEG400-in-*D*-limonene Pickering emulsions were prepared according to the emulsification process detailed elsewhere (Delgado-Sánchez et al., 2022). In brief, upon addition of the solid emulsifier into the continuous phase, the PCM was incorporated in the molten state at room temperature (≈23 °C), in the appropriate

proportion (see Table 1) and these compounds' mixtures were subjected to a high-speed homogenisation step for 5 min at 12,000 rpm and room conditions with the aid of a high-shearing rotor-stator homogeniser Ultra-Turrax T-25 (Ika-Werke, Staufen, Germany). The prepared Pickering PCEs were formulated with four different Aerosil®/PEG400 wt ratios, namely 0.01, 0.05, 0.1, and 0.5 while maintaining a constant PEG400/*D*-limonene weight ratio of 1:9 in all cases. Each PCE system was designated according to the applied nanoparticle:disperse phase weight ratio, as stated in Table 1. For clarity, a schematic representation of the emulsification process (Figure S1) has been included in the Supplementary Material.

2.3. Characterisation

Thermal transitions of raw materials and Pickering PCEs were analysed using a DSC250 (TA Instruments, USA), loading ~20 mg of sample in sealed Tzero pans, applying four modulated cooling–heating cycles between 40 and 90 °C under nitrogen. Thermal stability was assessed via TGA (Q50, TA Instruments) by heating samples in open aluminium crucibles from 30 to 600 °C (10 °C·min⁻¹, under nitrogen). Thermal conductivity of anhydrous PCEs was measured using the THB-100 (Linseis GmbH) with a THB A Metal sensor, reporting mean values from triplicate measurements. Microstructural observations were performed with an Olympus BX52 microscope (C5050Z camera), acquiring images of freshly prepared emulsions at 25 and −40 °C, while droplet size distributions and the mean diameters ($D_{3,2}$) were obtained by laser diffraction (Mastersizer Hydro 2000S, Malvern Panalytical) at room temperature. Rheological behaviour was characterised using an MCR 501 (Anton Paar) at 25 °C for flow curves (1–1000 s⁻¹) and during cooling ramps (25 to −30 °C; 10 s⁻¹; 1 °C·min⁻¹) with a serrated 50 mm plate-plate geometry (0.5 mm gap), while low-temperature analyses (−45 °C) were conducted on an Ares-G2 (TA Instruments) using a 25 mm serrated geometry (0.5 mm gap) for flow tests (0.001–100 s⁻¹) and frequency sweeps (0.03–100 rad·s⁻¹) within the Linear Viscoelastic Range. Surface and interfacial tensions were measured using a Sigma 703D tensiometer (Biolin Scientific) via the Wilhelmy plate method. Further experimental details are available in the Supplementary Material.

3. Results and discussion

3.1. Thermal characterisation

Firstly, the short-term thermal cycling stability of the formulated PCEs was assessed through four successive cooling–heating cycles. Fig. 1a illustrates the cycle evolution of the heat-flow thermogram for PCE_0.5, while Fig. 1b collects the final-cycle curves for all PCEs and the neat components.

Pure PEG400 exhibited a dominant crystallisation peak at −8.3 °C and a melting peak at 1.6 °C, with corresponding enthalpies of 103.8 and 107.0 J g⁻¹, respectively. These values align with previous reports on PEG400-based nanofluids and confirm the characteristic supercooling behaviour of this PCM (Chereches et al., 2022). A secondary crystallisation–melting pair at −21.1 °C and −17.6 °C was also observed, consistent with earlier studies attributing such features to multiple

Table 1

Composition in weight percentage (wt.%) of Phase Change Pickering Emulsion and SiO₂/PEG400 wt ratios,.

Designation	D-limonene (wt. %)	PEG400 (wt. %)	SiO ₂ (wt. %)	SiO ₂ /PEG400 (wt./wt.)
PCE_0.01	89.9	10.0	0.1	0.01
PCE_0.05	89.6	10.0	0.5	0.05
PCE_0.10	89.1	9.9	1.0	0.10
PCE_0.50	85.7	9.5	4.8	0.50

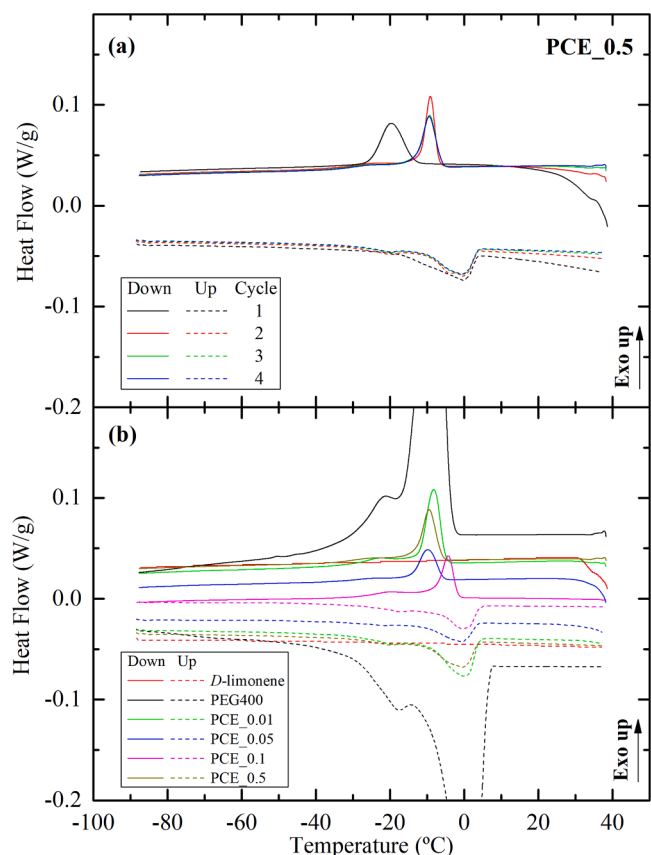


Fig. 1. Evolution of the DSC thermograms of emulsion PCE_0.5 over four cooling-heating cycles (a) and heat flow thermograms resulting from the fourth cooling-heating cycle of the main compounds and PCEs (b).

crystallisation pathways and the formation of lamellae with different thicknesses (Paberit et al., 2020). In contrast, *D*-limonene, used as the continuous phase, showed no thermal transitions within the examined temperature range.

Importantly, the PCEs retained the qualitative phase-change behaviour of PEG400 after emulsification, indicating that neither the presence of Aerosil® R805 nanoparticles nor the *D*-limonene matrix significantly disrupted the intrinsic thermal transitions of the PCM (Aydın and Toprakçı, 2021). Although the first thermal cycle induced a shift in the crystallisation peak (from $-19.7\text{ }^{\circ}\text{C}$ to $-9.1\text{ }^{\circ}\text{C}$), attributed to the thermal history of the as-prepared PCEs (Paberit et al., 2020). The initial DSC cycle primarily reflects the native droplet structure and interfacial state, whereas subsequent cycles exhibit nearly overlapping thermograms after thermal conditioning, indicating stable phase-change behavior without a significant impact on energy storage performance. This reproducibility across cycles confirms stable phase-change behaviour and indicates that the initial shift does not meaningfully affect the energy-storage performance of the emulsions. Overall, the results clearly demonstrate the excellent thermal reliability of the emulsified PEG400 for sub-zero temperature applications (Jouhara et al., 2023). Similar behaviour was observed across all SiO_2 :PEG400 ratios, as shown in the Supplementary Material (Figures S2-S5), whereas pure PEG400 displayed stable thermograms from the first cycle onward.

The emulsification process produced only minimal reductions in the T_m and T_c temperatures, particularly at higher nanoparticle loadings ($\geq 0.1\text{ wt.}\%$). This is a favourable outcome, as some PCE systems reported in the literature suffer from partial miscibility between phases, which reduces stored energy density (Delgado-Sánchez et al., 2021). Therefore, at high nanoparticle loads the normalised latent heats of crystallisation and melting remained close to those of neat PEG400, with

ΔH_c ranging from 93 to 103 J g^{-1} and ΔH_m from 88 to 98 J g^{-1} (see Table 2). These values confirm that the PCM retains most of its latent heat capacity within the emulsified structure.

At lower nanoparticle concentrations, however, insufficient stabilisation of the disperse phase led to partial phase separation, reflected in larger deviations in enthalpy values. Overall, the PCEs demonstrated strong cycling stability and high energy density, with only marginal reductions attributable to emulsification.

On the other hand, the DSC analysis revealed an apparent supercooling of approximately $8\text{ }^{\circ}\text{C}$ in all the formulated PCEs, quantified as the difference between the peak temperatures of melting and crystallisation ($\Delta T = T_m - T_c$). It is important to note, however, that these peak values represent only the extrema of the thermal transitions, which in practice occur over a broader temperature interval. During real operation, the working temperature of a TES system would be selected within the region where the melting and crystallisation ranges overlap (Barz et al., 2019; Barz and Sommer, 2018), allowing both processes to proceed concurrently over part of the cycle. Under such conditions, the effective supercooling experienced by the material, and therefore its influence on charging and discharging behaviour, may be considerably less pronounced than suggested by the peak-to-peak hysteresis alone. A rigorous evaluation of the impact of this hysteresis on system-level performance, including Coefficient of Performance (COP) or exergy efficiency in a vapour-compression cycle, would require dedicated experiments under realistic operating conditions or pilot-scale configurations. As the present study is intended as a preliminary investigation focused on formulation, characterisation, and proof-of-concept suitability, such an analysis lies beyond its scope. Nevertheless, the need for a more detailed assessment of the operational efficiency of these emulsions in service conditions has been identified as an essential direction for future work.

Beyond latent heat storage, the ability of the emulsions to store and transfer sensible heat was evaluated through measurements of isobaric heat capacity (C_p) at temperatures representing both liquid ($25\text{ }^{\circ}\text{C}$, $5\text{ }^{\circ}\text{C}$) and solid ($-45\text{ }^{\circ}\text{C}$, $-60\text{ }^{\circ}\text{C}$) states of the considered PCM. PEG400 exhibited C_p values consistent with literature (Marcos et al., 2017), increasing with temperature and decreasing by approximately 29% in the solid state at $-45\text{ }^{\circ}\text{C}$. The PCEs followed a similar trend, with crystallisation causing a $\sim 13\%$ reduction in C_p at $-45\text{ }^{\circ}\text{C}$.

Because fumed silica nanoparticles possess a much lower C_p value ($0.605\text{--}0.767\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$) than *D*-limonene ($1.376\text{--}1.506\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$), increasing nanoparticle content led to a progressive decrease in the overall C_p of the emulsions (Akilu et al., 2017). The most pronounced reduction occurred between 0.1 and 1 wt.% nanoparticles. Interestingly, at higher concentrations, C_p increased again, likely due to gelation phenomena that enhance interparticle interactions, consistent with the rheological behaviour discussed later (see Fig. 8).

Thermal conductivity (λ) was measured at room temperature using the Transient Hot Bridge method, and the resulting values were gathered in Fig. 2. At low nanoparticle loadings, the PCEs exhibited enhanced thermal conductivity relative to the continuous phase, despite *D*-limonene having a lower λ ($0.130\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) than PEG400 ($0.182\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). However, increasing the nanoparticle concentration beyond 0.1 wt.% resulted in a decrease in λ , reaching values as low as $0.141\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Although higher nanoparticle concentrations typically improve thermal conductivity (Yu et al., 2026) the opposite trend here may be explained by viscosity effects: at low nanoparticle contents, reduced viscosity can promote convection currents during measurement, artificially inflating λ values. Such convective contributions are known to cause deviations from expected conductive behaviour in low-viscosity multiphase systems (Paul et al., 2010).

The reduction in thermal conductivity at higher nanoparticle loadings may translate into a lower heat-exchange rate in practical TES equipment, potentially slowing the charging and discharging processes. However, this limitation could be mitigated either by optimising the nanoparticle concentration or by incorporating thermally conductive

Table 2

Thermal parameters extracted from the DSC analyses of raw materials and PCEs.

Sample	R805	D-limonene	PEG400	PCE_0.01	PCE_0.05	PCE_0.1	PCE_0.5
T_m (°C)	-	-	-8.2	-0.3	-0.6	-0.5	-0.5
$T_{m, onset}$ (°C)	-	-	-30.7	-27.2	-41.8	-34.8	-28.5
ΔH_m (J·g ⁻¹ PEG400 ⁻¹)	-	-	107.0	104.4	73.8	93.5	103.3
T_c (°C)	-	-	-8.2	-8.2	-9.8	-4.3	-9.4
$T_{c, onset}$ (°C)	-	-	-3.8	-5.1	-5.7	-1.7	-6.0
ΔH_c (J·g ⁻¹ PEG400 ⁻¹)	-	-	103.8	100.3	67.9	88.2	98.0
$C_{p, 25^\circ C}$ (J·g ⁻¹ ·°C ⁻¹)	0.767	1.506	2.238	1.431	1.382	1.327	1.595
$C_{p, 10^\circ C}$ (J·g ⁻¹ ·°C ⁻¹)	0.688	1.462	2.237	1.403	1.349	1.297	1.558
$C_{p, -45^\circ C}$ (J·g ⁻¹ ·°C ⁻¹)	0.620	1.376	1.574	1.197	1.214	1.173	1.422
$C_{p, -60^\circ C}$ (J·g ⁻¹ ·°C ⁻¹)	0.605	1.354	1.441	1.160	1.181	1.137	1.388

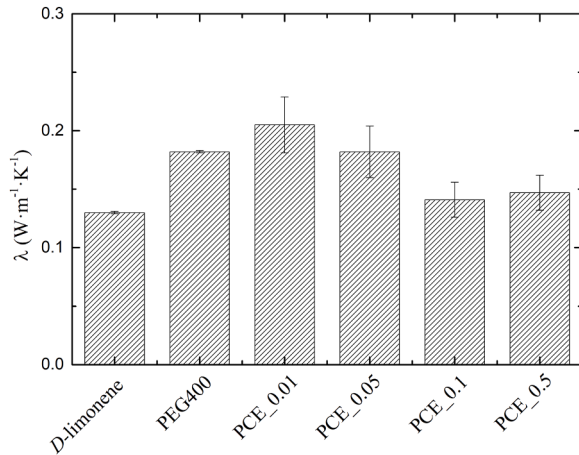


Fig. 2. Thermal conductivity values for all PCEs and PEG400 at 25 °C.

additives, which would enhance the effective heat-transfer rate while preserving the stabilising function of the particles (Mirahmad et al., 2025; Li et al., 2023).

Thermal stability was further examined through thermogravimetric analysis (TGA) under N₂ (see Fig. 3 and Table 3). The raw materials displayed distinct single-step decomposition patterns: *D*-limonene decomposed between 77.7 and 111.0 °C, while PEG400 decomposed between 301.9 and 386.6 °C, leaving negligible residues of 1.61% and 0.20%, respectively (Cherecheş et al., 2022). These results confirm the relatively low thermal stability of *D*-limonene ($T_{Onset} \sim 77.7$ °C) and the much higher stability of PEG400 ($T_{Onset} \sim 301.9$ °C). Aerosil® R805 nanoparticles, as expected, showed excellent thermal stability up to ~ 200 °C, followed by a minor mass loss ($\sim 4.5\%$) associated with desorption of physically bound water and decomposition of surface-grafted silane groups (Li et al., 2018).

The PCEs exhibited a two-step decomposition process, with the first stage (97.3–158.9 °C) corresponding to volatilisation of *D*-limonene and the second (256.3–375.4 °C) to PEG400 degradation (Fig. 3b). Increasing nanoparticle content produced only slight increases in $T_{5\%}$ and final residue (see Table 3), indicating that the nanoparticles impart a modest stabilising effect in these formulations. From an application standpoint, the thermal-stability profiles of the PCEs indicate that all formulations possess decomposition onset temperatures far above any conditions encountered in cold-storage or ultra-low-temperature TES systems. This ensures that neither volatilisation of the continuous phase nor degradation of the PEG-based PCM would occur during operation, even under transient thermal excursions or equipment malfunction. The slight increase in $T_{5\%}$ and residual mass with higher nanoparticle loadings suggests a marginally improved resistance to thermal degradation, which may be advantageous for long-term cycling stability. Although thermal stability is not typically a limiting factor in sub-zero TES applications, these results confirm that the formulated emulsions

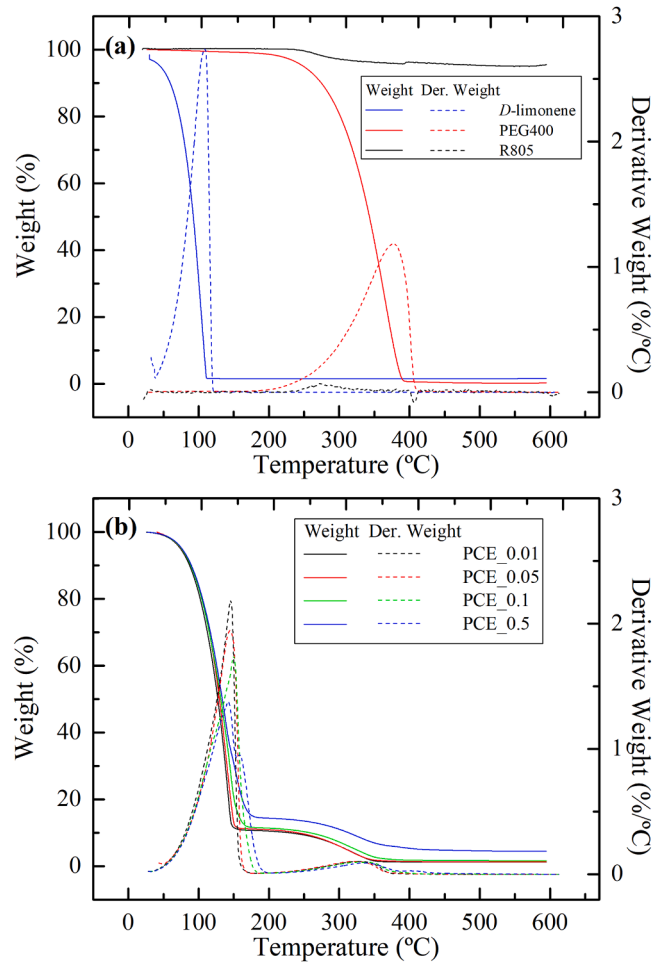


Fig. 3. Thermogravimetric and derivative curve results of raw materials (a) and prepared phase change emulsions (b).

provide a sufficiently wide safety margin for handling, storage, and integration into refrigeration equipment.

3.2. Microstructural analysis

Owing to the great impact of the micro-morphology of the PCE on their macroscopic properties, optical images were taken at 25 °C (without polarizers) and -40 °C (with crossed polarisers), above and below the freezing point of PEG400, and the resulting micrographs have been collected in Fig. 4. As can be noticed in the images obtained at 25 °C, i.e. quite above the PEG400 melting point, silica nanoparticles properly stabilise PEG400 into *D*-limonene, thus resulting in suitable Pickering PCEs with a homogeneous and well-dispersed spherical-like

Table 3

Thermogravimetric results of raw materials and prepared PCEs.

Sample	D-limonene	PEG400	R805	PCE_0.01	PCE_0.05	PCE_0.1	PCE_0.5
T _{Max,1} (°C)	104.8	-	-	140.4	139.3	144.6	137.0
T _{Max,2} (°C)	-	365.3	261.8	317.7	313.6	316.0	325.6
T _{Onset,1} (°C)	77.7	-	-	105.2	106.7	102.4	97.3
T _{Onset,2} (°C)	-	301.9	237.3	261.2	256.3	263.0	272.9
ΔW ₁ (%)	95.5	-	-	89.3	88.8	88.5	85.6
ΔW ₂ (%)	-	99.8	4.5	9.5	9.8	9.8	9.9
T _{5%} (°C)	45.7	249.5	>600	74.4	75.3	75.8	76.5
R (%)	1.61	0.23	95.55	1.24	1.34	1.63	4.45

droplets distribution without aggregation.

In addition, when PCEs are cooled down to -40 °C, below the crystallisation temperature of PEG400, optical images under cross-polarised light clearly point out the appearance of birefringent bright regions within the droplets, confirming the crystalline state of the disperse phase, previously reported from DSC experiments. In general, even though crystallization causes a slight circularity deviation of the disperse phase due to the crystal growth, no large deviation of the spherical shape is pointed out. However, it is important to note that, at low nanoparticle content, droplet size undergo a remarkable increase. Then, it appears that some particles are associated together after crystallization, as PEG crystals protrude from the interphase of the droplet and are linked to the neighbouring crystals. This led to changes in the PCE microstructure during cooling-heating cycles and even to the destabilisation of the emulsion during service.

Such microstructural destabilisation at low nanoparticle loadings has direct implications for practical TES operation. When crystallisation-induced coalescence or droplet growth occurs, the emulsion may develop local inhomogeneities that lead to fluctuations in heat flow, reduced interfacial area, and impaired heat-exchange efficiency during charging and discharging. These instabilities can ultimately compromise the predictability and reproducibility of the thermal response, resulting in sub-optimal performance of the PCEs when integrated into TES equipment. Ensuring sufficient interfacial stabilisation, either by maintaining nanoparticle concentrations above the critical threshold or by adopting complementary stabilisation strategies, is therefore essential to guarantee reliable long-term operation under repeated cooling-heating cycling.

Additionally, the droplet size distribution (DSD) of all Pickering PCEs was also evaluated at room conditions via laser diffraction technique (Fig. 5) and mean Sauter diameters gathered in Table 4. As can be noticed, all samples exhibit a unimodal dispersion of droplet sizes, which are shifted to smaller sizes as nanoparticle content raises. This results in a quantitative reduction in $D_{3,2}$, from 14.0 (PCE_0.01) to 3.03 μm (PCE_0.1).

In general, different factors may affect the droplet size in Pickering emulsions such as nanoparticle concentration, relative amount of disperse and continuous phases and the mechanical energy applied for emulsification. However, since the presented emulsions have been submitted to similar processing conditions and present a constant ratio of disperse to continuous phase of 0.11, it can be deduced that the nanosilica content will exert the predominant influence. Then, the evolution of the Sauter mean diameter with nanoparticle content follows a pattern previously reported for other authors, characterised by an exponential decrease, reaching a plateau at high concentrations, that seems to indicate a limit to the minimum droplet size that can be achieved (Fig. 6a). However, as previously reported (Frelichowska et al., 2010), the plateau observed would correspond to a lack of efficiency in the emulsification process as higher mechanical mixing energy or ultrasonic processing would allow for smaller droplet sizes. Therefore, silica nanoparticles would be in excess in this plateau. As stabilisation is achieved by adsorption of Pickering particles at the interface, it is generally accepted that larger amounts of nanoparticles enable a larger interfacial area to be stabilised. Subsequently, in the event that all of the

added nanoparticles were found to be adsorbed to the interface, that is to say, no excess of particles would remain in the bulk dispersing phase, it can be deduced that the diameter would be proportional to the phase ratio as follows (Frelichowska et al., 2010):

$$D_{3,2} = \frac{6}{\rho_{\text{PEG}} a_{\text{SiO}_2}} \frac{W_{\text{PEG}}}{W_{\text{SiO}_2}} \quad (1)$$

Where W_{PEG} and W_{SiO_2} are the mass content of PEG400 and Pickering particles, respectively, ρ_{PEG} is the density of the disperse phase above the melting point at 25 °C (1.13 g cm^{-3}) and a_{SiO_2} is the interfacial area per unit mass of silica at full coverage of the droplet. Here, this value was assumed to follow the predictions for a dense monolayer given by Arditty et al. (2003):

$$a_{\text{SiO}_2} = \frac{3}{\phi_e \cdot 2 \cdot \rho_{\text{SiO}_2} \cdot D} = 62.4 \frac{\text{m}^2}{\text{g}} \quad (2)$$

Where D is the diameter of elementary nanoparticles (12 nm), ρ_{SiO_2} is the density of pure silica (2.2 g cm^{-3}), and $\phi_e = 0.91$ is the fractional area occupied by spherical particles as a 2D hexagonal close packing. Then, Fig. 6b presents experimental and calculated values from (1) and enables the evaluation of the diameter resulting from each concentration, in order to ascertain whether it attains the predicted values. This is achieved only when all nanoparticles are dedicated to stabilising the emulsion and maintain a comparable surface structure in accordance with the concentration. However, Fig. 6b clearly shows a positive deviation from the model and then, for a given concentration ratio, the resulting droplet diameter is larger than when the entire mass of silica is arranged in a monolayer. Therefore, this outcome indicates the presence of a significant amount of silica nanoparticles in either of the disperse or continuous phase, according to the compatibility and affinity between them.

If it is assumed that the equilibrium is reached after emulsion processing, the position of the nanoparticles is controlled by thermodynamics and then, theoretically predicted by the so-called 'wetting parameter' (ω), which can be calculated as follows (Elias et al., 2007):

$$\omega = \frac{\gamma_{\text{SiO}_2-\text{PEG}} - \gamma_{\text{SiO}_2-\text{Lim}}}{\gamma_{\text{PEG-Lim}}} \quad (3)$$

Where $\gamma_{\text{SiO}_2-\text{PEG}}$ and $\gamma_{\text{SiO}_2-\text{Lim}}$ are the interfacial tensions or interfacial energies between the silica nanoparticles and polyethyleneglycol (PEG) and D-limonene (Lim), respectively, and $\gamma_{\text{PEG-Lim}}$ is the interfacial tension between both phases. Theoretically, for values of $\omega > 1$, nanoparticles are expected to be located in the D-limonene phase; if $\omega < -1$, they will be in the PEG phase, and eventually for values in the range $-1 < \omega < 1$, nanoparticles are confined at the interphase between both phases.

Interfacial tension between the solid (SiO_2) and fluid phases (F) can be estimated by means of the well-known Owens and Wendt equation (Elias et al., 2007):

$$\gamma_{\text{SiO}_2-F} = \gamma_{\text{SiO}_2} + \gamma_F - 2\sqrt{\gamma_{\text{SiO}_2}^d + \gamma_F^d} - 2\sqrt{\gamma_{\text{SiO}_2}^p + \gamma_F^p} \quad (4)$$

Where γ_{SiO_2} and γ_F are overall surface free energies of SiO_2 and the continuous (D-limonene) or disperse (PEG400) phases, and superscripts d and p refers to the dispersive and polar components of surface tension

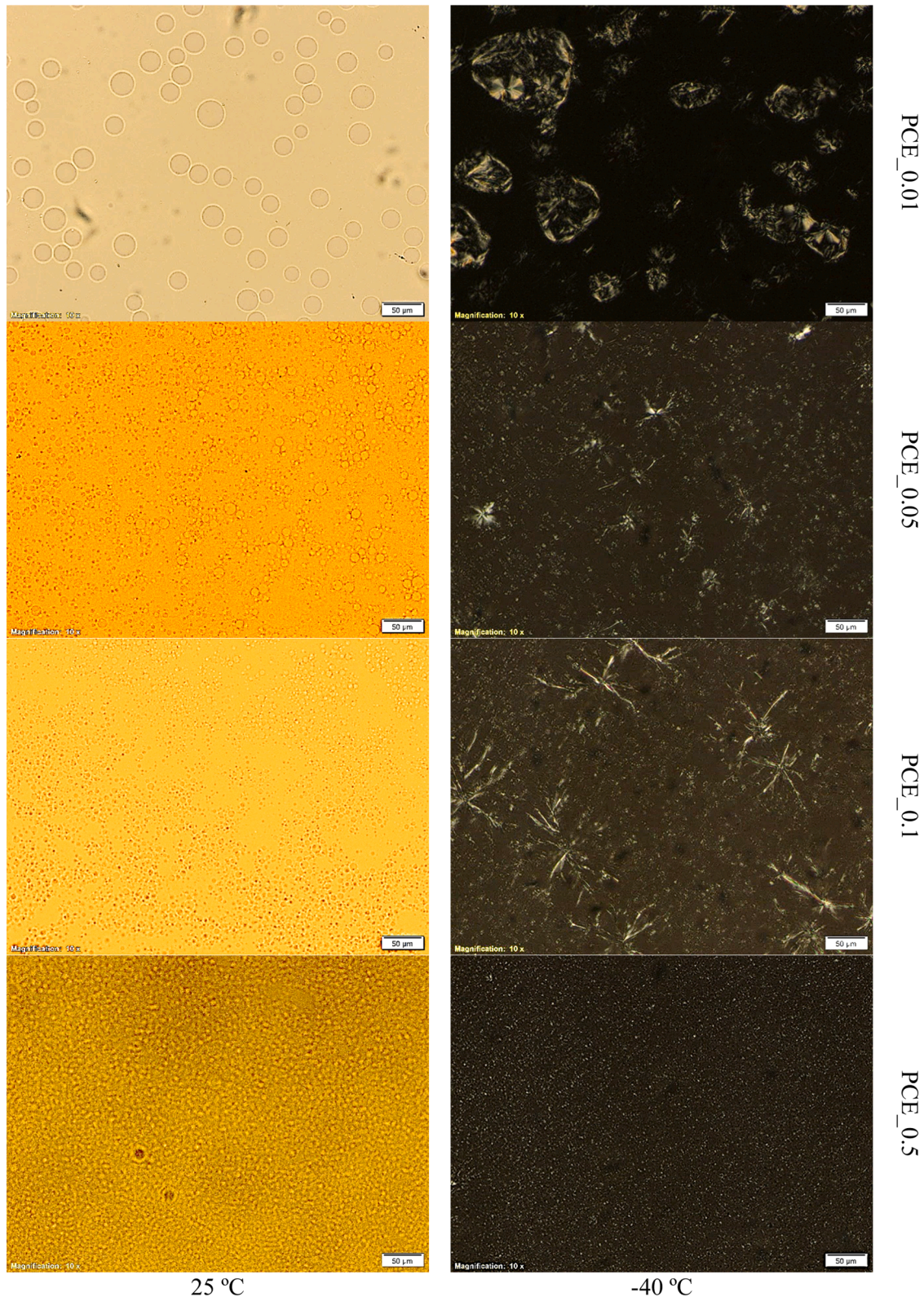


Fig. 4. Optical micrograph of fresh Pickering phase change emulsion at 25 °C (without polarizers) and -40 °C (with crossed polarizers).

summing $\gamma = \gamma^d + \gamma^p$, gathered in Table 5. Surface tension of neat liquid phases (γ_{Lim} , γ_{PEG}) and interfacial energy between them were experimentally measured by the Wilhelmy plate method (Table 5). Values for nanoparticles and dispersive component of PEG400 were taken from the investigations of Elias et al. (2007) and Sesigur et al. (2014), while for *D*-limonene was extracted from the study of Huang and Zhang (2025)

assuming 1.2% of polar component.

From (4) and Table 5, the estimated wetting coefficient for our system is 1.78, pointing out that nanoparticles present a stronger thermodynamic affinity for the *D*-limonene phase than for PEG400. Therefore, this outcome is consistent with the strong deviation of the model presented in Fig. 6b indicating that a significant quantity of particles may be

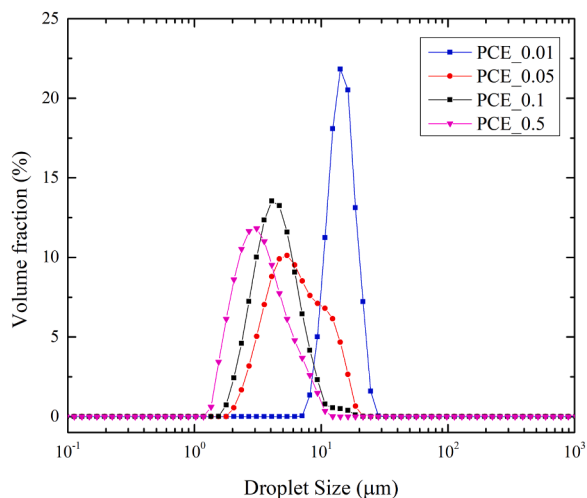


Fig. 5. Impact of Aerosil® R805 content on the PCE droplet size distribution.

Table 4

Sauter mean ($D_{3,2}$) diameter as a function of the Aerosil® R805 content.

Pickering Emulsion	$D_{3,2}$ (μm)
PCE_0.01	14.00
PCE_0.05	5.54
PCE_0.1	4.07
PCE_0.5	3.03

dispersed in the *D*-limonene phase. However, even though the calculated value of ω falls slightly outside the theoretical range of preferential interphase localisation, the experimental evidence in this work demonstrates that the hydrophobic nanoparticles display clear interfacial activity, as reflected by the reduction in droplet size and enhanced resistance to coalescence with increasing particle loading. This behaviour is consistent with Pickering-type limited coalescence, where

adsorbed particles control droplet size and act as a steric barrier at the interface (Peito et al., 2022; Hatchell et al., 2022).

3.3. Rheological behaviour

The viscous response of the formulated PCEs was analysed at 25 and -30 °C under shear conditions and the ensuing flow curves were gathered in Fig. 7a and b, respectively. As can be observed, the neat components, *D*-limonene and PEG400, exhibited Newtonian behaviour at 25 °C, with viscosities of approximately 0.0009 and 0.07 Pa·s, respectively.

At 25 °C, emulsification of PEG400 with low concentrations of surface-modified silica nanoparticles (up to PCE_0.1) produced only a slight increase in viscosity, with values remaining close to those of the continuous phase. This indicates that the emulsions maintain high flowability at low nanoparticle loadings. A mild shear-thinning behaviour emerged at low shear rates, becoming progressively more pronounced as the nanoparticle concentration increased.

A substantial change occurred when the SiO₂:PEG400 ratio was further increased. In particular, PCE_0.5 displayed a three-order-of-magnitude increase in viscosity at low shear rates compared to low-silica formulations, together with a strong shear-thinning response (Fig. 7a). This dramatic thickening reflects the formation of a more structured internal network, driven by both the increased number of stabilising particles and the reduction in droplet size.

To quantitatively describe the non-Newtonian behaviour at 25 °C, the flow curves were fitted to the Ostwald–de Waele model:

$$\eta = K \cdot \dot{\gamma}^{(n-1)} \quad (5)$$

Table 5

Overall surface free energies and their dispersive and polar interactions of all components and interfacial tension of PEG-Lim.

Sample	γ (mJ·m ⁻²)	γ^d (mJ·m ⁻²)	γ^p (mJ·m ⁻²)
SiO ₂	32.0	30.0	2.0
PEG	38.9	23.34	15.56
<i>D</i> -limonene	35.3	22.2	3.1
PEG-Lim	38.9	-	-

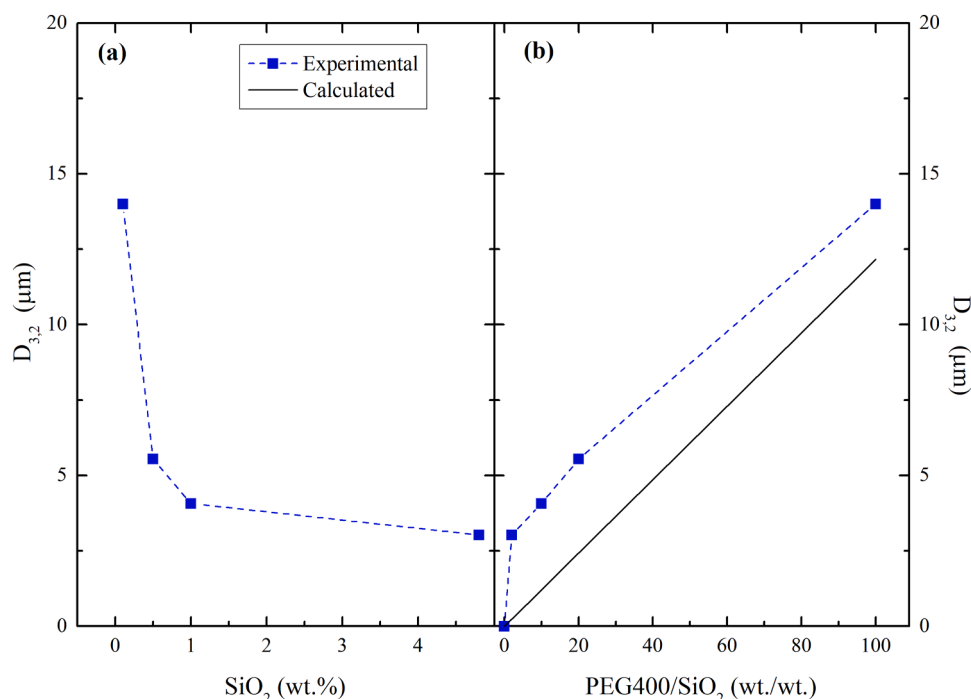


Fig. 6. Evolution of the droplet diameter $D_{3,2}$ (a) with nanoparticle content (b) with the weight ratio PEG400 to nanoparticle.

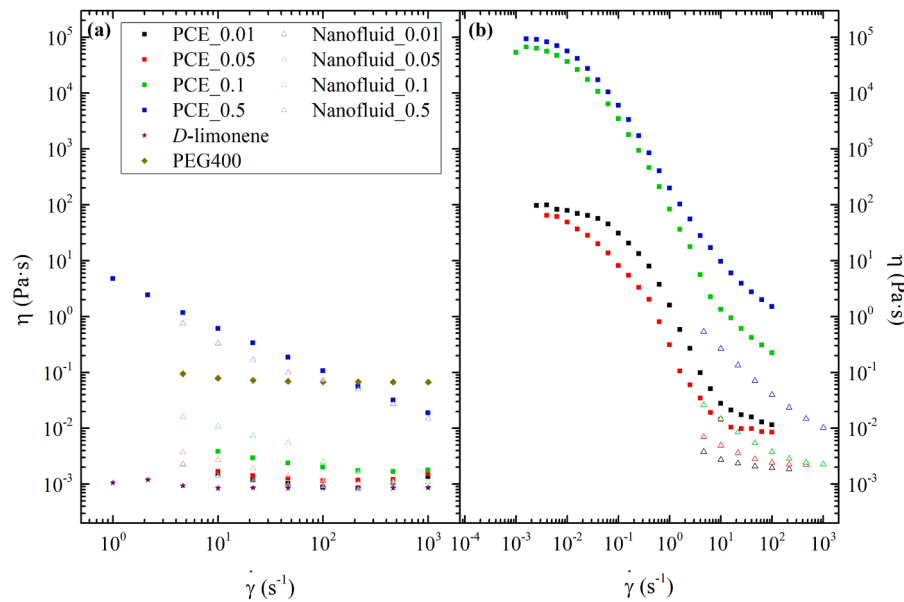


Fig. 7. Flow curves for the main components and PCE obtained at (a) 25 and (b) −30 °C.

where K is the consistency index and n the flow index (Huang and Petermann, 2015). The nonlinear regression was carried out using Levenberg–Marquardt Method, which provided the full statistical assessment of the Ostwald–de Waele fits. The agreement between the model and the experimental data was excellent, as reflected by an adjusted R^2 value above 0.978. The residual sum of squares and the reduced chi-square were extremely small relative to the magnitude of the measured viscosities, indicating minimal deviation between the fitted curve and the experimental points. The parameter estimates were statistically robust, and the residuals showed no systematic trends, confirming the suitability of the Ostwald–de Waele model for describing the shear-dependent behaviour at 25 °C. The fitting parameters (Table 6) confirm that PCE_0.5 exhibits the highest consistency index and the lowest flow index, indicating a strong pseudoplastic character and a high sensitivity to shear. The thickening effect cannot be attributed solely to the disperse phase, given its relatively low concentration (~10 wt.%). Instead, the combined influence of droplet size reduction, particle-induced structuring, and nanoparticle interactions within the continuous phase plays a dominant role.

Because of the hydrophobic silica nanoparticles affinity for the *D*-limonene phase, those not used for Pickering stabilisation would be dispersed through this phase, forming a nanofluid phase within the continuous medium. To isolate the effect of nanoparticles, nanofluids with equivalent silica concentrations were also characterised. As shown in Fig. 7a, these nanofluids exhibit a clear thickening effect, consistent with the known behaviour of Aerosil® R805 in non-polar media.

Previous studies (Tadjarodi and Zabihi, 2013) have shown that these nanoparticles tend to form branched aggregates or clusters, increasing the effective hydrodynamic diameter and inducing shear-thinning behaviour.

Interestingly, at 25 °C, nanofluids display higher viscosities than the corresponding emulsions at low shear rates. This is attributed to the localisation of nanoparticles at the droplet interface in PCEs, which reduces their effective concentration in the bulk continuous phase. However, at the highest silica loading (PCE_0.5), the emulsion viscosity surpasses that of the nanofluid. This inversion suggests that the emulsion microstructure, particularly the formation of a droplet network, contributes significantly to the overall viscosity at high particle concentrations (Fig. 4).

At −30 °C, the flow behaviour further changes with a significant increase in viscosity upon the crystallisation of the disperse PEG phase (see Table 2). All formulated multiphase systems showed a pronounced non-Newtonian response, with a *S*-shaped flow curve characterised by an apparent zero shear viscosity (η_0), followed by the shear-thinning region, and the subsequent apparent viscosity at an infinite shear rate (η_∞). Therefore, these flow curves obey the Cross-model equation and were accordingly fitted (Cross, 1965):

$$\eta = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{1 + (C \cdot \dot{\gamma})^m} \quad (6)$$

Where m and C depict the slope shear-thinning region and the relaxation time that marks the transition to the shear-thinning regime,

Table 6

Model fitting parameters for PCE's flow curves at 25 °C and −30 °C.

Parameter	T (°C)	PCE_0.01	PCE_0.05	PCE_0.1	PCE_0.5	
K (Pa·s ⁿ)	25	-	-	0.007 ± 0.001	4.657 ± 0.087	Ostwald
n		-	-	0.73 ± 0.02	0.14 ± 0.01	
$R_{Ostwald}^2$		-	-	0.978	0.998	
K (Pa·s ⁿ)	−30	0.052 ± 0.003	0.014 ± 0.001	9.11 ± 1.09	53.1 ± 6.33	Ostwald*
n		0.67 ± 0.02	0.89 ± 0.02	0.17 ± 0.04	0.20 ± 0.04	
$R_{Ostwald}^2$		0.987	0.882	0.993	0.993	
η_0 (Pa·s)	−30	83.66 ± 2.69	62.62 ± 2.81	64528.24 ± 1516.08	97155.72 ± 1043.06	Cross
η_∞ (Pa·s)		0.01 ± 0.00	0.01 ± 0.00	0.20 ± 0.00	1.20 ± 0.00	
C (s)		13.20 ± 0.93	39.14 ± 2.98	74.16 ± 3.08	75.24 ± 1.50	
m		1.65 ± 0.00	1.55 ± 0.00	1.60 ± 0.00	1.42 ± 0.00	
R_{Cross}^2		0.985	0.982	0.994	0.999	

(*) Fitting range 10–100 s^{−1}.

respectively. The nonlinear regression of the Cross model was also carried out using Levenberg–Marquardt Method, which generated the complete statistical evaluation of the fits. All samples exhibited excellent agreement with the model, with adjusted R^2 values exceeding 0.98. The reduced chi-square values and residual sum of squares were small compared with the magnitude of the experimental viscosity data, confirming that the fitted curves closely reproduced the measured flow behaviour. The residuals were randomly distributed, indicating the absence of systematic deviations. The fitted parameters were statistically stable, and the associated 95% confidence intervals were narrow. The ensuing fitting parameters were drawn and collected in Table 6. As can be seen, all these flow curves were suitably fitted to the Cross model, corroborating their pseudoplastic flow behaviour at low-temperature conditions, upon liquid-to-solid phase transition of the considered PCM.

In addition, the structuring effect of the SiO_2 nanoparticles at -30°C was once again observed in the nanofluid curves, as was the effect at 25°C but this slight viscosity increase of nanofluids after the temperature drop does not explain the flow behaviour of emulsions at -30°C .

In general, the phase change of the disperse phase and the increase in the nanoparticle load yield much more structured systems, judging by the remarkable increase reported of η_0 and η_∞ and by the raise of the relaxation time parameter (C), which is intrinsically related to the molecular freedom of movement, i.e. time required for structural rearrangements (Bourbon et al., 2010). Therefore, the results suggest that the development of a more densely packed structure has led to higher molecular movement restriction (Table 6).

Additionally, due to the PCM phase transition from the liquid to the solid state, a significant growth in the apparent viscosity was detected as the temperature was reduced from 25°C to -30°C . This effect is attributed to the reduced particle mobility and droplet deformability and the appearance of crystalline structure which favours the development of a network of emulsion droplets affecting the bulk emulsion. This can lead to an unusual dependence of shear stress on shear rate as previously stated by Chatterjee et al. (2017) when assessing the phase transition impact on the rheological properties of paraffin wax-water Pickering emulsions. As in our case, these authors pointed out a maximum followed by a minimum in the σ - $\dot{\gamma}$ curves (see Figure S6 in the Supplementary Material), at temperatures below the melting point of the disperse phase. This maximum is attributed to the formation of a crystalline network and its subsequent shear-induced disruption while the path to the minimum is caused by the progressive breakdown of the physical extended structures. Consequently, such crystallite disruption might be responsible for the unusually high shear-thinning region slope values of around 1.55 exhibited by the evaluated PCEs (Table 6).

The impact of phase change process on PCEs with different nano-sized stabilising agent proportion was also evaluated by means of rotational downward temperature ramps from 25 to -30°C applying a cooling rate of $1^\circ\text{C}\cdot\text{min}^{-1}$ under a constant shear rate (10 s^{-1}) and the resulting apparent viscosity values versus temperature were gathered in Fig. 8.

According to the previous flow tests (see Fig. 7), the structuring effect of the SiO_2 nanoparticles incorporated into the PCE can be confirmed within the whole temperature range evaluated in Fig. 8. Additionally, pure PEG400 displayed at the onset the crystallization an acute increase in the viscosity as temperature decreased, as a consequence of the lower deformation of crystallites when compared with the liquid PCM (Huang et al., 2009; Delgado-Sánchez et al., 2022), even achieving values out of the measurement range of the device, as reported in a previous investigation when assessing stearic acid-based phase change emulsions (Delgado-Sánchez et al., 2022).

Besides, due to the low disperse phase concentration (10 wt.%) and the relatively high shear rate used (10 s^{-1}), the crystallization process is, in general, barely perceptible. Indeed, SiO_2 -based PCEs just reported a steady slight increase in their apparent viscosity, whose onset transition temperature shifted to lower values when compared against that one

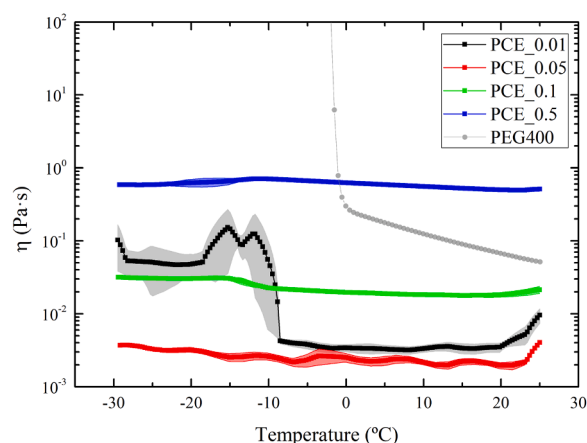


Fig. 8. Downwards temperature ramps under shear deformation for all PCEs ($1^\circ\text{C}\cdot\text{min}^{-1}$).

reported by pristine PEG400, owing to the incorporation of an additional interface thermal resistance, as well as the thermal isolation properties associated to fumed silica nanoparticles, hence hampering the heat transfer through the sample.

Surprisingly, PCE_0.01 emulsion containing the lowest nanoparticle content exhibited a sharp increment in its viscosity at -8.5°C , equivalent to the $T_{c,onset}$ extracted from the DSC experiments conducted under static conditions (Table 2). This outcome is attributed to a destabilisation process as a consequence of the notable rise in droplet size after crystallization (Fig. 5). Thus, PCM crystallisation in the *D*-limonene medium occurred at such a low nanoparticle loading that crystals were favoured to protrude from the droplet interface, leading to partial coalescence. Therefore, the occurrence of larger crystallite formation with subsequent disruption may be responsible for such a large increase in viscosity (Fig. 8) (Lu and Tassou, 2012).

Nonetheless, although steady shear experiments (Fig. 7) reported relatively high apparent viscosity values, mainly at low shear rates and at low temperatures, regardless of the SiO_2 :PEG400 ratio applied, PCEs' flow properties seem to fall within the acceptable interval for industrial applications (Royon et al., 1998) throughout the whole temperature range studied.

The strong dependence of viscosity on both nanoparticle loading and temperature has clear implications for TES operation. Higher silica concentrations produce a marked thickening effect, which would translate into increased pumping power and higher circulation costs when the emulsions are used as secondary coolants. Upon cooling, the progressive structuring of the system further elevates the apparent viscosity and may increase the pressure drop across pipes and heat-exchange components. The cooling-ramp experiments confirm that, although most formulations exhibit only a gradual viscosity rise due to the low disperse-phase content and the applied shear, insufficiently stabilised systems such as PCE_0.01 can undergo abrupt viscosity jumps associated with crystallisation-induced droplet growth and partial coalescence. Such events may lead to transient flow instabilities or localised increases in resistance to flow, potentially affecting the uniformity of heat transfer during charging and discharging. These observations highlight a formulation trade-off, that is, while higher nanoparticle contents enhance emulsion stability and suppress crystallisation-driven coalescence, they also yield more structured, more viscous systems that may challenge pumpability at low temperatures. Conversely, very low nanoparticle loadings favour flowability but risk microstructural destabilisation during phase change. Identifying an optimal stabiliser concentration is therefore essential to balance long-term stability with acceptable viscosity and pressure-drop levels under realistic TES operating conditions.

PEG400-dispersions were subjected to a viscoelastic characterisation

within the Linear Viscoelastic Region, thus assessing their viscoelasticity while preserving their structural properties, and their mechanical spectra were shown in Fig. 9. At 25 °C, only the emulsion with the highest particle concentration (PCE_0.5) presents a viscoelastic behaviour characterised by a predominantly elastic character, while the others do not show any elasticity (i.e. they show the terminal or Newtonian region of the viscoelastic spectrum). Therefore, at a nanoparticle content lower than 5 wt.%, the formation of structures in the nanofluid plus the contribution of the disperse phase is sufficient to cause an increase in viscosity and an incipient shear thinning behaviour, but not enough to produce a significant elastic response.

Therefore, PCE_0.5 at 25 °C and all emulsions at −45 °C, showed a predominant elastic behaviour, whose elastic moduli (G') remained always higher than viscous function (G''), within the whole frequency range evaluated, presenting a negligible frequency dependence, denoting their strong-gel like character. This happens despite the prepared PCEs have been demonstrated to flow properly upon crystallisation of the considered PCM. This gel behaviour results from PEG400 particle interactions favoured by the nanoscale flocs or agglomerate structures in the continuous phase, which is actually a nanofluid of hydrophobic silica in *D*-limonene. An increase in nanoparticle content on the one hand improves the nanoscale structuring which by itself leads to a gel response, due to development of a network of nano-agglomerates in the nanofluid. On the other hand, larger nanoparticle content gives rise to a reduction in the average droplet size, thereby inducing an effect of structuring of the disperse phase leading to the formation of a three-dimensional structure, as is clearly evident in Fig. 4. Finally, the crystallisation of the disperse phase leads to its solidification and greatly reduces the deformability and mobility of the droplets. Consequently, the synergistic effect of these processes results in a structuring phenomenon, thereby enhancing the viscoelastic response and increasing G' values by a factor of 600 upon increasing the silica nanoparticle content from 0.1 to 1 wt.%. This underscores the substantial impact of the stabilising agent on the ultimate properties of PCEs (Wang et al., 2018).

The rheological results provide complementary evidence that stabilisation in these emulsions cannot be ascribed solely to a bulk 'network effect' or exclusively to Pickering-type interfacial adsorption. The pronounced increase in viscosity and viscoelastic moduli, together with the emergence of a microstructural network in the continuous phase at higher nanoparticle loadings, indicates that structuring of the *D*-limonene phase effectively slows droplet mobility and drainage, thereby hindering coalescence. At the same time, the clear reduction in droplet size and enhanced resistance to coalescence with increasing nanoparticle concentration demonstrate a substantial contribution from

interfacial adsorption, consistent with Pickering-type limited coalescence and in agreement with previous reports describing the coexistence of interfacial adsorption and three-dimensional particle networks in particle-stabilised systems (Ren et al., 2023; Alison et al., 2016). Overall, the stabilisation mechanism in the synthesised PCEs is best interpreted as the synergistic action of interfacial nanoparticle adsorption and bulk network formation, rather than the result of a single dominant mechanism.

3.4. Cooling and pumping performance

To assess the potential of the synthesised anhydrous PCEs for indirect refrigeration applications, the volumetric enthalpy change (ΔH_v) over their full usable temperature range was evaluated and compared with well-established commercial secondary refrigerants. Four benchmark fluids commonly used in supermarkets, heat pumps, ice rinks, and other indirect systems were selected, including 30 wt.% ethylene glycol/water, 30 wt.% propylene glycol/water, 20 wt.% NaCl brine, and 20 wt.% CaCl₂ brine, following Melinder's thermophysical property compilations and IIR/ASHRAE practice (Melinder, 1998; Melinder, 2006). To ensure thermodynamic consistency across materials, all enthalpy values were expressed as changes relative to a common reference state, defined as the minimum working temperature (freezing point) of each fluid.

For the benchmark fluids, which do not undergo phase change, the volumetric enthalpy change was calculated as:

$$\Delta H_{v,Benchmarks} = \int_{T_{Min}}^{T_{Max}} \rho(T) \cdot c_p(T) \cdot dT \quad (7)$$

where $\rho(T)$ and $c_p(T)$ were taken from the ASHRAE Handbook (ASHRAE 2021), and T_{Min} corresponds to each fluid's freezing point, considered its minimum working temperature.

For the formulated PCEs, the volumetric enthalpy change was computed as:

$$\Delta H_{v,PCE} = \int_{T_{Min}}^{T_m} \rho(T) \cdot c_p(T) \cdot dT + \int_{\lambda(T_{m,i})}^{\lambda(T_{m,i})} \rho(T) \cdot d\lambda + \int_{T_m}^{T_{Max}} \rho(T) \cdot c_p(T) \cdot dT \quad (8)$$

where c_p and λ were obtained from modulated DSC measurements, and ρ was estimated experimentally using a pycnometer, as detailed in the Supplementary Material. This approach yields the integral volumetric enthalpy change curves shown in Fig. 10a, covering the full operational range of the PCEs from −85 °C to +20 °C.

The comparison reveals that, although the emulsions exhibit lower sensible heat capacity than conventional secondary refrigerants, their operational window is vastly broader, extending from approximately −85 °C to +20 °C. When integrated across this entire interval, the PCEs store and transport substantially more energy per unit volume than the benchmark fluids, all of which become unusable at significantly higher temperatures due to crystallisation, phase separation, or excessive viscosity. In contrast, the PCEs remain pumpable (as confirmed in the rheological analysis) and thermally active throughout the full sub-zero range, enabling continuous heat absorption and release where commercial brines and glycols cannot operate. This wide temperature span compensates for the modest latent heat associated with the 10 wt.% PCM loading, resulting in a higher cumulative volumetric enthalpy change across the full working domain. Quantitatively, when evaluated up to a maximum operating temperature of −5 °C, the formulated PCEs deliver cumulative volumetric enthalpy change values up to approximately 2.4-fold higher than those of the commercial benchmark fluids, underscoring the substantial energy-storage advantage arising from their exceptionally broad working temperature window.

Such performance is particularly advantageous in ultra-low-temperature refrigeration, cryogenic thermal buffering, biomedical cold-chain logistics, freeze-thaw stabilisation, and thermal management

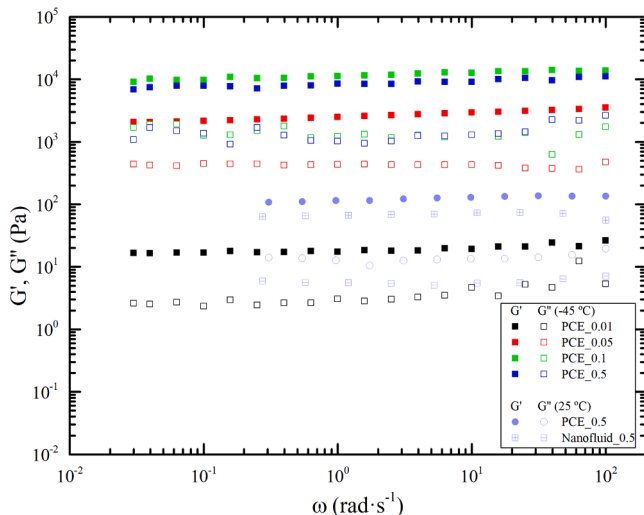


Fig. 9. SAOS moduli as a function of frequency for all PCE at −45 °C.

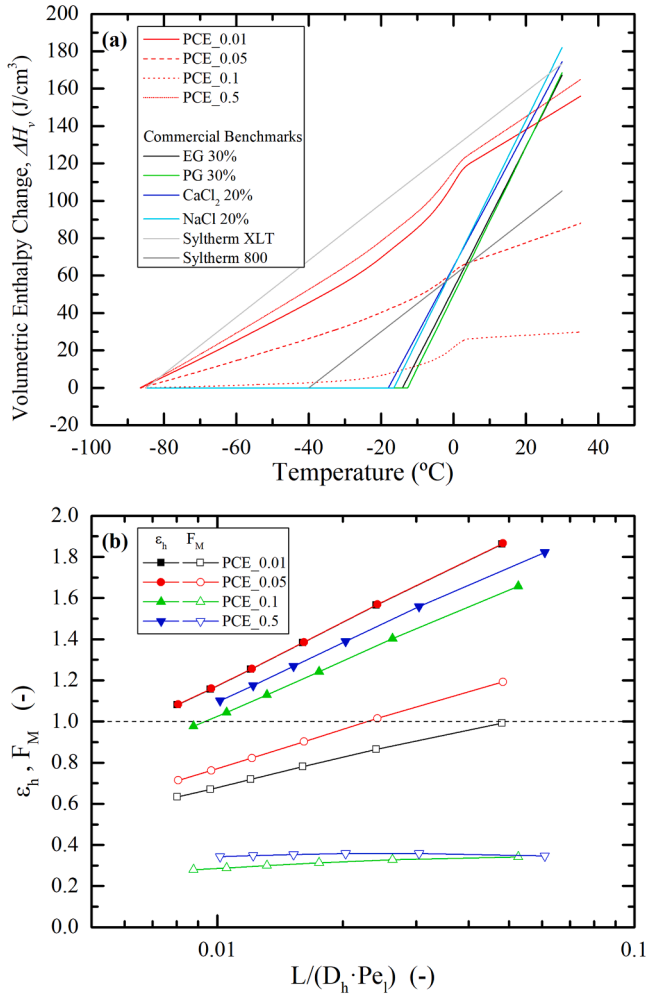


Fig. 10. Integral volumetric enthalpy change of the formulated PCEs compared with four commercial benchmark fluids (a) and dependence on Pe of F_M and ε_h (b).

processes requiring transitions between -80 °C and $+5$ °C, for which no conventional secondary refrigerant can simultaneously provide fluidity and thermal capacity.

It is important to note that the ΔH_v does not exhibit a strictly monotonic dependence on nanoparticle content, as this parameter reflects the combined influence of the phase-transition enthalpy, sensible heat and the temperature-dependent density of each formulation.

Finally, this study represents a preliminary step toward a new class of secondary refrigerants. While further optimisation is possible—such as enhancing the sensible heat through additives that increase the effective heat capacity (Shirazi and Meghdadi Isfahani, 2026; Said et al., 2023)—the present results already demonstrate that these emulsions offer a distinctive industrial advantage by combining a uniquely broad operating range with integrated volumetric enthalpy change values competitive with temperature-limited commercial fluids.

Additionally, refrigeration performance of PCEs was also estimated reproducing the flow conditions established by Ho et al. (2014) for a minichannel heat sink for Peclet numbers (Pe) in the range $Pe=665$ – 3250 . The experimental setup was composed of ten rectangular channels of 1 mm width, 1.5 mm depth and 50 mm length (L), and a hydraulic diameter of $D_h=1.2$ mm. Cooling conditions were adapted to PCE characteristics, with a fluid inlet temperature below PCM crystallization ($T_i=-35$ °C) and an average wall temperature above its melting ($T_w=25$ °C). Accordingly, fluid properties were determined within this temperature range, and their average values were used in the

subsequent calculations (Fig. 2, Tables 2 and 6).

No matter the viscous behaviour of PCEs and *D*-limonene, flow regime can be determined by the generalized Reynolds number, which can be written for a power-law (Ostwald) fluid as follows:

$$Re_{PL} = \left(\frac{D_h^n u_f^{2-n} \rho_f}{8^{n-1} K} \right) \left(\frac{4n}{3n+1} \right)^n \quad (9)$$

The velocity (u_f) of the fluids evaluated (PCEs or *D*-limonene) were determined from the above range of Peclet numbers ($Pe_f=u_f \rho_f c_{pf}/\lambda_f$), where ρ_f , c_{pf} and λ_f are average density, specific heat capacity, and thermal conductivity of the tested fluid in the temperature range considered. PCE consistency (K) and flow (n) indexes were obtained by fitting Eq. (6) at shear rates out of the previously commented flow instability region (above 10 s⁻¹) (Table 6). For the same mass flow rates fed to the heat sink of PCEs and *D*-limonene, emulsions presented values of $Re_{PL}<100$, whereas *D*-limonene showed $Re_{PL}<400$. In both cases Re values are within a laminar flow regime.

The heat-transfer efficiency, which accounts for the cooling enhancement achieved by adding PCM to *D*-limonene, can be defined as (Ho et al., 2013):

$$\varepsilon_h = \frac{h_b}{h_l} \quad (10)$$

where h_b and h_l denote the average heat-transfer coefficients of the PCM emulsion and its continuous phase (*D*-limonene), respectively. Laminar convection heat transfer coefficients were calculated using the Hausen correlation for *D*-limonene (Bergman et al., 2011),

$$Nu_l = 3.66 + \frac{0.0668 Gz_l}{1 + 0.04 Gz_l^{2/3}} \quad (11)$$

whereas heat transfer coefficients for PCEs were determined with the correlation proposed by Ho et al. (2014) for $Pe=665$ – 3250 :

$$Nu_b = 8.193 \left(\frac{Pe_b}{L/D_h} \right)^{-0.022} \left(1 + \frac{c_m}{Ste (1+Sb)} \right)^{-0.112} \quad (12)$$

where Nusselt number was calculated for every tested fluid (f) as $Nu_f=h_f D_h/\lambda_f$ and Graetz number as $Gz_f=(u_f \rho_f c_{pf} D_h^2)/(\lambda_f L)$. Stefan number (Ste) and the modified inlet subcooling parameter (Sb) were obtained as follows (Ho et al., 2014; Yang et al., 2019):

$$Ste = \frac{c_{pb} (T_w - T_i)}{c_m \Delta h_m} \quad (13)$$

$$Sb = \frac{T_m - T_i}{T_w - T_i} \quad (14)$$

where c_m is the PCM weight fraction in the PCEs and, respectively, Δh_m and T_m are their melting enthalpy and temperature obtained by DSC (Table 2).

Fig. 10b depicts the heat-transfer efficiency versus a dimensionless parameter ($L/D_h Pe$), which is the reciprocal of the Graetz number. The heat-transfer effectiveness increases when ε_h exceeds unity, and the larger its value, the greater the improvement in heat-transfer performance compared with *D*-limonene as cooling fluid. For the operating conditions considered, the results point out that the heat-transfer effectiveness increases as the Pe number (or fluid velocity) or emulsion stabilizer decreases, and when channel length is longer.

However, the observed effectiveness of the PCEs in enhancing convective performance needs to be further evaluated by comparing Figures of Merit (F_M), which relate improvements in average heat transfer coefficients to the associated increase in pumping power. The F_M is defined as follows (Ho et al., 2013):

$$F_M = \frac{\left(\frac{h_b}{h_i}\right)}{\left(\frac{N_b}{N_i}\right)^{\frac{1}{3}}} \quad (15)$$

where N_b and N_i are the pumping powers of PCEs and *D*-limonene at the same flow rates (m_f), which were calculated as follows (Ho et al., 2011):

$$N = 2 f u_f^2 \left(\frac{L}{D_h}\right) m_f \quad (16)$$

where friction factor was calculated as $f = 16/\text{Re}_{PL}$.

As seen in Fig. 10b, F_M increases as the reciprocal of Graetz number does. This suggests that the balance between the enhancement of heat transfer and the penalty of pressure drop improves as the PCE flow rate decreases (i.e., the Pe number or fluid velocity decreases) or as the length of the heat sink is longer. Fig. 10b also shows that F_M closes or exceeds unity as the concentration of emulsion stabilizer is lower. As reported by Ho et al. (2011), the substantially higher pressure drop induced by Pickering stabilizer and PCM droplets (much greater than that of pure *D*-limonene) results in much lower performance of emulsions PCE-0.1 and 0.5, if compared with pure *D*-limonene or PCEs formulated with lower concentrations of Aerosil® 805. These results suggest that emulsions PCE 0.01 and PCE 0.05 would outperform pure *D*-limonene as replacement working fluids in forced convection under selected flow and setup arrangements.

4. Conclusions

This work successfully formulated low-temperature phase-change emulsions using polyethylene glycol 400 as the disperse phase and *D*-limonene as the continuous phase, stabilised by surface-modified fumed silica nanoparticles. The influence of the nanoparticle-to-PCM ratio on emulsion performance was examined through thermal energy-storage capacity, thermal conductivity, microstructural organisation, stability, and rheological behaviour. The resulting PCEs exhibited homogeneous droplet dispersions and highly cycling-stable phase change transitions at sub-zero temperatures. Although silica nanoparticles had only a minor effect on the energy storage capacity, a minimum concentration of approximately 0.05 wt.% was required to prevent crystallisation-induced coalescence and phase separation, establishing a clear stabilisation threshold for reliable operation. Despite the insulating nature of silica slightly reducing heat-transfer rates, the nanoparticles significantly enhanced thermal stability, with onset decomposition temperatures well exceeding the operating range of sub-zero TES systems.

Droplet size showed strong sensitivity to nanoparticle concentration, decreasing markedly at higher Aerosil® R805 loadings. This behaviour, together with enhanced resistance to coalescence, aligns with a Pickering-type limited-coalescence mechanism in which hydrophobic nanoparticles adsorb at the interface and act as steric barriers to droplet growth. At insufficient stabiliser levels, crystallisation promoted droplet growth and partial coalescence, potentially generating local heat-transfer inhomogeneities during operation. These findings indicate that stabiliser concentrations below 0.05 wt.% should be avoided in TES applications requiring repeated cooling-heating cycling.

Rheological analysis showed that the emulsions remained highly flowable at low nanoparticle loadings, whereas higher silica contents promoted the formation of a structured particulate network that increased viscosity and shear-thinning behaviour. Cooling to -30°C further increased viscosity due to PEG400 crystallisation and particle-induced structuring, although all formulations apparently remained within acceptable limits for pumping and circulation in industrial TES equipment. This highlights a formulation trade-off between enhanced stability at higher nanoparticle contents and increased pumping-power requirements.

A volumetric-enthalpy change comparison with four commercial secondary refrigerants demonstrated that, despite modest latent-heat content, the PCEs benefit from an exceptionally broad operational window (-85°C to $+20^\circ\text{C}$). When evaluated up to -5°C , they delivered cumulative volumetric enthalpy change values up to 2.4-fold higher than those of benchmark brines and glycols, positioning them as promising candidates for ultra-low-temperature and cryogenic applications where conventional coolants fail due to crystallisation, phase separation, or excessive viscosity. Under forced-convection conditions, heat-transfer effectiveness increased with flow rate and decreased stabiliser content, while Figure-of-Merit analysis showed that lightly stabilised formulations maintain a favourable balance between thermal enhancement and pumping power.

Overall, this study establishes the fundamental structure-property-performance relationships governing anhydrous Pickering PCEs, focusing on formulation and proof-of-concept characterisation. As this work represents an initial step toward a new class of secondary refrigerants, the evaluation of these materials under service-like operating conditions will be essential to more clearly define their practical application scenarios in refrigeration and cold-energy-storage systems. Additionally, the present work does not address biodegradability, environmental persistence, or potential ecotoxicological impacts of the developed anhydrous PCEs. These aspects, including their possible contribution to microplastic accumulation, lie beyond the scope of this study and should be rigorously evaluated in future research.

CRedit authorship contribution statement

Adrián Tenorio-Alfonso: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Clara Delgado-Sánchez:** Methodology, Investigation, Data curation. **Antonio Guerrero:** Writing – review & editing, Validation, Supervision, Conceptualization. **Pedro Partal:** Writing – review & editing, Formal analysis, Conceptualization. **Francisco Javier Navarro:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jirefrig.2026.106967](https://doi.org/10.1016/j.jirefrig.2026.106967).

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