Universidad de Huelva

Departamento de Ingeniería Química, Química Física y Ciencias de los Materiales



Development of oil-in-oil phase change emulsions with enhanced heat storage properties

Memoria para optar al grado de doctora
presentada por:

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Fecha de lectura: 31 de mayo de 2024

Bajo la dirección de los doctores:

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Huelva, 2024



UNIVERSITY OF HUELVA

Department of Chemical Engineering, Physical Chemistry and Materials Science

DEVELOPMENT OF OIL-IN-OIL PHASE CHANGE EMULSIONS WITH ENHANCED HEAT STORAGE PROPERTIES

PhD Thesis

Doctoral Programme in Industrial and Environmental Science and Technology

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Huelva, 2024

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DESARROLLO DE EMULSIONES ACEITE EN ACEITE DE MATERIALES DE CAMBIO DE FASE CON PROPIEDADES MEJORADAS DE ALMACENAMIENTO TÉRMICO

Tesis Doctoral

Programa de Doctorado en Ciencia y Tecnología Industrial y Ambiental

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Huelva, 2024

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Memoria presentada por Clara Delgado Sánchez para aspirar al Grado de Doctor con Mención Internacional por la Universidad de Huelva

Clara Delgado Sánchez

La presente tesis ha sido realizada en el Departamento de Ingeniería Química, Química Física y Ciencia de los Materiales de la Universidad de Huelva bajo la dirección del Dr. Francisco Javier Navarro Domínguez y Dr. Pedro Partal López, los cuales autorizan su presentación:

Dr. Francisco Javier Navarro Domínguez Dr. Pedro Partal López

Huelva, 2024

Agradecimientos

No sé cómo empezar estos agradecimientos, pero lo que sí sé es que tengo mucho que agradecer. Hay muchas personas que me han acompañado en este viaje o en esta locura de una segunda tesis doctoral y gracias a ellos estoy aquí.

En primer lugar, quiero dar las gracias a mis directores de tesis, al Dr. Francisco Javier Navarro Domínguez y Dr. Pedro Partal López, por acompañarme y guiarme en este camino. Esta tesis no habría sido posible sin ellos. Muchas gracias por la confianza que siempre habéis puesto en mí, por la paciencia, por hacerme sentir valorada y respetada, por la libertad que siempre me habéis dado y por ayudarme a sacar lo mejor de mí. Gracias Javi, hoy y siempre, por ser la primera persona en apostar por mí, porque voy a recordar toda la vida como el profesor de reactores con el que jamás había intercambiado dos palabras me escribió un email para proponerme pedir una beca de colaboración con él. Fue la primera vez que me plantee pisar un laboratorio y aquí sigo. No imagino esto sin estar bajo tu ala, en serio, ni a nadie mejor con quien trabajar; gracias por cuidarme y hacerme crecer. Y gracias Pedro, por estar siempre, por confiar, por sacar lo mejor de mí, por aceptarme en tu grupo de trabajo, por la motivación. Tu entusiasmo siempre será inspirador, es un honor poder trabajar contigo. Gracias a ambos por frenar muchos de mis golpes, enseñarme y ayudarme; siento los dolores de cabeza. Ha sido un honor y una verdadera suerte contar con vuestra supervisión.

A la Dra. Vanessa Fierro y Dr. Alain Celzard, por acogerme en el *Institut Jean Lamour – CNRS* (Epinal, Francia), abrirme de nuevo las puertas del laboratorio y darme total libertad para trabajar allí durante los tres meses de estancia. Gracias por concederme de nuevo la oportunidad de trabajar con vosotros y de crecer profesionalmente. Epinal siempre será casa.

También quiero dar las gracias a todos los miembros del *Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS)* y, en especial, al *Grupo de Ingeniería de Fluidos Complejos* por acogerme, darme la oportunidad de crecer como investigadora con vosotros. Me considero una privilegiada por formar parte de esta gran familia, y por haberos encontrado tanto en lo profesional como en lo personal. En especial quiero dar las gracias a Concha, por estar siempre disponible para ayudar y para escuchar, porque si al final consigo presentar esta tesis será gran parte gracias a ti. También gracias a María José por ser maravillosa y ser tantas veces mi aporte de vitalidad necesario, gracias por preocuparte por mí, por cuidarme y quererme; y gracias a Cuadri, Paco, … a todos en verdad, porque es un placer compartir el día a día con vosotros.

Quiero dar las gracias a Adri y a Espe, por ser los mejores amigos del universo, yo no sé qué haría sin vosotros, ni lo quiero saber! Gracias por cuidarme, por haber estado y por estar para

absolutamente todo, os quiero mucho. Gracias a mi chulito por ser el mejor. A Ortegi por dejar que siguiera siendo su pupila, a mi veci que la quiero, a Isa y a Elena por el infinito cariño que siempre me dais, a Luis, a Ana, a Coraima, a Rodri, a Manuelillo, a Manue (Toro) por traernos luz, … Gracias chicos por ser compis de trabajo, pero sobre todo por ser amigos. Gracias por quererme y por ser lugar seguro. También quiero dar las gracias a Sergio por estar ahí siempre para todo a pesar de la distancia. A mi Jime y a mi César que los quiero con el alma por seguir siendo mi paz. A mis amigos del pueblo, a las niñas y a sus peques por el apoyo y por ser un punto de aire fresco en mi vida.

Y por último quiero darle las gracias a mi familia, porque han sido unos años duros, pero hemos estado juntos y somos más fuertes. Gracias abuelos por todo el amor. Abuelo, te echo de menos. Papa, Mama e Irenea, gracias por cuidarme, por estar conmigo siempre, por no dejarme caer jamás, por confiar en mí, por ser mi ancla, por el amor y apoyo incondicional, no soy nada sin vosotros, os quiero más que a nada en este mundo.

Siento que entre la Clara que empezó está tesis y la que hoy escribe estas palabras, hay un abismo. Ahora soy más madura, más fuerte, más valiente, más responsable, más en paz conmigo misma y sobre todo más libre. Ha sido un camino largo, pero ha merecido la pena.



"There is nothing like returning to a place that remains unchanged to find the ways in which you yourself have altered"

"No hay nada como volver a un lugar que no ha cambiado, para darte cuenta de cuanto has cambiado tú"

Nelson Mandela

A mis padres

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Chapter I: Introduction

I/1. Summary

Addressing today's sustainability and energy transition challenges requires a move towards innovative technologies. Phase Change Material Emulsions offer a promising solution for the efficient storage and transfer of thermal energy. By integrating phase change materials into heat transfer fluids, the energy storage capacity of these fluids is enhanced. The purpose of this thesis is to formulate non-aqueous emulsions of phase change materials using two oily phases. This represents a significant advance by extending their service temperature range and improving their long-term chemical and thermal stability. This research suggests new possibilities for innovative applications, such as high-efficiency solar collectors, industrial heat recovery, intermediate-high temperature systems, refrigeration, or cold energy storage systems.

During the PhD thesis, two groups of stable non-aqueous phase change materials were developed. The first group consists of emulsions formulated with polyethylene glycol of molecular weight approximately 4000 g/mol, with a melting point of 60 °C, dispersed in silicone oil. These emulsions are considered pioneering in the scientific literature, opening a new field of study. The development of these systems overcame several challenges, including the absence of data on appropriate emulsifiers for oil-in-oil dispersions and the requirement for the system to remain stable after the solid-liquid transition of the dispersed phase. The findings suggested that silicone surfactants are a viable option for stabilization. They also revealed not only the difficulty of their stabilisation but also the effect of composition (surfactant and dispersed phase concentrations) and processing conditions (agitation, temperature, time, etc.) on the final morphological, rheological and thermo-physical properties of phase change material emulsions. The properties mentioned were significantly influenced by changes in structure, particularly by the crystallinity, crystallisation mechanisms, or their modification, of the dispersed phase (phase change material) of the emulsion, as well as its partial compatibility with the other components.

On the other hand, a second group of stable stearic acid emulsions dispersed in silicone oil have been developed. These emulsions have a melting point of 70 °C and maintain their crystallinity after processing. They also improve the thermal storage properties compared to polyethylene glycol emulsions. The emulsions showed high physicochemical and thermal stability under mechanical-thermal cycles, withstanding

more than 100 heating-cooling cycles. This proves their stability during in-service operations. Therefore, they have demonstrated significant potential as novel heat transfer fluids in thermal energy storage systems, owing to their high phase change enthalpy of 22.32 J/g in emulsions containing 10%wt. of phase change material. Additionally, they retained their stability and storage capacity almost entirely for a minimum of one month.

Furthermore, the thesis explored the potential use of phase change emulsions as lubricants and found a significant reduction in the friction factor across the entire temperature range when compared to silicone oil. Therefore, the study proposes the use of these emulsions as a new intelligent lubricant due to its thermal storage capacity, which enables it to buffer temperature changes.

Finally, the thesis confirms the innovation of the research and the successful transfer and application of the results in industry through the application for a patent. It describes emulsions of non-aqueous phase change materials suitable for use in a temperature range of 100 to 800 °C.

In summary, the main challenges encountered in the development of these emulsions are specified in this thesis, and the importance of their thermal stability and reliability in practical applications is highlighted.

I/2. Resumen

El avance hacia unas tecnologías innovadoras es una cuestión fundamental para abordar los actuales desafíos de sostenibilidad y transición energética. En este contexto, las Emulsiones de Materiales de Cambio de Fase ofrecen una solución prometedora para el almacenamiento y transferencia eficiente de energía térmica. De este modo, al integrar materiales de cambio de fase en fluidos de transferencia de calor, se mejora la capacidad de almacenamiento energético de éstos. Así, el propósito de esta tesis conlleva formular emulsiones no acuosas de materiales de cambio de fase, es decir, mediante la utilización de dos fases oleosas, lo cual representa un avance significativo al permitir ampliar su rango de temperatura de servicio y mejorar su estabilidad química y térmica a largo plazo. Asimismo, esta investigación abre nuevas posibilidades para aplicaciones innovadoras, como pueden ser su uso en colectores solares de alta eficiencia, recuperación de calor industrial, sistemas de temperatura intermedia-alta o para sistemas de refrigeración o de almacenamiento de energía fría.

A lo largo de la tesis doctoral se han desarrollado dos grupos de materiales de cambio de fase no acuosas estables. El primer grupo de emulsiones, formulado con polietilenglicol de peso molecular aproximado 4000 g/mol, con un punto de fusión de 60 °C, dispersado en un aceite de silicona, se consideran pioneras en la literatura científica, abriendo un nuevo campo de estudio. La formulación de estos sistemas superó numerosos desafíos, como la falta de datos sobre emulsionantes adecuados para dispersiones aceite en aceite o la necesidad de que el sistema se mantenga estable después de la transición sólido-líquido de la fase dispersa. Los resultados propusieron tensioactivos siliconados como una alternativa eficiente para la estabilización. También se puso de manifiesto no solo la dificultad de su estabilización, sino también el efecto de la composición (concentraciones de tensioactivo y fase dispersa) y las condiciones de procesado (agitación, temperatura, tiempo, etc.) en las propiedades morfológicas, reológicas y termo-físicas finales de las emulsiones de materiales de cambio de fase. Estas propiedades también se vieron significativamente afectadas por los cambios de estructura y principalmente por la cristalinidad, los mecanismos de cristalización o la modificación de estos, de la fase dispersa (material de cambio de fase) de la emulsión y, así como, su compatibilidad parcial con el resto de componentes.

Por otro lado, también se ha desarrollado un segundo grupo de emulsiones estables de ácido esteárico, que presenta un punto de fusión de 70˚C, disperso en aceite de silicona, la cuales mantienen su cristalinidad después del procesado y mejoran las propiedades de almacenamiento térmico respecto de las emulsiones de polietilenglicol. Estas emulsiones evidenciaron una elevada estabilidad físico-química y térmica bajo ciclos mecánico-térmicos (soportando más de 100 ciclos se calentamiento-enfriamiento), comprobando su estabilidad durante las operaciones en servicio. De esta forma, presentaron un gran potencial como nuevos fluidos de transferencia de calor en sistemas de almacenamiento de energía térmica gracias a su entalpía de cambio de fase de 22.32 J/g en emulsiones con un 10%wt. de material de cambio de fase. Además, ellos mantenían su estabilidad y capacidad de almacenamiento prácticamente intactas durante, al menos, un mes.

Adicionalmente, se exploró su potencial uso como lubricantes, observándose una reducción significativa del factor de fricción, en todo el intervalo de temperaturas, en comparación con el aceite de silicona. De este modo se plantea el uso de las emulsiones con material de cambio de fase como un nuevo lubricante inteligente con habilidad de amortiguar cambios de temperatura gracias a su capacidad de almacenamiento térmico.

Finalmente, la notable innovación de la investigación y la efectiva transferencia y aplicación de los resultados en la industria queda constatado a través de la solicitud de una patente de invención. En ella se detalla emulsiones de materiales de cambio de fase no acuosas aptas para aplicaciones en un rango de temperatura de 100 a 800 °C.

En resumen, esta tesis especifica los principales desafíos encontrados en el desarrollo de estas emulsiones y resalta la importancia de su estabilidad y fiabilidad térmica en aplicaciones prácticas.

I/3. Justification

Given the urgent socio-economic challenges and the critical need for sustainable energy solutions, the development of innovative technologies holds significant promise in driving the transition towards a circular economy. The escalating global warming crisis highlights the pressing need for action. Climate change, pollution concerns, and the depletion of finite fossil fuel reserves are some of the issues that have led to heightened awareness and encouraged scientific communities worldwide to prioritize sustainable energy initiatives. As energy demands continue to rise, there's a clear need not only to promote renewable energy sources but also to enhance energy storage capacity and optimize production processes for maximum efficiency. However, despite the pivotal role of renewable energy in emission reduction, it is essential to address the intermittent nature of these sources. Therefore, promoting energy storage is crucial.

Within the realm of energy storage systems, thermal energy storage (TES) emerges as a particularly intriguing option. Furthermore, among the various TES methods available, one of the most innovative and attracting is the use of phase change materials (PCM). These PCMs undergo a phase transition process, such as solid to liquid or vice versa, during which they absorb or release large amounts of energy. This inherent ability of PCMs to store and release thermal energy at specific temperatures makes them essential in TES systems.

One way to integrate PCM into energy storage systems is by adding them to heat transfer fluids (HTFs), creating PCM Emulsions (PCMEs). PCMEs consist of a carrier fluid, often water, serving as the continuous phase, with dispersed PCM particles acting as the disperse phase. They not only enable the possibility of using the same medium for both transport and energy storage thanks to their pumpability, but also facilitate high heat transfer rates due to the increase in the specific surface area of the PCM, updating HTF

design and operation. PCMEs can be employed for several applications, including industrial waste heat recovery, solar harvesting systems, heating, ventilation, and air conditioning, secondary refrigerants, among others. However, all the PCMEs developed so far have used water as continuous phase thereby restricting the operational temperature range.

In this context, this thesis proposes a novel approach: the **development of oil-in-oil phase change emulsions**. By producing oil-in-oil PCMEs, the main goal is to enable the transport of matter and heat in systems under extreme pressure and temperature conditions while ensuring superior long-term chemical stability. These emulsions show great promise but require significant scientific and technological advancements.

To our knowledge, no previous studies have explored such non-aqueous PCM dispersions as heat transfer fluids for heating/cooling loops. This presents an exciting opportunity for pioneering research and innovative applications like temperature regulation in various industries, solar and geothermal thermal energy storage, as well as industrial waste heat recovery, to enhance the energy storage capacity of conventional HTFs. Furthermore, oil-in-oil PCMEs may also find application in the field of the lubrication industry. To the best of our knowledge, the literature does not contain scientific publications on O/O emulsions formulated with PCMs for lubrication, which is a great opportunity to explore new application fields that deserve to be studied.

Developing these emulsions builds upon liquid-liquid regular non-aqueous emulsions (without phase change), also known as oil-in-oil, anhydrous, or waterless emulsions. However, a significant challenge lies in the scarcity of suitable emulsifiers for oil-in-oil interfaces, an even greater challenge arises when there is a phase change in the dispersed phase. Such new dispersions with enhanced rheology, heat transfer and heat storage capability need to be designed with advanced physical-chemical and thermo-rheological properties to work in extreme performance environments, involving very low and high temperatures, and high-pressure conditions.

Overall, the ongoing research and development in this field aim to develop innovative and efficient oil-in-oil PCMEs that contribute to more effective and eco-friendly heat storage systems, helping to reduce energy consumption and greenhouse gas emissions.

I/4. Objectives

The main goal of the thesis is to study the formulation and processing of novel water-free PCMEs with high heat storage capacity and enhanced rheological and thermal properties. Such fluids will be designed to work at high temperatures, to overcome the performance limitation of water-based dispersions. To that end, oil-in-oil emulsions, containing PCMs will be designed providing them with new functionalities. Compared to the traditional HTFs and lubricating dispersions, these new emulsions will present higher heat storage capacities and heat transfer rates, along with a tailored rheology adapted to product application.

As a result, this thesis will generate a suitable scientific and technological background for the development of new emulsions to be used in a wide interval of temperatures (ranging from low temperatures to high thermal/pressurized conditions). With this aim, the methodology proposed for the design of these fluids address:

- Formulation of O/O emulsion, which will involve the selection and characterization of the immiscible oily phases (carried fluid + PCM) and its corresponding emulsifier, according to the nature of the immiscible phases.
- Processing conditions will be optimized for selected formulations, as a function of emulsification shear conditions, temperature, and time. Depending on the phase change temperature of the dispersed phase, emulsification will need to be performed at high temperatures (over the melting point of the PCM).
- Emulsion performance will be evaluated at in-service conditions, characterising the stability, morphology, rheological behaviour and thermal properties involving a heat transfer assessment in a heating/cooling loop, lubricating capability by tribological and technological tests, long-term fluid ageing and compatibility with metals.

Specific Objectives:

1. Select the compounds (for the dispersed and continuous phases) to be part of phase change emulsions, based on their thermo-rheological and thermal properties.
2. Identify and select the emulsifiers (surfactant, Pickering particles, or blends) in terms of emulsion stability and compatibility with the constituents.
3. Optimize the formulation of PCME, evaluating the effect of the concentration of PCM and stabilising agent; and the crystallinity of the PCM before and after the emulsifier process.

4. Study how processing variables (shear device, temperature, pressure and time) affect the final properties of emulsions.
5. Determine the laws that relate the processing-structure-properties in simple formulations, in order to extrapolate them to complex formulations.
6. Analyse the capacity of the emulsions to capture heat and to dampen temperature changes.
7. Identify the most suitable emulsion for heat storage applications.

I/5. Structure

This Ph.D. is structured into five chapters, beginning with this introductory Chapter I, which provides an overview of the research's summary, justification, objectives, and structure of the present research work. Chapter II delves into the state of the art, aiming to offer a comprehensive understanding of thermal energy storage, including its primary challenges and issues. Additionally, it provides an in-depth exploration of PCM, covering various implementation methods. Special emphasis will be placed on PCM emulsions, which are the focus of this research. Lastly, the chapter will discuss the current research advancements in non-aqueous emulsions to contextualize the study of non-aqueous PCM emulsions, the primary subject of this thesis. Chapter III sets out the general experimental details of this research work, looking at materials, methods of preparation and equipment used to conduct it. Chapter IV presents the experimental results and discussions stemming from the various studies undertaken in this Ph.D. endeavour. This chapter is subdivided into five distinct sections. The first four subsections feature articles—three of which have been published and one under review—in peer-reviewed scientific journals of high impact factor, while the final subsection showcases a patent. These scientific articles represent a ground-breaking milestone in HTF research, marking the first-ever publications of non-aqueous PCMEs. They detail the formulation and characterization of two systems, exploring the influence of PCM crystallinity on emulsion properties and highlighting the potential of these systems for thermal energy storage applications. Among these articles, the final one under review introduces a novel application of PCMEs as lubricants with energy storage capabilities. Additionally, the patent addresses the limitations of water-based emulsions' service temperatures, thus extending the potential application range of non-aqueous PCMEs to more extreme high-temperature

environments. Lastly, Chapter V provides a comprehensive summary of the key findings and conclusions drawn from this research endeavour.

Chapter II: State of the art

II/1. Global context

II/1.1. Energy challenges: efficiency and storage

The issue of global warming is of paramount concern, primarily stemming from the significant release of carbon dioxide (CO_2) emissions resulting from the combustion of fossil fuels over the past century. This climate change, together with the pollution problems, the depletion of fossil fuels, the current demand for energy and the increasing future energy forecasts are some of the major problems that society in general and the scientific community, in particular, are beginning to prioritise. It is precisely the latter, the increasing future energy forecasts, that requires a constant effort to improve production processes just as to increase energy storage capacity, all to achieve optimum energy efficiency. Consequently, current trends are not only oriented towards the promotion of electrification, primarily sourced from clean and sustainable alternatives such as wind, solar energy, and alternative fuels like hydrogen but also pay special attention to energy saving and efficiency as a way of contributing to the sustainability of resources (Fig. 1. Outline of some of the challenges facing society in general and the scientific community in particular.Fig. 1).

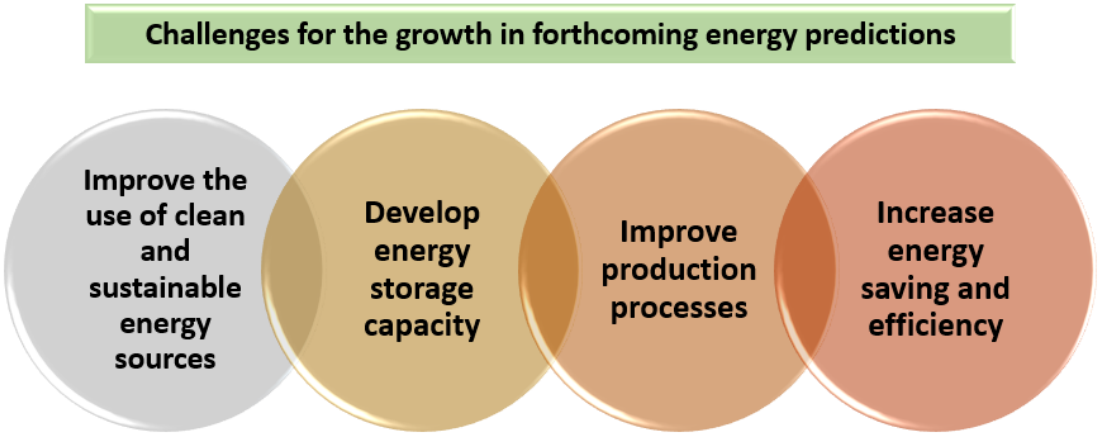


Fig. 1. Outline of some of the challenges facing society in general and the scientific community in particular.

Forecasts for the year 2040 point to an increase in energy world consumption of approximately 28% (Heydari et al., 2023), which would cause the major environmental problems mentioned at the beginning of this section. Thus, conducting a comprehensive

analysis of energy consumption across various sectors and identifying those with the potential for improvement through scientific research is a vital undertaking. Certainly, the energy landscape within the European Union reveals that the residential sector consumes approximately 40% (Ürge-Vorsatz et al., 2015), while the industrial sector accounts for only 25% (van Dijk et al., 2008). Remarkably, the European Union has set a priority goal to reduce energy use for building climate control by 50% by the year 2050 (Berge and Johansson, 2012).

Within this context, heating, ventilation, and air conditioning (HVAC) systems represent a substantial share of energy utilization. Therefore, optimizing and enhancing energy efficiency within HVAC systems through scientific research are integral aspects of comprehensive energy conservation efforts towards a sustainable and energy-efficient future. Energy efficiency and energy storage are intertwined in a way that helps optimize energy use, reduce waste, enhance the reliability of energy systems, and promote the integration of renewable energy sources. This synergy is crucial for creating a more sustainable and resilient energy infrastructure.

However, while renewable energy sources undoubtedly play a pivotal role in emission reduction, it is essential to address the intermittent nature of these sources (Sinsel et al., 2020). This highlights the critical need for efficient energy storage solutions to ensure a continuous and reliable supply of clean energy, mitigating the intermittency and unpredictability of renewables particularly when they are not actively producing. A wide diversity of renewable energy storage systems exists as depending on the application some of their characteristics make them more suitable than others. While conventional wisdom often points to batteries or supercapacitor as the primary means of energy storage, alternative methodologies, including, compressed air, hydrogen and thermal energy storage (TES), are gaining prominence (Aneke and Wang, 2016; Mahlia et al., 2014).

II/1.2. Thermal energy storage (TES)

TES is widely acknowledged as a method for incorporating renewable energy sources into the electricity generation and plays a pivotal role in the realm of energy management and sustainability for several compelling reasons. As we have been saying, it allows the integration of the renewable energies by ensuring a steady and reliable source that does not depend on weather conditions, decoupling in that way the energy production and consumption and enabling the storage of excess thermal energy when supply exceeds

demand and its release when needed. This load-shifting capability helps in efficiently managing energy demand, reducing grid stress, and avoiding peak energy usage, which often relies on fossil fuels. It leads to decreased greenhouse gas emissions associated with conventional heating and cooling methods, contributing to environmental sustainability. Thus, TES is of particular interest and significance in using this essential technique for solar thermal applications such as HVAC systems (Osterman and Stritih, 2021) because of its intermittent nature. Moreover, TES also covers similar problems arising in engineering applications such as the waste heat recovery systems where the waste heat availability and utilization periods are different. In general, industrial activities have a huge potential currently underutilized for waste heat recovery at any given moment (Papapetrou et al., 2018). Nowadays, TES is used in several industries being the most recurrent application the space comfort and electricity generation but also are used in the process itself such as the manufacture of construction materials, mining and the metallurgical industry in general (Laing et al., 2011; Miró et al., 2016). Storing heat at higher temperatures is also one of the most used applications in industry as enables heating provision without the need for heat pumps to raise fluid temperatures (Mahon et al., 2022).

Depending on the time length of the stored thermal heat, storage capacity, temperature range, cost or, for example, temporal range of the decoupling, the choice of the TES will depend. Thermal energy storage is generally classified into three primary methods depending on how this storage takes place (Fig. 2): sensible heat storage, latent heat storage and thermochemical storage.

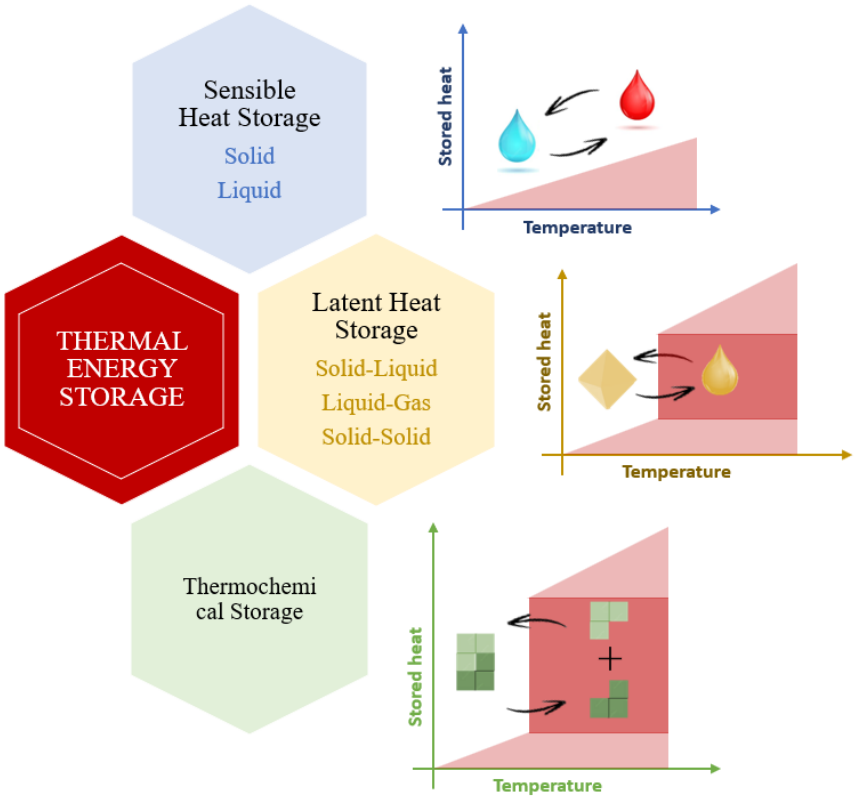


Fig. 2. Classification of thermal energy storage technologies.

The most traditionally used method is sensible heat storage. It involves altering the temperature of a heat transfer fluid or solid material to store or release heat. The amount of heat stored will be proportional to the density, specific heat, volume and variation of temperature of the storage material. Typically, it has been used to raise the temperature of water at low-temperature applications as hot water tanks or of rocks at high-temperature applications. However, nowadays, it is widely used not only with those more traditional systems but also with others, such as molten salts for high-temperature applications such as power plants (Hu et al., 2023), particle or packed beds in different temperature ranges (Gautam and Saini, 2020; Zhang et al., 2023) or thermal oil systems very interesting for heating systems or industrial processes (Mawire, 2016).

Latent heat storage, on the other hand, is an evolving technology that has gained significant interest in recent times as it allows storing large amounts of energy in relatively small masses with minimal temperature variations. Despite being a technology that is continuously under development and still has a lot of potential to be discovered, it is already being applied with great success (Jouhara et al., 2020). As the name implies, these materials store latent heat during a phase change in the storage media, it undergoes solid–solid, liquid–gas, and solid–liquid phase transformations. These so-called **phase**

change materials (PCMs) are very interesting since they may provide a high energy storage density and have the capacity to store significantly more energy per unit mass compared to sensible heat storage. For example, in the case of water, 80 times as much energy is required to melt 1 kg of ice as to raise the temperature of 1 kg of water by 1 °C. This means that a much smaller weight and volume of material is needed to store a certain amount of energy.

Lastly, thermochemical storage involves reversible chemical reactions that absorb and release heat during the endothermic and exothermic reaction steps, respectively. Despite the substantial potential of this storage method over sensible or latent heat systems due to its ability to achieve high energy densities, it is not widely used and remains in the phase of active development and research (Han et al., 2022; Yilmaz et al., 2020). This is primarily because these systems are significantly more complex, making it challenging to maintain their cyclic stability and reversibility (Sunku Prasad et al., 2019).

Thus, if we focus on the storage capabilities, commercial feasibility and durability aspects of the three TES systems, some of them may be more interesting than others. The longevity of sensible heat storage materials is roughly 20 years, which is significantly longer when compared to latent heat storage materials, with a lifespan of around 5 years, and thermochemical energy storage, which boasts a lifespan of about one-tenth that of sensible heat storage materials. Moreover, among these different types, latent heat storage can be used in a higher operating temperature range (Nazir et al., 2019).

II/2. Phase Change Materials (PCM)

As mentioned earlier, thermal energy storage (TES), particularly focusing on latent heat storage using phase change materials (PCMs), is gaining prominence as an effective approach. PCMs possess the remarkable capability to absorb and release significant amounts of latent heat during phase transitions that occur within a well-defined temperature or a limited range of temperature, making them highly efficient. Therefore, the selection of the PCM is crucial for the development of a latent heat thermal energy storage system, along with a thorough understanding of heat transfer mechanisms within the PCM. Over the years, various materials have been investigated for use as PCMs, including hydrated salts, paraffin waxes, polymeric materials, and eutectic materials, with studies examining the correlation between their properties and their heat storage capacity at desired temperatures (Pielichowska and Pielichowski, 2014).

II/2.1. Classification

PCMs are primarily classified based on two criteria: the temperature range of the phase change and the nature of the phase change itself.

The classification according to temperature range is closely linked to the potential applications of latent heat energy storage, a topic that will be thoroughly explored in the subsequent sections on applications (section “II/2.3” and section “II/3.4”). In general, PCMs can be classified into three main groups based on the temperature ranges at which the phase transition occurs. These include low-temperature PCMs, with phase transition temperatures below 15 °C, commonly employed for cold energy storage in air conditioning and the food industry (Nie et al., 2020); mid-temperature PCMs, the most commonly used, with phase transition temperatures ranging from 15 to 150 °C, extensively applied in solar, medical, textile, electronic, and energy-efficient applications within buildings (Zhang et al., 2018); and high-temperature PCMs, characterized by phase transitions exceeding 150 °C, primarily developed for industrial applications (Miró et al., 2016). These classifications underscore the versatility and applicability of PCMs across diverse fields, as they find use in various specific applications such as space applications (between -40 and -10 °C), refrigeration or freezing systems (from -45 to -10 °C), solar heating systems or building external envelopes (≈ 50-60 °C), heating, ventilation, and air conditioning (≈ 8-25 °C), internal insulation systems for residences (≈ 15-30 °C), industrial waste heat recovery (<150 °C), or intermediate temperature solar collectors (100-250 °C).

On the other hand, the PCM are also classified into sub-categories depending on the type of phase change that occurs: the liquid-gas, solid-gas, solid-solid, and solid–liquid phase transformation, and vice versa. Fig. 3 summarizes the TES materials and their corresponding phase change categories.

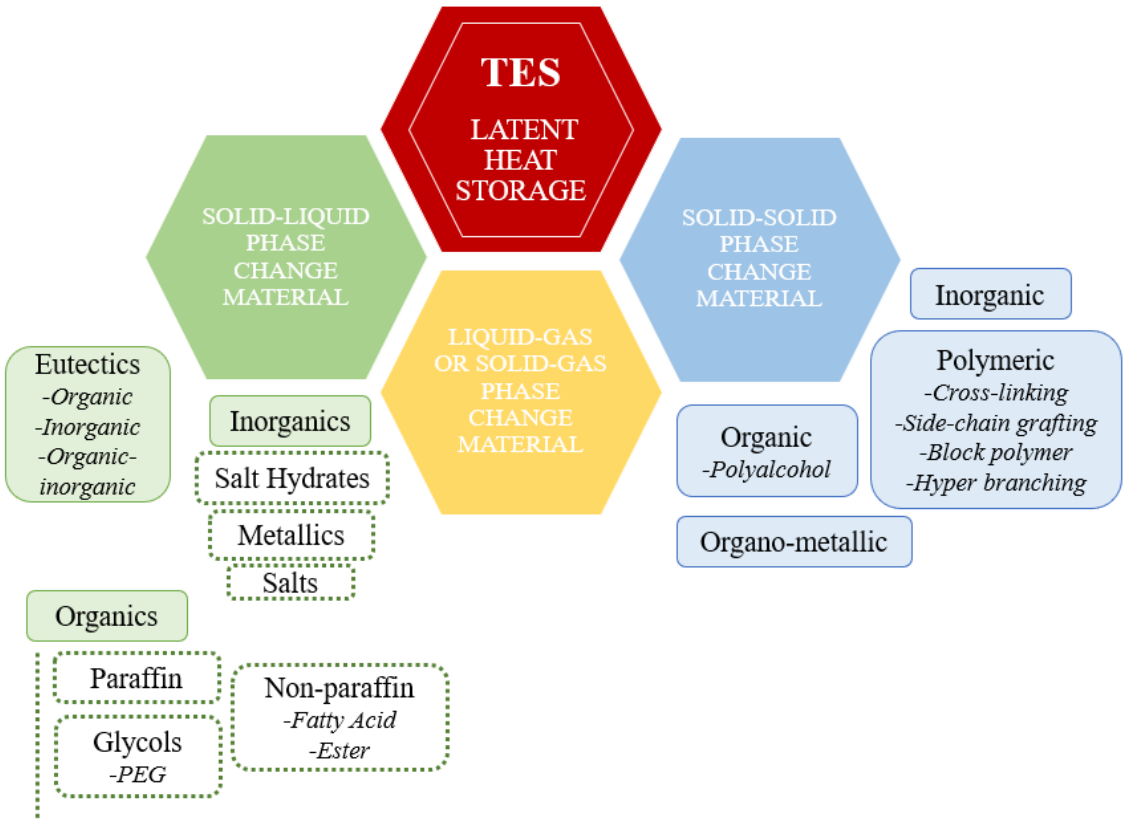


Fig. 3. Classification of PCMs.

TES systems involving solid-gas or liquid-gas phase transitions face several inherent limitations and impracticalities, including substantial volume demands, large volumetric alterations associated with the phase transition, and elevated system pressures, despite exhibiting notable phase transition latent heat capacity (Nazir et al., 2019). However, despite these challenges, some systems utilize liquid-gas PCMs, such as organic materials for heat management in hydrogen generators (Kwak et al., 2021) or the well-known water-steam system, commonly employed at temperatures ranging from 100 °C to 200 °C, albeit requiring robust materials resistant to high pressures to ensure safety (Danehkar and Yousefi, 2022).

In contrast, solid-solid PCMs absorb and release heat through reversible transitions between different crystalline structures. These transitions may involve conversions from a crystalline state to a semicrystalline or amorphous state. Solid-solid PCMs offer significant advantages, such as mitigating the risk of PCM leakage beyond phase transition temperatures and eliminating substantial volume fluctuations (Fallahi et al., 2017). Despite these promising characteristics, solid-solid PCMs have not gained widespread usage, primarily due to the limited discovery of materials with a substantial latent heat capacity comparable to more prevalent solid-liquid systems. However, in

recent years, there has been a growing interest in the research and development of these materials, with increasing exploration in various applications, such as passive solar buildings using organic plastic crystals (Chandra et al., 2005) or solar-driven wearable applications with polyurethan based PCMs (Shi et al., 2020).

Lastly, solid-liquid PCMs, which have demonstrated economic viability for energy storage systems, are the most widely utilized. Despite entailing a volume change, typically around 20 % or less, this variation is not as significant and does not pose potential engineering challenges as transitions involving solid-gas or liquid-gas phase changes. Consequently, these materials are considerably easier to manage and integrate into systems, contributing to their widespread adoption in various applications. Numerous materials exhibiting this type of phase change have been studied and utilized for energy storage applications (Zhang et al., 2018).

Each type of solid-liquid PCM has its advantages and limitations, making them suitable for specific applications based on factors such as temperature requirements, thermal conductivity, stability and cost-effectiveness. The choice of PCM depends on the particular needs of the system or process it is intended for. Based on their chemical composition, PCMs have the following forms: organic PCMs, inorganic PCMs, and eutectic mixture PCMs. This classification can be also seen in Fig. 3.

Organic PCMs

Organic PCMs are constituted by a wide range of materials including paraffins, fatty acids, esters, alcohols and other organic compounds. Generally, these PCMs are notable for their advantageous characteristics, such as chemical stability and high phase change enthalpy with self-nucleation, facilitating crystallization without excessive supercooling. Moreover, they undergo congruent melting processes, enabling phase change cycles without phase segregation.

In particular, on the one hand, paraffin waxes, composed of hydrocarbon chains ranging from 8 to 15 carbon atoms, and pure paraffin with chains ranging from 14 to 40 carbon atoms, offer versatility in temperature range suitability, making them applicable across a wide spectrum of thermal energy storage needs (Gulfam et al., 2019). Their non-corrosive, non-reactive nature and thermal stability within the designated range prevent degradation issues, contributing to their reliability in long-term applications (Soliman, 2020).

On the other hand, recent decades have witnessed intensive development in phase change heat storage materials, particularly focusing on fatty acids and their esters and compositions (Sarı and Kaygusuz, 2003; Yuan et al., 2014). Studies have demonstrated that these materials maintain their heat storage properties practically constant over several thousand thermal cycles(Chaudhari et al., 2013). Derived from biosourced raw materials like animal fats and vegetable oils (e.g., beef tallow, margarine, coconut oil, castor oil), they are sustainable, biodegradable, non-toxic, and exhibit lower flammability. Additionally, their excellent thermal stability and compatibility with polymers make them suitable for diverse applications (Liston et al., 2016). However, they may be more corrosive than paraffin and relatively more expensive.

Organic PCMs also include alcohols, which exhibit unique properties. Alcohols such as glycerol and ethylene glycol offer advantages such as high heat capacity, non-toxicity, and compatibility with various materials (Gunasekara et al., 2017b). Glycerol, due to its relatively low melting point and high latent heat of fusion, is very suitable for applications requiring moderate temperature ranges. Ethylene glycol, commonly used in antifreeze formulations, possesses a wide operating temperature range and excellent thermal stability, making it ideal for applications requiring high-temperature thermal energy storage. Additionally, alcohols can be easily modified to tailor their properties to specific application requirements, further enhancing their versatility (Tang et al., 2017).

Despite these advantages, organic PCMs encounter challenges such as low thermal conductivity, restricting their efficacy in certain heat transfer applications like TES. Additionally, issues such as volume changes during phase transition and flammability necessitate careful consideration to ensure safe and efficient utilization. Overall, organic PCMs present a promising path for thermal energy storage, combining performance, affordability, and environmental sustainability (Kenisarin, 2014).

Inorganic PCMs

Two kinds of inorganic compounds can be used as PCMs: hydrated salts and metals. While hydrated salts have been extensively researched for their PCM applications (Liu et al., 2012), metals remain relatively underexplored in this regard. In general, inorganic PCMs offer notable advantages, such as high thermal conductivity, high enthalpy, low volume change during phase transition, and non-flammability. However, they are also subject to drawbacks, including incongruent melting leading to phase segregation, poor

nucleating properties contributing to supercooling, and corrosiveness in case of hydrated salts or toxicity and limited compatibility in the case of metals.

Hydrated salts, typically denoted by the formula $AB{\cdot}nH_2O$, undergo phase change primarily through dehydration reactions. These salts exhibit varying melting behaviours, classified as congruent, incongruent, or semi-congruent, depending on their solubility in hydration water at the melting temperature. Incongruent melting, where the released water is insufficient to dissolve the formed crystalline salt, often leads to density differences, phase separation, and sedimentation. Scientists have made considerable efforts to overcome their problems such as salt segregation or supercooling, favouring TES applications due to their large latent heat of fusion, suitable phase transition temperatures, and economic feasibility (Kenisarin, 2010).

On the contrary, metallic PCM materials have garnered less attention in PCM technology, primarily due to weight penalties, despite their high reliability and repeatability (Pielichowska and Pielichowski, 2014). However, their potential for high heat of fusion per unit volume makes them attractive candidates when volume is a critical factor. Yet, their use poses unique engineering challenges, notably their high thermal conductivity compared to other PCMs. Metallic alloys, particularly those based on abundant elements like aluminum, copper, magnesium, and zinc, exhibit significant phase transition heat per unit mass and volume (Sun et al., 2007). Several studies have focused on determining specific heat, latent heat of fusion, and corrosion under thermal cycling conditions, highlighting their potential for TES applications (Sharma et al., 2009).

Eutectic PCMs

Eutectic PCMs are compositions of two or more components, whether organic, inorganic, or a combination thereof, that undergo congruent melting and freezing, forming a mixture of component crystals during crystallization. Unlike some PCM compositions that may exhibit segregation upon phase transition, eutectics typically melt and freeze without segregation, as they freeze into an intimate mixture of crystals, minimizing the opportunity for component separation (Sharma et al., 2009). Eutectic mixtures offer versatility in tailoring new PCM with explicit thermal properties, such as phase change temperature and latent heat, to suit specific applications. A state-of-the-art study on PCM mixtures have explored eutectic compositions and other variants, demonstrating the usefulness of phase equilibrium characteristics from mixture phase diagrams in select and prepare reliable PCMs for thermal energy storage (Gunasekara et al., 2017a). In this

manner, an extensive collection of eutectic mixtures can be synthesized. Consequently, there exists a wealth of numerical and experimental investigations focusing on the preparation and development of binary and ternary organic eutectic mixtures (Singh et al., 2021). An interesting example of such materials is eutectic mixtures of fatty acids thanks to their ability to achieve phase change temperatures suitable for various TES applications, such as building conditioning or textiles, where temperatures around 25 °C are often required. While most fatty acids have phase change temperatures above this range, eutectic blends can yield PCMs with lower phase change temperatures, enhancing their utility. For instance, the eutectic mixture of decanoic acid (melting at 31.6 °C) and hexadecanoic acid (melting at 62.9 °C) enables the attainment of a PCM with a melting temperature of 25 °C (Kahwaji and White, 2018). So, once the existence of these materials was discovered, it opened the door for researchers to explore and fabricate eutectics using other PCMs with even superior performance.

II/2.2. Selection criteria

The selection of PCM depends on the specific requirements of the system or process it is intended for. Each type of PCM offers distinct advantages and limitations, making them suitable for specific applications. Selecting a PCM involves the evaluation of various criteria related to its thermophysical, kinetic, chemical, and economic properties. Factors such as temperature requirements, thermal conductivity, and cost-effectiveness, as well as the specific needs of the system or process, influence PCM selection. General desirable properties for PCMs include a small volume change, compactness, easy handling, and high thermal energy density, among others (Sharma et al., 2009).

To delve further into these important properties, we can consider the following aspects. Thermal properties play a crucial role in PCM selection, including factors such as melting temperature within the desired operating range, high phase transition latent heat per unit volume, high specific heat, and high thermal conductivity of both phases to support the heat absorbing and releasing process (Lin et al., 2018). Physical properties like minimal volume change during phase transition, low vapour pressure at the operating temperature, congruent melting, and high density are also important considerations. Moreover, kinetic properties, such as no supercooling, high nucleation rate, and adequate crystallization rate, contribute greatly to PCM performance. Chemical properties are also essential for PCM suitability, including long-term thermo-chemical stability, reversible freeze/melt

cycles, compatibility with surrounding materials, non-corrosiveness, and non-toxic, non-flammable, and non-explosive characteristics indeed. And, additionally, PCMs should be readily available in large quantities at low cost (Oró et al., 2013).

Despite the ideal criteria, most PCMs do not fully meet all requirements for an adequate storage media. However, recent progress in material design, including advancements in nanomaterials, offers opportunities for improving performance and extending the lifetime of PCM systems. Practical difficulties may arise in the application of PCM, such as density changes, phase segregation, supercooling, or low thermal conductivity. Nevertheless, several techniques have been explored to address these challenges. These include incorporating metallic fillers, using finned tubes, or embedding PCM in graphite matrix to enhance thermal conductivity (Ji et al., 2014); addition of nucleators to decrease supercooling (Beaupere et al., 2018) or mechanical agitation that can be employed to mitigate density changes.

Overall, PCM selection involves balancing multiple criteria to ensure optimal performance, reliability, and cost-effectiveness for specific thermal energy storage applications.

II/2.3. Implementing PCM in industrial systems: practical applications and strategies

As has been discussed, heat or cold storage has gained significant interest due to its ability to harness residual energy and make renewable energies manageable. Systematic investigations into PCMs began after the oil crises, with research and development in PCMs intensifying notably by the late 1990s (Hasnain, 1998). While there remains considerable demand for research spanning from fundamental principles to applications in many areas, PCM technology is now considered mature in certain sectors, moving away from being solely a subject of research and development.

During the 1970s and 1980s, interest in PCM applications grew, particularly in solar systems for thermal energy storage, large solar plants, and smaller domestic applications such as hot water systems. The construction sector, which accounts for approximately 40 % of total energy consumption, stands out as one of the most advanced in PCM utilization. Industrial applications are also significant, given their high energy demand as in refrigeration facilities, for instance (Mehling et al., 2022).

The significance of PCMs for thermal energy storage, as well as the classification and properties of these materials discussed in previous sections, are closely linked to their practical applications. In this regard, this section will explore the main current applications, categorizing them according to the mode of PCM incorporation or utilization, as these concepts are interrelated.

There are several techniques developed and tested for the use of PCM. In general, these techniques encompass both direct utilization in their bulk form and incorporation into other systems like slurries or shape-stabilized composites. The incorporation into these latter types of systems can be done directly or through encapsulation. Encapsulation, a widely employed method (Huang et al., 2023), offers notable advantages in preventing any contact with the environment, preventing PCM from flowing away in the liquid phase, if the phase change is, for example, solid-liquid, and providing a defined surface for heat exchange. However, encapsulation also introduces challenges such as reduced thermal conductivity and complexity in the production process that involves, firstly, the encapsulation (by chemical or physical means), separation, washing, drying and further dispersion into the selected system, which leads to a high production cost (Jamekhorshid et al., 2014).

Having outlined the various techniques for PCM utilization, we now turn our attention to their practical applications. By categorizing these applications based on how PCMs are employed, we can gain insights into their diverse uses and the impact they have across different sectors:

Bulk material

Direct utilization of PCM involves its application without incorporation into another structure or integration with another phase to impart specific properties, that is, the bulk PCM is used. This method is widely used in various processes, such as solar heat storage, building materials or thermal energy storage systems. It involves large-scale containers or vessels filled with PCM (Nardin, 2014). These containers can be strategically placed within buildings or industrial facilities to absorb and store thermal energy during off-peak hours, then release it when needed to supplement heating or cooling systems (Abu-Hamdeh and Alnefaie, 2019). This approach helps to reduce energy consumption and costs by shifting peak demand periods and optimizing overall energy usage. Additionally, “large-encapsulation” techniques represent also another form of direct utilization. GlassX AG, for instance, produces translucent, thin glass elements filled with PCM, enabling

them to store heat akin to a concrete wall (Mehling et al., 2022). These translucent elements function by absorbing solar radiation and internal heat while also serving as design elements in architectural applications.

Shape-stabilised materials

Shape-stabilized PCMs represent a significant advancement in PCM technology, offering versatile applications across various fields. These materials are mainly composite materials where PCM is combined with another substance or structure to modify its properties or introduce entirely new ones. One of the primary objectives in shaping these materials is to achieve form stability, which addresses the leakage problem often associated with solid-liquid PCMs. Researchers have dedicated considerable efforts over the past few decades to develop a wide range of form-stable phase change materials. Those materials can remain in a solid state with no liquid leakage, even at temperatures higher than their phase change temperature, demonstrating remarkable shape stability, which simplifies handling. Numerous review articles have extensively covered different aspects of that kind of materials, including supporting materials, thermal conductivity enhancement, energy conversion, micro-/nano-encapsulation technologies, and their applications (Chinnasamy et al., 2023; Zhang et al., 2022). This research has paved the way for the development of innovative PCM solutions that offer enhanced performance and reliability in various practical applications.

Most PCMs inherently possess low thermal conductivity which limits their effectiveness in certain applications. However, by incorporating PCM into various types of support structures, such as metallic, carbon-based, or polymer matrix composites, with components having higher thermal conductivity, it is possible to enhance their performance (Sheng et al., 2021; Su et al., 2022). This approach not only improves heat transfer efficiency but also ensures shape stability.

PCM shape-stabilized materials find significant applications in the construction industry, particularly in enhancing the energy efficiency of buildings. One of the most notable applications is integrating PCM into building materials, offering passive thermal management solutions (see Fig. 4). Unlike conventional approaches where PCM is added as a separate layer (Cao et al., 2019), shape-stabilized PCM is integrated directly into the structure of building components. By incorporating PCM into building materials, such as gypsum boards, plaster, concrete, and clay, the latent heat energy storage capacity of these materials is significantly enhanced (Bondareva and Sheremet, 2022; Feldman et al., 1991;

Salgado et al., 2020). Form-stable compositions, combining PCM with porous structure materials, offer another promising heat storage solutions in buildings. To maximize PCM integration into porous structures, vacuum impregnation techniques are employed. This advancement enables widespread production of building materials, such as wood fiberboards (Qi et al., 2020), and the binding of PCM to textile fabrics.

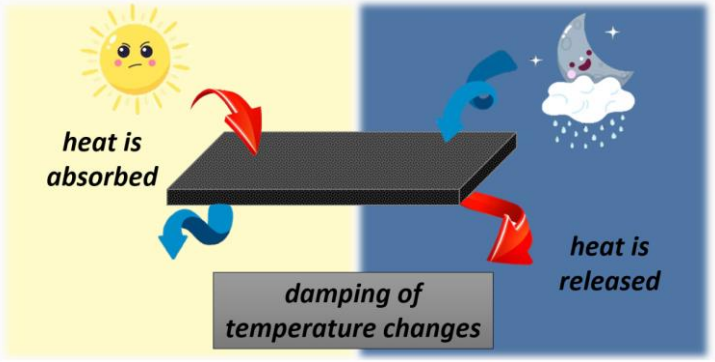


Fig. 4. Scheme of a thermal damping system in buildings.

The textile industry offers a promising opportunity for utilizing shape-stabilized PCMs too. Alongside impregnation methods, advancements now allow for the direct incorporation of microencapsulated PCM into fibres (Sun et al., 2015). This innovation enables the creation of clothing materials and sleeping equipment with enhanced heat storage capabilities, providing superior comfort and warmth, particularly in colder regions ("Outlast - market leader for climate regulating materials," n.d.). Additionally, encapsulated PCM incorporation extends to various applications, such as highway pavement, to mitigate abrupt temperature changes (Ma et al., 2013); medical prostheses (Wernke et al., 2015) and the food industry (Alehosseini and Jafari, 2019).

Slurries

A prevailing trend in recent years is the shift from single-phase fluids to solid-liquid PCM dispersions, known as phase change slurries (PCSs) given their high energy storage density. These slurries are engineered to optimize heat transfer rates, thereby achieving higher energy storage densities while retaining fluid pumpability. Typically, PCSs consist of a carrier fluid, often water, serving as the continuous phase, with dispersed PCM particles acting as the dispersed phase. By leveraging both the latent heat capacity of the PCM and the sensible heat capacity of the carrier fluid, PCSs efficiently store and transfer thermal energy more effectively than traditional alternatives (Delgado et al., 2012).

PCSs encompass a range of types, including 1) ice slurries; 2) phase change emulsions (PCMEs), where a PCM is directly dispersed in a liquid continuous phase, using a stabiliser; 3) microencapsulated phase change slurries, where a PCM is encapsulated and suspended in the continuous phase; 4) semi-clathrate and clathrate hydrate slurries, consisting of fine solid hydrate particles in water, constituting a special molecular structure; and 5) shape-stabilized slurries, composed of shape-stabilized materials suspended in the continuous phase. The utilization of PCSs offers numerous advantages, positioning them as versatile solutions for both thermal storage and heat transfer applications (Youssef et al., 2013). The pumpability of these innovative fluids allows their dual functionality as both transport mediums and energy storage reservoirs streamline system design and operation. Enhanced by the elevated surface-to-volume ratio, PCSs boast high heat transfer rates, optimizing energy exchange efficiency. This attribute, coupled with the slurries' higher heat capacity, results in lower pumping power requirements, further enhancing overall system efficiency. Furthermore, these novel fluids offer a thermal energy storage density advantageous over conventional sensible heat storage systems, making them a competitive alternative. Depending on the particular application and in-service temperature, these slurries need to be designed to optimally fulfil not only the general goal of maximizing thermal energy storage capacity but also secondary objectives such as enhanced thermal conductivity, higher heat transfer coefficients, temperature stabilization, reduced pressure drop, etc. Examples of potential applications of phase change slurries in energy storage and heat exchange systems are industrial waste heat recovery (80–200 °C), solar heating systems (50–60 °C), heating, ventilating, and air conditioning (8–25 °C), data centres and servers (25–32 °C), space applications (−40 to −10 °C), cold storage for air conditioning (5-12 °C), secondary refrigerants to the refrigeration system (-4-80 °C) (Liu et al., 2012; Saeed et al., 2019), etc.

In particular, encapsulated PCSs play a crucial role in preventing PCM leakage and potential solidification within ducts, thereby enhancing system effectiveness and reliability. So far, the investigations on encapsulated PCM are mostly on its fabrication methods and thermal properties (Fang et al., 2008; Pan et al., 2012) and on the flow and heat transfer characteristics through tubes (Inaba et al., 2003). Nevertheless, several drawbacks limit their applicability at an industrial scale: the potential additional costs associated with the encapsulation process; the integrity and durability of the capsules

against pump-induced stresses (Ran et al., 2020); and the negative effect of the shell on the thermal conductivity (Chen et al., 2018) all of them essential for maintaining efficient system operation. While with PCME, the main challenge lies in sustaining stable emulsions during the phase change (Chatterjee et al., 2017). However, these systems hold great potential due to the minimal thermal resistance of the protective surfactant layer between the continuous phase and the PCM (Delgado et al., 2012). This characteristic, compared to encapsulated materials, further enhances their promise.

In general, the PCSs find application across various industrial sectors due to their versatility and effectiveness. These slurries, especially semi-clathrate and clathrate hydrate slurries, have emerged as key components in secondary refrigeration systems and air conditioning units, serving as efficient heat transfer fluids. The PCSs have also been highly employed for waste heat recovery (Du et al., 2021). Additionally, they are employed as media for storing cold energy, making them invaluable in various industrial processes requiring precise temperature control (Eisapour et al., 2020; Kim et al., 2023). Overall, they are increasingly favoured for their ability to optimize energy usage and reduce environmental impact in industrial cooling applications. PCSs find widespread use in the food and beverage industry for refrigeration and preservation, ensuring the freshness and quality of perishable products (Chananipoor et al., 2021). They are also indispensable in the pharmaceutical sector, providing temperature-controlled storage solutions for medications and vaccines, thereby maintaining their efficacy and stability.

In summary, the real-world applications of PCMs highlight their versatile role in addressing energy challenges across various industries, emphasizing the ongoing need for research and innovation in this area. Whether it is improving thermal comfort and energy efficiency in buildings with PCM-incorporated construction materials or optimizing energy storage and transfer in industrial settings, PCMs have proven their versatility and efficacy. Furthermore, their potential goes beyond traditional uses, with emerging applications in cutting-edge technologies like electronic, human body or mobility applications (Mehling et al., 2022).

II/3. Phase Change Emulsions (PCMEs)

As discussed in the preceding section, PCMEs represent a cutting-edge approach to the development of advanced HTFs for diverse industrial applications. Unlike encapsulated PCSs, PCMEs involve dispersing molten PCM directly into a carrier liquid, often with the aid of surfactants to reduce interfacial tension. The phase change temperature of the emulsion can be tailored to meet the temperature requirements of heating or cooling applications by selecting appropriate PCMs. These emulsions offer several advantages, such as a shell-free structure, smaller droplet size, ease of production, reduced production costs, and enhanced heat transfer efficiency. Despite increasing interest, the literature on PCMEs, particularly focusing on oil-in-water emulsions, remains relatively sparse compared to encapsulated PCSs. However, ongoing research continues to uncover new insights into the thermal storage properties, stability, and rheological behaviour of PCM emulsions, driving innovation in this promising field.

In this context, numerous PCMs, predominantly paraffins, have been effectively emulsified in water using various techniques and surfactants over the years. Some examples include the following. One of the earliest PCME formulations reported in the literature introduced a mixture of n-alkanes emulsified using an ultrasonic generator with a commercial non-ionic surfactant (Royon and Guiffant, 2001). Additionally, tetradecane nanoemulsion was achieved via a phase inversion temperature method employing a combination of Tween60 and Span60 (Schalbart et al., 2010). Hexadecane emulsion was obtained through high shear dispersion and ultrasonic dispersion methods (Günther et al., 2010), while tetradecane and hexadecane were emulsified using a rotor-stator system with SDS and Tween40 (L. Huang et al., 2010). Other methodologies include emulsifying paraffin using the Incursion Method (Zou et al., 2010) and creating a mixture of paraffin and ethylene propylene diene monomer (EPDM) in petroleum ether with a blend of 1-dodecanesulphonic acid sodium salt (DAS) and sorbitan monooleate (Span-80) (Ding et al., 2019).

In addition to these examples, it is worth noting that various types of emulsions as a function of their drop size, as well as different specific techniques employed for their production, have been extensively explored in the literature. Furthermore, a deeper examination of their thermal properties, stability, rheological behaviour and technological applications will be provided in the subsequent sections.

II/3.1. Classification

Emulsions are versatile liquid dispersions comprising two or more immiscible liquids. They can be classified based on various criteria, such as the type of dispersed phase and carrier fluid, or the size of the droplets they contain. On the one hand, commonly, these liquids include water and oil, resulting in various types of emulsions such as binary water-in-oil (W/O) or oil-in-water (O/W) emulsions, as well as more complex configurations like oil-water-oil (O/W/O) and water-oil-water (W/O/W) emulsions. Additionally, there are cases of emulsions formed by oil-in-oil (O/O) configurations. The choice of emulsion type depends on several factors, including the method of preparation, properties of stabilizing additives, and specific application requirements. In the case of PCMEs, the O/W emulsion is particularly prevalent due to its stability and lower viscosity. This characteristic is crucial as PCMEs are intended for circulation within systems where minimizing pump power is essential. It is worth noting that while oil-in-oil (O/O) emulsions exist for other applications, no studies have formulated these emulsions using PCMs (Shao et al., 2015).

On the other hand, emulsions can also be classified based on the size of the droplets they contain. This classification scheme considers the diameter of the droplets, which is often indicative of the emulsion's stability. PCMEs exhibit three primary categories based on droplet size. Micro-emulsions, characterized by their thermodynamically stable behaviour, have droplet diameters ranging from 10 to 100 nm. In contrast, mini-emulsion (also known as nano-emulsion) and macro-emulsion systems, with droplet sizes ranging from 100 to 1000 nm and over 1 μm, respectively, often display a milky appearance and are prone to breakdown through coalescence and flocculation. Consequently, they are both kinetically and thermodynamically unstable (Liu et al., 2022).

The type of emulsion is also influenced by factors such as the method of preparation, properties of the stabilizing additive, and various other considerations.

II/3.2. Fabrication

When it comes to developing an emulsion, two crucial considerations must be taken into account: the selection of an appropriate stabilizer, which can be either a surfactant or nanoparticles and the chosen emulsification method.

The choice of stabilizer is essential for ensuring the stability of the emulsion by preventing droplet coalescence and aggregation. The right amount of surfactants in emulsions is also very important to the properties of final products. For PCMEs, the most common emulsifiers are non-ionic and ionic small molecule surfactants, which are characterized by a polar hydrophilic head group and a nonpolar hydrophobic alkyl tail (Shao et al., 2015). These surfactants play a critical role in forming a thin protective layer at the interface between water and oil, effectively preventing droplet aggregation. Alternatively, nanoparticles can also be employed as stabilizers of pickering PCMEs, offering advantages such as enhanced stability and tunable properties (Zheng et al., 2022).

Emulsifying methods for emulsion preparation can be classified into two groups: high-energy methods and low-energy methods. High-energy methods, such as mechanical stirring, ultrasonication, and high-pressure homogenization, involve the application of intense energy to break down the PCM into smaller droplets within the carrier liquid, resulting in a finer and more uniform emulsion. On the other hand, low-energy methods, such as the phase inversion temperature method and phase inversion composition method, rely on phase transitions or changes in composition to achieve emulsification without the need for extensive mechanical energy (Liu et al., 2022).

II/3.3. Characteristics

Understanding the key characteristics of PCMEs is paramount for optimizing their performance and stability in various applications. This section delves into three critical aspects of PCMEs: their rheological and thermal properties, the phenomena of hysteresis and supercooling, and the challenges associated with ensuring their stability over time.

Rheological and thermal properties

Understanding the rheological and thermal properties as well as their complex relationship is essential for optimizing energy recovery and transport processes, particularly in the context of PCMEs.

More precisely, to use phase change dispersions as heat transfer and energy storage fluids, these dispersions must meet some specific requirements. On the one hand, they must present the appropriate thermo-rheological behaviour to facilitate fluid transport with a minimum pumping requirement (Delgado et al., 2005; Steffe, 1996). In addition, PCM emulsions should be stable over a long period of storage, and able to resist the thermo-

mechanical load cycles in pump systems (Ho and Iverson, 2014). On the other hand, they must exhibit high heat capacity and thermal conductivity, high resistance to high-temperature thermal cycles and interfacial properties that facilitate a high heat transfer coefficient, as well as being environmentally friendly and compatible with metals used for pipes, tanks, etc. (Delgado et al., 2012; Huang et al., 2009).

It is important to note that rheological and thermal properties influence each other, creating a complex interplay that affects fluid dynamics and heat transfer mechanisms. For instance, the non-Newtonian behaviour not only affects Reynolds numbers but also influences Prandtl and Grashof dimensionless numbers. These parameters play crucial roles in empirical heat transfer correlations, particularly in determining Nusselt numbers under different heat transport conditions, such as forced convection or combined free/forced convection. Likewise, flow and consistency indexes, parameters of the Oswald de Waele viscous model, further modulate the non-Newtonian and non-isothermal character of convective heat transport mechanisms. In this sense, several studies on PCMs have pointed out the significance of this relationship. Thus, Saarinen et al. investigated turbulent convective heat transfer of n-decane-in-water nano-emulsions, correlating heat transfer coefficients with Reynolds numbers for turbulent regimes (Saarinen et al., 2015), while Ni et al. conducted similar studies for laminar flow (Ni et al., 2017).

Additionally, it has been reported that viscous properties significantly influence the performance and efficiency of thermal energy systems in practical applications (Drissi et al., 2019). For example, an increase in viscosity gives rise to not only a greater pressure drop (and greater pumping power) but also leads to a reduction in fluid turbulence, resulting in a decrease in the heat-transfer coefficient. On the contrary, a more apparent shear-thinning non-Newtonian behaviour leads to higher heat transfer coefficients.

In summary, recognizing and understanding the intricate interplay between rheological and thermal properties is crucial for optimizing PCMEs' performance in energy recovery and transport processes.

Hysteresis and supercooling

When different results between the measurements of the cooling and heating processes are obtained, this phenomenon is called hysteresis; nevertheless, hysteresis is commonly understood as a material property. In the case of inorganic materials, the hysteresis phenomenon is much more noticeable than in the case of organic materials. Hysteresis

and supercooling, while related, are distinct phenomena in the context of PCM. Hysteresis refers to the phenomenon where different results are observed between the cooling and heating processes, influenced by both material properties and measurement conditions. On the other hand, supercooling specifically refers to the difference between a substance's melting and freezing points, resulting in delayed phase change and reduced system efficiency (Evans et al., 2006). In PCMEs, supercooling is primarily caused by shifts in nucleation mechanisms, transitioning from heterogeneous to homogeneous processes (Günther et al., 2010), particularly evident in nano-emulsions with smaller droplet sizes (Zhang et al., 2015). While many PCMs do not exhibit supercooling in macroscopic settings, the phenomenon becomes apparent in microscopic geometries (Shamseddine et al., 2022). Nucleating agents have been extensively explored to mitigate supercooling by promoting nucleation (Liu et al., 2021). However, resolving the supercooling issue in PCMEs remains challenging due to various factors beyond nucleation effects. For instance, the varied crystallization behaviours of alkanes under different conditions, such as bulk versus micro/nanoconfinement, contribute to the complexity of the issue, thus underscoring the significant influence of droplet size in this phenomenon (Cholakova and Denkov, 2019). Hexadecane emulsions prepared using three different surfactants highlighted the impact of surfactant type on emulsion supercooling (Li Huang et al., 2010). Therefore, addressing supercooling remains a substantial obstacle in advancing high-performance thermal energy storage systems in general and PCMEs in particular.

Stability

The stability of PCMEs is a critical aspect governed by several interrelated factors. These factors include the physicochemical properties of the PCM and the surfactants used for emulsification, as well as the emulsion preparation method.

Certain key aspects affecting stability are common to most emulsions, such as interfacial tension, droplet size distribution, concentration of stabilizing agents or thermodynamic considerations such as Ostwald ripening, coalescence, and sedimentation. Additionally, external factors such as temperature fluctuations, mechanical agitation, and storage conditions can also influence emulsion stability (Tadros, 2016).

However, there are several factors inherent to PCMEs themselves that pose unique challenges. Thus, the main challenge of stabilizing PCMEs arises from the intrinsic phase transition behaviour of the PCM. During the phase transition, the physical state of the PCM droplets within the emulsion changes, leading to alterations in volume, density, and

interfacial properties (Evans et al., 2006), potentially resulting in instability and eventual breakdown of the emulsion.

For instance, during the phase transition, PCMs typically undergo a significant volume change (Mehling and Cabeza, 2008). For example, during the solid-to-liquid transition, the PCM volume usually increases, exerting mechanical stress on the surrounding emulsion structure. This volume change can disrupt the stability of the emulsion and lead to phase separation or coalescence of droplets. Moreover, this phase change affects the interfacial properties of PCM droplets, as solid PCM droplets may exhibit different surface energies and interactions with the surrounding medium compared to liquid PCM droplets. These changes in interfacial properties can influence the stability of the emulsion by altering the balance of interfacial forces that govern droplet dispersion and interaction (Evans et al., 2006). Additionally, phase change can accelerate Ostwald ripening due to the difference in solubility and diffusivity between solid and liquid phases.

On the other hand, thermal cycling, which is essential for the applicability of these systems, can induce additional stress on the emulsion structure (Huang et al., 2009), leading to fatigue and eventual breakdown of the emulsion, particularly if the emulsion components are not designed to withstand thermal cycling.

Overall, mitigating these challenges requires careful consideration of the phase transition behaviour of the PCM, selection of emulsifiers and stabilizers capable of adapting to the changing interfacial properties of PCM droplets during phase transition, and optimization of emulsion formulation and processing parameters to enhance stability and prevent phase separation or coalescence. While many research studies acknowledge the difficulty of finding stabilizers capable of addressing these challenges, few delve into the intricate details of each of the aforementioned aspects, essential for advancing our understanding with PCMEs.

II/3.4. Applications

In a previous section (II/2.3), it has been discussed the numerous industrial applications of PCSs, highlighting systems already in the market. However, in this section, our focus shifts to exploring the potential applications of the PCMEs. Unlike several PCSs, which have established industrial applications, PCMEs are currently in the development stages, and there are limited publications available regarding their commercial or industrial-level application. Nevertheless, it is widely acknowledged that PCMEs hold great potential for

numerous applications across various industries. This section, it is delved into the potential applications of PCMEs and examines their promising role in enhancing energy efficiency and sustainability in diverse sectors.

Solar thermal and photovoltaic systems

PCMEs can be used in solar thermal energy storage systems to collect and store solar energy for later use, helping to save energy, reduce costs, and lessen environmental impact by using renewable energy sources. Zou et al. successfully formulated PCMEs with great potential as novel HTFs for solar thermal systems as they proved effective in reducing power consumption rates as the concentration of PCM increased (Zou et al., 2010). PCMES have also been used as HTFs for directly absorbing heat in solar collectors by incorporating graphite nanoparticles (Wang et al., 2016) or nanoplatelets (Wang et al., 2019) to enhance their ability to absorb solar radiation, boosting overall performance.

Finally, in photovoltaic (PV) technologies, Feng et al. explored the use of paraffin-in-water nano-emulsions as innovative cooling fluids to improve the efficiency of PV modules (Feng et al., 2021).

Heating, ventilation, and air conditioning (HVAC) systems

The industrial application of PCMEs in HVAC systems is one of the most advanced areas of development. By integrating PCMEs into HVAC systems, heat transfer efficiency and temperature regulation can be significantly enhanced, resulting in improved energy efficiency and greater indoor comfort (Shao et al., 2015).

Numerous studies have highlighted the efficacy of PCMEs in HVAC applications, providing adaptable solutions for passive cooling, temperature regulation, and energy-efficient HVAC operation, especially within thermal energy storage systems. For instance, Huang et al. have demonstrated the potential of PCMEs in air-conditioning installations, proposing their utilization not only in cooling facilities but also to replace water in storage piping systems, thereby enhancing the heat storage capacity of buildings (Huang et al., 2009).

Indeed, the use of paraffin emulsions in water stands as one of the most researched areas due to its potential as a two-phase secondary refrigerant for air conditioning applications (Wang et al., 2017). These PCMEs have also been extensively studied as thermal media in cooling-supply networks, offering cost reduction compared to traditional water-based systems. Moreover, Delgado et al. conducted a comparative analysis of the storage

capacity of a tank filled with either water or a low-cost PCME, showing the higher energy storage density of the PCME-based tank (Delgado et al., 2015). Furthermore, the research was focused not only on the formulation of the emulsion but also on optimizing the tank charging process and design to enhance energy storage density.

Electronics Cooling

The thermal management of electronic devices is increasingly challenging due to rising power densities and miniaturization. PCMEs provide an efficient solution for cooling electronic components by absorbing and dissipating heat during operation (Ho et al., 2021). Several studies have integrated water-based nano-PCMEs of n-hexadecane (Liu et al., 2006) or n-eicosane (Ho et al., 2021), for example, into thermal interface materials and small tubular channels, enhancing heat transfer efficiency and preventing overheating, thus prolonging the lifespan and reliability of electronic devices. One sector of particular interest, where much research is focused, is electric vehicles, especially zero-emission or hybrid models, whose lithium-ion batteries are highly sensitive to operating temperatures. The research efforts in this area are not only focused on nano-emulsions mainly of paraffin (Wang et al., 2020) but also on their instrumental development (Cao et al., 2020).

II/4. Non-aqueous emulsions

As mentioned earlier in the section on phase change material emulsions, an emulsion is characterized as a thermodynamically unstable system consisting of two or more immiscible phases. The macroscopic destabilization of these systems is prevented by the addition of an appropriate surfactant. Nowadays, the majority of all commercially available emulsions incorporate an aqueous phase, with a vast body of scientific literature existing in this field. Nevertheless, the presence of water is not indispensable, as emulsions could, in principle, be formulated with any pair of immiscible liquids, giving rise to the so-called anhydrous emulsions, also known as non-aqueous or oil-in-oil emulsions (Imhof and Pine, 1997a; Vold, 1965).

Anhydrous emulsions have not received much attention, as systematic studies on this topic are not well-documented, and the number of scientific publications addressing it remains relatively modest (Crespy and Landfester, 2011). However, this dearth of scientific knowledge and technological advancement contrasts with the escalating

demand for anhydrous emulsions across a diverse array of applications (Zia et al., 2020) (*Fig. 5*).

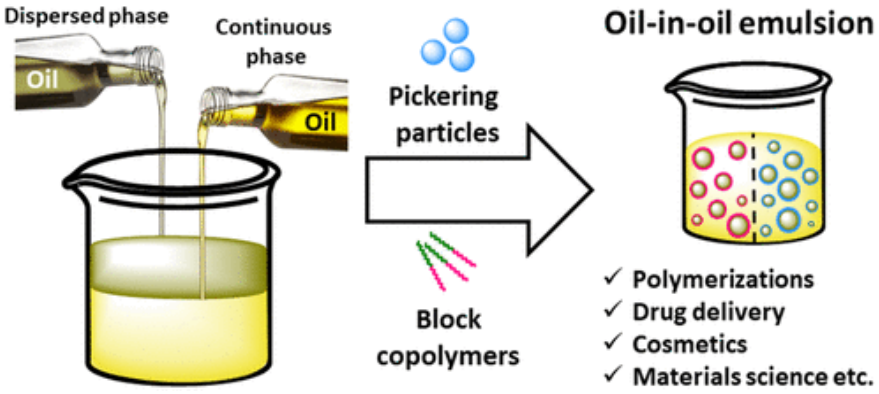


Fig. 5. Oil-in-oil emulsion manufacture and applications (Zia et al., 2020).

Since the early studies in the 1960s (Hamill et al., 1965; Hamill and Petersen, 1966a, 1966b) where olive oil-in-glycerin systems were first tested, the majority of studies in this domain have focused on investigating cosmetic or pharmaceutical formulations. On one hand, systems have been prepared to comprise biocompatible oils such as polyethylene glycol, paraffin, or glycerol esters stabilized with block copolymers (Atanase and Riess, 2014, 2013), which hold significant relevance in these industries due to their utility as bases for topical applications. On the other hand, other systems involving castor oil/silicone oil combinations exhibit noteworthy potential in pharmaceutical applications, where they can serve as solvents for medications or as suspension vehicles (Jaitely et al., 2004; Suitthimeathegorn et al., 2007, 2005). Additionally, emulsions prepared with soybean oil or sunflower oil dispersed in propylene glycol have been investigated for nutritional formulations comprising edible and non-toxic ingredients (Ceballos et al., 2014; Nanjwade et al., 2011; Patel et al., 2006).

Furthermore, non-aqueous emulsions can serve as alternatives to conventional aqueous emulsions in situations where the presence of water is undesirable. This scenario arises in cases involving water-sensitive reactions that exclude the use of certain catalysts or radical monomers. Similarly, non-aqueous emulsions are pertinent when elevated temperatures beyond the boiling point of water are required. This limitation, for instance, hinders the utilization of non-aqueous emulsions as a technique to produce nanostructured polymeric materials. The study carried out by Crespy and Landfester illustrates these applications, where droplets suspended in ethylene glycol within a stable mini-emulsion

were employed as reactors for the reduction of silver nitrate into silver nanoparticles followed by their subsequent polymerization (Crespy and Landfester, 2009). Another example is the work carried out by Klapper et al., who synthesized polymeric latex particles using dimethylformamide suspended in alkanes with carefully designed copolymers as stabilizers, thus enabling the use of water-sensitive catalysts (Klapper et al., 2008). Furthermore, the efforts of Lin et al. merit mention, as they facilitated the stabilization of deoxyArbutin, a skin-whitening agent prone to degradation in aqueous solutions, within polyol-in-silicone emulsions utilizing siliconated surfactants (Lin et al., 2011). Another example can be found in cleaning systems sensitive to oxide formation, such as engines or other systems where the application of electric fields is necessary (Ha and Yang, 2000). Additionally, they can be employed as templates for sol-gel processes in the preparation of microspheres, nanoparticles, and microstructures (Riess et al., 2004), among other applications. The droplets of a stable emulsion obtained with formamide as the continuous phase, isoctane as the dispersed phase, and a block copolymer as the emulsifier serve as templates for the creation of highly ordered macroporous materials like titanium, silica, and zirconium (Imhof and Pine, 1998, 1997b).

II/4.1. Phase selection

The first critical aspect that shapes the future applications of new anhydrous emulsions is the search for a suitable pair of immiscible phases. This involves predicting the miscibility of phases across a broad temperature range and assessing their behaviour in response to surfactant addition (Cameron and Sherrington, 1996; Vold, 1965). Certain pairs of immiscible compounds have been extensively investigated, such as castor oil/silicone oil or formamide/silicone oil, which can be stabilized solely by specific surfactants (Imhof and Pine, 1997a; Jaitely et al., 2004; Suitthimeathegorn et al., 2005), a theoretical framework is lacking to determine the applicability of other compounds that could function as continuous or dispersed phases, along with the selection of an appropriate emulsifier. Furthermore, it remains unclear which combination of molecular or thermodynamic properties can confidently predict the stability of a system under a given surfactant.

The initial step towards addressing these issues involves selecting the two immiscible phases, taking into consideration that this attribute is significantly influenced by the polarity of the solvents. In this manner, their immiscibility could be assessed using the

Hildebrand solubility parameter (δ) (Hildebrand and Scott, 1964), which provides a numerical estimation of the interaction degree for non-polar or slightly polar substances and can serve as a valuable solubility indicator, as materials with different δ values are highly likely to be immiscible. Following these indications, predictions could be made, for instance, that emulsions of polyethylene glycol (δ = ~ 20 $MPa^{1/2}$) (Adamska et al., 2007) and silicone oil (δ = 15.4 $MPa^{1/2}$) (Ylitalo et al., 2006) could be stabilized with an appropriate emulsifier.

Thus, when formulating non-aqueous emulsions, an alternative approach could involve replacing the water in an existing water/oil or oil/water emulsion with a non-aqueous compound. In this context, the chosen compound should possess significant polarity to render it immiscible with oils and to serve as an effective solvent for the solvophilic segment of surfactant molecules.

II/4.2. Formulation of non-aqueous emulsions

Formulation of non-aqueous emulsions becomes an extremely complex task, primarily due to the lack of data concerning the availability of suitable surfactants in such systems. Not only is data regarding the selection of immiscible pairs for non-aqueous emulsion formulation lacking but there are also relatively few studies addressing the optimal surfactant selection for them. There exist only studies that analyse the emulsifying effects of numerous ionic and non-ionic surfactants in very specific non-aqueous systems, observing the efficiency of each in stabilizing the respective system. However, these studies often fall short of exploring deeply the physicochemical, rheological, and microstructural properties of the resulting emulsions. For instance, McMahon et al. examined the emulsifying effects of over 15 surfactants in the non-aqueous binary system of glycerol and olive oil (McMahon et al., 1963). Additionally, blends of commercial emulsifiers ArlacelsTM and polysorbates were prepared and tested at various hydrophilic-lipophilic balance (HLB) values, yielding stable emulsions using several of these agents and combinations in specific systems (Hamill et al., 1965; Hamill and Petersen, 1966a, 1966b; Imhof and Pine, 1997a; Magdassi and Frank, 1986; Petersen et al., 1964). Castor oil emulsions in silicone oils have been stabilized with Triton-X-100, where the polysorbate-type surfactants or sorbitan esters like Tween 80 or Span 60 do not function (Jaitely et al., 2004). Lastly, Imhof and Pine also developed stable concentrated emulsions of oil in formamide and oil in sulfoxide using commercially available non-

ionic surfactants. This likewise demonstrated that several other polar liquids do not yield stable anhydrous emulsions with these surfactants (Imhof and Pine, 1998, 1997a, 1997b).

On the other hand, in the early 1970s and more recently, research conducted by Atanase and Riess (Atanase and Riess, 2013) and Suitthimeathegorn et al. (Suitthimeathegorn et al., 2005) have indicated that block copolymers containing two distinct structural segments that are selectively soluble in either of the immiscible phases could prove to be more effective than low molecular weight surfactants. This offers a genuine possibility for stabilizing non-aqueous emulsions, imparting enhanced steric hindrance against coalescence. Various reports have already demonstrated the requirement for high molecular weight surfactants for the efficient stabilization of non-aqueous emulsions (Crespy and Landfester, 2009; Imhof and Pine, 1997a), and if such a surfactant stands a structure with two incompatible blocks, each selectively soluble in either of the immiscible liquids, it could indeed be suitable. However, despite having identified certain effective surfactants for specific systems, the precise combination of physicochemical or molecular properties governing emulsifying capacity remains far from clear. As a result, the search process unfolds as an iterative trial-and-error approach. The only established insight in the study of two non-aqueous phase (oily) or polar solvent-oil systems is that hydrogen bonding distinctly plays a more significant role than polarity (Imhof and Pine, 1997a). Additionally, there are no established guidelines for stabilizing two immiscible non-polar oils or polar solvent-oil phases, as the hydrophilic-lipophilic balance (HLB) criteria cannot be applied to these systems.

Thus, the absence of a specific surfactant selection criterion for non-aqueous systems underscores the need for research that provides technologists and the industry with a toolkit, data, and/or protocols that offer a starting point or assistance in the search for the appropriate surfactant. This approach could enhance the success rate in formulating new anhydrous emulsions, saving study time, avoiding excessive empiricism that entails testing all available emulsifiers before finding one that works and facilitating the formulation of stable non-aqueous emulsions.

II/4.3. Properties and stability of non-aqueous emulsions

Similar to conventional aqueous emulsions, anhydrous emulsions are also thermodynamically unstable systems that can reach kinetic stability due to the presence of surfactant agents. Generally, the destabilization of dispersion can arise from a

combination of different destabilization phenomena or mechanisms, such as creaming/sedimentation, coalescence, flocculation, and droplet coarsening (Ostwald ripening). Most of these mechanisms are interlinked, rendering their separation quite challenging (Delgado-Sánchez et al., 2017; Saidi et al., 2020). Detecting these phenomena at an early stage is of vital importance for enhancing emulsion stability and optimizing formulation development. Moreover, understanding how various types of instabilities can be influenced by changes in experimental parameters such as surfactant concentration, temperature, processing time, etc. is highly significant. Parameters like temperature, dispersed phase concentration, agitation speed, or processing time play a pivotal role in achieving an optimal formulation and stable emulsion. Presently, these matters have not been extensively investigated for this type of emulsions; only limited studies exist where the effect of temperature on non-aqueous emulsions has been analysed (Reichmann and Petersen, 1973), or rheological behaviour has been studied to determine optimization for specific systems (Cameron and Sherrington, 1996; Ha and Yang, 2000).

For years, the main destabilization mechanisms of numerous aqueous emulsions have been studied extensively using various techniques (Schramm, 2005; Tadros, 2013). However, investigations into unconventional emulsions, like the ones under consideration, are notably limited and nearly absent. It is known solely that the Ostwald ripening process plays a significant role in the stability of these non-aqueous emulsions. This phenomenon has been found to occur considerably faster than in aqueous systems due to the higher (albeit still low) solubility of oils in non-aqueous polar solvents (Cameron and Sherrington, 1996; Imhof and Pine, 1997a).

In conclusion, these types of systems hold great promise in numerous applications, yet their utilization remains limited due to the lack of studies in this field. This highlights the necessity to promote research endeavours that contribute to the development of literature and understanding in this area.

II/4.4. Non-Aqueous Phase Change Emulsions

Research on non-aqueous emulsions of phase change materials (non-aqueous PCMEs) represents entirely uncharted territory, particularly when juxtaposed with conventional water-in-oil or oil-in-water. However, these oil-in-oil PCMEs could offer significant advantages in applications requiring thermal energy storage, such as building heating and cooling systems, solar thermal energy systems, and industrial processes. Unlike existing

aqueous PCM formulations, which often utilize water as either the main component of the continuous phase (Chatterjee et al., 2017; L. Huang et al., 2010) or the dispersed phase (Ji et al., 2021), oil-in-oil PCMEs have the potential for improved chemical and thermal stability, as well as a wider operational temperature range.

Future technological advancements are aimed at developing complex structured fluids capable of functioning in single-stage refrigeration systems operating at temperatures as low as -45 °C or Ultra Low Temperature (ULT) freezers reaching down to -100 °C (Li et al., 2019). Utilizing non-aqueous PCMEs, based on carrier fluids with low freezing temperatures, presents a promising approach to addressing this challenge. However, the current lack of research in this area highlights the need for further exploration from both technological and scientific perspectives.

Similarly, in high-temperature applications, the use of PCMEs could be a promising approach for thermal energy storage and heat transfer in various practical applications, including solar thermal capture, waste heat recovery or thermal management of electronic systems. However, like their counterparts in cold energy applications, the reliance on water-based dispersions poses limitations on the upper-temperature range. Despite this limitation, the direct utilization of PCMs with phase change temperatures in medium to high-temperature ranges (100-300 °C) and high temperatures (>300 °C) is widely practised (Kenisarin, 2010). These systems play a crucial role not only in energy recovery but also in acting as a temperature regulator in chemical reactions, improving temperature distribution in the reactor, and mitigating temperature fluctuations. Consequently, a significant challenge lies in developing emulsions suitable for highly efficient thermal solar collectors, industrial waste heat recovery, and similar applications (Wang and Zhai, 2010).

Furthermore, oil-in-oil PCMEs hold potential applications in the lubrication industry. Traditional lubricating emulsions are commonly employed in milling, threading, or bearings, where high-pressure and temperature conditions can lead to metal oxidation and deformation during work. Consequently, a significant challenge for lubricating emulsions is to expand the operational range to enable lubrication in environments requiring extreme temperatures. Moreover, considering that lubrication involves the formation of a lubricating film between moving contact surfaces, some oil-in-oil emulsions (without phase change) have been proposed as capable of achieving suitable lubricating film thickness (Forbus, 2004). What's more, incorporating a PCM as the dispersed phase in

oil-in-oil emulsions could introduce new and intriguing functional properties to these lubricants. As suggested by (Lerasle et al., 2016) for aqueous emulsions, PCM could absorb heat generated during lubrication, particularly in engine operations, thereby attenuating peak in-service temperatures and prolonging lubricant lifespan. These innovative non-aqueous PCMEs may offer improved heat transfer (cooling) characteristics, enhancing their overall performance in lubrication applications.

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Chapter III: Materials and Methods

III/1. Materials

III/1.1. Continuous phase

Silicone Oil

All the emulsions formulated in this work employed silicone oil, specifically for industrial use (polydimethylsiloxane, viscosity 0.1 Pa·s at 25 °C) supplied by Esquim S.A. (Spain), as the continuous phase. The linear polymer backbone end-capped with trimethylsilyl groups consists of alternating silicon and oxygen atoms with methyl attached to the tetravalent silicon centres (Fig. 6). Renowned for its exceptional physicochemical properties, silicone oil serves as an outstanding carrier fluid. Its attributes include high stability, both chemically and thermally, along with low viscosity (Somasundaran et al., 2006). Furthermore, its commendable heat-transfer characteristics make it widely employed in various applications, such as heating baths, diffusion pumps, and oil-filled heaters.

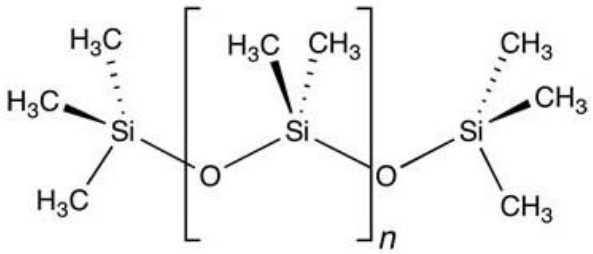


Fig. 6. Generalised chemical structure of silicone oil.

III/1.2. Disperse phase

Polyethylene glycol 4000

Polyethylene glycol 4000 (PEG4000), with an average molecular weight of 4000 g/mol (range: 3500–450 g/mol), was supplied by Panreac Química S.A. (Spain). Its remarkable latent heat fusion, approximately 165 kJ/g, coupled with a melting peak temperature of 58-61 °C, makes it highly suitable as the PCM of encapsulated PCSs for various applications of thermal energy storage and temperature regulation (Sun et al., 2021). Additionally, PEG 4000 (Fig. 7) was selected in the past for some emulsions due to its chemical and thermal stability, nonflammability, non-toxicity, non-corrosiveness, and cost-effectiveness (Jang et al., 2015; Sharma et al., 2015). These attributes, alongside its

viscosity and solubility characteristics, make it particularly suitable for pharmaceutical and healthcare applications too (D'souza and Shegokar, 2016; Fruijtier-Pölloth, 2005; Mojsiewicz-Pieńkowska, 2015; Schalau and Aliyar, 2015).

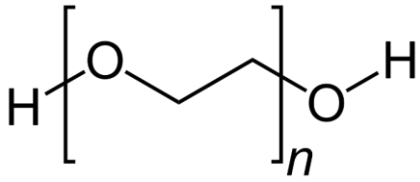


Fig. 7. Generalised chemical structure of PEG.

Stearic Acid

Stearic acid, obtained from Sigma-Aldrich (Spain), was also used as a disperse phase in the PCMEs formulated in this thesis. With a melting point of 69 °C, it boasts a high latent heat of fusion, around 199 kJ/kg, comparable to that of paraffin (Sharma et al., 2009). The latter makes stearic acid a promising candidate for latent heat storage systems. Notably, its melting temperature and latent heat of fusion exhibit minimal variation over thermal cycles, indicating excellent thermal reliability (Chaudhari et al., 2013; Masoumi et al., 2019). Its phase change temperature, approximately 69 °C, makes it suitable for medium-temperature applications like solar air heaters or solar domestic hot water systems (Du et al., 2018; Wen et al., 2018). In addition, stearic acid is a safe, cheap, and environmentally friendly PCM fatty acid (Fig. 8).

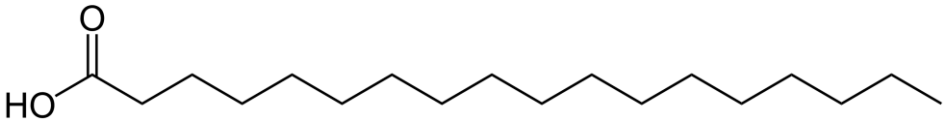


Fig. 8. Chemical structure of stearic acid.

III/1.3. Surfactant

Formulating stable non-aqueous emulsions involves a significant challenge, primarily due to the limited availability of data regarding suitable surfactants for such systems. The absence of guidelines for surfactant selection to stabilize immiscible non-polar oils has led to extensive testing of various surfactant types before achieving stable formulations.

Initially, four conventional low molecular weight non-ionic surfactants were evaluated: Span 20 (hydrophilic–lipophilic balance (HLB) = 8.6), Tween 20 (HLB = 16.7), Polysorbate 80 (HLB = 15), and Cremophor® ELP (HLB = 12–14), procured from

Sigma Aldrich. Despite their proven efficacy in oil-in-water emulsions, these surfactants failed to stabilize the non-aqueous emulsions, resulting in rapid phase separation.

Subsequently, silicone-based surfactants, characterized by a comb-like structure with pendant groups attached along the polydimethylsiloxane main chain, were investigated. Initially, these surfactants appeared promising due to their high molecular weight, which promotes steric hindrance in such systems, and their silicone backbone, which enhances miscibility in the continuous phase.

Three high-performance silicone surfactants, kindly provided by Dow Corning Corporation (Midland, USA), went under study: **DOWSIL™ ES-5300** (Lauryl PEG-10 Tris(Trimethylsiloxy)silylethyl Dimethicone; HLBcalculated = 3), **DOWSIL™ 5225C** (Cyclopentasiloxane (and) PEG/PPG-18/18 Dimethicone; HLBcalculated = 2) and **DOWSIL™ ES-5226 DM** (Dimethicone (and) PEG/PPG-18/18 Dimethicone; HLBcalculated = 2). These surfactants were evaluated within the PEG4000/silicone oil system, with particular emphasis on their interaction and performance. Among these candidates, **DOWSIL™ ES-5226 DM** emerged as the most effective, boasting a structure similar to that represented in Fig. 9 with PEG and PPG groups grafted onto a polydimethylsiloxane backbone.

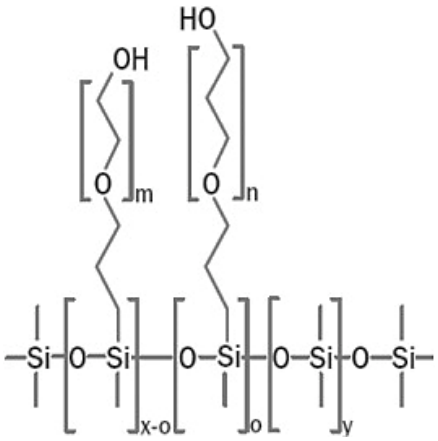


Fig. 9. Example of the comb-like structure of silicone surfactants.

Another silicone emulsifier, **ABIL CARE XL 80** (Bis-PEG/PPG-20/5 PEG/PPG-20/5 Dimethicone (and) Methoxy PEG/PPG-25/4 Dimethicone (and) Caprylic/Capric Triglyceride; calculated HLB = 11), graciously provided by Evonik Nutrition & Care GmbH (Germany), emerged as a notable addition to the investigation. Comprising approximately 82% silicone polyether-based emulsifiers and 18% Caprylic/Capric Triglyceride, this surfactant was subjected to rigorous testing alongside the previously

mentioned candidates. Upon evaluation, ABIL CARE XL 80 demonstrated exceptional performance, showcasing its potential to optimize the stearic acid/silicone oil system.

This outcome highlights the importance of comprehensive surfactant selection and underscores the intricate interplay between molecular composition and emulsion stabilization.

III/2. Experimental procedures

III/2.1. Phase change emulsion preparation

The preparation of all non-aqueous PCMEs takes place with the incorporation of the PCM into silicone oil using a rotor-stator homogenizer Ultra-Turrax T25 (IKA, Germany) operating at 20000 rpm (Fig. 10). This process occurred at a temperature exceeding the melting point of the PCM and involved the utilization of an emulsifier.



Fig. 10. Ultraturrax™ T25 digital high shear mixer and dispersing accessory.

Emulsions with varying amounts of dispersed phase and surfactant were systematically prepared to investigate their impact on emulsion characteristics. It is noteworthy that the selection of surfactant concentration in each system was based on its demonstrated stabilizing properties across all emulsions following preliminary assessments. Moreover, independently of those studies in which the effect of the amount of surfactant in the systems is analysed, the amount of surfactant was selected to be the lowest amount able to keep the system highly stable.

The standard procedure for preparing PCMEs involved initially dissolving the surfactant in the continuous phase, silicone oil, at the processing temperature (typically 80 °C). This temperature, set 10 – 20 °C above the phase change temperature of the disperse phase, ensured optimal conditions for emulsion formation. Subsequently, the PCM, preconditioned at 80 °C to ensure its liquid state, was added drop by drop to the pre-prepared solution. The resulting mixture underwent emulsification at 20000 rpm for 10 min using the Ultra-Turrax T25. The resulting emulsions, referred to as fresh emulsions, were designated according to their components and composition.

III/2.2. Stabilisation procedure

Following the preparation outlined in Section III/2.1, certain PEG4000 in silicone oil emulsions underwent a post-treatment process to enhance their stabilization.

The selected fresh emulsions were subjected to post-processing, which involved maintaining them under low-shear agitation at a specific temperature for a certain time. This was achieved using a four-bladed stirrer rotating at 500 rpm, attached to an IKA RW-20 stirring device (Germany) (

Fig. 11).



Fig. 11. IKA RW20 Stirrer and a 50 mm four-bladed impeller.

For further investigation, the effect of the post-processing temperature was explored by conducting it for 24 h at different temperatures: 80 °C, 120 °C, and 150 °C. Additionally, the effect of mixing time was studied by extending the post-processing duration of a chosen emulsion for up to one week at 80 °C. These emulsions were referred to as post-processed emulsions.

III/2.3. Binary mixtures preparation

Binary mixtures comprising all components of the emulsion (continuous phase, dispersed phase, and surfactant) were formulated to investigate their mutual interactions individually. This involved combining each component with the other two separately to analyse how they interacted with each other in the absence of other factors.

These samples were prepared with mass ratios similar to the main formulation studied, mirroring the procedures employed for the preparation of both fresh and post-processed systems.

III/3. Characterisation techniques

For comprehensive insights into the properties of non-aqueous PCMEs, various characterization techniques have been employed. These methods examine the morphological, rheological, tribological, and thermophysical characteristics of these non-aqueous emulsions. They focus on factors such as phase change cycle stability, compound interactions, and modification of disperse phase crystallinity, providing valuable information about emulsion formulation and processing.

III/3.1. Differential scanning calorimetry

Understanding the thermal properties of PCMEs is fundamental for their application. Differential Scanning Calorimetry (DSC) analysis, conducted on both individual phase components of the emulsion and on the PCMEs with different mass fractions, provides critical insights into their suitability for heat storage applications.

DSC is a thermal analysis technique used to measure changes in heat flows associated with material transitions such as melts, glass transitions, phase changes, and curing by measuring the difference in heat flow rate between a sample and an inert reference with temperature. Hence, DSC measurements provide both qualitative and quantitative data on endothermic (heat absorbing) and exothermic (heat evolving) processes.

DSC tests were obtained by using a Q-250 DSC calorimeter (TA Instruments, USA) (Fig. 12). Around 5–10 mg of samples were subjected to the following procedure: (a) a first heating scan from room temperature to 120 °C was carried out to remove the thermal history of the sample; (b) a cooling ramp, to −80 °C; and (c) a second heating ramp, to

the same final temperature used for the first heating scan. The selected conditions were: heating/cooling rates of 10 °C min^{-1} and a flow of 50 mL/min N_2 as the purge gas.



Fig. 12. TA Q-250 differential scanning calorimeter.

The DSC curves show the exothermic crystallisation process and the endothermic melting process of the measured systems. Thus, all thermal events of the emulsions and their pure components were identified, as well as the enthalpy values, the crystallization and melting temperatures and the apparent specific heat and capacities of the samples. The temperature at which the PCM starts to melt was obtained from the point of maximum slope of the leading side of the transition peak and extrapolating the heat flow baseline on the same side (T onset); the temperature peak was the point at which the largest deviation of the heat flow signal from the virtual baseline is measured (T peak) and the enthalpy of the phase change (ΔH) was calculated as the area under the peak by numerical integration. The procedure for obtaining some of these parameters is illustrated in Fig. 13.

All the results are the average of three replications of each one of the three different batches of the emulsions prepared.

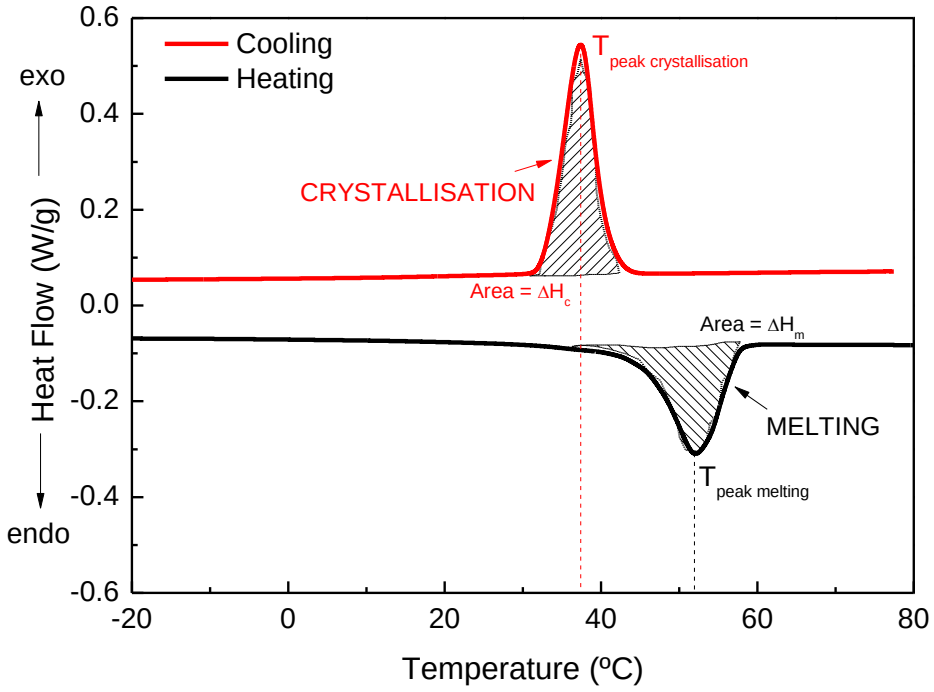


Fig. 13. Standard Exo up Heat Flux DSC Spectrum of a phase change material. The curve shows the exothermic crystallization process and the endothermic melting process.

III/3.2. Rheological characterisation

The rheological behaviour of the PCMEs plays a crucial role in optimizing product performance and characteristics. Rheological properties are closely linked to the final structure of the emulsion, including factors such as disperse phase volume fraction, phase viscosities, droplet size, and stability. Understanding these properties is essential for assessing the suitability of PCME systems as HTF, as they can significantly influence the heat transfer process. Consequently, the rheological characteristics of the PCMEs and their pure component were performed in terms of viscous flow behaviour (which accounts for the material's resistance to flow) and linear viscoelastic properties (related to the material's microstructure when still in an unperturbed state) using different types of rheometers (both controlled-stress and controlled-strain), to assess their stability and applicability.

Before any of the proposed tests, the sample was always allowed to rest and reach equilibrium for at least 15 min at the testing temperature. To ensure accurate rheological results, all the tests were carried out at least twice to ensure the repeatability of the results.

Steady-state tests

Isothermal viscous flow measurements, below the crystallization temperature and above the melting point of the dispersed phase, were carried out in a controlled-strain rheometer Ares-G2 (TA Instruments, USA) equipped with a Couette geometry (cup of 30 mm diameter and bob of 27 mm diameter and 42 mm length) on steady rotational shear mode (Fig. 14). Tests were performed by progressively applying an increasing stepped shear rate ramp from 0.01 to 1000 s^{-1}.

In addition, downward and upward temperature ramps were performed by imposing a 1 °C/min gradient from 90 to 30 °C, at the constant shear rate of 1 s^{-1} to study the evolution of the apparent viscosity during the phase change process.

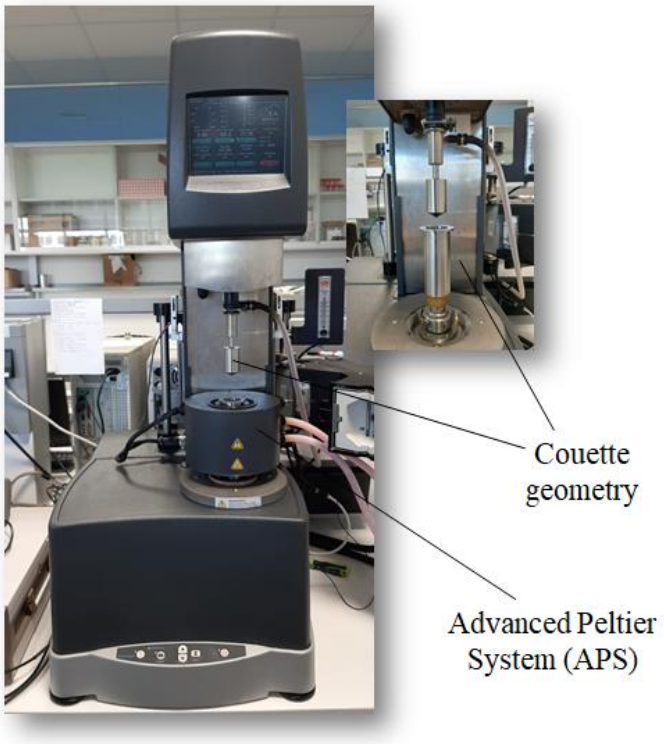


Fig. 14. Setup and detail of the strain-controlled rheometer equipped with an Advanced Perlier System and a Couette geometry.

Dynamic tests

Small-amplitude oscillatory shear (SAOS) tests were conducted to obtain information about the developed microstructure of the PCMEs, especially after the crystallization of the disperse phase. Indeed, characterizing the dynamic viscoelastic moduli within the linear viscoelastic region offers valuable insights into the structural integrity of the system under non-destructive conditions.

Those properties of the PCMEs were investigated using the Physica MCR501 controlled-stress rheometer (Anton Paar, Austria), featuring a Peltier temperature controller for

precise thermal regulation (Fig. 15). Initially, stress sweep tests at 1 Hz were conducted to determine the linear viscoelastic range (LVR), covering a stress range from 0.01 to 5000 Pa. Subsequently, SAOS frequency sweep tests were performed within the established LVR, ranging frequencies from 0.03 to 100 rad/s.



Fig. 15. Setup of the Physica MCR501 controlled-stress rheometer.

Tests were carried out over a temperature range of 30 °C to 90 °C, with incremental temperature steps of 5-10 °C. To ensure consistency across measurements and minimize the wall-slip effect, SAOS tests were uniformly conducted using the rheometer equipped with serrated plate-plate geometry (1 mm gap and 50 mm diameter).

Rheo-SALS tests

Rotational rheological measurements were duplicated for selected PCMEs, employing Small-Angle Light Scattering (SALS) analysis. This approach aimed to comprehend the significant viscosity and microstructural changes observed in the emulsions after the phase transition of the PCM, in the two types of rheological tests explained previously.

This method enabled the observation of significant fluctuations in sample density and orientation, as well as the impact of deformation direction on the behaviour of the emulsion's dispersed phase within the shear field during phase transition. The Rheo-SALS system was integrated with the above-mentioned Anton Paar MCR 501 rheometer, featuring a specially designed glass plate-plate geometry (PP43/GL-HT) with a gap of

0.188 mm. A laser beam with a wavelength of $\lambda = 658$ nm illuminated the sample vertically between crossed polarizers, interacting with the crystallizing sample's microstructure and causing scattering. The scattered light, transmitted through the sample, was captured on a screen and recorded using a CCD camera. This scattering was angle-dependent, allowing for polarized and depolarized measurements. A scheme of the Rheo-SALS system setup can be seen in Fig. 16.

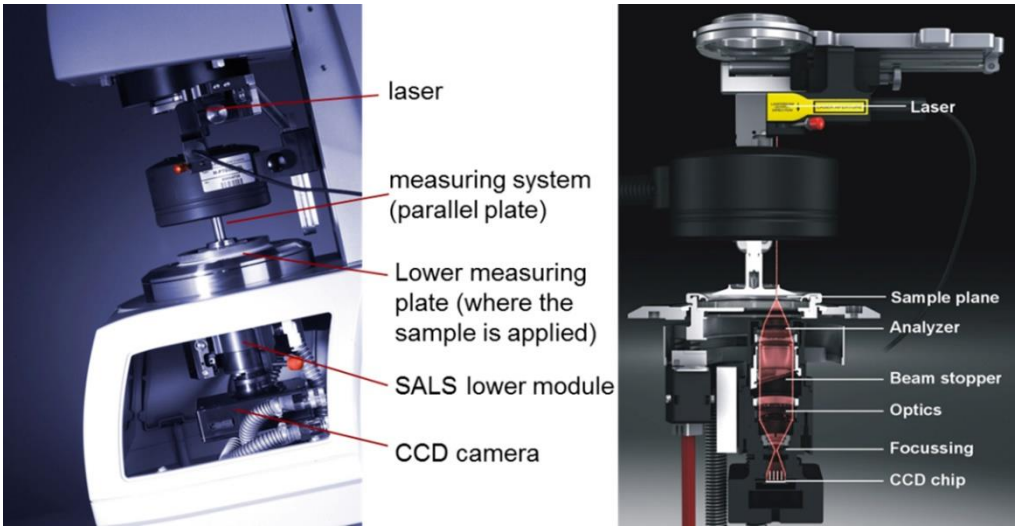


Fig. 16. Rheo-SALS setup (Läuger, 2006).

III/3.3. Tribological measurements

Tribology is a field crucial for assessing emulsion lubricating properties, wear resistance and friction behaviour. By studying how emulsions interact with surfaces under different conditions, we gain insights into their suitability for various applications, such as lubrication in machinery or reducing friction in mechanical systems. Tribological analyses help evaluate the performance and durability of emulsions in real-world scenarios, ensuring their effectiveness and longevity in practical applications.

Tribological properties of the formulated PCMEs were evaluated in the aforementioned Physica MCR 501 controlled-stress rheometer coupled with a ball-on-three-plates tribological cell (detailed in Fig. 17).

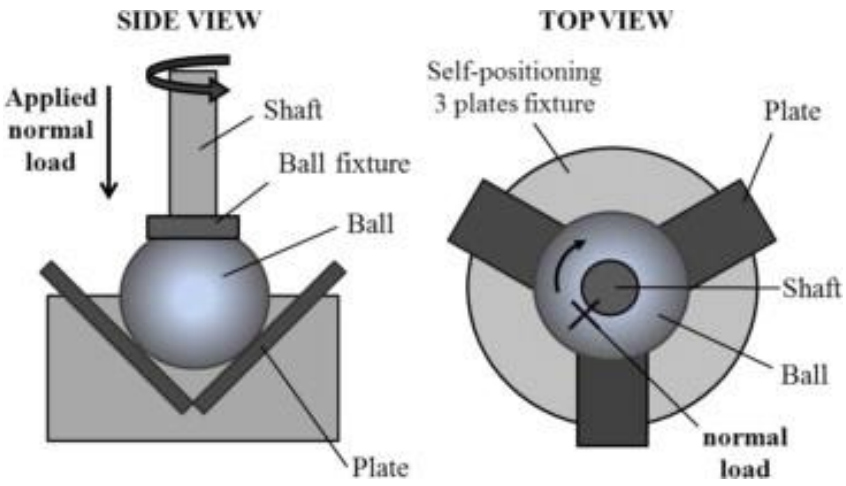


Fig. 17. Schematic representation of the tribology cell (Martín-Alfonso and Valencia, 2015).

The experimental configuration involves a lower measuring geometry with three 45°-inclined steel plates (1.4301 AISI 304, 0.21 μm roughness, 80 HRB hardness) where the PCMEs were positioned. Additionally, an upper measuring geometry includes a fixed 6.35 mm-radious bearing ball (1.4401 grade 100 AISI 316). This arrangement, known as the ball-on-three-plates configuration, enables the friction coefficient (μ) determination. This coefficient is calculated as the ratio between the applied normal force (F_N) and the measured friction force (F_F) (see Equation 1).

$$\mu = \frac{F_F}{F_N} \qquad (1)$$

Therefore, the stationary friction coefficient of all formulated stearic acid-in-silicone oil PCMEs on steel-steel contact was evaluated over time at constant temperatures (both below and above the phase change temperature of the dispersed phase), using a normal force of 20 N and a rotational speed of 10 rpm. This specific sliding velocity was chosen to ensure comparability of the stationary friction coefficients among the different emulsions under the same test conditions.

Furthermore, tribological heating and cooling temperature ramps were conducted, ranging from 40 to 100 °C and vice versa, while applying a constant normal force of 20 N and a heating/cooling rate of 1 °C·min^{-1}. Each tribological experiment was repeated at least five times using fresh samples, with a measurement duration of 120 s per data point to ensure stable friction values.

III/3.4. Microstructural characterisation

Microstructural characterization techniques, such as optical microscopy and X-ray diffraction (XRD), are essential for providing detailed knowledge of the morphology and phase distribution of materials. On the one hand, optical microscopy allows for the visualization of the microstructure of samples at a microscopic level, enabling the observation of features such as particle/droplet size, shape, and distribution within the PCMEs. This technique is particularly useful for examining the physical structure of emulsions and identifying any changes that may occur during processing or storage.

On the other hand, XRD is a powerful tool for analysing the crystalline structure of materials. By exposing a sample to X-ray radiation, XRD measures the diffraction pattern produced by the sample's atomic arrangement. This information can be used to determine the presence of crystalline phases, their orientation, and their degree of crystallinity. In the context of PCMEs, XRD can be employed to investigate the crystalline structure of the dispersed phase, providing valuable data on its thermal behaviour and phase transitions.

Morphological characterisation

Optical microscopy was used to study the morphology and microstructure of the emulsions. This technique uses visible light and a system of lenses to magnify images of small samples, and thus, it can be used as above mentioned to determine the shape, size and size distribution of microscopically dispersed particles, droplets or aggregates, reaching resolutions in the order of 0.5 μm.

In this case, microphotographs for microstructural characterisation of the PCMEs were taken using a polarized light optical microscope (PLOM) Olympus BX52 (Japan) with a digital camera Olympus C5050Z (objectives of 10x and 20x) and coupled with an LTS-350 Heating-Freezing Stage controlled by a Linkam TP94, manufactured by Linkam Scientific Instruments (UK). The whole setup can be observed in Fig. 18.

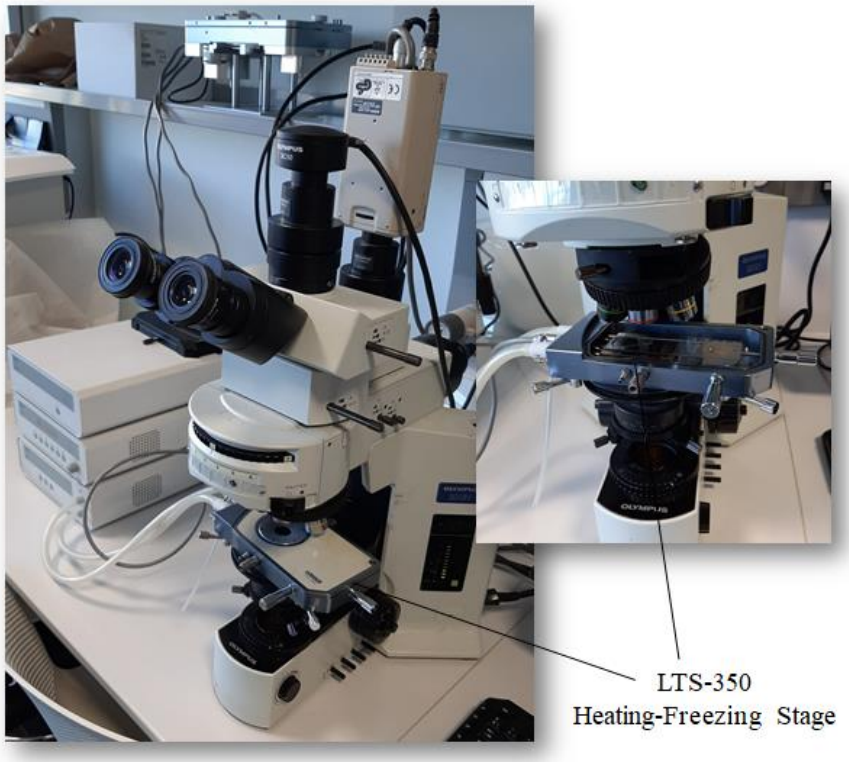


Fig. 18. Setup and detail of the optical microscope equipped with Heating-Freezing Stage.

Optical images of samples were obtained under ordinary and cross-polarized light at different temperatures, ranging from 20 to 90 °C, so that their properties at temperatures above and below the melting point can be observed. The cross-polarised light does show the appearance of birefringent bright regions that indicate the formation of crystals in the sample. In Fig. 19, an example is shown of a micrograph taken under polarized light. In this image, all the bright areas correspond to the crystalline structure of stearic acid at room temperature. This visual effect of brightness is due to the interaction of polarized light with the crystalline structures of stearic acid.

Samples were carefully poured onto a sample holder (76 × 26 mm) and spread under a glass coverslip at temperature over the melting point and then conditioned to the measurement temperatures, to avoid the alteration of the crystalline structures in the sample preparation. The droplet size of the emulsions was determined from the analysis of the diameter of a minimum of 100 emulsion droplets using ImageJ software. Droplet size values have been reported as means ± standard deviation statistically determined by analysis of variance (ANOVA, $p < 0.05$) employing the statistical package SPSS 18.

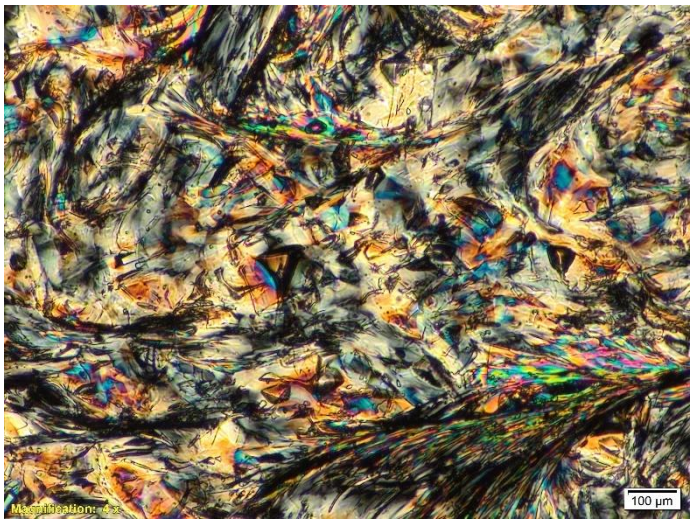


Fig. 19. Micromorphology of pure stearic acid at 30 °C under cross-polarised light.

X-ray Diffraction (XRD)

X-ray crystallography is a technique used for the identification of crystalline phases of various materials and the quantitative phase analysis after the identification. The properties and functions of materials largely depend on the crystal structures. In this technique, an X-ray beam passes through the crystals of the substance under study. The beam is scattered in several directions due to the symmetry of the grouping of atoms and, by diffraction, gives rise to a pattern of intensities. This pattern can be interpreted according to the location of the atoms in the crystal, applying Bragg's law (Kacher et al., 2009).

The crystal structure of stearic acid pure and the phase change stearic acid/silicone oil emulsions were analysed using a D8 Advance X-ray diffractometer (Fig. 20) (Bruker-AXS, Germany) at room temperature (25 °C). The X-ray diffraction pattern was obtained under the following instrumental conditions: 30 mA, 40 kV, angle 2θ: 4° and 59.9°, step size = 0.019°. A copper Kα/K target (λ = 1.54) was used for the generation of the X-rays. All the samples were prepared by placing a small amount on a supporting glass slide of 25 × 25 mm^2, which was heated over stearic acid melting temperature (80 °C) to flatten and obtain approximately 1 mm thick followed by a cooling to room temperature. Afterwards, the sample-containing slide was located at the centre of a metal holder, externally shaped to be allocated in the instrument.



Fig. 20. D8 Advance X-ray diffractometer.

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Chapter IV: Results and Discussion

Chapter IV: Results and Discussion

Algunos de los trabajos científicos publicados, debido a restricciones relativas a derechos de autor, han sido retirados de la tesis. En sustitución de los documentos ofrecemos la siguiente información: referencia bibliográfica, enlace al texto completo y resumen.

- Delgado Sánchez, C., Cuadri Vega, A. A., Navarro Domínguez, F. J. & Partal López, P. (2021). Formulation and processing of novel non-aqueous polyethylene glycol-in-silicone oil (o/o) phase change emulsions. Solar Energy Materials and Solar Cells, 221, 110898. DOI: https://doi.org/10.1016/j.solmat.2020.110898

Enlace al texto completo: https://doi.org/10.1016/j.solmat.2020.110898

Resumen:

Oil-in-oil phase change emulsions, composed of phase change materials (PCMs) dispersed in a continuous oily medium, have never been reported in the literature. The current study involves the formulation, stabilisation and characterisation of novel anhydrous emulsions of polyethylene glycol (PEG4000) as PCM in silicone oil. Emulsions with different dispersed phase concentrations were evaluated by analysing the viscous flow properties, optical microscopy and modulated differential scanning calorimetry. The results evidence that the emulsions can be pre-stabilised at 80 °C, under high shear conditions, by selecting an adequate silicone surfactant but undergo a severe destabilisation after a cooling and heating cycle. Nevertheless, a post-processing protocol (low shear agitation at 80 °C for 24 h) leads to thermal cycle resistant and storage stable non-aqueous dispersions. This process gives rise to a reduction of the shear-thinning character of the emulsion, shifts the melting and crystallization temperature of the PEG4000 to lower values and reduce its crystallinity. This is attributed to partial compatibility of the crystalline fraction of PEG4000 with other compounds of the emulsion.

- Delgado-Sánchez, C., Partal, P., Martín-Alfonso, M. J., & Navarro, F. J. (2021). Role of crystallinity on the thermal and viscous behaviour of polyethylene glycol-in-silicone oil (o/o) phase change emulsions. In Journal of Industrial and Engineering Chemistry (Vol. 103, pp. 348–357). Elsevier BV. https://doi.org/10.1016/j.jiec.2021.08.003

Enlace al texto completo: https://doi.org/10.1016/j.jiec.2021.08.003

Resumen:

Stable polyethylene glycol-in-silicone oil phase change emulsions were successfully prepared with a selected silicone surfactant. These oil-in-oil (o/o) emulsions have been scarcely examined up, despite the highly remarkable properties of both phases for energy recovery applications and cosmetic/pharmaceutical compositions. The objective

of the present work was to study the effect of composition (surfactant and disperse phase concentrations) and the post-processing conditions (further agitation at the processing temperature for 24 h) on the final features of the emulsion. For this purpose, optical morphology, thermo-physical and the rheological behaviour of the emulsions and binary blends of their compounds were measured and analysed. Special attention has been paid to structural changes and crystallinity modifications of the emulsion disperse phase. The observed miscibility of the silicone surfactant and silicone chains with the disperse phase reduces its crystallinity degree and modifies in the crystallization mechanism of the polyethylene glycol, from heterogeneous to homogeneous nucleation. Interestingly, the change in the disperse phase crystallinity remarkably modifies final thermal and rheological properties of the emulsion.

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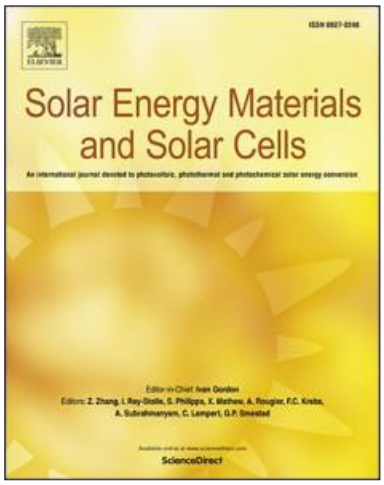
IV/1. Article 1

Formulation and processing of novel non-aqueous polyethylene glycol-in-silicone oil (o/o) phase change emulsions

Clara Delgado-Sánchez, Antonio Abad Cuadri, Francisco Javier Navarro, Pedro Partal

Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS), Universidad de Huelva, Campus de "El Carmen", 21071, Huelva, Spain

Published in:



SOLAR ENERGY MATERIALS AND SOLAR CELLS
Publishing company: ELSEVIER
Editor-in-Chief: Ivan Gordon
Volume 221, 110898
Year 2021
ISSN 0927-0248
DOI 10.1016/j.solmat.2020.110898
Impact Factor (2021) 7.305

Category	***Journal rank/Total journals***	***Quartile***
MATERIALS SCIENCE, MULTIDISCIPLINARY	*83/345*	*Q1*
PHYSICS, APPLIED	*29/161*	*Q1*

IV/2. Article 2

Role of crystallinity on the thermal and viscous behaviour of polyethylene glycol-in-silicone oil (o/o) phase change emulsions

Clara Delgado-Sánchez, Pedro Partal, María José Martín-Alfonso, Francisco Javier Navarro,

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Published in*:*



Journal of Industrial and Engineering Chemistry
Publishing company: ELSEVIER
Editor-in-Chief: Jun Yeob Lee
Volume 103, 348-357
Year 2021
ISSN 1226-086X
DOI 10.1016/j.jiec.2021.08.003
Impact Factor (2021) 6.760

Category	***Journal rank/Total journals***	***Quartile***
ENGINEERING, CHEMICAL	*23/142*	*Q1*

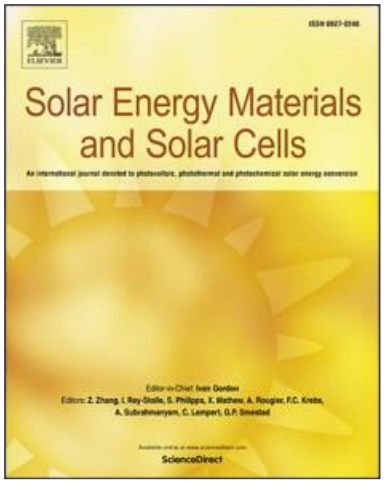
IV/3. Article 3

Oil-in-Oil emulsions of stearic acid dispersed in silicone oil with enhanced energy storage capability for heat transfer fluids

Clara Delgado-Sánchez, Pedro Partal, María José Martín-Alfonso, Francisco Javier Navarro,

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Published in*:*



SOLAR ENERGY MATERIALS AND SOLAR CELLS
Publishing company: ELSEVIER
Editor-in-Chief: Ivan Gordon
Volume 245, 111893
Year 2022
ISSN 0927-0248
DOI 10.1016/j.solmat.2022.111893
Impact Factor (2022) 6.900

Category	***Journal rank/Total journals***	***Quartile***
MATERIALS SCIENCE, MULTIDISCIPLINARY	*80/344*	*Q1*
PHYSICS, APPLIED	*26/160*	*Q1*

Solar Energy Materials & Solar Cells 245 (2022) 111893

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Oil-in-Oil emulsions of stearic acid dispersed in silicone oil with enhanced energy storage capability for heat transfer fluids

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ARTICLE INFO

Keywords:
Non-aqueous emulsion
Phase change material (PCM)
Phase change material emulsion (PCME)
Rheology
Stability

ABSTRACT

Non-aqueous phase change emulsions are very unknown and promising multifunctional fluids consisting of phase change materials dispersed in carrier fluids, both being oily phases. The oil-in-oil phase change emulsions allow the possibility of using the same medium for latent heat storage and transport under more extreme pressure and temperature conditions. In this paper, stable emulsions composed of stearic acid with a melting point of 68–71 °C dispersed in silicone oil have been developed. Stearic acid-in-silicone oil emulsion samples with different phase concentrations were evaluated by analysing their thermophysical properties, viscous and viscoelastic behaviour and microstructure. Emulsion properties below the melting point of the phase change material were greatly influenced by the concentration of the disperse phase. Thus, as the temperature lowered, a well-developed three-dimensional network of stearic acid crystalline structures interconnected with each other was formed. Furthermore, emulsion physicochemical and thermal stabilities were examined and proved under several mechanical–thermal cycles, withstanding more than 100 cycles in the calorimeter. The results indicate that stearic acid-in-silicone oil emulsions are an attractive candidate for energy storage applications with a phase change enthalpy in emulsions with the 10 wt% of phase change material of 22.32 J/g.

1. Introduction

Thermal energy storage (TES) systems are widely used worldwide for efficient utilization and conservation of off-peak power, waste heat and intermittent energy sources, cleverly exploiting clean energy resources and decreasing energy consumption [1,2]. An efficient, attractive and innovative method of storing thermal energy storage is latent heat storage. Then, the so-called phase change materials (PCMs) use the latent heat of the phase transition to quickly store and release a large amount of energy during the phase changing process, at a constant temperature [3,4]. Thus, PCMs have recently received considerable attention as they substantially contribute to harvest cheap and clean energy from waste heat sources and solar energy, for direct uses or converting to electricity [5,6]. In addition, they also present the potential for effective heat management in various applications such as building, industry or electronic devices [7]. Furthermore, PCMs can be added to conventional heat transfer fluids (HTFs), obtaining latent functionally thermal fluids that exhibit a higher specific heat storage capacity than conventional HTFs. Therefore, they show promising applications in many fields of renewable energy conversion, production, and storage since they remain in a fluid state throughout the phase change process, allowing for easy pump transportation and circulation in the energy storage systems [8–10].

In general, four broad categories are used to classify the thermal fluids that work with latent heat: (1) ice slurries, i.e., mixtures of ice particles and an aqueous solution; (2) clathrate hydrate slurries (CHSs); (3) microencapsulated PCM slurries (MPCMSs), in which the PCM encapsulated into microcapsules and further dispersed into HTFs; and (4) phase change material emulsions (PCMEs), which are formed by dispersing PCM droplets into the continuous phase, usually water, with the help of the surfactants that reduce the interfacial tension between the two phases [11]. The PCMEs, compared with the others PCM systems, show greater potentials and present several advantages, including a simple preparation process, negligible thermal resistance, good operation stability and low cost, which make them an excellent HTF.

Most of the PCME existing literature used as novel HTFs are manufactured by incorporating PCMs into water with the aid of emulsifiers [12–14]. However, the aim of this work is to develop PCMEs by using two non-aqueous phases for thermal energy storage application, of which, to the best of our knowledge, little work has been done so far. In the literature, there are some studies of non-aqueous emulsions

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https://doi.org/10.1016/j.solmat.2022.111893
Received 1 March 2022; Received in revised form 2 June 2022; Accepted 11 July 2022
Available online 17 July 2022
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Nomenclature

English Letter

T	temperature (°C)
G′	loss modulus (Pa)
G″	storage modulus (Pa)
n	flow index (−)
Ks	consistency index (Pa s^n)
R^2	coefficient of determination
ST	stearic acid
SO	silicone oil

Abbreviation

TES	thermal energy storage
PCM	phase change material
HTF	heat transfer fluid
CHS	clathrate hydrate slurries
MPCM	microencapsulated PCM slurries
PCME	phase change material emulsion
DSC	differential scanning calorimetry
HLB	hydrophilic-lipophilic balance
SAOS	small-angle light scattering
PLOM	polarized light optical microscope

Greeks

λ	wavelength (nm)
ΔH	enthalpy change (J/g)
η	viscosity (Pa s)
$\dot{\gamma}$	shear rate (s^{-1})

Subscripts

m	melting
c	crystallization

especially for cosmetic and pharmaceutical applications [15,16] and other uses covering crystallization processes within emulsified systems, especially in the food industry [17,18]. However, there is almost no research concerning non-aqueous PCMEs as latent functionally HTFs. Only recently, the authors have begun to study and develop anhydrous PCMEs in previous work [19,20], facing the lack of information regarding the availability of suitable surfactants in such systems and pointing out the difficulty in developing such systems. In that sense, these previous works noted the importance of a good selection of immiscible phases, since a partial compatibility of the phases would mean a loss of their energy storage properties.

These almost totally unknown non-aqueous phase change emulsions would not only present the advantages that slurries bring to heat transfer applications, such as the possibility of using the same medium for transport and storage, the high heat transfer rate due to the increase of the specific surface area of the PCM or the easy of pumping transportation and circulation [9], but also all those related to the use of oily phases, making a difference. Thus, anhydrous PCMEs would allow the transport mass and heat in systems where the pressure and temperature conditions are more extreme [21], those systems could withstand much higher temperature and pressure peaks than current aqueous systems without being degraded. Moreover, they will provide a better long term chemical stability. And, additionally, this study of non-aqueous phase change emulsions will lay the groundwork for the use of PCME in applications with phase change temperatures above 100 °C, offering the advantage of the emulsions to applications where the current water-based dispersions have been restricted due to the upper temperature limit. Therefore, this work can be considered as preliminary work for the next major challenge, the development of emulsions that can be used in high efficient thermal solar collectors (100 °C), industrial heat recovery (<150 °C) [22], and low and intermediate temperature solar collection systems (100-250 °C) [23].

Before going any further, it is worth noting that emulsion cooling below the disperse phase melting point will lead to droplets solidification and, therefore, the formation of a suspension of solid particles. Even though it would be more accurate to call them dispersions (being emulsions above the disperse phase melting point and suspensions below the crystallization temperature), the term phase change material emulsion (PCME) is widely accepted in the literature and will be used throughout this study.

In this work, novel non-aqueous emulsions prepared with stearic acid and silicone oil were explored for developing PCMEs. Stearic acid is a very promising PCM for latent heat storage systems since its variation in both melting temperature and latent during repeated heating/cooling cycles in service is negligible and, therefore, shows a good thermal reliability as PCM [24,25]. Moreover, its phase changing temperature of around 69 °C makes it suitable for applications in the medium temperature range such as solar air heater, solar domestic hot water systems, flat-plate solar collectors, etc. [3,26]. In addition, stearic acid is a safe, cheap, and environmentally friendly PCM fatty acid. On the other hand, silicone oil has been selected as a continuous phase because it is highly stable (chemically and heat resistant) and presents a low viscosity [27].

With this aim, a comprehensive investigation of the thermorheological characteristics of stearic acid-in-silicone oil emulsions stabilized using a silicone surfactant has been carried out. Firstly, the thermophysical properties of the emulsion to secure their applicability for thermal energy storage were evaluated. Secondly, the viscous and viscoelastic behaviour were studied on the basis of the obtained rheological properties and finally, the microstructure was also examined.

2. Materials and methods

2.1. Materials

Non-aqueous stearic acid-in-silicone oil (o/o) phase change emulsions are dispersions of stearic acid droplets in silicone oil stabilized by a selected surfactant. Stearic acid (melting point of 69 °C) was purchased from Sigma-Aldrich (Spain) and a selected industrial silicone oil, ESQUIM FH-100, (polydimethylsiloxane, viscosity 0.1 Pa s at 25 °C) was supplied by Esquim S.A. (Spain). The emulsion was stabilized by a silicone-based non-ionic emulsifier, ABIL Care XL80 (Bis-PEG/PPG-20/5 PEG/PPG-20/5 Dimethicone (and) Methoxy PEG/PPG-25/4 Dimethicone (and) Caprylic/Capric Triglyceride; $HLB_{calculated} = 11$), which was kindly supplied by Evonik Nutrition & Care GmbH (Germany).

2.2. Sample preparation

Non-aqueous dispersions were prepared according to the method detailed elsewhere [19], i.e. mixing all the components of the emulsions by a high shear rotor-stator homogeniser, at 80 °C. The emulsions were prepared at the stearic acid/silicone oil (i.e. disperse/continuous phase) weight ratios of 1/99, 5/95 and 10/90, while keeping the surfactant/-disperse phase weight ratio constant at 1/10. Fig. S2 shows a likely structural formulation of the surfactant and its possible stabilisation mechanism in the present emulsion. It is worth mentioning that such a concentration of surfactant was selected thanks to a pre-study where the lowest possible amount of surfactant to maintain a highly stable system was selected. The minimisation of the amount of surfactant was carried out because there was evidence in several studies with others PCMEs that the surfactant presence can reduce the crystallinity of the dispersed

Nomenclature

English Letter

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Greeks

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especially for cosmetic and pharmaceutical applications [15,16] and other uses covering crystallization processes within emulsified systems, especially in the food industry [17,18]. However, there is almost no research concerning non-aqueous PCMEs as latent functionally HTFs. Only recently, the authors have begun to study and develop anhydrous PCMEs in previous work [19,20], facing the lack of information regarding the availability of suitable surfactants in such systems and pointing out the difficulty in developing such systems. In that sense, these previous works noted the importance of a good selection of immiscible phases, since a partial compatibility of the phases would mean a loss of their energy storage properties.

These almost totally unknown non-aqueous phase change emulsions would not only present the advantages that slurries bring to heat transfer applications, such as the possibility of using the same medium for transport and storage, the high heat transfer rate due to the increase of the specific surface area of the PCM or the easy of pumping transportation and circulation [9], but also all those related to the use of oily phases, making a difference. Thus, anhydrous PCMEs would allow the transport mass and heat in systems where the pressure and temperature conditions are more extreme [21], those systems could withstand much higher temperature and pressure peaks than current aqueous systems without being degraded. Moreover, they will provide a better long term chemical stability. And, additionally, this study of non-aqueous phase change emulsions will lay the groundwork for the use of PCME in applications with phase change temperatures above 100 °C, offering the advantage of the emulsions to applications where the current water-based dispersions have been restricted due to the upper temperature limit. Therefore, this work can be considered as preliminary work for the next major challenge, the development of emulsions that can be used in high efficient thermal solar collectors (100 °C), industrial heat recovery (<150 °C) [22], and low and intermediate temperature solar collection systems (100-250 °C) [23].

Before going any further, it is worth noting that emulsion cooling below the disperse phase melting point will lead to droplets solidification and, therefore, the formation of a suspension of solid particles. Even though it would be more accurate to call them dispersions (being emulsions above the disperse phase melting point and suspensions below the crystallization temperature), the term phase change material emulsion (PCME) is widely accepted in the literature and will be used throughout this study.

In this work, novel non-aqueous emulsions prepared with stearic acid and silicone oil were explored for developing PCMEs. Stearic acid is a very promising PCM for latent heat storage systems since its variation in both melting temperature and latent during repeated heating/cooling cycles in service is negligible and, therefore, shows a good thermal reliability as PCM [24,25]. Moreover, its phase changing temperature of around 69 °C makes it suitable for applications in the medium temperature range such as solar air heater, solar domestic hot water systems, flat-plate solar collectors, etc. [3,26]. In addition, stearic acid is a safe, cheap, and environmentally friendly PCM fatty acid. On the other hand, silicone oil has been selected as a continuous phase because it is highly stable (chemically and heat resistant) and presents a low viscosity [27].

With this aim, a comprehensive investigation of the thermorheological characteristics of stearic acid-in-silicone oil emulsions stabilized using a silicone surfactant has been carried out. Firstly, the thermophysical properties of the emulsion to secure their applicability for thermal energy storage were evaluated. Secondly, the viscous and viscoelastic behaviour were studied on the basis of the obtained rheological properties and finally, the microstructure was also examined.

2. Materials and methods

2.1. Materials

Non-aqueous stearic acid-in-silicone oil (o/o) phase change emulsions are dispersions of stearic acid droplets in silicone oil stabilized by a selected surfactant. Stearic acid (melting point of 69 °C) was purchased from Sigma-Aldrich (Spain) and a selected industrial silicone oil, ESQUIM FH-100, (polydimethylsiloxane, viscosity 0.1 Pa s at 25 °C) was supplied by Esquim S.A. (Spain). The emulsion was stabilized by a silicone-based non-ionic emulsifier, ABIL Care XL80 (Bis-PEG/PPG-20/5 PEG/PPG-20/5 Dimethicone (and) Methoxy PEG/PPG-25/4 Dimethicone (and) Caprylic/Capric Triglyceride; $HLB_{calculated} = 11$), which was kindly supplied by Evonik Nutrition & Care GmbH (Germany).

2.2. Sample preparation

Non-aqueous dispersions were prepared according to the method detailed elsewhere [19], i.e. mixing all the components of the emulsions by a high shear rotor-stator homogeniser, at 80 °C. The emulsions were prepared at the stearic acid/silicone oil (i.e. disperse/continuous phase) weight ratios of 1/99, 5/95 and 10/90, while keeping the surfactant/-disperse phase weight ratio constant at 1/10. Fig. S2 shows a likely structural formulation of the surfactant and its possible stabilisation mechanism in the present emulsion. It is worth mentioning that such a concentration of surfactant was selected thanks to a pre-study where the lowest possible amount of surfactant to maintain a highly stable system was selected. The minimisation of the amount of surfactant was carried out because there was evidence in several studies with others PCMEs that the surfactant presence can reduce the crystallinity of the dispersed

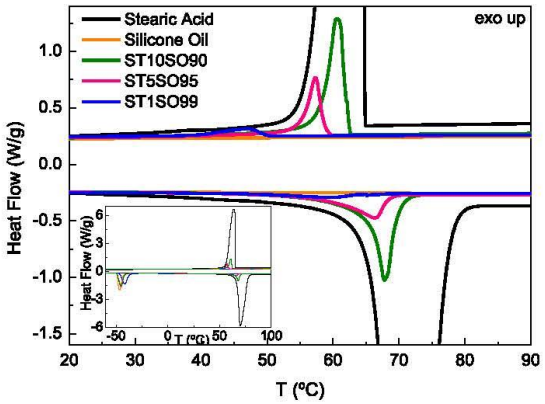


Fig. 1. DSC crystallization and melting curves of the PCMEs with different mass fractions of the stearic acid and the pure components. Inset: more open-ended scale.

clear trend [24,30].

On the other hand, melting and crystallization temperatures clearly decrease with silicone oil content. This observed depression in the melting point and heat of fusion is usually correlated with molecular interactions among the different constituents of the emulsion with the stearic acid that partially disrupts the crystalline structure and, probably, leads to crystallites of smaller sizes. Considering the T onset, which is less affected by heating/cooling rates of the DSC test, it is important to underline that whereas the largest freezing point drop is of about 16 °C, the melting point is modified in a little greater extent specially for the sample ST1SO99 (T_c drops approximately 18 °C). This fact is consistent with the partial compatibility of ST with other molecules inducing a more homogeneous crystallization. As a consequence, the super-cooling degree is almost non-existent for T onset, and rises from 7 to 15 °C for T peak, which is in line with other phase change systems found in literature [31,32]. Therefore, the melting and crystallization events in emulsions seem to be affected by the emulsification process and the concentration of the dispersed phase, particularly at low ST content i.e. emulsion ST1SO99. This effect is probably caused by the high ratio silicone oil/ST resulting much more affected by the processing conditions. This agrees with numerous thermal reliability studies that have been carried out on stearic acid applying repeated working cycles, where similar behaviour where the phase change temperatures and enthalpies decrease slightly has been observed after strong processing [30,33]. Moreover, it is also likely that silicone oil and surfactant form a protective barrier that slows down the crystallization process.

For industrial applications, a PCME must present a suitable thermal stability after a long-term utility period and be able to resist cyclic repeated melting and crystallization cycles. In this sense, a thermal cycling test was conducted to determine the thermal reliability of prepared PCMEs. Fig. 2 portrays DSC curves of ST10SO90 after 100 thermal cycling and shows negligible changes in the melting and crystallization curves after thermal cycling. Therefore, in terms of thermal reliability, stearic acid-in-silicone oil emulsions can be potentially considered for thermal energy storage and transport applications.

Finally, not only in terms of thermal reliability but also in terms of thermal storage capacity the present emulsions show interesting features. Similar values of phase change enthalpy (ΔH_m) of ST10SO90, 21.51 ± 3.6 J/g, have been observed in others aqueous PCMEs. Those PCME with the same application and with analogous PCM (usually paraffins) concentration exhibit very similar values such as 23.3 J/g or 21.1 J/g [28], 19.3 J/g [34], or even lower ones such as 16.5 J/g [35] and 13.9 J/g [8]. Although some of these aqueous emulsions can been prepared with higher PCM concentrations and, therefore, higher phase change enthalpies, the great advantage of the of the here-developed anhydrous PCMEs is the possibility of reaching working temperatures much above the boiling point of water. Moreover, as noted in the introduction, this development may serve as a basis for the development of new non-aqueous PCME with applications in others temperature ranges.

3.2. Rheological measurements

The rheological behaviour of emulsions has become increasingly important for today's formulator in optimising the performance and the attributes of final products [36]. Then, the rheological properties are closely related to their final structure, dispersed phase volume fraction, viscosities of the phases, droplet size or stability of the emulsion [37]. Hence, the rheological characteristics of samples will also have a major influence on the heat transfer process, making it necessary to test the applicability of the PCME systems as HTFs.

3.2.1. Steady-state flow measurements

During in-service operations, stearic acid-in-silicone oil emulsions must be able to recover their rheological properties, after being subjected to a heating-cooling cycle. Therefore, this would give us information on how suitable our material is to be applied as a latent functionally HTF. For this purpose, heating/cooling temperature sweep tests, at a constant shear rate of 1 s^{-1}, were performed to check the

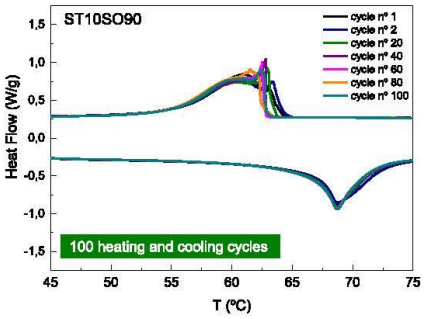


Fig. 2. DSC spectra of ST10SO90 after thermal cycling.

Table 1
Thermo-physical properties of the stearic acid and the PCMEs.

	CRYSTALLIZATION				MELTING			
	T_c onset (°C)	T_c peak (°C)	ΔH_c (J/g)	ΔH_c (J/g of ST)	T_m onset (°C)	T_m peak (°C)	ΔH_m (J/g)	ΔH_m (J/g of ST)
Stearic Acid	64.3 ± 0.8	62.9 ± 0.9	231.74 ± 8.3	231.74 ± 8.3	66.9 ± 0.1	70.9 ± 1.1	229.13 ± 8.3	229.13 ± 8.3
ST10SO90	62.3 ± 0.9	60.6 ± 0.1	22.32 ± 4.4	225.45 ± 44.9	65.4 ± 0.3	67.7 ± 0.4	21.51 ± 3.6	217.22 ± 36.6
ST5SO95	59.1 ± 0.4	57.4 ± 2.2	10.68 ± 0.7	214.65 ± 10.7	59.4 ± 0.5	66.5 ± 0.3	10.38 ± 0.6	208.64 ± 8.0
ST1SO99	48.2 ± 1.6	44.5 ± 2.9	2.2 ± 0.1	220.46 ± 12.3	48.6 ± 2.1	60.1 ± 1.8	1.98 ± 0.1	197.91 ± 10.9

stability of the system. Subsequently, steady state flow curves at different temperatures and linear viscoelastic properties of the resulting emulsions at different temperatures were also evaluated.

In order to study the evolution of the apparent viscosity during the phase change process, Fig. 3 (A) collects the viscosity dependence on temperature of the ST10SO90 system, measured at a shear rate of 1 s^{-1} while subjecting sample to a 1 °C/min cooling/heating ramp. After processing, the sample was cooled from 90 °C to 40 °C at 1 °C/min and then heated from 40 °C to 90 °C at the same rate. As can be seen, during the cooling stage, emulsion viscosity slowly increases until 65 °C where undergone a sharp rise, and thereafter the evolution is slowed down again. This jump in viscosity matches with the onset of the crystallization peak of the dispersed phase observed in DSC scans in Fig. 1. On the other hand, during the subsequent heating cycle, viscosity follows the reverse pathway with the increasing temperature, but with a more abrupt drop at around 65 °C, agreeing with the melting peak of the disperse phase (see again Fig. 1). The small variations between the outward and return paths are consequence of the different mechanisms involved in the melting and crystallization processes that gives rise to the supercooling phenomenon [38]. Additionally, during the heating cycle, an unusual peak in viscosity is observed at around the melting point of stearic acid, followed by a sharp drop to approximately the starting values, which can be related to the melting of the disperse phase and the collapse of its crystalline structure. Regarding the viscosity maximum, this behaviour has been also reported in the literature for similar systems and its origin is a matter of debate [39,40]. However, it seems to be related to a change in the microstructure of the droplets because of the shape relaxation while the subsequent increase of temperature [39,41]. From the operational point of view, a positive fact is that after the cooling and heating cycle, the emulsion is able to retain the previous viscous properties even after being subject to a phase change, point out a suitable rheological stability.

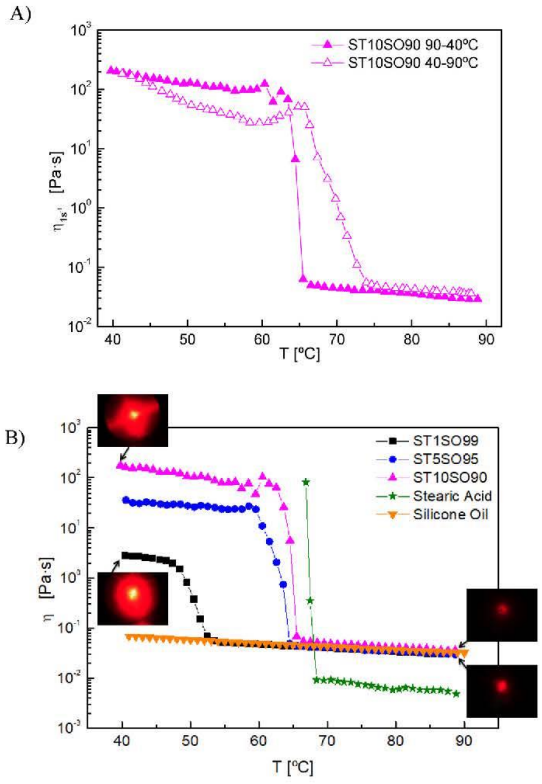


Fig. 3. Temperature dependent viscosity at 1 s^{-1} under 1 °C/min heating/cool ramps conducted on: A) ST10SO90 emulsion (cooling and heating) and B) pure components and stearic acid-in-silicone oil emulsions at different disperse phase concentration (cooling). Inset of SALS crossed-polarizers images.

Fig. 3 (B) shows same testing as above, but only during the cooling ramp, at different disperse phase concentrations. Going deeper in the analysis of their behaviour with decreasing temperature, again, all emulsion viscosities increase rapidly once the phase change process takes place, as the dispersed phase begins to solidify at the freezing temperature. This behaviour is attributed to the formation of solid particles with a much higher viscosity than the liquid droplets and, therefore, less prone to deformation under shear stress [42]. This is in line with the evolution of pristine ST, with a much lower viscosity in molten state and clearly larger values below the freezing point of the solid state (exceeding the instrument limit). In this sense, the apparent viscosity of PCMEs below the freezing point reaches higher values with increasing the dispersed phase concentration. This fact gives clear indication that the development of stearic acid crystals exerts a major role in the rheological behaviour of PCMEs, as has been reported by other authors [28,32]. It is also noteworthy that the steep rise in viscosity occurs at lower temperatures as the concentration of stearic acid decreases, which is fully in line with DSC results of the previous section, where the crystallization temperature decreased accordingly.

In order to more accurately interpret the reported viscosity changes, small-angle light scattering (SALS) analyses were carried out on the emulsions at the extreme temperatures of the range covered (90 and 40 °C). The scattering patterns obtained from the crossed-polarized rheo-SALS analysis are shown as insets in Fig. 3 (B). There were significant differences in the scattering patterns obtained at the start and end of the cooling ramp. Initially, at 90 °C, emulsion displays no scattering with crossed-polarizers configurations (note that central dot is caused by the main beam), as expected for the molten state of any crystallisable structures. However, with decreasing temperature, both an increase in the scattered intensity as well as change in shape to elliptical or four-lobe pattern are observed, which proves the appearance of stearic acid crystals growth during crystallization [43]. A trend to a circularly symmetric pattern means that growing morphologies tend to randomization in space which is expected for the low concentration of crystalline structures (see the inset in ST1SO99 emulsion, Fig. 3 (B)) [44]. Then, the appearance of an indistinct circular pattern may be related to the development of random array of quasi-crystallites smaller than the wavelength of the incident beam [45]. In emulsions with a higher concentration of stearic acid (inset in ST10SO90, Fig. 3 (B)), depolarized SALS image seems to evolve into a four-lobe pattern, a characteristic signature of spherulitic overgrowing morphologies or the existence of rod-like crystalline structures [44,46].

After analysing and confirming that this system can be stable during the phase change process, a more detailed study of the rheological properties of the emulsion before and after the phase change was carried out.

At high temperatures, above the melting point of stearic acid, all emulsions show a Newtonian behaviour with similar viscosity values to the silicone oil, whereas the viscosity of pure stearic acid is significantly lower at 90 °C (Fig. 4 (A)). An increase in the disperse phase concentration does lead to a shorter separation between droplets and a significantly higher specific surface area, both enhancing the interaction between droplets and usually leading to a viscosity raise [47,48]. Thus, it would be expected a higher viscosity with increasing concentration of disperse phase. However, this is not the result found at high temperature. Even though the effect of the droplet size is analysed in detail in the next section, this result seems to be related to the relatively low concentration of the dispersed phase, where the influence of droplet size on the viscosity is of minor importance and the formation of

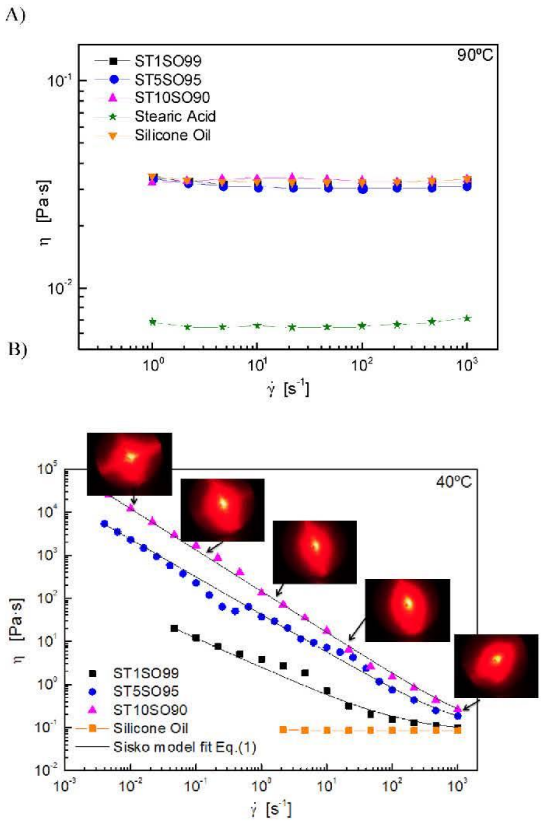


Fig. 4. Viscous flow curves of emulsions and pure components at: A) 90 °C and B) 40 °C, the curves of the emulsions were calculated by Eq. (1). Inset of SALS crossed-polarizers images.

non-flocculated emulsions, as can be clearly seen in Fig. 4 (A) [49].

On the contrary, as can be observed in Fig. 4 (B) at 40 °C, after crystallization, the disperse phase concentration exerts a major influence on the flow curves of dispersions and modifies their rheological behaviour. Then, all samples display a remarkable shear-thinning response, characterised by a drop of up to five orders of magnitude in viscosity and with a trend to reach a limiting viscosity in the high shear rate region.

As a result, the Sisko model fits fairly well the flow behaviour obtained over the whole shear rate range studied ($R^2 > 0.99$) and is useful for analysing this tendency:

$$\eta = \eta_\infty + K_s\,\dot{\gamma}^{n-1} \tag{1}$$

where K_s and n are the consistency and flow indexes, respectively, and η_∞ is the high-shear-rate limiting viscosity. These fitting parameters are shown in Table 2. The decrease in flow index (and $n < 1$) with increasing disperse phase concentration reflects a more apparent shear-thinning behaviour. Even though this result could be partially attributed to the viscosity increase of the stearic acid droplets after their solidification during phase change, the magnitude of the modification in the flow behaviour is not consistent with these moderately diluted non-flocculated dispersions. Therefore, this result hints structural changes in the emulsion microstructure related to the crystallization of the steric acid, apart from the solidification of the dispersed phase.

Table 2
Values of Sisko's model parameters.

Sisko's model parameters				
	η_∞ (Pa s)	Ks (Pa s^n)	n (−)	R^2
ST10SO90	*0.078*	*145.00*	*0.04*	*0.999*
ST5SO95	*0.085*	*41.81*	*0.12*	*0.998*
ST1SO99	*0.080*	*2.43*	*0.31*	*0.990*

As deduced from Fig. 4 (B), a notable increase in viscosity values is noticed as concentration rises, which is in line with the previously reported apparent viscosities in the low-temperature zone of the temperature sweeps shown in Fig. 3 (B) and *Ks* evolution gathered in Table 2. Moreover, parameters recorded in Table 2 reveal that larger disperse phase concentrations lead to a more complex microstructure with stronger inter-droplet interactions that provoke an increase in the flow resistance and, therefore, in the consistency index, K_s [31].

On the other hand, all systems present an interesting trend to reach a similar high-shear-rate limiting viscosity, close to that of the oil forming the continuous phase (see η_∞ values in Table 2). This reveals that dispersion microstructure is highly susceptible to shear, which is clearly positive from the application standpoint because, commonly, industrial processing and pumping operations involve shear rates within the intermediate-high shear regime (1-1000 s^{-1}) [50]. More specifically, shear rates of 1 s^{-1} are typical shear rates of fluid drainage [51], the range 10–10000 s^{-1} are typical shear rates for mixing and stirring, and 100 –1000 s^{-1} for pipe flow [52]. As an example, it can be mentioned that lubricant greases with a marked shear thinning behaviour and having much higher low-shear apparent viscosities (approximately 10^7 Pa s) can be successfully pumped in piping flow experiments [53].

Finally, the SALS images (inset Fig. 4 (B)) also give us information about the effect of applied shear in rotational measurements under isothermal conditions. Preferential orientation of scatters along the flow direction is the consequence of elongated crystalline structures (threads) [44,54]. Differences, as in the case of static measurements shown in the inset of Fig. 3 (B), result from the stronger impact of the applied deformation and the significant effect of the increase in deformation on the pre-formed structure. As crystalline structures are supposed to be rigid and confined into the disperse phase, this behaviour is consistent with their orientation close to the shear direction. Then, this pattern in the polarized rheo-SALS set-up suggests that there is a continuous structure in the flow direction [46]. Then, whereas liquid PCM particles are spherical, after crystallization, solid and distorted particles are expected to appear. The distorted shape results in a higher surface area of the particles that may strengthen the interaction forces. Therefore, such an interrelated microstructure would largely affect the flow behaviour and becomes stronger as PCM content increases [55]. Consequently, at low shear rates it leads to a notable viscosity increase and, as shear rate rises, the progressive orientation of the structures gives rise to the viscosity fall. This behaviour is very common for emulsions of phase-shifting materials and has been previously reported [14,28,56].

Dynamic viscoelastic moduli within the linear viscoelastic region provide a fingerprint of the viscoelastic system under non-destructive conditions and give structural information in a regime where excitation does not disturb the equilibrium microstructure of the sample. Thus, the system rheology is examined without disrupting its structure as continuous shear techniques (i.e. viscous flow tests) do.

Oscillatory frequency sweep tests were conducted to obtain information about the developed microstructure after crystallization. The response of the dynamic measurements, the storage (or elastic) modulus G' and the loss (or viscous) modulus G'' are shown in Fig. 5. Each system was also investigated at different temperatures within the application temperature range, since temperature had an important effect on viscoelastic properties, especially when a phase change material is involved.

At low temperature, frequency sweep curves show that the elastic

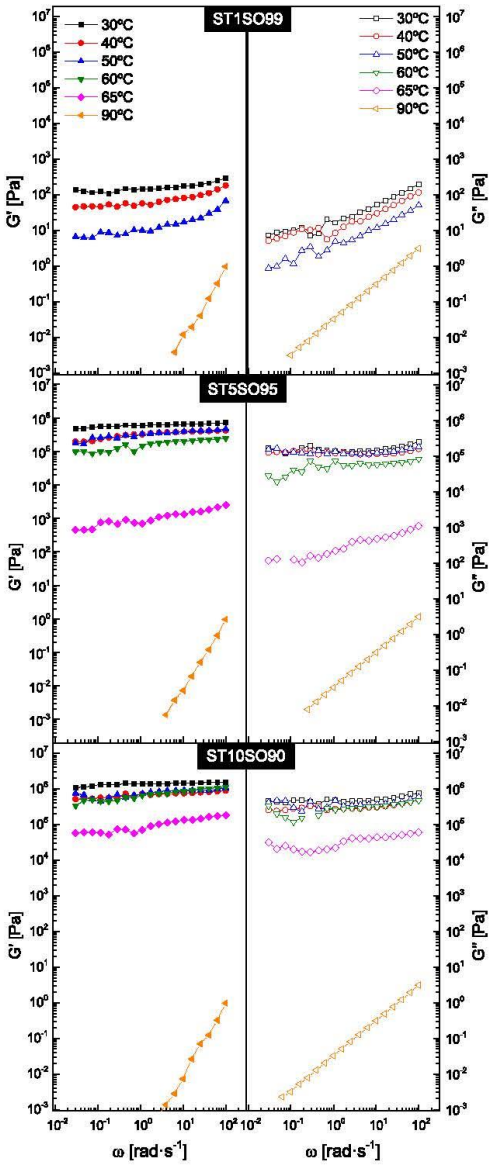


Fig. 5. Storage (*left-hand column*) and Loss (*right-hand column*) moduli as a function of frequency of the emulsions: A) ST1SO99, B) ST5SO95 and C) ST10SO90, at different temperatures.

modulus is almost independent of frequency and remains clearly above the loss modulus (Fig. 5), which develops (or tends to develop) a minimum that depends on the testing temperature and concentration. Therefore, the so-called "plateau region" is noticed pointing out the formation of a gel-like structure when the disperse phase remains in its solid crystalline state [57].

From Fig. 5, it is obvious that the liner viscoelastic behaviour of dispersions strongly depends on the disperse phase concentration, especially when ST content increases from 1 to 5 wt%. Thus, ST1SO99 presents lower G′ and G″ values and a crossover between both linear viscoelastic functions at high frequencies, and exhibits a less evident plateau region. Higher disperse phase concentrations (samples ST5SO95 and ST10SO90) induce a more developed plateau region and a remarkable rise of four orders of magnitude in both moduli. Then, larger dispersed phase concentration favours the formation of stronger gel-like characteristics [58]. Thus, as the volume fraction of the disperse phase increases, the number of stearic acid crystals grows, decreasing the distance between the droplets and increasing the total area of the interface [39,59].

In general, below the melting point of the stearic acid, as temperature increases, both G' and G'' undergo a progressive lowering, while maintaining their rheological behaviour (Fig. 5). At temperatures close to the phase change, the plateau region becomes less evident, and then, a weaker gel is formed as temperature increases.

The reported rheological behaviour that emerges at temperatures around and below the dispersed phase change may be related to the formation of well-developed three-dimensional network as a consequence of the crystallization of the disperse phase. Thus, the formed crystalline structures are probably interconnected with each other, enhancing the network rigidity as temperature lowers [60]. In addition, taking into account that in the molten state a non-flocculated dispersion of spherical droplets is obtained and the disperse phase concentration is relatedly low (Fig. 5), the solidification of the PCM may be accompanied by other processes that significantly change the microstructure of the sample. According to this, such viscoelastic behaviour is consistent with a microstructure where stearic acid forms a crystalline network expanded through the whole volume, swollen by the silicone oil. Thus, the solid-like stearic acid deformable network would contribute to the enhancement of elastic and viscous properties.

As shown in Fig. 5, before the phase change, when the temperature raises, both moduli decrease very slightly in all samples, in line of the previously reported evolution of the apparent viscosity with temperature (Fig. 3).

It is worth mentioning that, unexpectedly ST10SO90 seems to show a minor increase of the viscoelastic functions at 60 °C (Fig. 5 (C)) which approximately corresponds the onset of the melting process in Fig. 1. This is consistent with the local viscosity maximum observed in the temperature sweeps portrayed in Fig. 3, which is more intense as disperse phase concentration increases. This outcome is probably caused by the consolidation of the network structure of the crystalline structures due to the onset of a phase change. The liquefaction of the dispersed phase initially leads to a shape relaxation process and, at concentrations high enough, to the jamming of the dispersed structures due to their expansion giving rise to a change in the network. Similar behaviour was observed in other systems where a phase change of one of the system components takes place [39,40].

At temperatures close to melting point disclosed in Table 1 (50 °C for ST1SO99 and 65 °C for ST5SO95 and ST10SO90) the drop of viscoelastic moduli become more apparent and slopes of these functions increases, but G' still remains over G'' (for ST1SO99 a crossover appears at high frequencies) pointing out a small network weakening. In all systems, the gel collapses sharply at higher temperatures (e.g., 90 °C), with a sudden drop of G′ and G''. Thus, a fluid-like behaviour or the terminal region of the mechanical spectrum is observed, where G''>G′ and both moduli exhibit a power-law dependence on frequency with log-log slopes of 1 and 2, respectively. Finally, it is worth noting that the transition temperature from gel-like to liquid-like response lowers as concentration does, particularly for ST1SO99, in line with the viscosity evolution during cooling reported in Fig. 3 (B).

3.3. *Microstructure*

As already mentioned, the macro-properties of the samples are closely related to their micro-morphologies [61]. Thus, optical images of samples were obtained at two different temperatures (before and after

the melting point of the PCM, Fig. 6 row (1) and Fig. 6 row (2), respectively) at different disperse phase concentrations (see the columns of Fig. 6). Fig. 6 also gathers images of the emulsions at 40 °C with cross-polarized light to identify the presence of crystalline structures and their distribution throughout the sample (Fig. 6 row (3)).

At 90 °C, above their melting point, where both phases are low-viscosity liquids, optical microscope clearly shows a fairly homogeneous distribution of isolated stearic acid droplets, dispersed in a silicone oil continuous medium (Fig. 6 (A1), (B1) and (C1)). Therefore, at high temperature, when the disperse phase is melted, all emulsions present a non-flocculated microstructure, a fact that would explain their Newtonian flow behaviour.

From these micrographs, the calculated diameters of the droplets slightly increase with the dispersed phase fraction, (3.41 μm in ST1SO99, 4.19 μm in ST5SO95 and 6.58 μm in ST10SO90). According to those results, mean particle size increase with disperse phase concentration. However, their contribution to the bulk viscosity is not high enough to modify the emulsion flow behaviour, due to the relatively low concentration or volume fraction of the disperse phase. Therefore, at 90 °C, the viscosity of the emulsions becomes close to the continuous phase viscosity (Fig. 4 (A)).

On the other hand, during cooling, the microstructure of the emulsion is greatly modified evolving from a non-flocculated state to a more complex arrangement (see Fig. 6 row (2)). Thus, self-assembled structures clearly appear when the temperature of the sample decreases to 40 °C, as a consequence of the crystallization of the disperse phase, as can be seen by inspecting the same samples under cross-polarized light in Fig. 6 row (3), where the light areas correspond to crystals of stearic acid [62]. The crystal microstructure exhibited various morphologies depending on disperse phase concentration. These crystals may protrude from the freezing droplets inducing self-shaping depending on crystal morphology [63], and can be ranged from thin crystallised layer to larger droplets that crystallise in a globular form. Higher concentrations of stearic acid in the emulsion tended to large rod-like structures. As an example, ST5SO95 allows us to analyse the development of the new microstructures, since a three-dimensional crystalline network can be observed together with small globules of crystallised particles (Fig. 7). This can also be seen more clearly in Fig. 8 with lower magnifications. There are many studies currently discussing about the different crystallization mechanisms of droplets in emulsions [64,65]. It has even been shown that the polydispersity of the emulsion affects the rate of crystallization and, therefore, any structure that may form [66]. The latter, together with the different droplet sizes and quantities, explains

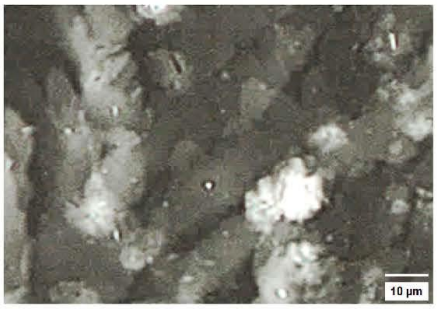


Fig. 7. Detail of the micromorphology under cross-polarized light of ST5SO95.

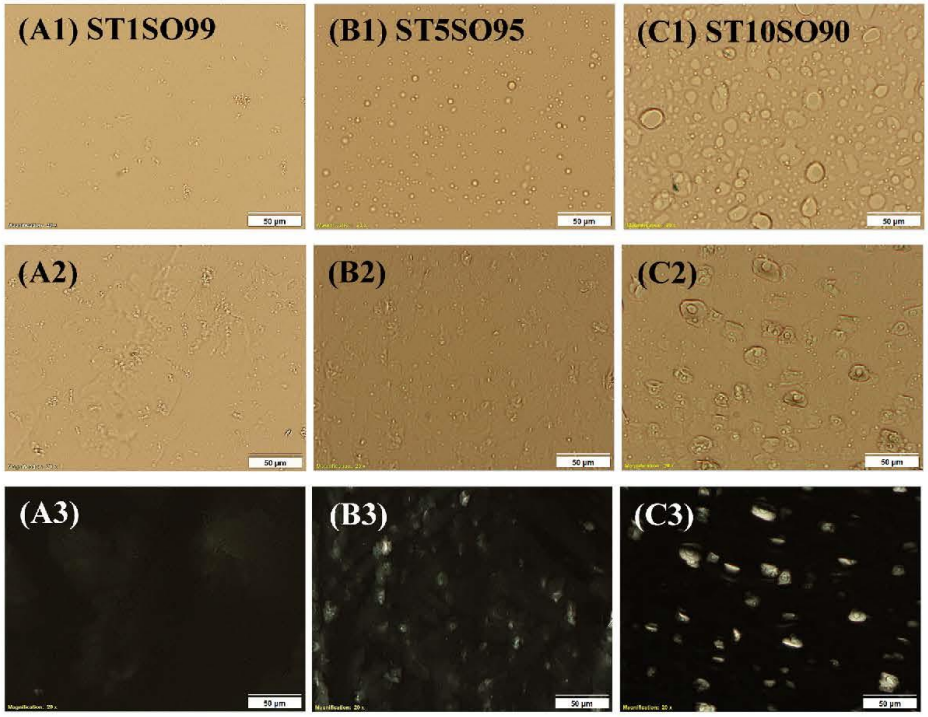


Fig. 6. Micromorphology of the phase change emulsion at different concentrations: column (A) ST1SO99, column (B) ST5SO95, column (C) ST10SO90; under an optical microscope (20x): row (1) at 90 °C; row (2) at 40 °C; row (3) at 40 °C under crossed-polarized light.

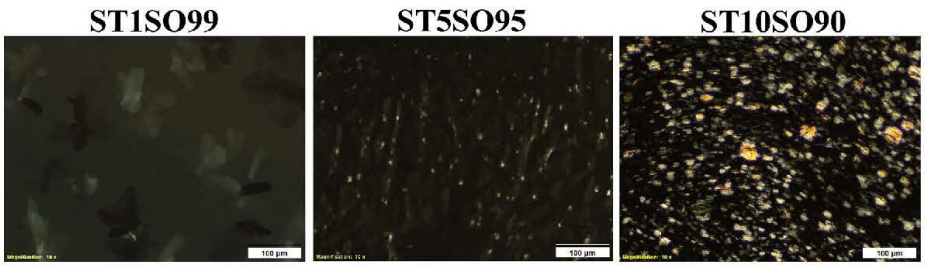


Fig. 8. Micromorphology under cross-polarized light of the phase change emulsion at different concentrations under an optical microscope (10x).

why different structures are observed in emulsions with different dispersed phase concentrations.

What is clear is that non-spherical shapes are triggered by the crystal formation into the droplets upon emulsion cooling. As was assumed in the previous section, emulsion droplets deviated from the initial spherical shape, resulting in a higher surface area of the particles, strengthening the interaction force, which is very common in crystallised systems [32,42]. It has also been observed that crystals protruded from the droplet interface and a three-dimensional network are formed developing an extended microstructure in the system. Therefore, this complex crystal deformable microstructure with strong inter-droplet interactions is consistent with the above results and would explain the reported rheological properties.

Finally, the emulsions microstructure at high temperature has been also evaluated after experiencing 10 heating-cooling cycles. According to the micrographs shown in Fig. 9, PCMEs only showed a slight increase in droplet size after thermal cycling (4.189 μm in ST1SO99, 4.785 μm in ST5SO95 and 6.922 μm in ST10SO90). This result points out that the stearic acid-in-silicone oil emulsions exhibit good thermal stability and is reliable with the results obtained in the previous analyses. Thus, even though droplets are broken by PCM crystals during the cooling cycle, initial microstructure of the emulsion is recovered when reheated up to 90 °C, revealing the high effectiveness of the surfactant.

4. Conclusions

At present, formulating a non-aqueous PCME for thermal storage and heat transfer applications is both promising and challenging. This study assesses in detail the thermal and rheological performance of stearic acid-in-silicone oil emulsions as well as their microstructural and viscoelastic properties at different temperatures. The obtained results make evident that a stable PCME can be successfully fabricated by selecting an appropriate silicone surfactant.

Emulsions were characterised by a Newtonian behaviour at high temperature, above the melting point of the PCM, and a pronounced non-Newtonian shear thinning behaviour, described quantitatively by the Sisko model, at temperature below the melting point of the PCM. After crystallization, the results show an increase in low-shear-rate viscosity of up to 5 orders of magnitude for the most concentrated emulsion. This increase was due to the occurrence of an interrelated microstructure of crystals which would largely affect the flow behaviour of the emulsion and becomes stronger as PCM content increases. Indeed, structural information obtained by non-destructive essays shows as a well-developed three-dimensional network of crystalline structures interconnected with each other was formed as a consequence of the crystallization of the dispersed phase. Interestingly, such a microstructure is highly susceptible to shear, which is clearly positive from the application standpoint, as industrial processing and pumping operations usually involve shear rates within the intermediate-high shear regime.

On the other hand, samples were subjected to heating/cooling temperature sweep tests under steady shear, optical microscopy and DSC, checking not only the rheological and microstructural stability of the system but also its thermal reliability during in-service operations. The present PCMEs were able to resist heating-cooling cycles and remain stable for at least one month, keeping their properties and heat storage capacity practically intact. Consequently, the PCMEs show great potential for use as a novel HTF in thermal energy storage systems. A more in-depth study about the energy transport characteristics and the evaluation of the performance in a pilot plat device, close to the industrial applications, will be the path to continue this study.

CRediT authorship contribution statement

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



Fig. 9. Micrographs of stearic acid-in-silicone oil emulsions at 90 °C after heating-cooling cycles.

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.

Data availability

Data will be made available on request.

Acknowledgements

Grant PID2020-116905RB-I00 funded by MCIN/AEI/10.13039/501100011033, grant P18-RT-4684 funded by EU-FEDER program and grant CTQ2017-89792-R funded by MCIN/AEI/10.13039/501100011033 and by "ERDF A way of making Europe", by the "European Union".

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solmat.2022.111893.

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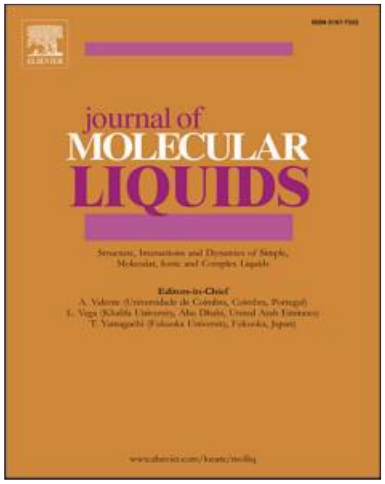
IV/4. Article 4

Innovative stearic acid-in-silicone oil (o/o) phase change material lubricating emulsions (PCMLEs): thermo-rheological and tribological properties

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Submitted to*:*



JOURNAL OF MOLECULAR LIQUIDS
Publishing company: ELSEVIER
Editor-in-Chief: T. Yamaguchi
ISSN 0167-7322
Impact Factor (2022) 6.000

Category	***Journal rank/Total journals***	***Quartile***
PHYSICS, ATOMIC, MOLECULAR & CHEMICAL	*4/35*	*Q1*

Journal of Molecular Liquids

Innovative stearic acid-in-silicone oil (o/o) phase change material lubricating emulsions (PCMLEs): thermo-rheological and tribological properties

--Manuscript Draft--

Manuscript Number:	MOLLIQ-D-24-01298
Article Type:	Full length article
Section/Category:	Lubricants, polymer solutions and melts
Keywords:	phase change emulsions, phase change materials, lubricants, wear, rheology
Corresponding Author:	Francisco Javier Navarro University of Huelva Huelva SPAIN
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Abstract:	This paper analyses the feasibility of using novel non-aqueous stearic acid-in-silicone oil (o/o) phase change material lubricating emulsions (PCMLEs). The novel use of these dispersions with heat storage capacity for lubricating applications can be considered a new approach since they have not yet been used for such purposes. In this study, PCMLEs consist of stearic acid, with a melting point of roughly 69 °C, as a dispersed phase change material in a continuous silicone oil medium. Samples were prepared by mixing different phase ratios, by high-shear processing and stabilised by a constant concentration of a silicone-based non-ionic surfactant. Taking into consideration the ability of stearic acid to absorb latent thermal energy during machinery operation, the potential application in lubrication has been assessed by means of stationary and temperature ramp friction tests. Moreover, the effect of the phase transition on the PCMLEs' rheological response has been analysed through stationary flow tests and frequency sweeps within the linear viscoelastic range at constant temperatures, below (40 ºC) and above (80 ºC) the melting process of the disperse phase. Additionally, their thermal properties and morphology were also studied through X-ray diffraction measurements (XRD), differential scanning calorimetry (DSC) and polarised optical microscopy. As a result, the reported rheological properties and microstructure led to the enhancement in tribological characteristics of PCMLEs since a significant reduction in the friction factor is evidenced, within the whole temperature range, when compared to the silicone oil.
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Innovative stearic acid-in-silicone oil (o/o) phase change material lubricating emulsions (PCMLEs): thermo-rheological and tribological properties

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Abstract

This paper analyses the feasibility of using novel non-aqueous stearic acid-in-silicone oil (o/o) phase change material lubricating emulsions (PCMLEs). The novel use of these dispersions with heat storage capacity for lubricating applications can be considered a new approach since they have not yet been used for such purposes. In this study, PCMLEs consist of stearic acid, with a melting point of roughly 69 °C, as a dispersed phase change material in a continuous silicone oil medium. Samples were prepared by mixing different phase ratios, by high-shear processing and stabilised by a constant concentration of a silicone-based non-ionic surfactant. Taking into consideration the ability of stearic acid to absorb latent thermal energy during machinery operation, the potential application in lubrication has been assessed by means of stationary and temperature ramp friction tests. Moreover, the effect of the phase transition on the PCMLEs' rheological response has been analysed through stationary flow tests and frequency sweeps within the linear viscoelastic range at constant temperatures, below (40 ºC) and above (80 ºC) the melting process of the disperse phase. Additionally, their thermal properties and morphology were also studied through X-ray diffraction measurements (XRD), differential scanning calorimetry (DSC) and polarised optical microscopy. As a result, the reported rheological properties and microstructure led to the enhancement in tribological characteristics of PCMLEs since a significant reduction in the friction factor is evidenced, within the whole temperature range, when compared to the silicone oil.

Keywords: phase change emulsions, phase change materials, lubricants, wear, rheology

1. Introduction

In recent years, there has been an increased emphasis on developing high-performance lubricants that can improve the efficiency and longevity of machines and equipment. Awareness of the critical importance of the use of lubricants in today's world is growing in the metalwork industry, especially in high-temperature applications such as in engines, turbines, bearings and other machinery that operate in extreme heat conditions where their life cycle is being undermined as a consequence of the generated friction and wear [1].

The choice of lubricant depends on the specific application, as well as factors such as operating conditions, temperature, pressure, and load. Thus, the use of mineral oils, one of the most commonly used lubricants on the market [2] entails disadvantages in terms of preserving their properties for sufficient periods, which, together with the low affinity with metal surfaces due to their non-polar characteristics [3], leads the lubricant community to look for enhanced formulations that allow the life cycle of machinery to be extended. For instance, in high-speed rolling processes, the temperature can easily reach 200 ºC due to the high forming pressure [3], seriously affecting those oil-based lubricants' properties due to their oxidation and the protective film rupture in metal contacts.

Within the lubricants used in metalworking, oil-in-water (o/w) emulsions have been reported to have good properties helping to improve tool life and workpiece quality [4,5]. They show an important compromise between the droplets' stability inside the emulsion, the ability to form a protective tribo-film, and the permanent supply to the contact area, which is required to get good tribological properties reducing friction and wear [6,7]. In this sense, o/w emulsions based on highly polar vegetable oils have been proposed by some authors trying to solve the compatibility issues with metal surfaces in these applications, providing better cooling and lubrication compared to pure oils, which can be beneficial for high-speed machining operations

[8,9]. However, those vegetable oils-based emulsions may also have some drawbacks compared to other lubricants, such as some derived problems related to the generated carbon residues during the process that could make cleanliness difficult or affect the surface accuracy of the machined part [10]. Moreover, although these emulsions show a high surface affinity due to their polar components, they also present microbial growth and a limited range of temperatures in which they can effectively operate in stable conditions [11,12]. Understanding the tribology and rheology of emulsions at high temperatures is of principal importance to the application of the emulsions. Thus, some emulsion formulations have been used in high-temperature applications to provide not only lubrication but also cooling, through complex and not very well-known destabilisation and evaporation mechanisms of the aqueous phase [13].

Accordingly, the development of advanced lubricants, improving compatibility with metal, operating stably over a broad range of temperatures, as well as in humid and oxidising conditions, remains challenging. To solve these issues, oil-in-oil (o/o) emulsions could be an interesting option to explore in this field. This kind of emulsion is widely used in cosmetics and pharmaceuticals but their applications in lubrication are practically unknown, as there are only a few patents [14].

The use of phase change materials (PCMs) in lubrication is another emerging area of research that shows promise for improving the performance and efficiency of lubricants in various applications [15,16]. PCMs are materials that can store and release thermal energy by undergoing a phase transition, typically from a solid to a liquid state, at a specific temperature [17]. In lubrication, PCMs can be especially beneficial in high-temperature applications, where overheating can cause premature wear and damage to the machine as they can be used to absorb excess heat and maintain a more stable operating temperature, which can improve the overall performance and reliability of the system. To the best of our knowledge, there are only a few

88 studies investigating the development of novel lubricant formulations that incorporate PCMs
89 and those studies are extremely recent. They incorporate PCM to form composites, either by
90 injecting it directly into a porous matrix [18] or through the incorporation of microcapsules
91 into an elastomeric matrix [15], but none of them use emulsion-based technologies.

92 Therefore, the incorporation of PCM, as the disperse phase, to formulate the so-called phase
93 change material lubricating emulsions (PCMLE), would allow to open the path to a new
94 approach for lubricating applications. Then, PCMLEs will combine the advantages of
95 o/o emulsions such as thermal and chemical stability, at high temperatures, with improved heat
96 storage capacity of the PCM, better heat transfer rate associated with the larger specific surface
97 area and adequate pumpability [19]. In general, non-aqueous phase change material emulsions
98 have only recently been investigated by the authors for their use in energy storage applications
99 [20] and, as far as we know, it has never before been studied for lubrication purposes.

100 In a very recent study [21], despite the lack of information regarding that kind of emulsions,
101 the authors successfully reported a fully stable PCM dispersion, stearic acid-in-silicone oil
102 emulsion, with potential as a lubricant for high-temperature applications, together with the
103 capability of storing and releasing thermal energy. In particular, silicon oil-based lubricants
104 have been previously reported as thermally stable materials, more specially
105 polydimethylsiloxane (PDMS) silicone oil has proven to be an excellent alternative as an
106 external lubricant coating in stainless-steel contacts with outstanding tribological
107 characteristics, at high shear rates [22]. Moreover, the use of stearic acid as the dispersed phase
108 of the emulsion is also advantageous since, as saturated fatty acid, it has been previously
109 employed as a significant lubricating additive to reduce wear and friction in tribological contact
110 [23]. Thus, in addition to the improvement in chemical compatibility with metal surfaces, the

phase change process of the dispersed phase, at 69 °C, would help to decrease the surface temperature of a bearing, improving its performance and reducing the risk of failure.

Therefore, the focus of this research was the thermorheological and tribological assessment of novel PCMLE in pursuit of feasible lubricating material. For that purpose, PCMLEs bearing different proportions of dispersed stearic acid were subjected to a comprehensive characterisation, comprising tribological stationary and temperature ramps, rheological flow tests and small amplitude oscillatory shear analysis, as well as thermal, microstructural and morphological evaluation.

2. Materials and methods

2.1. Materials

Oil-based phase change material lubricating emulsions (PCMLEs) encompass phase change material's (stearic acid) droplets dispersed in a continuous oily phase (silicone oil) by using a selected stabilizer (surfactant). Thus, stearic acid (SA), whose melting temperature is centred at 69 °C, provided by Sigma-Aldrich (Spain) forms the disperse phase. A selected industrial low-viscosity silicone oil, ESQUIM FH-100 (polydimethylsiloxane - PDMS, viscosity 0.1 Pa·s at 25 °C) was supplied by Esquim S.A. (Spain) and regarded as the continuous phase. PCMLEs were stabilized by a silicone-based non-ionic surfactant, ABIL Care XL80 (Bis-PEG/PPG-20/5 PEG/PPG-20/5 Dimethicone (and) Methoxy PEG/PPG-25/4 Dimethicone (and) Caprylic/Capric Triglyceride; HLB calculated = 11), which was purchased from Evonik Nutrition & Care GmbH (Germany).

2.2. Sample preparation

PCMLEs were prepared following the emulsification process previously detailed in [21]. In brief, all compounds were firstly pre-conditioned at 80 °C, aimed at ensuring the liquid state

134 of stearic acid. Afterwards, the surfactant was dissolved in silicone oil, with the subsequent
135 dropwise addition of molten stearic acid, according to the proportions established in Table 1.
136 These mixtures were subjected to simultaneous homogenisation under high shear conditions
137 (20000 rpm) by using an Ultra-Turrax T25 homogeniser (IKA, Germany).

138 Table 1. Compositions of PCMLEs.
139

Sample	Weight ratio of Silicone Oil to Stearic acid	Silicone Oil (wt.%)	Stearic acid (wt.%)	Surfactant (wt.%)
SA10	90/10=9	89.11	9.90	0.99
SA5	95/5=19	94.53	4.98	0.49
SA1	99/1=99	98.90	1.00	0.10

140 **2.3. Methods**

141 **2.3.1. Rheological characterisation**

142 The rheological response of the developed PCMLEs was studied at the temperatures of 40 and
143 80 ºC, below and above the crystallisation/melting points of the stearic acid. First, rotational
144 viscous flow analyses were conducted within the shear rate range from 0.01 up to 100 s^{-1}, using
145 a controlled-strain Ares-G2 rheometer (TA Instruments, USA), fitted with a smooth Couette
146 geometry (cup diameter of 30 mm, bob diameter of 27 mm, bob length of 42 mm), with an
147 operating gap of 2 mm and a Peltier temperature control system. Small Amplitude Oscillatory
148 Shear (SAOS) tests were also carried out at 40 ºC, in a controlled-stress rheometer
149 Physica MCR 501 (Anton Paar, Graz, Austria), between the frequency range from 0.03 to
150 100 rad·s^{-1}, using a plate-plate geometry (50 mm diameter, 1 mm gap) within the Linear
151 Viscoelastic Region (LVR) evaluated in previous Stress Sweep experiments conducted at 1 Hz.

2.3.2. X-ray diffraction measurements (XRD)

The crystalline structure of pure stearic acid and the PCMLE were analysed using a D8 Advance X-ray diffractometer (Bruker-AXS, Germany) at room temperature (25 °C). The X-ray diffraction pattern was obtained under the following instrumental conditions: 30 mA, 40 kV, angle 2θ: 4° and 59.9°, step size = 0.019°. A copper Kα/K target (λ = 1.54) was used for the generation of the X-rays. All the samples were prepared by placing a small amount on a supporting glass slide of 25 × 25 mm^2, which was heated over stearic acid melting temperature (80 °C) to flatten and obtain approximately 1 mm-thick film followed by cooling to room temperature. Afterwards, the sample-containing slide was located at the centre of a metal holder, externally shaped to be allocated in the instrument.

2.3.3. Differential Scanning Calorimetry (DSC)

The thermal properties of the anhydrous PCMLEs were evaluated in a differential scanning calorimeter DSC250 (TA Instruments, USA). Hermetic aluminium pans, loaded with 5–10 mg of emulsion, were heated up to 30 °C and subsequently submitted to a double heating-cooling cycle from 30 to 80 °C, with a scan rate of 1 °C·min^{-1}, under inert purge of nitrogen (50 mL·min^{-1}). All thermal events, mainly melting and crystallisation processes were identified and characterized from the resulting thermograms. Therefore, the following parameters were estimated: the crystallisation/melting onset-temperatures (T_c^{onset} , T_m^{onset}) were obtained from the intersection point of the extrapolated baseline and the inflectional tangent at the beginning of the crystallisation/melting peaks from the cooling/heating scans; the crystallisation/melting peak-temperatures (T_c^{peak}, T_m^{peak}) was regarded as the temperature ascribed to the largest deviation of the heat flow signal from the virtual baseline; the crystallisation/melting enthalpies (ΔH_c, ΔH_m) were determined by the numerical integration of the area enclosed within the crystallisation/melting peaks.

2.3.4. Tribological characterisation

Tribological properties of the formulated PCMLE were evaluated in a Physica MCR 501 controlled-stress rheometer (Anton Paar, Graz, Austria) coupled with a ball-on-three-plates tribological cell [24]. The experimental setup comprises a lower measuring geometry with three 45°-inclined steel plates (1.4301 AISI 304, 0.21 μm roughness, 80 HRB hardness) where the PCMLEs were placed, together with an upper measuring geometry fitted with a fixed 6.35 mm-radious bearing ball (1.4401 grade 100 AISI 316). Such ball-on-three-plates configuration enables the friction coefficient (μ) determination as the ratio between the applied normal force (F_N) and the measured friction force (F_F) (see Equation 1).

$$\mu = \frac{F_F}{F_N} \qquad (1)$$

Therefore, the stationary friction coefficient of all formulated emulsions on steel-steel contact was evaluated over time at constant temperatures (40 and 80 °C), under 20 N of F_N and at the rotational speed of 10 rpm. Such sliding velocity was selected to compare the stationary friction coefficients of the different emulsions under the same test conditions. Additionally, tribological heating and cooling temperature ramps from 40 to 100 °C and the other way around, were also performed by applying 20 N of F_N and 1 °C·min^{-1} of heating/cooling rate. At least five replicates of each tribological experiment were carried out on fresh samples, establishing a duration of measurement per point of 120 s to ensure stationary friction values.

2.3.5. Optical microscopy

An Olympus System Microscope BX52 (Japan) fitted with a light polarizer and an Olympus Digital Camera C5050Z with an objective of 4x were used to analyse the morphology of the prepared PCMLE before and after the previously detailed tribological temperature ramps tests

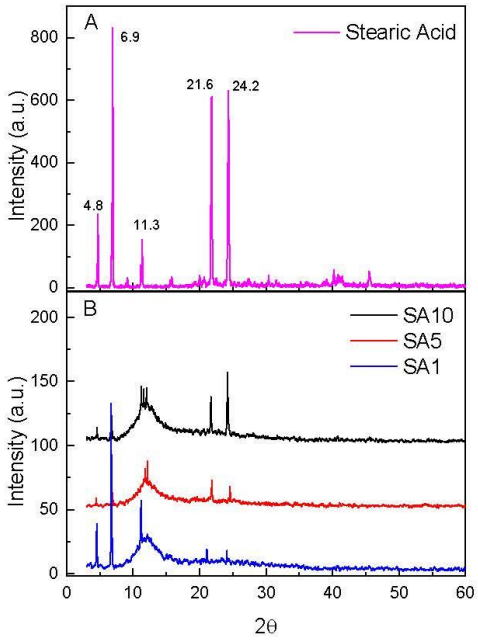
197 at room temperature. However, due to the abrasive wear mechanism obtained after friction tests
198 on steel-steel contact, this morphological characterisation was carried out after performing the
199 tribological temperature ramps tests on PMMA-steel contact. Thus, the lower measuring
200 geometry with three 45°-inclined steel plates was replaced by PMMA plates with similar
201 characteristics to the former to prevent metal wear and the subsequent presence of metallic
202 particles in the formulations. After tribological measurements, PCMLEs were carefully poured
203 into the sample holder (76 × 26 mm), obtaining the optical images under ordinary and cross-
204 polarized light.

205 Additionally, evaluation of the friction tracks remaining on the steel plates upon conducting
206 stationary tribological experiments at both temperatures (40 and 80 °C) was also conducted by
207 using optical microscopy at 4x magnification. The ensuing track values are reported as the
208 average resulting from the three steel plates after running six replicates.

209 ## 3. Results and discussion

210 ### 3.1. Crystalline structure of the disperse phase

211 The knowledge of the crystalline structure of dispersions is of paramount importance for the
212 proposed application, because it is directly related to the energy storage capacity since a large
213 crystallinity will lead to a high phase change enthalpy [25]. In this sense, Figure 1 shows the
214 wide-angle XRD patterns of pure stearic acid (Figure 1A) and stearic acid-in-silicone oil
215 emulsions (Figure 1B), which provides information about the crystal morphology of the
216 samples.



217

218 Figure 1. XRD patterns of a) pure stearic acid and b) non-aqueous phase change material
219 lubricating emulsions (PCMLEs).

220 For pure stearic acid (Figure 1A), the XRD pattern is characterised by the presence of several
221 well-defined peaks, where those placed at 2Θ = 21.6° and 24.0° are attributed to interplanar
222 spacings of ordered molecules, pointing out its crystalline state [26,27]. Therefore, the melting
223 and crystallization of stearic acid crystals, presented in DSC thermograms (Figure 2), are
224 responsible for the thermal energy storage and release during heating and cooling.

225 Concerning PCMLEs, on the one hand, XRD spectra display a large diffraction halo at around
226 12° (Figure 1B) which is ascribed to the continuous silicone oil phase of the emulsion, since
227 similar profiles have been reported for amorphous polydimethylsiloxane elsewhere [28,29]. On
228 the other hand, for all PCMLEs, the same conspicuous diffraction peaks attributed to the stearic
229 acid can be noticed as well, but with intensities proportional to the disperse phase ratio.

Particularly, the mentioned maxima corresponding to the interplanar spacing of stearic acid (21.6° and 24.0°), were not shifted with concentration, a fact that points out that the stearic acid exists in its crystalline form in all emulsions, even for the least concentrated one, at room temperature. These results also indicated that the internal crystal structure of stearic acid was not affected during the emulsification process [30].

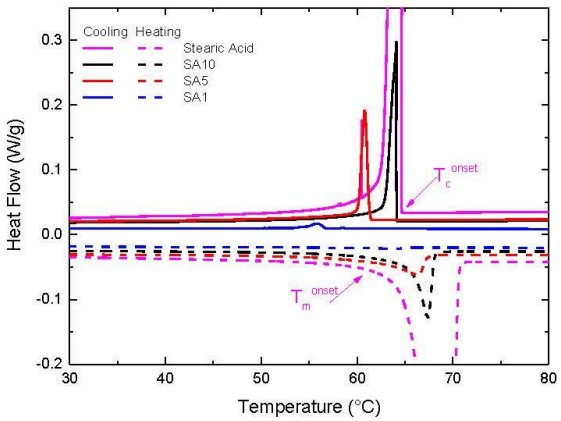


Figure 2. Heating and cooling DSC scans at 1 ºC·min^{-1}, for pure stearic acid and PCMLEs.

This is consistent with the results obtained in the DSC measurements (Figure 2 and Table 2) where it can be observed that the normalised enthalpies of the stearic acid, in the emulsion were practically unaffected and hence the total crystallinity. However, Figure 2 and Table 2 point out a clear decrease of phase change temperatures (T_m^{peak} and T_c^{peak}) when disperse phase concentration does, a fact that reveals partial compatibility of crystal structures of stearic acid with silicone oil and surfactant. Therefore, even though stearic acid crystal spacing is unaltered after emulsification i.e. disperse phase presents similar nano-scale morphology, this outcome is usually attributed to the partial disruption of the micro-crystalline structure, as a consequence of the high shear processing, which led to smaller size of crystals formed [21].

247 Table 2. Physicothermal properties of stearic acid and PCMLEs after applying tribo-
248 temperature tests.

CRYSTALLIZATION					
	DSC				Friction curves *
Sample	T_c^{onset} (°C)	T_c^{peak} (°C)	ΔH_c (J/g)	ΔH_c (J/g SA)	T_c^{frict} (°C)
Stearic Acid	64.6	64.7	225.2	225.2	-
SA10	64.1	64.1	21.2	213.8	72.7
SA5	61.3	60.8	10.4	208.6	69.6
SA1	56.6	55.9	1.8	180.2	51.1

249

250

MELTING					
	DSC				Friction curves*
Sample	T_m^{onset} (°C)	T_m^{peak} (°C)	ΔH_m (J/g)	ΔH_m (J/g SA)	T_m^{frict} (°C)
Stearic Acid	67.1	68.6	223.2	223.2	-
SA10	65.7	67.4	22.0	221.9	52.2
SA5	61.3	66.3	10.5	210.6	59.3
SA1	55.0	63.8	1.1	112.1	54.0

251 * T_m^{frict} and T_c^{frict} were calculated from tribo-temperature curves (Figure 9)

252 It is worth mentioning that, according to DSC results, solid stearic acid crystals are present
253 after cooling emulsions, below the phase change interval and, therefore, led to the development
254 of a suspension of solid structures. By contrast, above the melting interval, liquid melted
255 droplets dispersed in the silicone phase would form a genuine emulsion. Therefore, although
256 the concept of phase change material emulsion is extensively accepted, and so used along this
257 paper, strictly speaking, it would be more appropriate to use a more generic term as dispersions
258 of PCM.

259

3.2. Rheological behaviour

Formulated PCMLEs were characterised under Small Amplitude Oscillatory Shear (SAOS) conditions at 40 °C, below the crystallization temperature of the disperse phase. Figure 3 collects the resulting complex modulus (G*) and loss tangent (tan δ = G''/G') as a function of applied frequency. According to this figure, under these conditions, all stearic acid-based dispersions exhibited a gel-like behaviour, typically characterised by a predominant elastic response (tan δ < 1) and a minimum value of loss tangent (see Figure 3B), while complex moduli showed an almost negligible reliance on the frequency magnitude.

However, as previously reported [21], both linear viscoelastic responses and gel stiffness are strongly concentration-dependent. This effect is especially remarkable when rising the disperse phase content from roughly 1 up to 5 wt.%, since it led to a significant increase in G^* values from 57 Pa up to $3.5 \cdot 10^5$ Pa (at 1 rad·s^{-1}) and, therefore, to gels with a more structured supramolecular network. Further the addition of stearic acid, from 5-10 wt.%, imparted the PCMLE with a stronger gel-like structure, at 40 ºC, with larger G^* values and a clear loss tangent minimum (see Figure 3B). This rheological behaviour is a consequence of the development of a three-dimensional network of crystallised stearic acid particles which are physically interconnected with each other [21]. By contrast, at low stearic acid content (SA1), a much weaker structured network is revealed by its viscoelastic response, with the lowest G^* values and the presence of a shoulder in loss tangent rather than a minimum [31].

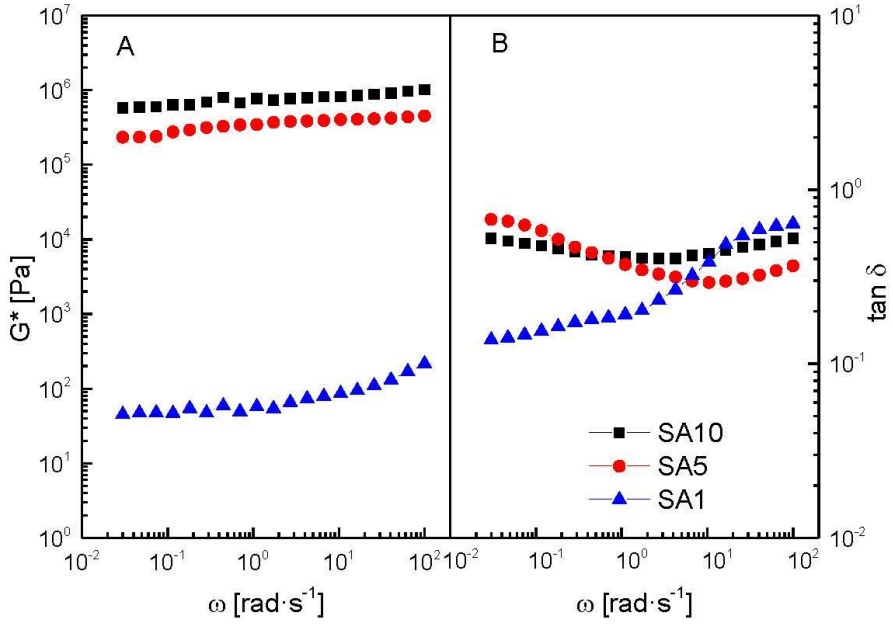
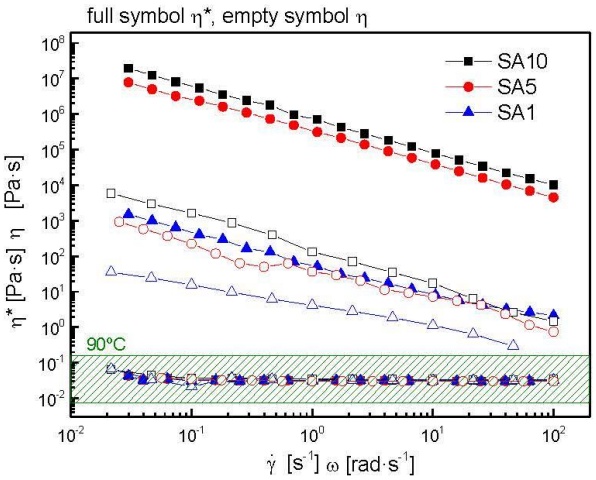


Figure 3. SAOS analysis results for all PCMLEs at 40 °C as a function of frequency, including a) complex modulus (G*) and b) loss tangent (tan δ).

The flow behaviour of the PCMLEs was also evaluated under steady-state conditions at 40 and 80 ºC, i.e., below and above the phase change of the stearic acid. Figure 4 displays the ensuing steady-state flow curves for all the stearic acid-based dispersions, i.e., the apparent viscosity (η) versus shear rate ($\dot{\gamma}$). As expected, stationary viscosity values of PCMLEs, at 40 ºC, are very sensitive to the disperse phase concentration, as in the case of SAOS measurements. In addition, is noteworthy that the melting of the continuous phase (see 80 ºC curves in Figure 4) dramatically modified the rheological response. Then, at 40 ºC, regardless of the dispersed

292 phase content, a sharp non-Newtonian behaviour can be observed, while a Newtonian response,
293 with similar values among samples, is evidenced at 80 °C upon melting of the stearic acid [21].
294 As an example, in the case of dispersion SA10 the apparent viscosity recorded at 1 s^{-1} decreased
295 from around 133.44 up to 0.032 Pa·s when heating to 80 °C (see Figure 4).



296

297 Figure 4. Complex viscosity (η*), at 40 °C, and steady-state apparent viscosity (η), at 40 and
298 80 ºC, for the formulated phase change emulsions.

299 Additionally, the applicability of the empirical Cox-Merz rule (see Equation 2) was also
300 analysed, according to which oscillatory complex (η^*) and apparent (η) viscosities can be
301 superimposed at equivalent frequency (0.01-100 rad·s^{-1}) and shear rate (0.01-100 s^{-1}) values,
302 i.e., $\dot{\gamma} = \omega$ [32,33], which is particularly useful to overcome the occurrence of likely
303 experimental limitations [32,34].

$$\eta(\dot{\gamma}) = \eta^*(\omega) \quad (2)$$

As can be deduced from Figure 4, at 40 ºC, the pseudoplastic behaviour of the stearic acid-based dispersions was also observed under SAOS conditions. However, the complex viscosity remained markedly superior to the steady-state counterpart, within the whole experimental range. As established in previous studies [34–37], such departure from the conventional Cox-Merz rule might be ascribed to the disruption of the microstructure as a consequence of the severe strain magnitude during the steady-state experiment, against small amplitude considered in the frequency sweeps, typically conducted in the pre-yield region. Furthermore, the magnitude of the deviation appeared to be more remarkable when raising stearic acid content above 1 wt.%, which is related to the mentioned development of a network of interacting particles [38]. In this concentration range, the much higher values of complex viscosities compared to steady-shear ones is a typical response of weak-gel networks which can withstand small oscillatory deformations but rupture under higher shear deformation in flow tests.

Consequently, to correlate both apparent and complex viscosities, which have been plotted in Figure 5, the generalized Cox-Merz rule has been considered in this study [34,37,38].

$$\eta^* = C \cdot \eta^{\alpha} \tag{3}$$

where C and α are experimental parameters, which are gathered in Table 3. According to the results, despite the inadequacy of the conventional Cox-Merz model for the considered PCMLEs, the introduction of the shift factor C and the power index α allowed to provide a proper correlation between both viscosities, for the evaluated PCM suspensions with a disperse phase content ranging from 1 up to 10 wt.%, which can be confirmed by the appropriate regression coefficients (R^2=0.99).

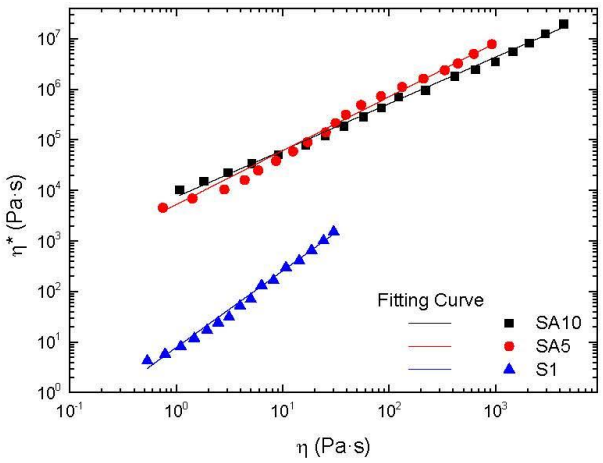
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326

327 Table 3. Generalized Cox-Merz fitting parameters for the studied PCMLEs.

PCMLE	C	α	R^2
SA10	7429.57 ± 212.76	0.92 ± 0.01	0.99
SA5	5250.12 ± 670.76	1.07 ± 0.02	0.99
SA1	7.82 ± 0.19	1.52 ± 0.01	0.99

328 On the other hand, the fitting parameter C is only slightly increased when raising the stearic
329 acid proportion above 5 wt.%, while experiencing a dramatic drop of around 99.9% below that
330 critical concentration (see Table 3), thereby evincing the significantly higher structured
331 network developed in SA10 and SA5, at 40 °C. Similarly, α presented values close to 1, at the
332 higher disperse phase content, while increasing around 70% for lower disperse phase
333 concentrations, therefore, revealing the higher susceptibility of its η* to the corresponding
334 steady-state properties.



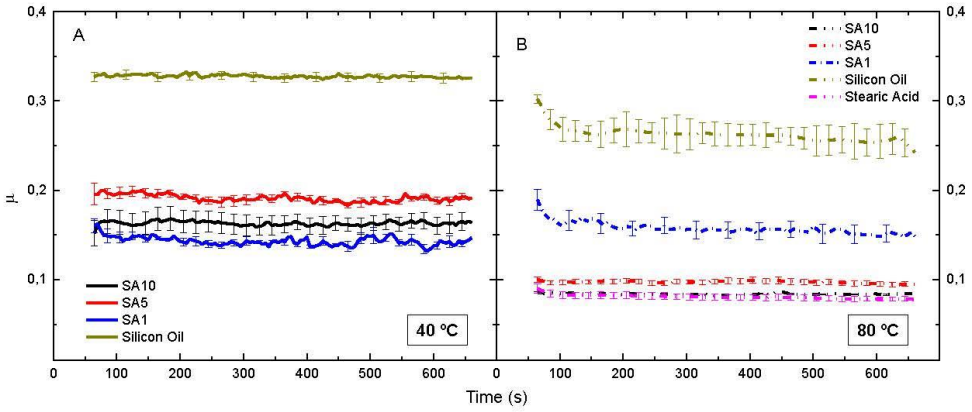
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336 Figure 5. Correlation between complex (η*) and apparent (η) viscosities, at 40 °C.

337 Consequently, values of the empirical parameters from the generalised Cox-Merz model can
338 therefore be used to estimate steady shear properties from small amplitude oscillatory shear
339 measurements for all PCMLEs at 40 °C.

340 **3.3. Tribological and thermo-physical properties**

341 Figure 6 shows the stationary friction coefficient curves of all PCMLEs when subjected to a
342 constant normal force of 20 N and a rotational speed of 10 rpm for 10 min. In this study, two
343 different temperatures (40 and 80 °C) were applied while testing to evaluate the tribological
344 behaviour of these emulsions, upon crystallisation of the dispersed phase and in its molten state.
345 As previously established, silicone oil by itself usually exhibits poor tribological
346 characteristics, with relatively high friction coefficients in comparison with other lubricating
347 oils [39,40].



348

349

350 Figure 6. Stationary friction coefficients of all formulated emulsions at a) 40 °C and b) 80 °C.

351 Interestingly, as can be deduced from Figure 6, a significant reduction in friction coefficients
352 was appreciated when using PCMLEs in tribological contact at both temperatures. Therefore,
353 an improvement of the tribological characteristics was obtained when dispersing stearic acid
354 in this oil, resulting in a remarkable drop in the friction coefficients together with the energy
355 storage capabilities [41]. In general terms, it should be noted that a temperature rise from 40 to
356 80 ºC, led to a significant decrease in the friction coefficients. This outcome is attributed to the
357 melting of the crystallized stearic acid (solid dispersions) that gave rise to the appearance of
358 liquid droplets in emulsions at 80 ºC.

359 In addition, some differences in the friction values can be noticed when modifying the amount
360 of stearic acid used to formulate them. As can be expected, the friction coefficients should be
361 decreased as the viscosity of emulsions increases since a thickened formulation would lead to
362 higher hydrodynamic pressures, thus promoting the entrainments of droplets into the
363 tribological contact [42]. However, for the measurements performed at 80 °C, the values of the
364 friction coefficients were reduced with stearic acid concentration but no differences in viscosity

were detected (Figure 4). In those systems, at 80 ºC, the disperse phase remains in its molten state, favouring a non-flocculated dispersion of spherical droplets within the continuous phase, where the relatively low volume fraction of stearic acid does not modify the emulsion flow characteristics [21]. This indicates that the tribological behaviour is not only affected by the viscous properties of materials but also by the emulsion microstructure. On the one hand, taking into account that the liquid stearic acid, at 80 ºC, presents the lowest friction coefficient, an increase of the disperse phase concentration of the emulsion is expected to progressively improve the lubricity, as it has been reported for water-based emulsions [43,44]. On the other hand, the droplet size of the disperse phase of the emulsion exerts a notable influence on friction and wear. In this sense, as pointed out by Wang et al. [42], larger droplet sizes could decrease friction as a consequence of the greater ease of being squeezed and entrained into the tribological contact, inducing coalescence and forming the protective friction film more easily. Therefore, the lowest emulsion friction values (0.08) were obtained for those PCMLEs containing a 10 wt.% of disperse phase with a diameter of droplets of 6.58 μm [21], where the protective film is more quickly generated, hence diminishing friction. Conversely, a lower concentration resulted in smaller droplet diameters (3.41 μm), as in the SA1 system, generating higher friction in the tribological contact (friction values of 0.15).

Nonetheless, at 40 ºC, i.e., at temperatures below its crystallization point, a different trend in the friction behaviour was identified, despite the low friction coefficients obtained. In this case, as it has been previously mentioned, stearic acid remains crystalline leading to a gel-like behaviour and a significant increase in the viscosity of the system (Figure 4). Thus, an increase in the amount of stearic acid gives rise to a decrease in the friction coefficients, which is in accordance with the rise of emulsion viscosity at 40 °C. Such crystalline structure brings about a major effect on viscosity for the most concentrated emulsions (SA10 and SA5). Thus, lower friction values were obtained for SA10 formulation (0.16) than those shown by suspensions

390 comprising 5 wt.% of disperse phase in its crystalline state (0.19 for SA5) due to the formation
391 of stronger microstructural networks. Moreover, stearic acid provides a high affinity to metal
392 surfaces due to the existence of polar components in its chemical structure, which favours
393 adherence to tribological contact. Thereby, a thicker tribo-film would be formed with higher
394 weight fractions of stearic acid, providing a higher separation between the tribological contact
395 and obtaining a uniform decrease in the friction coefficient [10,23]. An unusual behaviour was
396 displayed for SA1, which showed the lowest friction value (0.14) despite containing a smaller
397 amount of crystalline phase. However, the markedly different rheological properties and
398 microstructure could produce a different hydrodynamic lubrication regime, which may make
399 it not directly comparable to the others. Then, the much lower number of crystals in the SA1
400 emulsion, coupled with the friction-generated heat in a tribological contact, would explain this
401 decrease in the friction coefficients.

402 Concerning the wear of the metal surfaces, Figure 7 shows the scar diameters obtained after
403 performing the stationary friction tests under constant load and sliding speed for 10 min. This
404 wear is plotted as a function of the concentration of the disperse phase, comprising the phase
405 change emulsions at two different temperatures (40 and 80 °C). For tests carried out at a low
406 temperature, the existence of solid particles in the oil suspensions could lead to an increase in
407 wear, in comparison with those shown by pure silicone oil, as a consequence of particle sliding
408 during shear [45,46]. However, raising the concentration of stearic acid fosters the achievement
409 of a more structured supramolecular network and an increase in the tribo-film viscosity [21],
410 which, together with the greater number of polar groups and their affinity to metal surfaces,
411 allows for reduced wear [10]. However, as well as the friction coefficients, SA1 formulation
412 resulted in lower wear scar diameter values, probably due to lower concentration of the disperse
413 phase. Despite this, SA1 formulation displayed noticeable differences in wear surface in
414 comparison with the samples comprising higher amounts of stearic acid. As can be seen in

Figure 8, although all formulated dispersions exhibited abrasion characteristics, a lower wear diameter but with wide furrows and dark grooves with deep craters were obtained for suspension containing the lower amount of crystalline phase. In this case, metal particles dispersed freely into emulsion can easily get into the contact zone contributing to wear and generating abrasions [47,48].

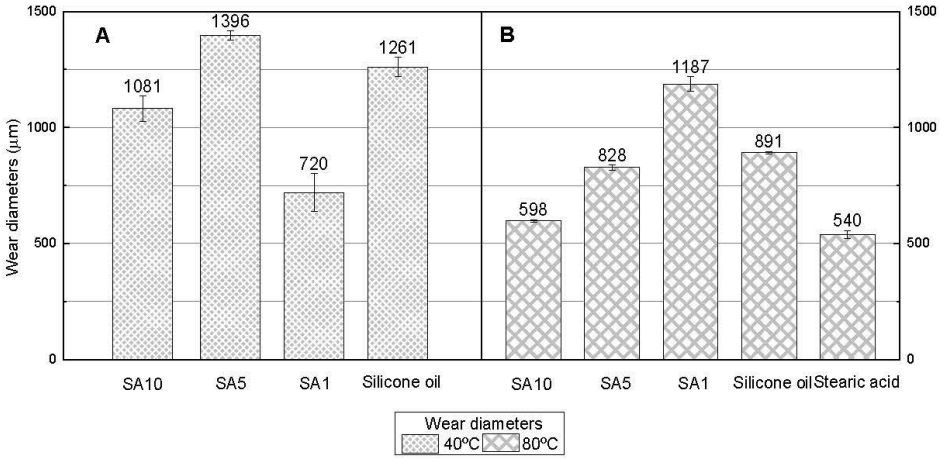


Figure 7. Wear scar diameters obtained after tribological tests conducted at a different temperature, taken from Figure 8: a) 40 and b) 80 °C.

Likewise, at high temperature, the wear scar diameters were reduced as the amount in the disperse phase concentration increased. In these formulations, although the viscosity of samples was quite similar to those found by the pure silicone oil at this temperature (80 °C) [21], the wear diameters decreased as a consequence of the easy formation of the wear-protective tribo-film [42]. Thus, larger droplets inducing coalescence and squeezing and entraining into the lubricant contact were obtained when adding a concentration of dispersed phase higher than 5 wt.%, easily generating a tribo-film that covers the metal surfaces and provides a noticeable decrease in wear.

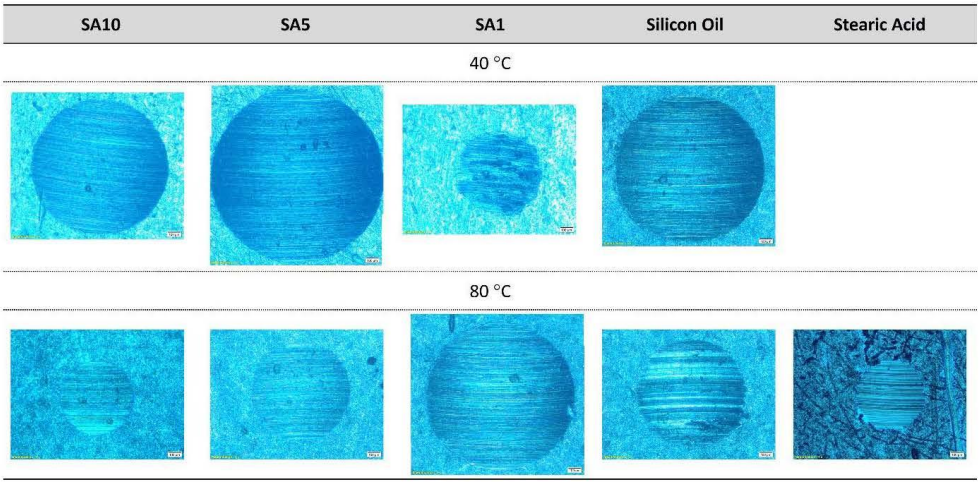


Figure 8. Wear scar images obtained by optical microscopy after tribological tests.

On the contrary, SA1 formulation showed a high wear scar diameter, even larger than that shown by the continuous phase, which can be attributed to the relatively low amount of stearic acid forming the non-flocculated dispersion. In this case, the smaller size droplets, which would need extra time to form the wear-protective tribo-film, produced relatively high friction at 80 °C (see Figure 6), causing abrasion wear on the metal surface and squeezing out metal particles from the contact zone. These expelled particles could accumulate around the edge of the wear scar as a consequence of the low viscosity of the systems, thus enlarging the scar diameter [48]. Finally, the PCMLE comprising the highest concentration (10 wt.%) of crystalline phase showed the lowest wear scar diameter, also displaying a smoother wear surface with softer abrasion as a result of the fast formation of the protective film adhered to the tribological contact.

Additionally, the effect of the phase change process and the recovery capacity of these formulations during friction were studied by applying tribological tests under heating and cooling temperature ramps in the 40-100 °C range and compared with DSC scans both

449 performed at 1 ºC·min^{-1}. Figure 9 shows the friction coefficients of the different PCMLEs and
450 their base components when applying 20 N of F_N, 10 rpm of velocity and 1 °C·min^{-1} of
451 heating/cooling rate. Moreover, although the Stribeck curves have not been described in this
452 work, a rough estimation of the Sommerfeld parameter [49] could be obtained by fixing normal
453 load and sliding velocity during the test. Therefore, taking into account that stationary friction
454 values were obtained under these constant conditions, the frictional behaviour of these
455 materials could be analysed as a function of both the viscous properties of each formulation
456 and the prevailing lubrication regime [50]. In general terms, as determined in stationary friction
457 tests, friction coefficients of PCMLEs were notably lower than those obtained by the pure
458 silicone oil in the whole range of temperatures studied. Moreover, these values were drastically
459 reduced as temperature raised, and vice versa, which could be related to two simultaneous
460 phenomena, i.e., the melting/crystallisation of the dispersed phase with modifying temperature
461 and the shifting throughout the different regimes of the Stribeck curve. In addition, as
462 previously mentioned, rheological data pointed out a clear dependence of viscosity on the
463 melting and crystallisation point of the stearic acid [21]. In this way, relatively high friction
464 values were obtained for all systems when applying low temperatures, which match with the
465 melting/crystallisation point of stearic acid obtained in DSC tests (Table 2), providing a higher
466 value of Sommerfeld parameter due to the higher viscosity of these formulations at low
467 temperatures. In this case, the Boundary regime could be dominant in these temperature ranges,
468 since relatively constant friction values were attained. However, as the temperature increased
469 and the sliding was maintained, the stearic acid on the contact surface melted due to the effect
470 of friction heat and temperature increase, which resulted in lower friction coefficients. This is
471 strongly influenced by the viscosity drop of several orders of magnitude that probably yields
472 the shift to the mixed lubrication regime where the friction coefficient is reduced [51].
473 Nonetheless, although the friction coefficient was variable throughout the temperature range

studied, it is noteworthy that after the heating and cooling cycles, the systems were able to recover their tribological properties upon their phase change, thus indicating great stability from the point of view of their friction characteristics.

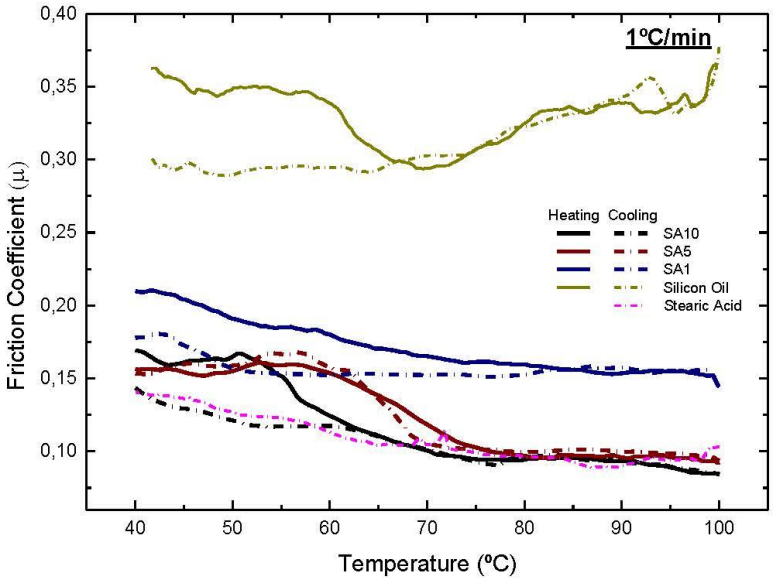


Figure 9. Friction coefficients of the different PCMLEs and their base components when applying tribological tests under heating and cooling temperature ramps.

Regarding the effect of disperse phase concentration, several differences can be also detected in the tribological curves. As previously stated, thermal characterisation was conducted on fresh PCMLEs and the effect of friction over the onset of melting (T_m^{onset}) and crystallisation (T_c^{onset}) points, and their corresponding enthalpies (ΔH_m, ΔH_c) is the subject matter of this study. Consequently, as can be seen from the thermal results collected in Table 2, the peak and onset melting and crystallisation temperatures (Figure 2), as well as their corresponding enthalpies have been calculated from DSC tests.

Furthermore, it is important to note that, a more pronounced shift in both phase change temperatures (from 9 to 12 °C), was appreciated in tribological temperature ramps in comparison with DSC data i.e. without shearing (see T_m^{onset}, T_c^{onset}, T_m^{frict}, T_c^{frict} in Table 2). This effect is in line with two observations which have a particular impact on the latter emulsion. Firstly, it is consistent with the idea that the protective barrier formed by silicone oil and surfactant slows down the process of crystallisation and melting. Secondly, a similar trend of reduced phase change temperatures and enthalpies was found in multiple thermal reliability studies on stearic acid after intense processing, which is the case for tribological testing [52,53]. On the other hand, as it is well known, the effect of shear/friction can significantly disturb the way crystals grow and melt, leading to changes in their thermal characteristics. Therefore, this result clearly indicates that the high shear rate in tribological tests exerts an evident contribution to the increase in the crystal nuclei density [54]. In addition, extra energy can be provided by this friction, which promotes both crystallisation and melting mechanisms and modifies their thermal points to early stages due to the easy particle diffusion under friction [55].

3.4. Optical microscopy

The influence of the tribological process on the crystal's formation in PCMLEs was also studied by optical microscopy analysis. Micro-morphology images were taken at room temperature over the fresh samples and upon application of tribological-temperature heating-cooling ramp tests on PMMA plates. Thus, Figure 10 shows the optical images with/without cross-polarised light for the three PCMLEs with different disperse phase concentrations, aimed at identifying the effect of friction force on the formation of crystalline structures, which can be seen as bright regions under cross-polarisers. Albeit the influence of the stearic acid concentration in PCMLE, detailed in a previous publication [20], the effect of friction on the crystallisation process of these emulsions was further evaluated in this research.

Firstly, according to the optical micrographs, the multiphasic nature of emulsions is revealed, with different shapes of the disperse phase that evolve from globular to needle-like or rod-like structures, depending on the disperse phase concentration. On the other hand, by inspecting the same samples under cross-polarized light in prior tribological tests (before shear), self-assembled crystalline structures are progressively developed for systems bearing PCM content above 1 wt.% (SA5 and SA10). Then, this three-dimensional crystalline network is responsible for the previously reported gel-like behaviour, that would explain the observed rheological properties.

A more remarkable effect could be noted after conducting tribological tests as shown in Figure 10. In this regard, the performance of the heating-cooling tribological temperature ramps over the formulated PCMLEs expectedly resulted in significantly lower crystallite sizes [56]. Consequently, over the course of these tribological measurements, not only liquid-to-solid phase change would likely alleviate the detrimental effect of the overheating generated in the tribological contact, but also the crystallite breakdown may contribute to the energy dissipation process. Therefore, bearing in mind the generally lower friction coefficient and the larger tribo-film viscosity ascribed to SA10, the energy required to be dissipated throughout its tribological characterisation might be relatively lower than that corresponding to PCMLEs bearing lower stearic acid proportions, hence yielding reduced wear scar values and larger crystallites after completion of the tribological experiment (see Figure 7). On the contrary, owing to the likely occurrence of abrasion wear during friction when considering emulsion SA1, as well as its superior frictional coefficient, an increase in the friction-generated energy within the tribological contact could be expected, resulting in smaller crystal size accordingly.

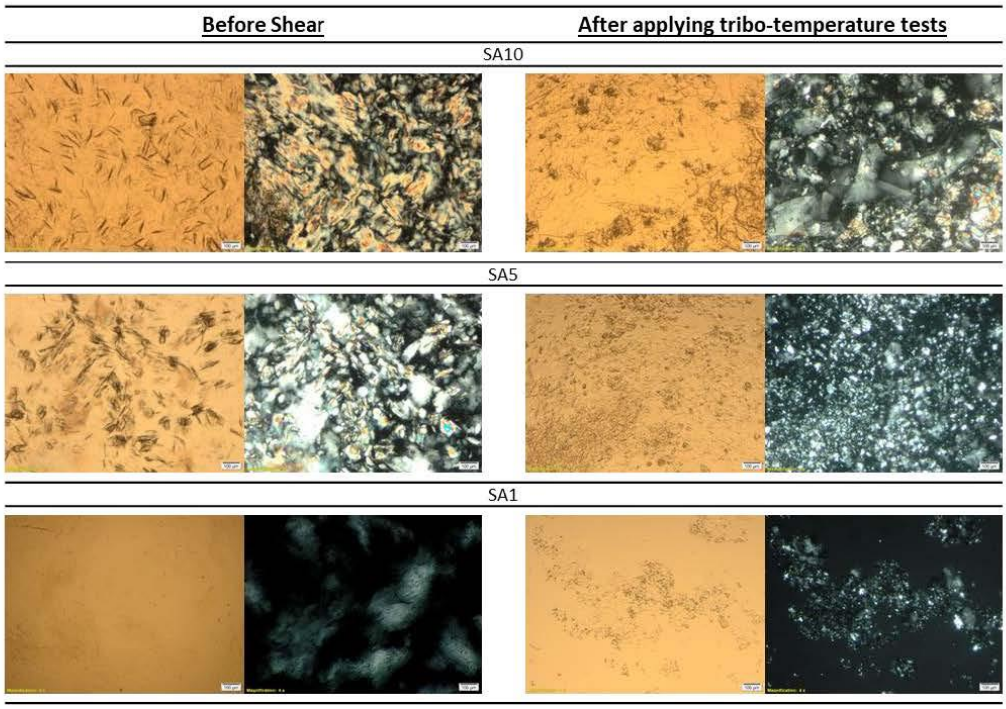


Figure 10. Micro-morphology images of PCMLEs, at 40 °C, taken over fresh samples and after application of tribological-temperature heating-cooling ramp tests.

4. Conclusions

Stable PCMLEs, composed of a dispersed stearic acid in silicone oil were successfully stabilised with an adequate non-ionic surfactant to be used as a novel lubricant with improved thermal characteristics. The reported rheological properties result in being strongly dependent on disperse phase ratio and testing temperature. Thus, at 40 °C, i.e. below the melting point of the disperse phase, stearic acid remains in a crystalline state and SAOS discloses a clear gel-like behaviour for disperse phase ratios equal to more than 5, as a consequence of the development of a three-dimensional network of crystal structures, whereas a much weaker structured network is noticed at lower ratios (SA1). However, the observed strong deviation of the empirical Cox-Merz revealed from the comparison with stationary flow tests and

546 tribological tests pointed out a high susceptibility to shear and the weakness of the developed
547 network, as demonstrated by optical observations. On the contrary, at 80 ºC, i.e. above the
548 melting interval of stearic acid, liquid melted droplets are dispersed in the silicone phase,
549 leading to a low viscosity Newtonian behaviour almost independent of concentration.

550 The reported rheological behaviour and developed microstructure led to a remarkable
551 improvement of the tribological characteristics since PCMLEs friction coefficients are lowered
552 compared to silicone oil. In addition, the melting of the disperse phase also gave rise to a
553 significant decrease in the friction coefficients. Finally, the heat storage capacity of PCMLEs
554 contributes to the delay of the phase change temperate in the tribological temperature ramp
555 test.

556 **Acknowledgements**

557 Grant PID2020-116905RB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and grant
558 TED2021-131284B-I00 funded by MCIN/AEI/10.13039/501100011033 and European Union
559 "NextGenerationEU"/PRTR. Clara Delgado and Adrián Tenorio also acknowledge financial
560 support from Junta de Andalucía through post-doctoral Grants DC 01228 (co-funded by the
561 EU Fondo Social Europeo (FSE)) and POSTDOC_21_00644, respectively.

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IV/5. Patent

OFICINA DE TRANSFERENCIA DE RESULTADOS DE INVESTIGACIÓN
UNIVERSIDAD DE HUELVA

SOLICITUD P202330101

EMULSIONES ANHIDRAS DE MATERIALES DE CAMBIO DE FASE PARA APLICACIONES DE MEDIA Y ALTA TEMPERATURA

RESUMEN

La invención se refiere a una emulsión anhidra que comprende un material de cambio de fase de naturaleza orgánica, inorgánica o mixta orgánica-inorgánica, que experimenta un cambio de fase a temperaturas entre 25 y 800 ºC, disperso en una fase continua de naturaleza orgánica, inorgánica o mixta orgánica-inorgánica y al menos un agente estabilizante, y a un procedimiento de preparación de la emulsión definida que comprende:

- a) dispersión de uno o más estabilizantes en una fase continua

- b) añadir el MCF en estado fundido a la mezcla obtenida en la fase continua anterior,

- c) una etapa de emulsificación.

TITULAR

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Número de solicitud:	P202330101	
Fecha de recepción:	10 febrero 2023, 12:35 (CET)	
Oficina receptora:	OEPM Madrid	
Su referencia:	PII-2023-002- Solic	
Solicitante:	Universidad de Huelva	
Número de solicitantes:	1	
País:	ES	
Título:	Emulsiones anhidras de materiales de cambio de fase para aplicaciones de media y alta temperatura	
Documentos enviados:	Descripcion-1.pdf (15 p.) Reivindicaciones-1.pdf (3 p.) Dibujos-1.pdf (9 p.) Resumen-1.pdf (1 p.) OLF-ARCHIVE.zip POWATT.pdf (11 p.) FEERCPT-1.pdf (3 p.)	package-data.xml es-request.xml application-body.xml es-fee-sheet.xml feesheet.pdf request.pdf
Enviados por:	CN=RODRIGUEZ QUINTERO JOSE - 27309420W,SN=RODRIGUEZ QUINTERO,givenName=JOSE,serialNumber=IDCES-27309420W,C=ES	
Fecha y hora de recepción:	10 febrero 2023, 12:35 (CET)	
Codificación del envío:	F4:7E:F1:67:38:4A:AD:67:DF:5C:06:E2:2A:53:AD:FD:33:C0:86:03	

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Emulsiones no acuosas de materiales de cambio de fase para aplicaciones de media temperatura

Campo de invención

La invención pertenece al campo técnico de las emulsiones de materiales de cambio de fase y comprende la formulación y método de preparación de éstas, con una orientación preferente hacia aplicaciones de almacenamiento y transporte de energía térmica en el intervalo de temperaturas medias comprendido entre 100 y 400 °C. Estas dispersiones están formadas por dos fases no acuosas inmiscibles, siendo la fase dispersa un material de cambio de fase (MCF) con una temperatura de transición de fase mayor a 100 °C, estabilizadas por micro/nano partículas (partículas "pickering") o por tensioactivos no iónicos.

Estado de la técnica

En la actualidad, los sistemas de almacenamiento de energía son utilizados ampliamente para la utilización eficiente y la conservación de la energía fuera de las horas punta, la utilización del calor residual y las fuentes de energía intermitentes, aprovechando inteligentemente los recursos energéticos y disminuyendo el consumo de energía. Un método atractivo e innovador para almacenar energía térmica son los llamados materiales de cambio de fase (MCF). Éstos son compuestos químicos que, al sufrir una transición de fase, almacenan o liberan grandes cantidades de energía en forma de calor latente a temperaturas constantes.

Estos materiales de cambio de fase pueden añadirse a los fluidos caloportadores convencionales, obteniendo fluidos térmicos funcionales que presentan una mayor capacidad específica de almacenamiento de calor por el uso del calor latente. En concreto, existen Emulsiones de Materiales de Cambio de Fase (EMCF) donde un material de cambio de fase se encuentra suspendido en forma de gotas en un fluido de transferencia de calor. Estos sistemas poseen un gran potencial de desarrollo futuro y muestran aplicaciones prometedoras en muchos campos de la conversión, producción y almacenamiento de energía, ya que permanecen en estado fluido durante todo el proceso de cambio de fase, lo que permite un fácil bombeo y circulación en los sistemas de almacenamiento y transporte de energía. Además, la insignificante resistencia térmica de la capa tensioactiva protectora entre la fase continua y el MCF, en comparación con los materiales encapsulados, las hacen aún más prometedores ya que favorecen la transferencia de calor durante el servicio.

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Hasta el momento, sólo se han desarrollado EMCFs que emplean agua como fluido portador, lo que limita fuertemente su rango de aplicación. A continuación, se hace referencia algunas patentes de EMCFs en el rango medio de temperatura, como puede ser emulsiones de alcanos puros o mezclas con una temperatura de cambio de fase entre 20-100 °C (CN107353878A, DE202009018635U1 o CN103146349A). También, se han descrito patentes de EMCFs para bajas temperaturas, empleando soluciones de compuestos que disminuyen el punto de congelación del agua, localizándose la temperatura de transición sólido-líquido en el rango de –30 y 0 °C (EP2127737A2 o CN109777366A).

Sin embargo, no se tiene constancia de EMCFs con aplicación en rangos de temperatura superiores a 100 °C ya que la fase acuosa limita el intervalo de uso. A pesar de esto, la utilización directa de MCF con temperaturas de cambio de fase, en rangos de temperatura medio-alto 100-300 °C y altos >300 °C, sí es un método ampliamente utilizado. Estos sistemas desempeñan un papel importante no solo en la recuperación de energía, sino que, además, pueden actuar como termorregulador en reacciones químicas, mejorando la distribución de la temperatura en el reactor y frenando la fluctuación de temperatura. Principalmente, estos MCFs en esos rangos de temperatura se utilizan para la captación de energía solar, la recuperación del calor residual industrial y aplicaciones similares. De esta forma, se contribuye a resolver los problemas de desajuste de la oferta y la demanda de energía térmica, reduciendo la inestabilidad y discontinuidad de ésta causada por factores como puede ser el clima. Una de las aplicaciones más utilizadas es concretamente la recuperación del calor de un flujo de gases de escape (off-gas) con alta energía generada en un proceso industrial (proceso industrial y de servicios) para evitar no sólo la pérdida de energía sino también problemas de contaminación.

En ambos rangos de temperatura, existen numerosas patentes relacionadas con esta utilización de MCFs para su uso en eficiencia energética. Por un lado, se puede encontrar patentes más relacionadas con el diseño del propio MCF que se va a utilizar en esos rangos de temperatura, como son CN104559936B (que emplea ácido adípico en el intervalo 150-160 °C) o CN113845886A (que usa mezclas de materiales para que haya distintas temperaturas de aplicación). Por otro lado, se encuentran patentes en la que el MCF se encuentra formando parte de otros compuestos (CN102585775B) como puede ser materiales con base carbonada (CN113621350A), cerámicas (CN109135683B y CN105790638B) o espumas metálicas (CN104135191A). El principal problema que presentan estos sistemas es que, durante el cambio de fase del MCF, se pueden producir fugas o filtraciones por el compuesto o la matriz. Para tratar de prevenir

estos problemas, se han descrito invenciones relacionadas con la fabricación de estructuras de núcleo-caparazón mediante encapsulación (CN109054758B) o el diseño de equipos o dispositivos donde almacenar estos MCFs (JP6040318B2 o CN102374812A).

Por tanto, no existen hasta el momento ninguna EMCF que pueda ser utilizada en aplicaciones donde la temperatura de cambio de fase es superior a los 100 °C. Las emulsiones no acuosas de MCF ofrecen la ventaja de poder ser utilizadas en aplicaciones donde las emulsiones basadas en agua tienen restringido el límite superior de temperatura. De esta forma, se pueden desarrollar emulsiones para utilizarlas en colectores solares de alta eficiencia, en recuperación de calor industrial y en sistema de baja e intermedia temperatura.

Descripción de la invención

La presente invención tiene como objetivo hacer frente a las limitaciones mostradas en el estado de la técnica, permitiendo la utilización de emulsiones con materiales de cambio de fase a temperaturas superiores a los 100 °C. Esta mejora se obtiene principalmente gracias a la utilización de emulsiones anhidras, mejorando así la funcionalidad de estos sistemas para su utilización en procesos de transporte y/o almacenamiento de energía que requieran temperaturas superiores a los 100 °C.

Las emulsiones no acuosas con MCF que se presentan en esta invención se consideran un tipo particular dentro del campo de las dispersiones. Estas emulsiones se obtienen emulsionando dos fases oleosas inmiscibles gracias a un agente estabilizante. La fase continua de la emulsión, un fluido oleoso, actuará de fluido portador y en ella se dispersa un MCF, como fase dispersa, con temperaturas de cambio de fase superiores a 100 °C. La dispersión efectiva del MCF en el fluido portador se lleva a cabo por acción mecánica utilizando un agente estabilizante, que puede ser un tensioactivo o partículas sólidas (emulsión tipo pickering), y empleando un agitador o dispersor, preferiblemente de alta cizalla. En esta invención se contempla las siguientes proporciones en peso: 1-90 % de fase dispersa o MCF, 0.01-10 % de agente estabilizante y el resto de porcentaje de fase continua.

En la presente invención, se entiende por fase continua los fluidos portadores no acuosos, de base oleosa, con baja viscosidad que faciliten el transporte del MCF y que presenten una adecuada resistencia a la temperatura. Los fluidos portadores pueden ser aceites vegetales, refinados o modificados de base vegetal (ricino, girasol, colza,

palma, soja, etc.), fluidos siliconados de alta temperatura (por ejemplo, polidimetilxilosanos), terpenos naturales o sintéticos (limoneno, terponoleno, pineno) o aceites sintéticos (aceites parafínicos, aromáticos, hidrocarbonados, etc), bifenilo y óxido de difenilo, mezclas de isómeros de dibencil bencenos o bencil tolueno, etc.

Como componentes de la fase dispersa, MCFs, se entienden en la presente invención los compuestos polares o apolares que presentan un cambio de fase sólido-líquido o sólido-sólido a temperaturas superiores a 100 °C. La invención incluye polialcoholes con transiciones sólido-líquido como alcoholes de azúcares (desde C4 Eritritol o C6 D-Mannitol hasta C24 Lactitol, con transiciones de 117, 120, 240 °C, respectivamente) y polialcoholes con transiciones sólido-sólido (como pentaeritritol (182 °C) o Tris(hidroximetil)metil aminometano (135 °C)). Además, la invención incluye alcanos industriales (trans-1,4-polibutadieno (145 °C), poliolefinas (polietileno de alta densidad y polipropileno (120-160 °C), sales metálicas de ácidos grasos (estearato de zinc (120 °C), calcio (140-160 °C), magnesio (150 °C), aluminio (150-170 °C), litio (220 °C), etc.) y otros compuestos (acetanilida (119 °C), ácido benzoico (121 °C), estilbeno (124 °C), benzamida (127 °C), urea (134 °C), ácido adípico (152 °C), etc.), entre otros.

En cuanto al método de estabilización de la fase dispersa en la fase continua, la presente invención considera tanto a las nano o micropartículas (tipo Pickering) como a los tensioactivos. En ambos casos, los agentes estabilizantes deben presentar una adecuada resistencia a la temperatura para el diseño de estas dispersiones. La invención entiende por partículas sólidas emulsionantes tipo pickering a nanopartículas de sílices pirogénicas modificadas superficialmente con distintas cadenas orgánicas en un rango de C8-C30 átomos de carbono (por ejemplo, Aerosil R106, Aerosil R805, Aerosil R974), nanotubos de carbono o grafeno (en su estado original o modificados), nanopartículas metálicas o óxidos metálicos (por ejemplo, Al_2O_3, TiO_2), etc. En cuanto a tensioactivos, se consideran preferentemente los de tipo no iónicos, como por ejemplo alquilfenoles etoxilados de cadena larga, copolímeros en bloque de alta temperatura (por ejemplo, el poliestireno-b-polietilenglicol o éster de metilmetacrilato (PS-PPEGMA)) y emulsionantes a base de silicona (en dos formas estructurales tipo peine y tipo bloque, con bloques injertados a medida, principalmente cadenas de polioxietileno y/o polioxipropileno).

El proceso de emulsificación de las presentes EMCF no acuosas, con MCF de temperaturas superiores a 100 °C, comprende las etapas detalladas a continuación. Inicialmente, todos los compuestos necesarios para la preparación de la emulsión son calentados a una temperatura superior a la temperatura de cambio de fase del MCF

utilizado. Una vez que todos los compuestos están atemperados, se dispersa el emulsionante (partículas o tensioactivo) en la fase continua de la emulsión hasta homogeneización. Finalmente, se añade el MCF a la mezcla hasta la formación de la emulsión. La emulsificación se realiza preferentemente por medio de un homogeneizador rotor-estator de alta cizalla (1-10 min, 2000-20000 rpm), y/o una sonda de ultrasonidos (0.5-5 min, 10-60 % amplitud, 20-40 kHz).

Las emulsiones preparadas presentan una adecuada estabilidad al almacenamiento en estático, a temperaturas superiores a la del cambio de fase, y a los ciclos térmicos sucesivos de calentamiento/enfriamiento.

Por lo tanto, en la presente invención se ha logrado estabilizar dos fases oleosas inmiscibles, siendo una de ellas un MCF, mediante la formación de una emulsión estable. Además, las dispersiones obtenidas pueden ser empleadas a temperaturas de servicio por encima los 100 °C para aplicaciones de almacenamiento y transporte de energía térmica. Una revisión del estado de la técnica indica que no se tiene constancia de invenciones similares, que puedan ser empleadas a temperaturas superiores a los 100 °C. Las EMCFs no acuosas propuestas en la presente invención incorporan una alternativa competitiva para los procesos de recuperación, almacenamiento o transporte de energía térmica a temperaturas superiores a 100 °C.

Descripción de las figuras

Figura 1. Termograma de calorimetría diferencial de barrido (DSC) del MCF.

Figura 2. Termograma de calorimetría diferencial de barrido (DSC) de un ejemplo de emulsión no acuosa de material de cambio de fase (EMCF).

Figura 3. Ensayo de flujo viscoso de un ejemplo de EMCF, a 0 °C (por debajo del punto de fusión de la fase dispersa) y a 140 °C (por encima del punto de fusión).

Figura 4. Espectro mecánico de una EMCF con la temperatura (desde 140 °C a 0 °C).

Figura 5. Microfotografías de la EMCF x10 aumentos tomadas a (a) 140 °C (b) 20 °C y (c) 20 °C con polarizadores cruzados.

Descripción detallada de la invención

La presente invención se refiere a la formulación y procesado de emulsiones no acuosas de materiales de cambio de fase cuya transición sólido-líquido o sólido-sólido se localiza a temperaturas superiores a los 100 °C, estabilizadas mediante emulsionantes no iónicos o mediante partículas, con propiedades de almacenamiento y/o transporte de energía.

El ejemplo que se incluye a continuación permite ilustrar los efectos beneficiosos de la presente solicitud, sin limitar la invención propuesta.

Ejemplo: Preparación de una EMCF no acuosa con Estearato de Zinc como MCF

Preparación de la emulsión: Se añade 0.45 g de agente estabilizador (nano-partícula de sílice, AEROSIL® R 805), en 36 g de fase continua (aceite de silicona) y se somete a agitación hasta homogenización. La mezcla se atempera a 140 °C y, a continuación, se añaden 9 g de fase dispersa (estearato de zinc, ZnS), previamente atemperado a 140 °C, y se emulsifica el sistema utilizando un homogeneizador de alta cizalla rotor-estator a una velocidad de 19000 rpm durante 5 min. Transcurridos 5 min, se obtiene una emulsión estable del estearato de zinc (material de cambio de fase) en aceite de silicona.

Con el objetivo de mostrar y verificar las características óptimas que poseen estas emulsiones para la aplicación de almacenamiento de energía térmica, se han analizado sus propiedades termo-físicas, reológicas, tanto en condiciones de flujo como oscilatorias y la morfología a través de microscopía óptica.

Inicialmente, se muestran los resultados de la caracterización termo-física. Las propiedades térmicas son claves para la aplicación de esta invención, ya que la emulsión debe presentar una buena capacidad de almacenamiento de energía. Por ello, en la Figura 1 y Figura 2 se muestran las curvas de los análisis de calorimetría diferencial de barrido, en condiciones de atmosfera inerte (N_2) a una velocidad de calentamiento/enfriamiento de 10 °C/min, para el MCF puro y para la EMCF no acuosa, respectivamente. A partir de ambos termogramas (Figura 1 y Figura 2) se pueden extraer los datos de entalpías de cristalización y fusión de ambos sistemas y las correspondientes temperaturas de cambio de fase. Estos datos se encuentran recogidos en el Tabla 1.

Tabla 1. Propiedades térmicas del MCF y la EMCF analizada.

	ΔHc (J/g ZnS)	Tc (°C)	ΔHm (J/g ZnS)	Tm (°C)
Estearato de Zinc	140.96	88.2	140.95	121.2
EMCF	136.43	82.5	134.37	119.2

En los resultados de la Tabla 1 se puede observar que el estearato de zinc tiene una alta capacidad de almacenamiento de energía térmica (141 kJ/kg). Esta entalpía de cambio de fase se mantiene casi inalterada una vez introducimos este MCF en la emulsión como fase dispersa. Se puede observar una muy ligera disminución de la entalpía y temperatura de cambio de fase, probablemente debido a la presencia de las nanopartículas estabilizantes que distorsionan ligeramente la cristalinidad del MCF. Sin embargo, en definitiva, la emulsión presenta una elevada capacidad de almacenamiento de energía en forma de calor latente y una pérdida insignificante de cristalinidad.

Después de comprobar su capacidad de almacenamiento de energía es necesario estudiar sus propiedades reológicas, ya que éstas darán información de su aplicabilidad como un fluido de caloportador, en las operaciones en servicio. La Figura 3 muestra las curvas de flujo antes y después del cambio de fase del MCF. La EMCF muestra un marcado comportamiento pseudo-plástico, con una caída de casi 4 órdenes de magnitud con el aumento de la velocidad de cizalla. La emulsión presenta este comportamiento a ambas temperaturas, siendo la viscosidad de la emulsión a 0 °C mayor que a 140 °C como cabría esperar debido a la cristalización de la fase dispersa. El comportamiento de flujo viscoso indica que la microestructura de la dispersión es muy susceptible a la cizalla, lo cual es claramente positivo desde el punto de vista de la aplicación porque,

comúnmente, las operaciones industriales de procesado y bombeo implican velocidades de cizalla dentro del régimen intermedio-alto (1-1000 s^{-1}).

Por otro lado, la Figura 4 recoge la respuesta viscoelástica (módulos de almacenamiento, G', y módulo de pérdidas, G") de la EMCF durante el proceso de cambio de fase. Es decir, su dependencia con la temperatura, a una frecuencia constante, dentro del intervalo viscoelástico lineal de la emulsión y empleando una geometría de platos paralelos rugosos de 50 mm de diámetro, mientras la muestra es sometida a una rampa de enfriamiento de 1 °C/min. Esta gráfica proporciona una caracterización viscoelástica bajo condiciones no destructivas y aporta información estructural de la muestra, ya que ésta se encuentra en un régimen donde su microestructura está en condiciones de cuasi-equilibrio. Después de procesar la emulsión, se le somete a una rampa de enfriamiento desde 140 °C a 0 °C a 1 °C/min. En la Figura 4 puede observarse que, durante el proceso de enfriamiento, los módulos viscoelásticos de la emulsión aumentan lentamente hasta 100 °C donde tiene lugar un aumento brusco de ambos módulos, y después continúan aumentando ligeramente de nuevo. Este salto en las propiedades viscoelásticas coincide con el inicio del pico de cristalización de la fase dispersa de la emulsión (MCF) (comprobar en la Figura 2). Las curvas viscoelásticas muestran un marcado comportamiento elástico (G'>G") en todo el rango de temperatura. Este comportamiento viscoelástico revela la elevada estabilidad mecánica de la EMCF en las condiciones de ensayo, lo cual, junto con la elevada capacidad de almacenamiento y liberación de energía, resulta de gran interés en el área de aplicación de los MCFs.

Por último, la Figura 5 muestra la estructura microscópica de la emulsión la cual influye de forma importante en sus propiedades macroscópicas anteriormente comentadas. Las imágenes al microscopio fueron obtenidas a dos temperaturas diferentes: antes y después del punto de cristalización del MCF, Figura 5 (a) y Figura 5 (b), respectivamente. La Figura 5 también muestra la imagen de la EMCF a 20 °C con polarizadores cruzados para identificar la presencia de estructuras cristalinas y su distribución homogénea en la emulsión (Figura 5 (c)).

REIVINDICACIONES

1. Emulsiones de material de cambio de fase no acuosas, formuladas con dos fases oleosas inmiscibles y un agente estabilizante; y caracterizadas por ser la fase dispersa un material de cambio de fase con una temperatura de cambio de fase por encima de los 100 °C.

2. Emulsiones según la reivindicación 1 donde el agente estabilizante se encuentra en las proporciones de 0.01 a 10 % en peso del total de la emulsión.
3. Emulsiones según la reivindicación 2 donde el agente estabilizante son partículas sólidas emulsionantes que comprenden sílices pirogénicas modificadas, nanotubos de carbono o grafeno, nanopartículas metálicas o óxidos metálicos y/o son tensioactivos que comprenden no iónicos, copolímeros en bloque de alta temperatura y emulsionantes a base de silicona.
4. Emulsiones según la reivindicación 1 donde la fase dispersa de la emulsión, es decir, el material de cambio de fase se encuentra en las proporciones del 1 al 80 % en peso de la emulsión.
5. Emulsiones según la reivindicación 4 donde el material de cambio de fase comprende materiales que presentan un cambio de fase sólido-líquido o sólido-sólido a temperaturas superiores a 100 °C seleccionado entre alcoholes de azúcar, polialcoholes, alcanos industriales, sales metálicas de ácidos grasos y otros compuestos.
6. Emulsiones según la reivindicación 1 donde la fase continua de la emulsión que es oleosa se encuentra en las proporciones del 20 al 98 % en peso de la emulsión.
7. Emulsiones según la reivindicación 6 donde la fase continua comprende un compuesto oleoso seleccionado de entre aceites vegetales, refinados o modificados de base vegetal, fluidos siliconados, terpenos naturales o sintéticos o aceites sintéticos.
8. Procedimiento para preparación de las emulsiones según la reivindicación 1 que comprende:
    a. Atemperación de los componentes de la emulsión a una temperatura superior a la temperatura de cambio de fase de la fase dispersa.
    b. Mezcla del agente estabilizante con la fase continua
    c. Adicción de la fase dispersa
    d. Dispersión de los compuestos
9. Procedimiento según la reivindicación 8 donde la etapa d se lleva a cabo utilizando un homogeneizador rotor-estator de alza cizalla a velocidades comprendidas entre los 2000 y 20000 rpm, durante un tiempo de emulsificación comprendido entre 1 y 20 minutos.
10. Procedimiento según la reivindicación 8 donde la etapa d se lleva a cabo utilizando una sonda de ultrasonidos de baja frecuencia (entre 20-30 kHz) con una amplitud de entre 10 y 60 %, durante un tiempo de emulsificación comprendido entre 0.5 y 5 minutos

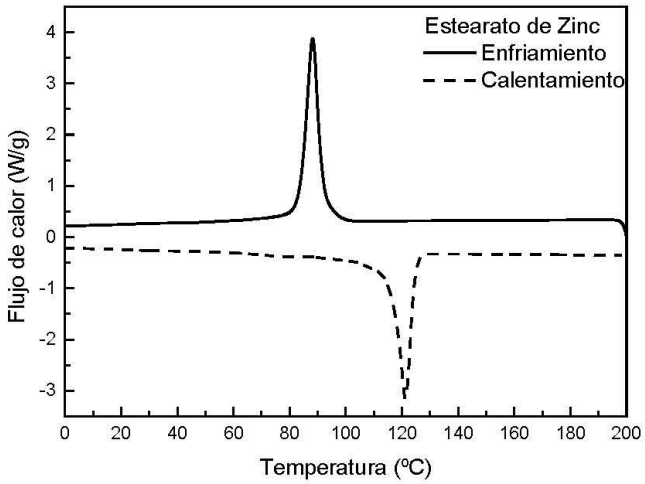
11. Emulsión no acuosa de material de cambio de fase obtenida en el procedimiento según cualquiera de las reivindicaciones 2 a 10.
12. Uso de la emulsión según la reivindicación 1 para su aplicación como fluido caloportador a temperaturas superiores a los 100 °C.

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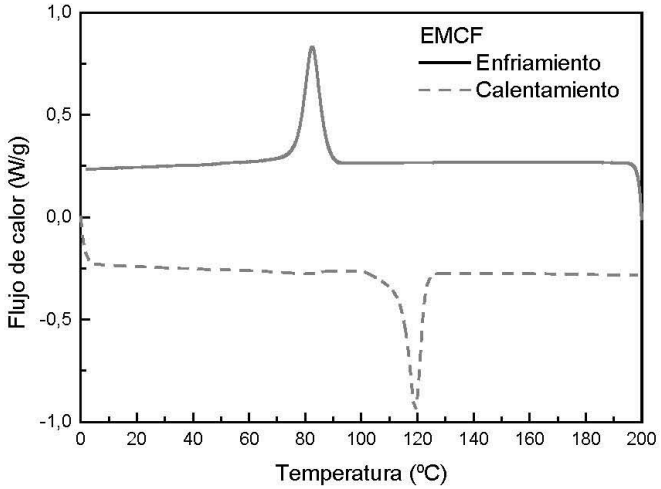
FIGURAS

FIGURA 1



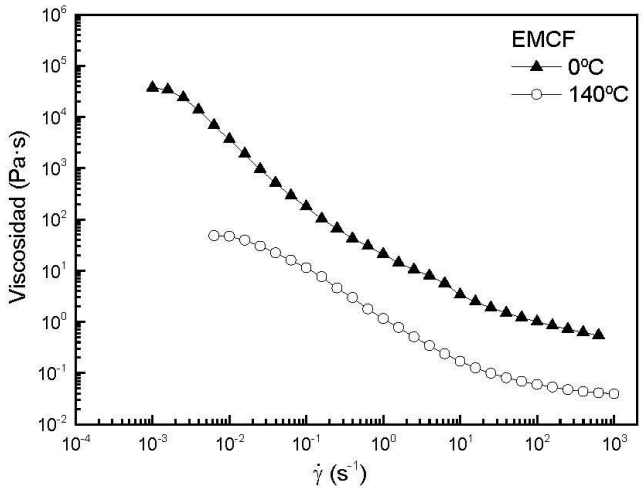
11

FIGURA 2


EMCF
Enfriamiento
Calentamiento
Flujo de calor (W/g)
Temperatura (ºC)
1,0
0,5
0,0
-0,5
-1,0
0
20
40
60
80
100
120
140
160
180
200

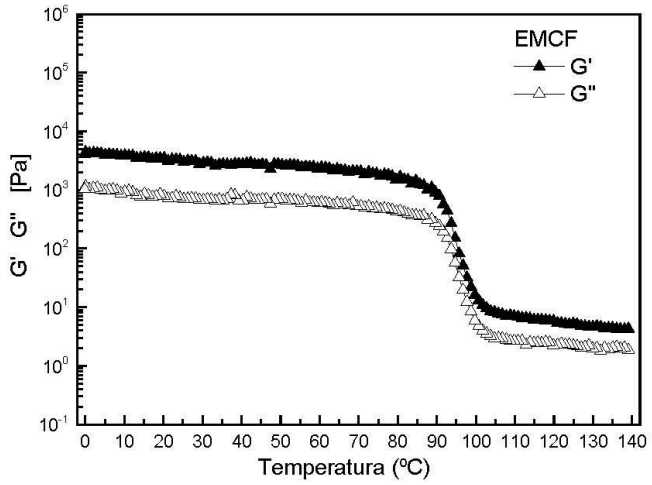
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FIGURA 3


EMCF
0ºC
140ºC
Viscosidad (Pa·s)
$\dot{\gamma}$ (s^{-1})
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}

13

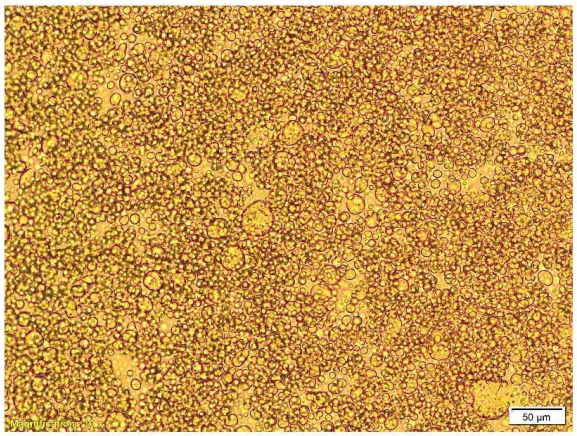
FIGURA 4


EMCF
G'
G"
G' G" [Pa]
Temperatura (ºC)
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140

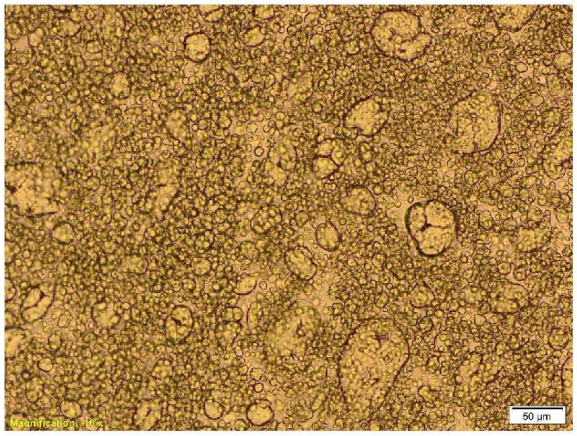
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FIGURA 5

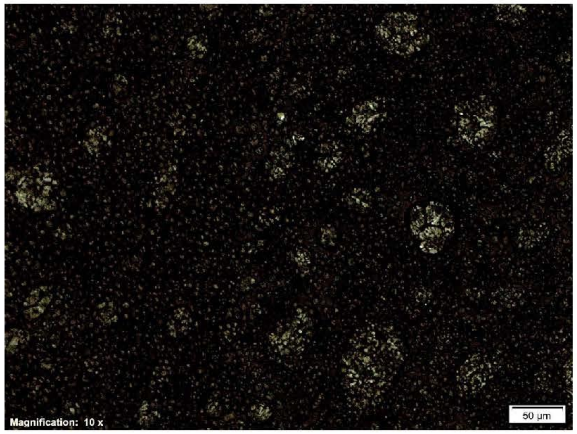
(a)



(b)



(c)



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Chapter V: General Conclusions

V/1. Conclusions

The experimental research for this PhD has yielded several major findings and conclusions which are described hereinafter:

- One of the key findings is that the formulation of non-aqueous PCMEs presents both promising opportunities and significant challenges for their utilization in thermal storage and heat transfer applications. The research has also emphasized the importance of carefully characterizing morphological, rheological and thermo-physical properties across varying temperatures. Although the formulation process can be complex, the detailed characterization provides essential insights into the behaviour of these systems. This lays a foundation for their potential applications in practical settings. Moving forward, this scientific understanding will be instrumental in optimizing the performance and efficacy of non-aqueous PCMEs in real-world applications.

- The search for a suitable surfactant to stabilize oil-in-oil emulsions, particularly those containing a PCM, presented significant challenges. However, silicone surfactants proved to be effective solutions for both formulations of PCMEs developed in this thesis: PEG4000-in-silicone oil and stearic acid-in-silicone oil emulsions. These silicone surfactants, characterized by a comb-like structure with pendant groups grafted onto a polydimethylsiloxane backbone, have demonstrated superior performance. The effectiveness of each block copolymer in stabilizing immiscible phases is due to its selective solubility. Compared to low molecular weight surfactants in oil-in-water emulsions, these surfactants provide significant steric stabilization, which enhances emulsion stability. These findings highlight the importance of careful surfactant selection in achieving stable PCMEs and emphasize the critical role of surfactant in this process.

- The crystalline structure of PCMEs is crucial for their energy storage capacity application, with higher crystallinity corresponding to increased phase change enthalpy. In stearic acid-in-silicone oil PCMEs, X-ray diffraction and DSC analysis indicate that stearic acid maintains its crystalline form consistently across various concentrations, processing conditions, and temperatures. However, the crystalline structure of PEG4000 in emulsions containing silicone oil appears to be influenced by several factors, including composition and processing conditions. These changes in the PCM's crystalline structure have been shown to significantly impact all final properties and performance of the emulsions, ranging from their rheological to thermal properties.

❖ All fresh emulsions of PEG4000 in silicone oil exhibit pronounced non-Newtonian shear-thinning behaviour at low shear rates, with a tendency to approach constant viscosity at higher shear rates. The viscous flow behaviour becomes more prominent with increasing PEG4000 concentration and surfactant content, reaching an optimal stability at 4 wt.% emulsifier. However, subsequent cooling and heating cycles cause complete destabilisation of the emulsion. The instability of fresh PEG4000-in-silicone oil emulsions is attributed to the needle-like crystallization of PEG4000. This causes protrusions from the dispersed phase that rupture the film between droplets, resulting in coalescence. To address this issue, a stabilization method called post-processing has been successfully implemented. This processing improves both the macro and micro stability of the emulsions, preventing phase separation and providing resistance to heating and cooling cycles.

❖ The viscous flow behaviour of PEG4000 PCMEs undergoes significant changes after post-processing, resulting in lower viscosities and alterations in microstructure characterized by larger droplet sizes. Furthermore, both post-processing and storage duration cause notable shifts in thermal behaviour, as observed in DSC scans, with decreasing melting and crystallization temperatures and a reduction in phase change enthalpies, indicating decreased crystallinity of PEG4000. The changes in the emulsion properties were caused by the infiltration of silicone oil and surfactant molecules into the dispersed phase, which altered the crystalline fraction of PEG4000. Increasing the surfactant content and silicone oil/PEG4000 ratio resulted in proportional decreases in melting and crystallization enthalpies, indicating a gradual decrease in PEG4000 crystallinity. Furthermore, it has been observed that more intense processing leads to changes in the crystallization mechanism of polyethylene glycol. This is indicated by the disappearance of heterogeneous crystallization peaks and the emergence of homogeneous low-temperature crystallization peaks. The shift in semicrystalline morphology of the dispersed phase is attributed to molecular diffusion, which results in reduced emulsion viscosity, loss of shear-thinning behaviour, and limitations in heat storage applications.

❖ The rheological behaviour of stearic acid-in-silicone oil emulsions varies depending on temperature conditions. When the temperature exceeds the melting point of the PCM, the emulsions exhibit a Newtonian behaviour with low viscosity. In this state, liquid melted droplets are dispersed within the silicone phase, and the viscosity remains relatively constant regardless of concentration. However, below the melting point of the

PCM, the emulsions exhibited non-Newtonian shear-thinning behaviour after the PCM crystallised. This behaviour was quantitatively described by the Sisko model. The viscosity at low shear rates increased significantly upon crystallisation, with the most concentrated emulsion showing an increase of up to five orders of magnitude. The increase in viscosity was due to the formation of a connected microstructure of crystals, which greatly affected the flow of the emulsion, especially as the PCM content increased. However, all systems showed a tendency to approach a similar high-shear-rate limiting viscosity, similar to that of the continuous-phase oil. This suggests that the dispersion microstructure is highly sensitive to shear, which is promising for practical applications. Industrial processing and pumping operations usually involve shear rates in the intermediate-high shear regime, which ranges from 1-1000 s^{-1}.

- In stearic acid-in-silicone oil emulsions, non-destructive analysis and microscopy reveal the formation of a well-defined three-dimensional network of interconnected crystalline structures resulting from the crystallization of the disperse phase. This phenomenon significantly influences the rheological properties, particularly concerning the dispersed phase ratio and testing temperature. For example, when the temperature is below the melting point of the dispersed phase, such as 40 ºC, stearic acid remains in its crystalline state. Concentrated emulsions exhibit a distinct gel-like behaviour according to SAOS analysis, which is attributed to the robust formation of the crystalline network. However, the high susceptibility to shear and the fragility of the developed network are highlighted by a significant deviation from the empirical Cox-Merz relationship, as observed in stationary flow tests.

- Stearic acid PCMEs underwent a comprehensive evaluation, including heating/cooling temperature sweep tests under steady shear, optical microscopy, and DSC analysis. The evaluation aimed to scrutinize their rheological behaviour, microstructural stability, and thermal reliability during in-service operations. The PCMEs demonstrated resilience against more than 100 heating-cooling cycles, maintaining stability for at least one month. Their inherent properties and heat storage capacity remained unchanged throughout this duration with a phase change enthalpy in emulsions with the 10 wt% of PCM of 22.32 J/g.

- The use of phase change material lubricating emulsions (PCMLEs) is a significant advancement in tribological engineering and industrial applications. PCMLEs are obtained by dispersing stearic acid in silicone oil, and offer enhanced thermal properties,

making them suitable for a wide range of industrial lubrication needs. The improvements observed in rheological behaviour, microstructure development, and thermal characteristics contribute to significant enhancements in tribological performance. The lower friction coefficients of PCMLEs compared to silicone oil, along with the significant decrease in friction coefficients due to the melting of the dispersed phase, highlight their effectiveness as lubricants. In addition, the heat storage capacity of PCMLEs is crucial in delaying the phase change temperature during tribological temperature ramp tests. This enhances their usefulness in various operational environments. Overall, PCMLEs provide a versatile and efficient solution for improving lubrication performance and extending the lifespan of mechanical equipment.

- PEG4000-in-silicone oil emulsions under specific formulation and processing conditions and stearic acid-in-silicone oil emulsions at all times have been identified as potential novel HTFs for thermal energy storage systems. The stearic acid-in-silicone oil emulsions have demonstrated resilience and stability against heating-cooling cycles while preserving their properties and heat storage capacity. Thus, this thesis has made significant achievements in this area. The thesis has successfully achieved its primary objective of obtaining **stable non-aqueous PCMEs capable of heat storage and transfer**. The next steps in advancing this study involve further investigation into the energy transport characteristics and performance evaluation in pilot plant devices, closer to industrial applications.

V/2. Conclusiones

La investigación experimental para este doctorado ha arrojado varios resultados y conclusiones importantes que se describen a continuación:

- Uno de los principales hallazgos es que la formulación de emulsiones no acuosas de materiales de cambio de fase presenta tanto oportunidades prometedoras como retos significativos para su utilización en aplicaciones de almacenamiento térmico y transferencia de calor. La investigación también ha puesto de relieve la importancia de caracterizar cuidadosamente las propiedades morfológicas, reológicas y termo-físicas a distintas temperaturas. Aunque el proceso de formulación puede ser complejo, la caracterización detallada proporciona conocimientos esenciales sobre el comportamiento de estos sistemas, sentando de este modo las bases de sus posibles aplicaciones en la práctica. En el futuro, este conocimiento científico será fundamental para optimizar el

rendimiento y la eficacia de las emulsiones no acuosas de materiales de cambio de fase en aplicaciones reales.

- La búsqueda de un tensioactivo adecuado para estabilizar las emulsiones de aceite en aceite, en particular las que contienen un material de cambio de fase, planteó importantes retos. Sin embargo, los tensioactivos de silicona demostraron ser soluciones eficaces para las dos formulaciones de emulsiones con materiales de cambio de fase desarrolladas en esta tesis: emulsiones de PEG4000 en aceite de silicona y de ácido esteárico en aceite de silicona. Estos tensioactivos de silicona, caracterizados por una estructura en forma de peine con grupos injertados en una columna vertebral de polidimetilsiloxano, han demostrado un rendimiento superior. La eficacia de cada copolímero en bloque para estabilizar fases inmiscibles se debe a su solubilidad selectiva en cada una de las fases. En comparación con los tensioactivos de bajo peso molecular en emulsiones de aceite en agua, estos tensioactivos proporcionan una estabilización estérica significativa, lo que mejora la estabilidad de la emulsión. Estos resultados ponen de relieve la importancia de una cuidadosa selección de los tensioactivos para conseguir emulsiones de materiales de cambio de fase estables y subrayan el papel crítico de los tensioactivos en este proceso.
- La estructura cristalina de este tipo de emulsiones es crucial para su capacidad de almacenamiento de energía, ya que a mayor cristalinidad mayor entalpía de cambio de fase. En las emulsiones de ácido esteárico en aceite de silicona, la difracción de rayos X y el análisis calorimétrico con DSC indican que el ácido esteárico mantiene su forma cristalina de forma consistente en todas concentraciones, condiciones de procesado y temperaturas. Sin embargo, la estructura cristalina del PEG4000 en emulsiones que contienen aceite de silicona parece estar influida por varios factores, como la composición y las condiciones de procesado. Se ha demostrado que estos cambios en la estructura cristalina del material de cambio de fase afectan significativamente a todas las propiedades finales y al rendimiento de las emulsiones, desde sus propiedades reológicas hasta las térmicas.
- Todas las emulsiones frescas de PEG4000 en aceite de silicona muestran un pronunciado comportamiento pseudoplástico a bajas velocidades de cizalla, con tendencia a aproximarse a una viscosidad constante a velocidades de cizalla más altas. Este comportamiento de flujo viscoso se acentúa al aumentar la concentración de PEG4000 y el contenido de tensioactivo, alcanzando una estabilidad óptima con un 4 %

en peso de emulsionante. Sin embargo, los ciclos posteriores de enfriamiento y calentamiento provocan la desestabilización completa de la emulsión. La inestabilidad de las emulsiones frescas de PEG4000 en aceite de silicona se atribuye a la cristalización en forma de aguja del PEG4000. Esto provoca protuberancias de la fase dispersa que rompen la película entre las gotas, lo que da lugar a la coalescencia. Para solucionar este problema, se ha aplicado con éxito un método de estabilización denominado post-procesado. Este procesado mejora tanto la macro como la microestabilidad de las emulsiones, evitando la separación de fases y proporcionando resistencia a los ciclos de calentamiento y enfriamiento.

- El comportamiento de flujo viscoso de las PCME de PEG4000 experimenta cambios significativos tras el post-procesado, dando lugar a viscosidades más bajas y alteraciones en la microestructura caracterizadas por tamaños de gota más grandes. Además, tanto el post-procesado como la duración del almacenamiento provocan cambios notables en el comportamiento térmico, como se observa en los resultados del DSC, con una disminución de las temperaturas de fusión y cristalización y una reducción de las entalpías de cambio de fase, lo que indica una menor cristalinidad del PEG4000. Los cambios en las propiedades de la emulsión se debieron a la infiltración de moléculas de aceite de silicona y surfactante en la fase dispersa, lo que alteró la fracción cristalina del PEG4000. El aumento del contenido de tensioactivo y de la relación aceite de silicona/PEG4000 dio lugar a disminuciones proporcionales de las entalpías de fusión y cristalización, lo que indica una disminución gradual de la cristalinidad del PEG4000. Además, se ha observado que un procesamiento más intenso provoca cambios en el mecanismo de cristalización del polietilenglicol. Así lo indica la desaparición de picos de cristalización heterogéneos y la aparición de picos de cristalización homogéneos a baja temperatura. Este cambio en la morfología semicristalina de la fase dispersa se atribuye a la difusión molecular, y provoca una reducción de la viscosidad de la emulsión, la pérdida del comportamiento pseudoplástico y limitaciones en las aplicaciones de almacenamiento térmico, entre otros efectos.
- El comportamiento reológico de las emulsiones de ácido esteárico en aceite de silicona varía en función de la temperatura. Cuando la temperatura supera el punto de fusión del material de cambio de fase, las emulsiones presentan un comportamiento newtoniano con baja viscosidad. En este estado, las gotitas líquidas fundidas se dispersan dentro de la fase de silicona, y la viscosidad permanece relativamente constante independientemente de la concentración. Sin embargo, por debajo del punto de fusión del

material de cambio de fase, las emulsiones mostraron un comportamiento no newtoniano pseudoplástico tras la cristalización del material de cambio de fase. Este comportamiento se describió cuantitativamente mediante el modelo de Sisko. La viscosidad a bajas velocidades de cizalla aumentó significativamente tras la cristalización, y la emulsión más concentrada mostró un aumento de hasta cinco órdenes de magnitud. El aumento de la viscosidad se debió a la formación de una microestructura conectada de cristales, que afectó en gran medida al flujo de la emulsión, especialmente a medida que aumentaba el contenido de ácido esteárico. Sin embargo, todos los sistemas mostraron una tendencia a aproximarse a una similar viscosidad límite a alta velocidades de cizalla, similar a la del aceite en fase continua. Esto sugiere que la microestructura de la dispersión es muy sensible al cizallamiento, lo que resulta prometedor para aplicaciones prácticas ya que las operaciones industriales de procesamiento y bombeo suelen implicar velocidades de cizalla en el régimen de cizallamiento intermedio-alto, que oscila entre 1-1000 s^{-1}.

- En las emulsiones de ácido esteárico en aceite de silicona, el análisis no destructivo y la microscopía revelan la formación de una red tridimensional bien definida de estructuras cristalinas interconectadas resultantes de la cristalización de la fase dispersa. Este fenómeno influye significativamente en las propiedades reológicas, sobre todo en lo que respecta a la proporción de fase dispersa y a la temperatura de ensayo. Por ejemplo, cuando la temperatura es inferior al punto de fusión de la fase dispersa, como 40 ºC, el ácido esteárico permanece en su estado cristalino. Según el análisis SAOS, las emulsiones concentradas presentan un comportamiento distinto, similar al de un gel, que se atribuye a la sólida formación de la red cristalina. Sin embargo, la alta susceptibilidad al cizallamiento y la fragilidad de la red desarrollada se ponen de manifiesto por una desviación significativa de la relación empírica de Cox-Merz, como se observa en las pruebas de flujo estacionario.
- Las PCME de ácido esteárico se sometieron a una evaluación exhaustiva, que incluyó ensayos de barrido térmico de calentamiento/enfriamiento bajo cizalla constante, microscopía óptica y análisis DSC. El objetivo de este estudio era analizar su comportamiento reológico, estabilidad microestructural y fiabilidad térmica durante las operaciones en servicio. Las PCME demostraron resistencia frente a más de 100 ciclos de calentamiento y enfriamiento, manteniendo la estabilidad durante al menos un mes. Sus propiedades inherentes y su capacidad de almacenamiento térmico permanecieron inalteradas durante todo este tiempo, con una entalpía de cambio de fase en emulsiones con un 10% en peso de PCM de 22.32 J/g.

- El uso de emulsiones lubricantes de materiales de cambio de fase (PCMLE) es un avance significativo en ingeniería tribológica y aplicaciones industriales. Las emulsiones lubricantes de materiales de cambio de fase se obtienen dispersando ácido esteárico en aceite de silicona, y ofrecen propiedades térmicas mejoradas, lo que las hace adecuadas para una amplia gama de necesidades de lubricación industrial. Las mejoras observadas en el comportamiento reológico, el desarrollo de la microestructura y las características térmicas contribuyen a mejorar significativamente el rendimiento tribológico. Los menores coeficientes de fricción de las PCMLE en comparación con el aceite de silicona, junto con la significativa disminución de los coeficientes de fricción debida a la fusión de la fase dispersa, ponen de relieve su eficacia como lubricantes. Además, la capacidad de almacenamiento de calor de las PCMLEs es crucial para retrasar la temperatura de cambio de fase durante las pruebas tribológicas de rampa de temperatura. Esto aumenta su utilidad en diversos entornos operativos. En general, las PCMLE ofrecen una solución versátil y eficaz para mejorar el rendimiento de la lubricación y prolongar la vida útil de los equipos mecánicos.
- Las emulsiones de PEG4000 en aceite de silicona en condiciones específicas de formulación y procesamiento y las emulsiones de ácido esteárico en aceite de silicona en todo momento se han identificado como posibles fluidos caloportadores novedosos para sistemas de almacenamiento de energía térmica. Las emulsiones de ácido esteárico en aceite de silicona han demostrado resistencia y estabilidad frente a los ciclos de calentamiento y enfriamiento, al tiempo que conservan sus propiedades y su capacidad de almacenamiento térmico. Así pues, esta tesis ha conseguido logros significativos en este campo. La tesis ha alcanzado con éxito su objetivo principal de **obtener PCME no acuosas estables capaces de almacenar y transferir calor**. Los próximos pasos en el avance de este estudio implican una mayor investigación de las características de transporte de energía y la evaluación del rendimiento en dispositivos de planta piloto, más cercanos a las aplicaciones industriales.

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