



Optimisation of water-free Phase Change Emulsions for cold energy storage

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Abstract

The transition to sustainable energy systems is essential for reducing reliance on traditional fossil fuels and combating climate change. In this context, advanced energy storage technologies, such as Thermal Energy Storage (TES) systems, play a pivotal role. These systems utilize Phase Change Materials (PCMs) that store thermal energy through solid-liquid phase transitions. To enhance their flow behaviour, these materials can be dispersed in heat transfer fluids, resulting in Phase Change Emulsions (PCEs). However, current PCEs are primarily water-based, which imposes certain technical limitations. This study, therefore, aims to develop a novel energy storage approach by formulating anhydrous PCEs using mixtures of D-Limonene, polyethylene glycol 400, and silica nanoparticles, with potential applications in cold energy storage. The research investigates the effect of nanoparticle concentration (ranging from 0.1% to 4.8%) on the thermal, microstructural, and rheological properties of the PCEs. The results demonstrate that emulsions with appropriate nanoparticle content (0.1-1%) exhibit favourable thermal and rheological performance, highlighting their potential for applications in cold chain logistics and thermal comfort.

Key words. Energy Storage, Pickering Emulsion, Phase Change Material, Polyethylene Glycol, *D*-Limonene

1. Introduction

With the increasing ambient temperatures, the demand for efficient cooling systems has become particularly important for applications ranging from thermal comfort to cold chain logistics for chemicals and perishable food products [1]. In this context, thermal energy storage (TES) utilizing Phase Change Materials (PCMs) has demonstrated significant advantages due to their inherently high energy storage capacity during the solid-liquid phase transition at a constant temperature [2]. Furthermore, the dispersion of PCMs within heat transfer fluids has proven to be an effective approach, providing adequate energy

storage capacity while maintaining suitable flowability and heat transfer performance, leading to the development of the so-called Phase Change Emulsions (PCEs) [3]. However, existing PCEs for cold energy applications remain predominantly water-based, which imposes certain technical limitations [4].

Therefore, this study aims to develop a series of anhydrous PCEs with potential applications in cold energy storage. Specifically, a cyclic monoterpene, *D*-limonene, was employed as the continuous phase, while polyethylene glycol 400 was utilized as the PCM. These PCEs were stabilized using silica nanoparticles, resulting in the formation of anhydrous Pickering PCEs. This study investigates the influence of nanoparticle concentration on the thermal, microstructural, and rheological properties of the formulated PCEs, with nanoparticle content varying from 0.1% to 4.8%.

2. Experimental

A. Materials

This study was intended to prepared Phase Change Emulsions, using a natural cyclic monoterpene (*D*-Limonene) as the continuous phase, and a low molecular weight-polyethylene glycol (PEG400) as the dispersed PCM. *D*-Limonene was purchased from ITW Reagents PanReac, while PEG400 were acquired in Sigma-Aldrich Merck Group. Hydrophobic surface-modified silica nanoparticles (Nano-SiO₂) were purchased from Evonik Operations GmbH and used as stabilising agent in the ensuing Pickering PCEs.

B. Emulsion preparation

Pickering PCEs were prepared with the appropriate *D*-Limonene/PEG400/Nanoparticles proportions, using a

rotor stator T 25 digital ULTRA-TURRAX® disperser, equipped with a S 25 N – 25 F dispersion tool (Ika-Werke). The samples were homogenized at high speed 6 (~12000 rpm) for 5 min at room temperature (~23 °C). Four different PCEs were prepared with a constant *D*-Limonene/PEG400 ratio of 9/1 and varying Nano-SiO₂ content, ranging from 0.1 up to 4.8% wt (see Table I).

Table I. – Pickering PCEs' formulation

Component	PCE			
	PE0.1	PE0.5	PE1.0	PE4.8
D-Limonene (g)	45.0	44.8	44.6	42.9
PEG400 (g)	5.0	5.0	5.0	4.8
Nano-SiO ₂ (g)	0.1	0.2	0.5	2.4

C. Morphological characterisation

Microscopic analysis was conducted using an Olympus Microscope BX52 (C5050Z Digital Camera). Optical micrographs were recorded on fresh samples at room conditions. Additionally, their droplet size distribution (DSD) was analysed through Laser Diffraction technique, using a Mastersizer 2000 particle size analyser (Malvern Panalytical).

D. Thermal properties

Thermal characterisation was evaluated utilizing a differential scanning calorimeter DSC250 (TA Instruments). All samples (~10 mg) were subjected to multiple cooling-heating cycles within the temperature range from -90 to 40 °C (50 mL/min N₂, 2 °C/min). In these modulated DSC experiments, a modulation amplitude of 0.30 °C for 60 seconds was considered

E. Rheological measurements

On the other hand, the evolution of the PCEs' viscosity at steady shear, within a shear rate range from 1 to 1000 1/s (25 and -30 °C), as well as over downward temperature ramps (10 1/s, 1 °C/min), was addressed using a Physica MCR 501 Anton Paar rheometer (50 mm diameter plate-plate geometry).

3. Results

First, the microstructure of the PCEs upon emulsification was analysed using laser diffraction and optical microscopy, with the resulting average droplet size diameters presented in Fig. 1.

As corroborated by the optical images, an appropriate dispersion of PEG400 within the continuous *D*-limonene phase was achieved. Additionally, an increase in Nano-SiO₂ content led to a significant reduction in the average droplet size. This reduction is likely to contribute to enhanced emulsion stability.

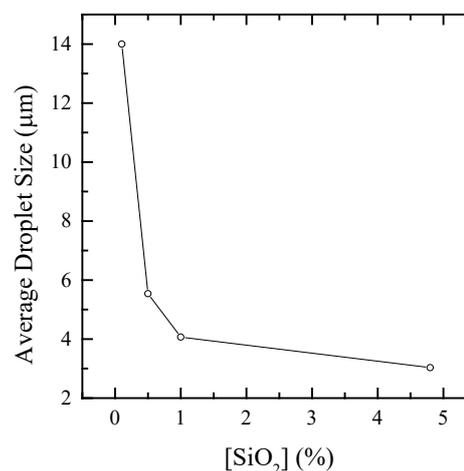


Fig.1. Average droplet size extracted from Laser Diffraction

With respect to their thermal properties, the formulated PCEs exhibited a stable and high thermal energy density throughout the cooling-heating cycles. The melting and crystallization transition temperatures, respectively recorded at -0.5 and -8.0 °C, remained largely unchanged upon emulsification in *D*-limonene, compared to the melting and crystallization temperatures of the pure PCM (-8.2°C). This fact makes these systems particularly suitable for applications in the cold energy storage industry, ensuring efficient thermal management within the desired operational range.

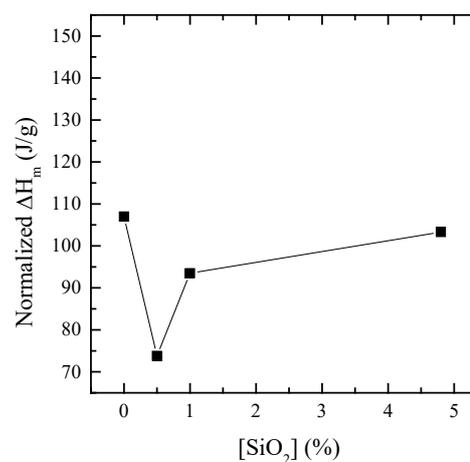


Fig.2. Normalized melting enthalpy of the formulated PCEs

Moreover, although the normalized energy storage capacity remained largely comparable to that of the pure PCM in most cases, partial phase separation was observed at low nanoparticle concentrations, resulting in a noticeable deviation from the expected energy storage capacity.

Furthermore, the rheological behaviour of these Pickering emulsions was assessed, with viscosity values relative to the Newtonian continuous phase measured as a function of shear rate (10–1000 s⁻¹) and temperature (20 – -30 °C), as plotted in Fig. 3 and Fig. 4, respectively. The results indicate that at low nanoparticle concentrations, the emulsions exhibited Newtonian response. However, as the Nano-SiO₂ content increased, a more pronounced pseudoplastic behaviour was observed. Despite the significant rise in viscosity with increasing nanoparticle content, as well as the liquid-to-

solid transition ascribed to the PCM, most of the formulated Pickering emulsions maintained apparent viscosity values within an optimal range for industrial applications across the temperature range of -30°C to 25°C.

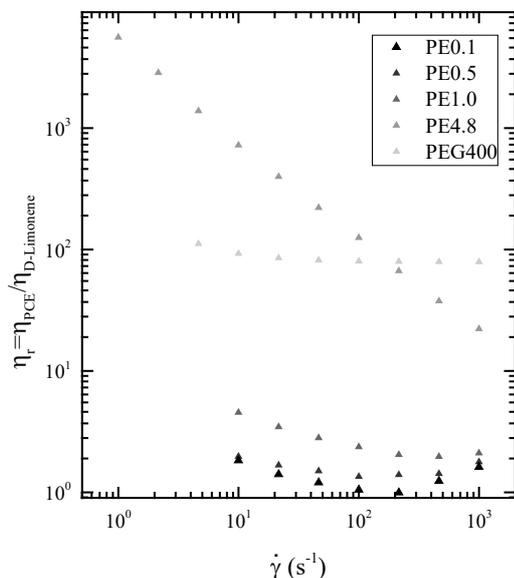


Fig.3. Relative viscosity as a function of shear rate (25 °C)

This appropriate viscosity behaviour, combined with their favourable thermal properties, makes these systems highly suitable for application in the cold energy storage industry, enabling efficient performance under relevant operational conditions.

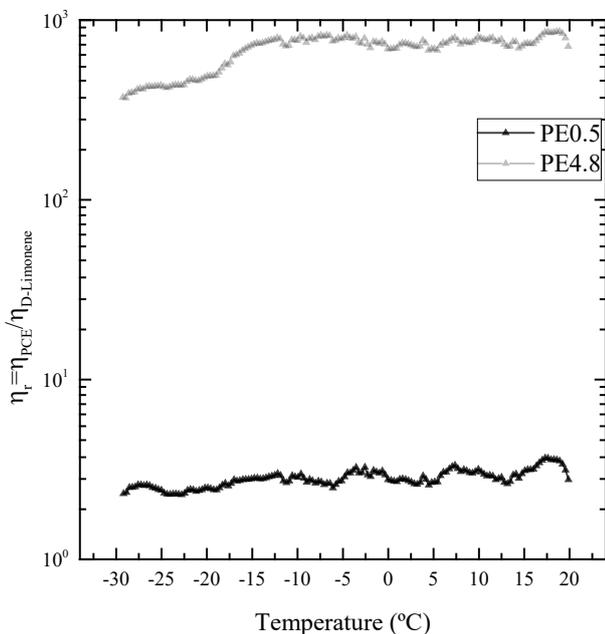


Fig.4. Relative viscosity (10 s⁻¹) as a function of temperature for selected emulsions

4. Conclusions

In this study, anhydrous Pickering Phase Change Emulsions were successfully formulated using *D*-limonene/polyethylene glycol 400/silica nanoparticles

blends, and the effect of stabilizing nanoparticle concentration was evaluated. The results indicated that the formulated PCEs exhibited a homogeneous droplet distribution. Moreover, emulsions containing an adequate nanoparticle content demonstrated promising thermal properties, as their phase transition temperatures remained within the appropriate operational range, while their energy storage capacity remained comparable to that of the pure PCM. Furthermore, the combination of these favourable thermal properties with appropriate viscosity behaviour confirms the suitability of these PCEs for cold energy storage applications, ensuring reliable performance under relevant operational conditions.

Acknowledgement

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