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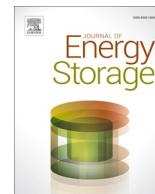
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Research papers

Insights on the degradation of capric acid as phase change material for long-term applications[☆]

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ABSTRACT

In this work, a protocol for evaluating the long-term thermal and chemical stability of capric acid is presented. Capric acid is a phase change material (PCM) employed as a latent heat thermal storage material to store/retrieve heat during the phase transition from solid to liquid or vice versa. The nature of the materials utilized for latent heat thermal batteries plays a vital role in their long-term performance for the different applications. Therefore, precisely investigating these material thermal and chemical stability is significant. The protocol consists of two tests (accelerated thermal cycling and thermal stress) in which the performance of the PCM will be investigated. A benchmark experiment for accelerated thermal cycling was performed where the impact of different parameters (heating/cooling rate and sample volume) was investigated for the initial 50 thermal cycles. This was followed by long-term accelerated thermal cycling for a total of 1500 thermal cycles (melting followed by crystallization). A thermal stress where the PCM stays in a liquid state was performed for the capric acid to investigate the impact of the higher temperature on the stability of the PCM. The thermal properties reliability over time was measured with differential scanning calorimetry (DSC), which indicated a variation of 3.2 % in onset phase change equilibrium temperature and 10.45 % in phase change enthalpy after 1500 thermal cycles. Gas chromatography (GC) and nuclear magnetic resonance spectroscopy (NMR) were performed to reveal that by-products are formed during capric acid thermal treatment. These results provide valuable guidance for the research community to design adapted thermal cycling protocols and select appropriate characterization methods, thereby enabling more accurate and reliable investigations of the long-term stability of organic PCMs.

1. Introduction

Humankind's high living standards contribute to increased energy consumption, which is harmful to the environment and disrupts nature. Across the globe, stakeholders are putting together policies to make our planet more sustainable and greener. Climate action, which is one of the 17 sustainable development goals of the United Nations to improve our planet, directs the use of environmentally beneficial energy sources [1]. The International Energy Agency reports that in 2022, half of the energy demand for the building sector was utilized for space heating and hot water applications responsible for a tremendous amount of carbon emissions [2]. To meet the massive energy demand with the least adverse impacts on the environment, there should be less reliance on fossil fuel energy sources. Renewable energy sources that have enough

potential to supply clean energy can be a good alternative source [3]. However, the intermittent nature of these energy sources restricts their direct integration into conventional systems.

Thermal energy storage (TES) technology that utilizes thermal batteries can mitigate the intermittent nature by storing thermal energy for later use. These thermal batteries can be integrated into existing systems to enhance overall system efficiency and reduce the supply/demand gap [4]. The TES thermal battery includes its simple working principle that includes charging, storing energy, and discharging. TES are classified as sensible heat storage, latent heat storage, and thermochemical heat storage based on the various operating principles used to store and retrieve thermal energy [5]. Latent heat thermal energy storage (LHTES) utilizes phase change material (PCM) as a thermal battery material that stores/retrieves heat energy with phase transition from, for example,

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Table 1
Properties of the material provided by the manufacturer [21].

Materials	Properties	Supplier
Capric acid	T_m : 27–32 °C Molecular weight: 172.26 g/mol Density: 0.893 g/cm ³ Purity: 98 %	Sigma Aldrich, Germany

solid to liquid and vice versa. LHTES is getting more attention due to the phase transition in a narrow temperature range and comparatively high energy density [6]. Detailed works have already been presented by utilizing latent heat thermal batteries for different thermal energy storage applications [7–9].

Phase Change Materials (PCMs) are primarily categorized as organic (carbon-based), inorganic (metallic and salt hydrate), and organic-inorganic mixtures based on their chemical composition. These different PCM types offer both advantages and disadvantages, making them suitable for various thermal energy storage applications [10]. Organic PCMs include alkanes, esters, sugar alcohols, fatty alcohols, and fatty acids. Among these, fatty acids have gained particular attention due to their properties, including excellent phase change reversibility, cost-effectiveness, eco-friendliness, and safety for human contact. The effectiveness of a thermal battery is largely determined by the stability of the PCM, which includes the reliability of the thermal properties and the compatibility of the PCM with its container [11]. Before selecting a PCM for any application, it is crucial to assess its long-term stability. Accelerated thermal cycling is a commonly employed technique to evaluate the lifespan of PCMs. This method involves subjecting the PCM under investigation to repeated charging and discharging cycles, simulating long-term use in a shorter timeframe [12].

Various experimental setups are utilized to perform the accelerated thermal cycling experiment, as summarized by Rathgeber et al. [13] in their technical survey. These experiments differ in sample size (0.5 mL to 154 L), cooling/heating rates (0.05 to 50 °C/min), and daily thermal cycle frequency (1 to 140 cycles). After performing multiple successive cycles (melting/freezing), the sample is investigated for thermal and chemical stability. Besides that, PCM stability can also be investigated with a thermal stress test. In the thermal stress test, the impact of temperature is investigated without the phase change process. Majo et al. [14] conducted accelerated thermal cycling and stress tests. These authors performed 1000 thermal cycles on capric acid, using a thermal

bath with a heating/cooling rate of 0.5 °C/min. The result shows a minimal change in melting onset temperature ($T_{m(\text{onset})}$ difference of 0.5 ± 0.0 °C) and a slight decrease in the enthalpy variation during fusion ($\Delta_{\text{fus}}H$ reduced by 6 ± 1 J/g). While FT-IR analysis showed no chemical degradation, Gas-Chromatography (GC) revealed additional peaks, leading the researchers to conclude that FT-IR may not be effective for detecting PCM chemical degradation. Martin et al. [15] conducted a study on the long-term stability of capric acid using a Bioer Gene Q T-18 thermocycler. A bioer thermocycler is generally utilized for biomedical applications where the temperature ramp can be done at a higher rate for small sample sizes. The accelerated thermal cycling (melting/solidification) was performed with this thermocycler. The 0.5 mL sample of capric acid was exposed to 2000 thermal cycles with cooling and heating rates ranging from 240 to 300 °C/min. To evaluate the thermal properties reliability, differential scanning calorimetry (DSC) was utilized, while chemical stability was examined using Fourier Transform Infrared Spectroscopy (FT-IR). Initial measurements showed a phase change equilibrium temperature ($T_{m(\text{onset})}$) of 31.5 °C and a latent heat of fusion ($\Delta_{\text{fus}}H$) of 150 J/g. After 2000 thermal cycles, these values remained nearly unchanged at 31.5 °C and 151 J/g, respectively. Furthermore, FT-

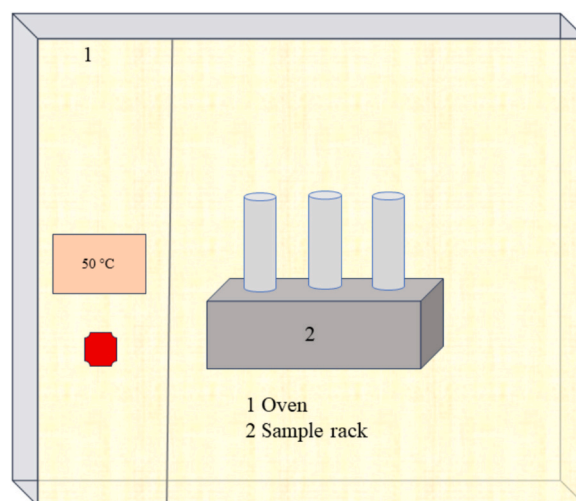


Fig. 2. Experimental setup utilized for the thermal stress test.

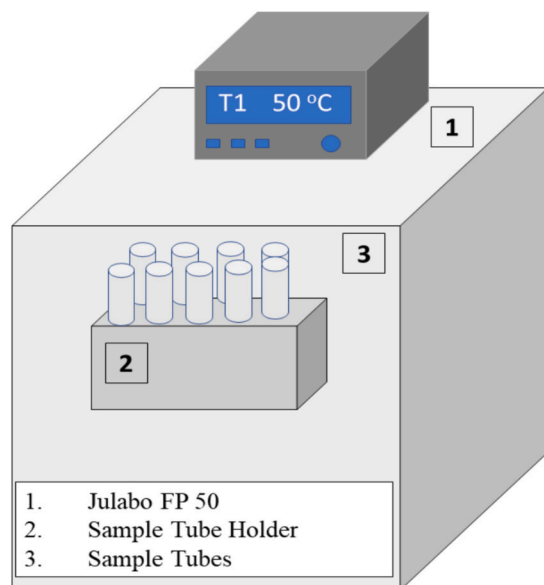
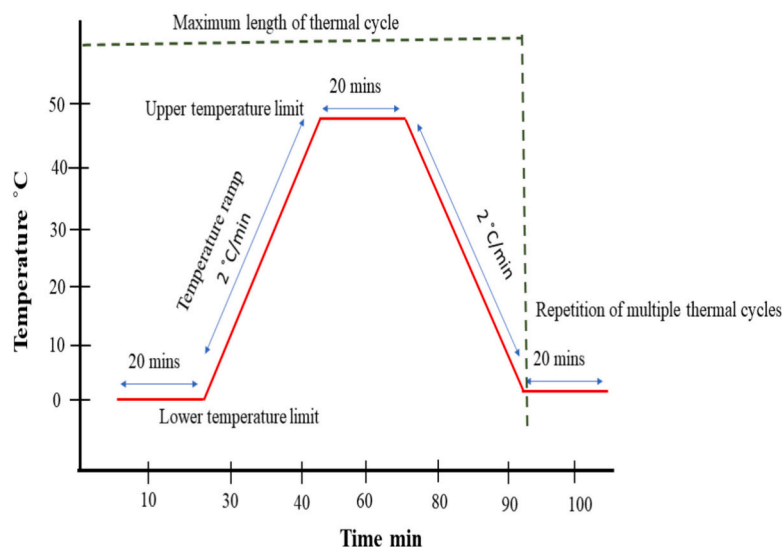


Fig. 1. Experimental setup and temperature profile utilized for accelerated thermal cycling.



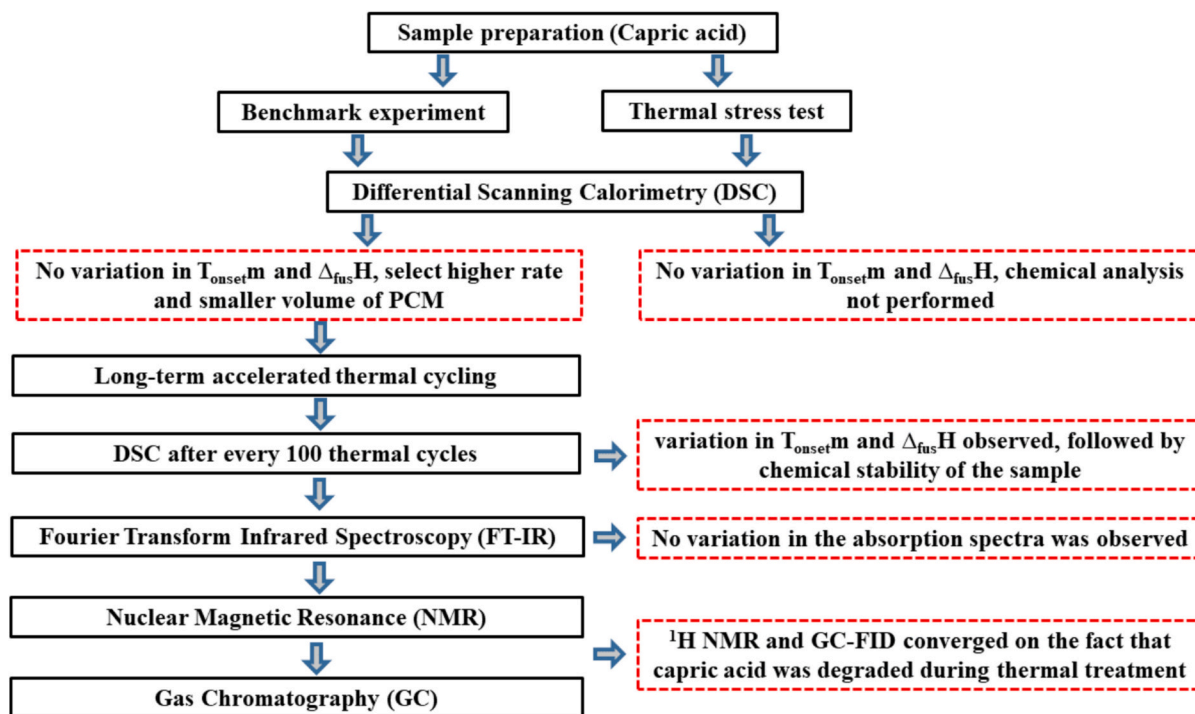


Fig. 3. Schematic overview of the workflow.

IR analysis confirmed the chemical stability of capric acid throughout the cycling process. The limitation of the FT-IR is its sensitivity, it's difficult to detect minor changes in the chemical structure of the sample. This observation was also found for other organic PCMs studied.

Sharma et al. [16] performed long-term stability investigations for 3000 thermal cycles on three fatty alcohols (1-Hexadecanol, Dodecanol, and 1-Ocatdecanol) using a BIOER TC-25/H thermal cyler. The thermal cyler was utilized to perform successive melting/solidification thermal cycles for the PCM. Their results showed more significant changes, with up to 9.4 % variation in phase change enthalpy and phase change equilibrium temperature shifts between -0.51 and 1 °C. Again, FT-IR analysis did not detect any chemical degradation in the cycled samples. Han et al. [17] conducted a thermal cycling study on a binary mixture of hexanediol and lauric acid using a refrigerated cooling/heating device (Julabo FP50-HL). The experiment was initiated with 10 g of sample, and 0.5 g was removed for analysis every 200 cycles, up to a total of 1000 cycles. Initial measurements showed a $T_{m(onset)}$ of 36.81 °C and a $\Delta_{fus}H$ of 179.01 J/g. After 1000 cycles, these values changed to 36.37 °C and 173.22 J/g, respectively. The variation in the $T_{m(onset)}$ and $\Delta_{fus}H$ were 0.44 °C and 5.79 J/g. FT-IR analysis shows the chemical structure remained intact throughout the process, with no detectable signs of degradation. Patel et al. [18] subjected bio-based PCM called POSO to 5400 thermal cycles in a controlled environment chamber (Model EC127, Sun Electronics). Their protocol involved heating and cooling at a rate of 3.5 °C/min between -10 °C and 60 °C. The initial T_m ($onset$) and $\Delta_{fus}H$ were 26.56 °C and 133 J/g, which changed to 27.12 °C and 116.10 J/g after cycling. As with the hexanediol/lauric acid mixture, FT-IR spectroscopy results didn't detect any changes in the chemical structure of POSO PCM throughout the thermal cycling process.

Kalidasan et al. [19] subjected RT50 (Rubitherm 50) PCM to accelerated thermal cycling in a custom-designed thermal cyler. A total of 3000 thermal cycles were performed, with temperatures alternating above and below their solid-liquid phase change points. The sample size was 2 g, with a heating rate of 15 °C/min and a cooling rate of 7 °C/min. The sample was analyzed in the DSC after every 500 thermal cycles to study the thermal properties. The initial thermal properties were a T_m

($onset$) of $44-45$ °C and $\Delta_{fus}H$ of 157.8 J/g. The variation in $T_{m(onset)}$ and $\Delta_{fus}H$ after 3000 thermal cycles were $2-3$ °C and 10.6 J/g. No chemical degradation was detected in the absorption spectra from the FT-IR analysis. Jacob et al. [20] studied the long-term thermal reliability of paraffin wax and palmitic acid binary mixture. The sample was subjected to 4000 thermal cycles, and a change of 1.45 °C and 6.53 J/g was evident, whereas the initial $T_{m(onset)}$ was 55.0 ± 0.2 °C and $\Delta_{fus}H$ 160.0 ± 3.2 J/g. However, no changes in the chemical structure of the PCM were observed by the FT-IR analysis.

Therefore, in scientific literature, it was evident that different parameters are utilized by all the authors for accelerated thermal cycling, and the technique utilized to investigate the chemical stability was not effective. Furthermore, despite widespread agreement among researchers on the importance of stability investigations, there is currently no standardized procedure for conducting these tests, and to date, a commercial device is not available in the market, but different self-designed equipment is utilized for long-term stability tests of PCM. Hence, this study aims to address this gap by contributing to the development of a general methodology for assessing pure organic PCM stability. The research focuses on capric acid as a model PCM, investigating the impact of various parameters on its degradation process during a benchmark experiment for accelerated thermal cycling. Hence, an initial experimental campaign is made for a total of 50 thermal cycles (melting/solidification) to study the influence of heating/cooling rates for different volume sizes of the PCM. These benchmark experiments will help to optimize the long-term accelerated thermal cycling performed for a total of 1500 thermal cycles by selecting the optimal parameters. A thermal stress experiment in which the temperature is maintained at a value higher than the melting temperature will provide insights into the impact of temperature on the degradation of the PCM. The thermal reliability of the PCM's thermophysical properties is evaluated using Differential Scanning Calorimetry (DSC).

Different chemical characterizations will be utilized to investigate the chemical structure of capric acid. The characterization will be first-hand to investigate the atomic and molecular level of the capric acid. These include FT-IR, proton nuclear magnetic resonance spectroscopy (1H NMR), Gas Chromatography associated with Mass Spectrometry

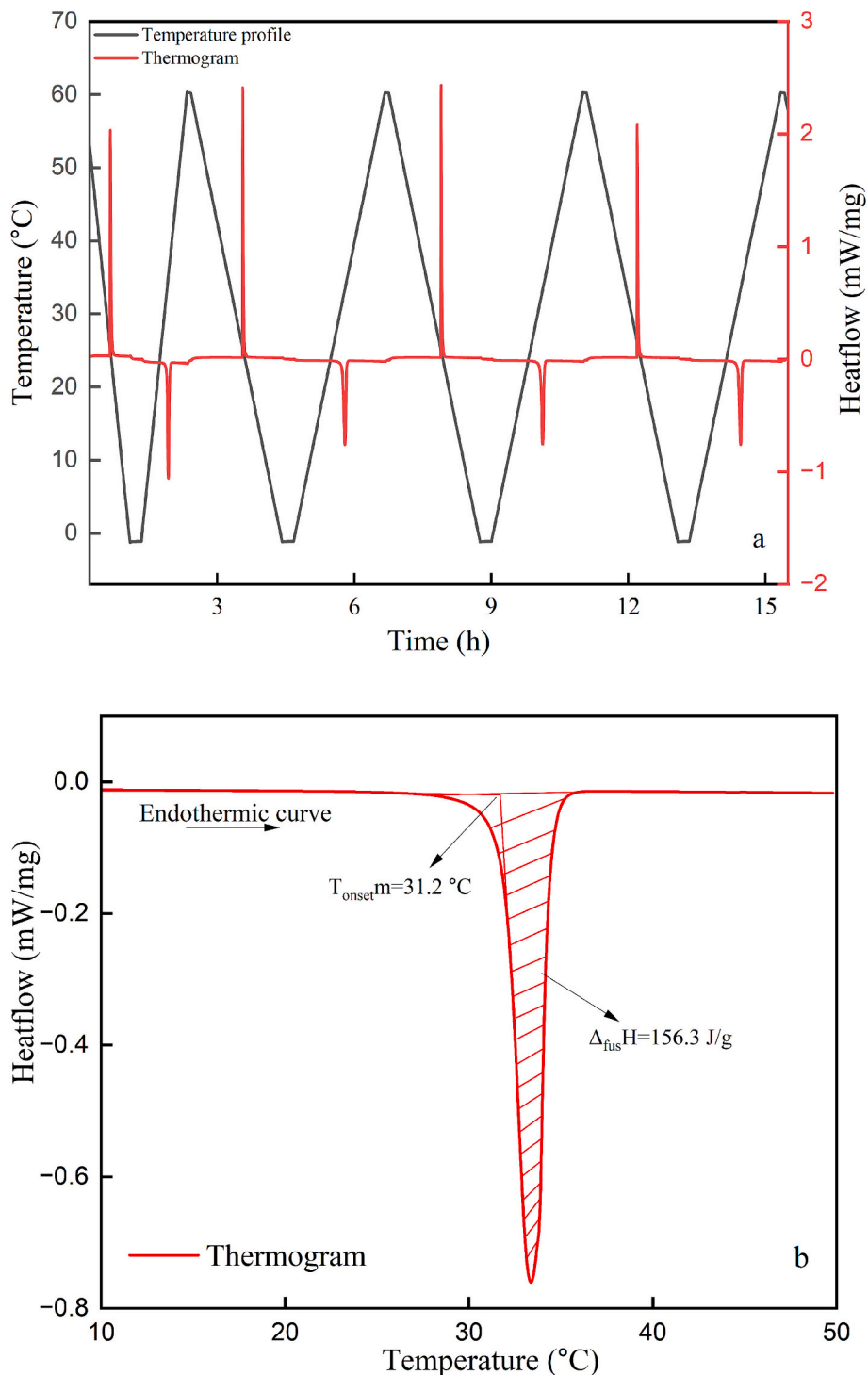


Fig. 4. DSC of capric acid, a) number of thermal cycles performed in DSC for one sample, and b) Endothermic thermogram of capric acid with uncycled sample.

(GC-MS), and Gas Chromatography with Flame Ionization Detection (GC-FID). The techniques utilized will give insights into capric acid chemical stability and purity level throughout the thermal cycling process. To the best of the author's knowledge, the by-products formed during capric acid degradation have not been fully identified and quantified previously in the open literature. The results from this work will give better insights into the mechanism of degradation of the PCM and could help to suggest strategies to limit it. This approach will enable more accurate assessments of PCM performance and endurance, ultimately advancing the field of thermal energy storage and management.

2. Materials and experimental methodology

2.1. Materials

This work considers capric acid a medium-chain fatty acid for investigation. Capric acid was provided by Sigma Aldrich, Germany, with a purity of 98 % [21]. Capric acid possesses a crystalline structure with a white color at room temperature. The material was utilized without further purification or processing for this study. The properties of the capric acid, according to the manufacturer, are presented in

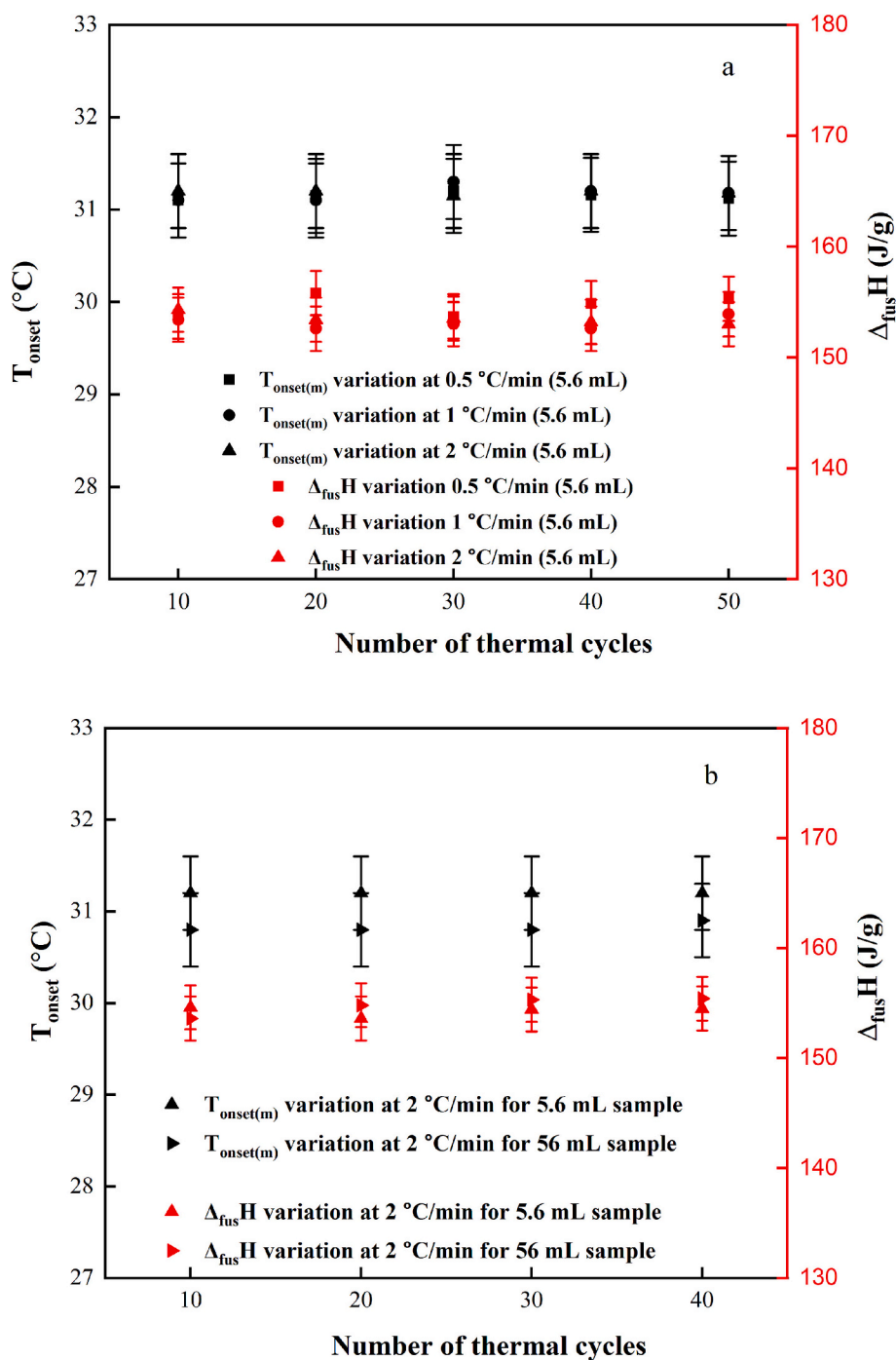


Fig. 5. Thermal properties variation with different parameters, a) impact of different heating/cooling rates during thermal cycling (0.5, 1, and 2 °C/min) and b) impact of different volumes (5.6 and 56 mL) during thermal cycling.

Table 1.

2.2. Experimental methodology

2.2.1. Accelerated thermal cycling

Successive charging/discharging cycles for the capric acid were performed in a controlled environment with a cooling and heating device (Julabo FP 50). The PCM is introduced into test tubes immersed in the machine's thermostatic bath (see Fig. 1). The upper and lower temperatures of the thermal cycle (charge + discharge) utilized in the bath were 50 °C and 0 °C. These limit temperatures are chosen to have a temperature difference of around 25 °C above and below the melting

temperature. To avoid quick temperature shifts and maintain good thermal equilibrium with the heat transfer fluid, the temperature is maintained at 0 °C for 20 mins, which is followed by a temperature ramp until 50 °C. The temperature is kept at 50 °C for 20 mins and a decrease in temperature is done until 0 °C. The temperature profile utilized is shown in Fig. 1 for a heating/cooling rate of 2 °C/min.

The accelerated thermal cycling was completed in two parts. The first part is the benchmark experiment where the impact of different heating/cooling rates (0.5, 1, and 2 °C/min) for the temperature ramps in the device and the impact of the volume (5.6 and 56 mL) of the PCM were studied. The two volumes, 5.6 and 56 mL correspond to 5 g and 50 g, respectively of capric acid. It was easier to control the mass to be sure

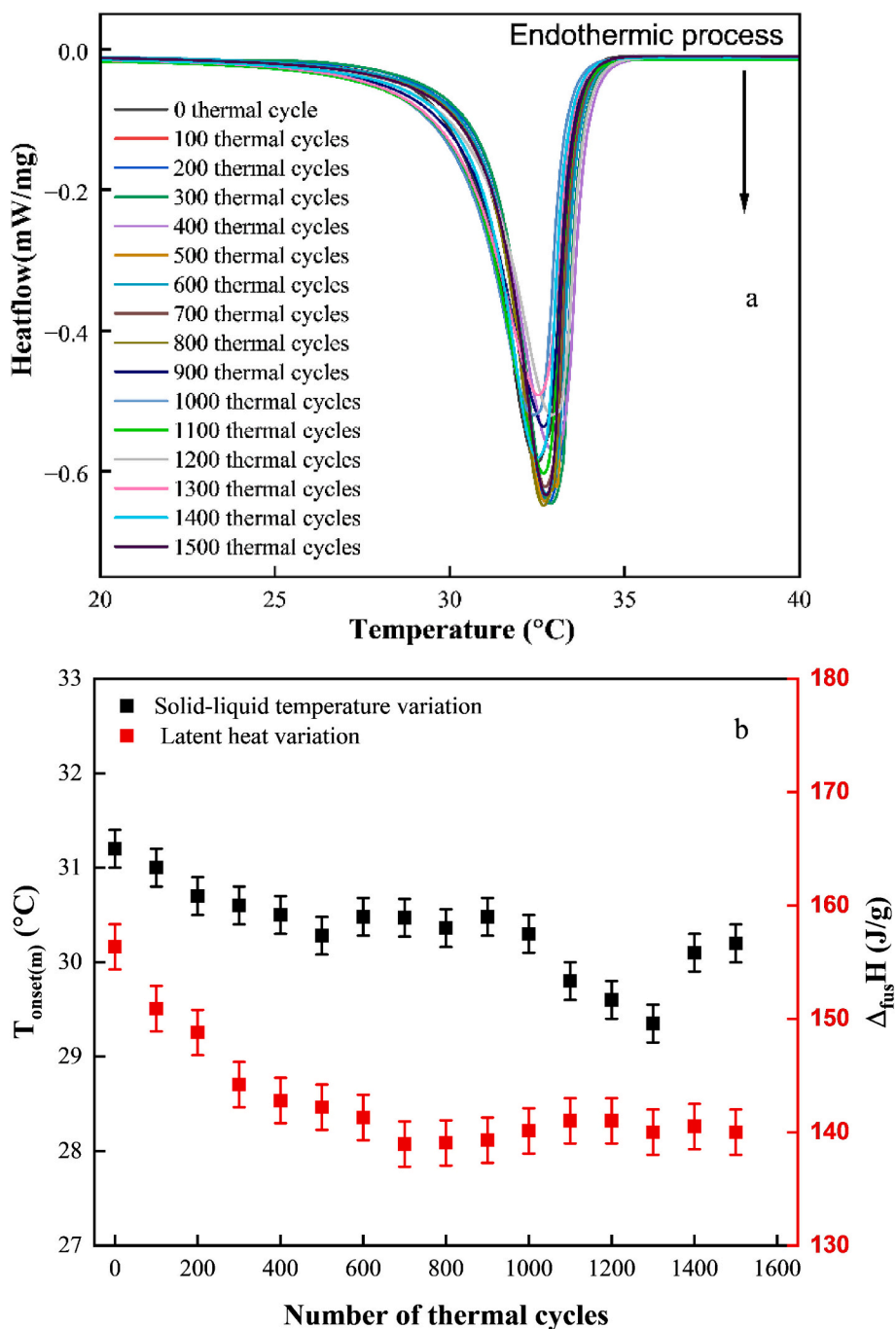


Fig. 6. Long-term thermal cycling of capric acid, a) thermograms of capric acid for 1500 thermal cycles and b) thermal properties variation of capric acid for 1500 thermal cycles.

to fix the volume. A total of 50 thermal cycles were performed. For the second part, only one cooling/heating rate and one volume were selected, taking into account the results of the benchmark (part 3.1.2). The selected cooling/heating rate was $2^{\circ}\text{C}/\text{min}$ with a volume of 5.6 mL of capric acid for a total of 1500 thermal cycles. A total of 15 samples in test tubes were exposed to the experimental campaign. The same thermal cycle is repeated to perform charging/discharging within the capric acid by storing/retrieving thermal energy. After each 100 thermal cycles, a sample was removed for further characterization.

2.2.2. Thermal stress experiment

This experimental campaign corresponds to the study of the PCM when it remains in a liquid state for a long time without crystallizing

once during the experiment. To investigate the thermal stress on capric acid, an oven (DHG-9032) was utilized as a controlled temperature chamber as shown in Fig. 2. The uncertainty of the temperature of the oven was $\pm 0.5^{\circ}\text{C}$. The temperature in the oven was set to 50°C , which is the same temperature as the maximum temperature utilized for the accelerated thermal cycling. This temperature is above the phase change equilibrium temperature. For 90 days, 3 samples of 35 g were exposed to the controlled environment. Among the three samples, one sample was removed every 30 days for analysis. Each sample was separately sealed in a glass bottle to avoid direct contact with the open environment. The objective of the test is to investigate the influence of temperature without a phase change process.

Table 2
Comparison of the results with open literature data for capric acid.

PCM	Capric acid [15]	Capric acid [14]	Capric acid [This study]
Cooling/heating rate (°C/min)	240/ 300	0.5	2
Volume of sample (mL)	0.5	–	5.6
Min temperature (°C)	15	18	0
Max temperature (°C)	70	40	50
Device utilized	Thermocycler (Bioer Gene Q T-18)	Thermal bath	Refrigerated cooling/heating device (Julabo FP50)
Number of thermal cycles	2000	1000	1500
T _{onset(m)} (°C) initial	31.5	32.3 ± 0.0	31.2 ± 0.4
T _{onset(m)} (°C) final	31.5	31.8 ± 0.0	30.2 ± 0.4
ΔH _{fus} (J/g) initial	150	159 ± 1	156 ± 2
ΔH _{fus} (J/g) final	151	153 ± 1	140 ± 2

2.2.3. Thermal and chemical stability investigation with various characterization techniques

2.2.3.1. Differential scanning calorimetry (DSC). The thermal properties of the PCM were investigated with differential scanning calorimetry (DSC) (MICRO-DSC7-EVO, SETARAM). DSC measures the difference in heat flow between a sample cell (PCM inside an aluminum cell in our case) and a reference (empty) cell as they are subjected to a controlled temperature program. The DSC analysis results in a thermogram, which gives detailed information for the phase change equilibrium temperature and the related change in enthalpy. Nitrogen gas was introduced at 1 bar pressure for the DSC analysis to provide an inert environment for the sample being tested. The sample analyzed in DSC had a volume of approximately 20 μL and was studied at a heating/cooling rate of 0.5 °C/min from 0 to 60 °C for the phase change process. The low cooling/heating rate and small volume were utilized to have good thermal equilibrium between the cell and the PCM. For the reliability of the result, each experiment performed in the DSC has a total of four thermal cycles. The first cycle was done to perform an initial melting and to ensure good contact between the sample and the cell. The average values of the equilibrium temperature of the phase change and the variation of the enthalpy of fusion, obtained from three successive thermal cycles, are presented for discussion. The DSC was calibrated in the usual way using three reference materials. The uncertainty of the measurements (±0.4 °C for the temperature in and ± 1.3 % for the change in enthalpy) was measured by testing octadecane (not used for the calibration) and comparing the values found with those in the standard data sheet.

2.2.3.2. Fourier transform infrared spectroscopy (FT-IR). The chemical stability of capric acid was investigated with FT-IR. Spectra were obtained using attenuated total reflectance (ATR) on a Thermo Nicolet IS50 FTIR spectrophotometer over the range 4000–450 cm⁻¹ for 64 scans with a resolution of 4 cm⁻¹. The spectra were acquired and analyzed using Omnic 9.8 software.

2.2.3.3. Proton nuclear magnetic resonance spectroscopy (¹H NMR). ¹H NMR spectra were recorded using a Bruker Ascend 400 MHz spectrometer at 25 °C with 64 scans and a time delay D1 of 5 s. The analysis was performed by dissolving 5–10 mg of capric acid in 0.5 mL of deuterated chloroform (CDCl₃). The spectra were acquired and analyzed using TopSpin software.

2.2.3.4. Gas chromatography (GC). Capric acid samples were analyzed using two gas chromatography instruments: one with a flame ionization detector (GC-FID) for a sensitive semi-quantitative determination and a second associated with a mass spectrometer (GC-MS) to identify by-products. To compare the results of both instruments, the Kovats retention index was determined with an alkane mix (C6-C16, Restek, Bellefonte, USA). External calibrations of identified by-products were not carried out, as commercial products of standard quality were not available.

Samples of capric acid were diluted at 2 mg mL⁻¹ in methanol (99.9 % liquid chromatography grade, Merck KGaA, Darmstadt, Germany) with 0.1 mg mL⁻¹ of Decane as internal standard IS (99.9 %, Sigma-Aldrich, Saint Louis, USA). Three methanol solutions of samples were prepared and analyzed in triplicates with GC-FID for the quantification of by-products. GC-FID measurements were performed with a Thermo Trace 1300 (Thermo Fischer Scientific, Waltham, USA) and an auto-sampler Thermo AI1310 (Thermo Fischer Scientific, Waltham, USA): 1 μL of samples were injected with a split ratio 1/100 at 200 °C on a TG-1MS column (60 m, 0.25 mm, 1 μm Thermo Scientific, Waltham, USA) with helium flow rate of 2 mL min⁻¹ for 26 min (oven program: 50 °C for 1 min, to 240 °C at 10 °C/min, 240 °C for 5 min). The FID detector was warmed at 225 °C with 350 mL min⁻¹ of air, 35 mL min⁻¹ of hydrogen, and 40 mL min⁻¹ of helium with a solvent delay of 5,5 min.

GC-MS measurements were performed with a GC Clarus680 (Perkin-Elmer, Waltham, USA) equipped with an autosampler and a mass spectrometer Clarus 600S (Perkin-Elmer, Waltham, USA). 1 μL of samples were injected with a split ratio 1/1 at 250 °C on an Elite-5MS column (60 m, 0.25 mm, 1 μm, Perkin-Elmer, Waltham, USA) with helium flow rate of 2 mL min⁻¹ for 22 min (oven program 40 °C for 1 min, to 240 °C at 10 °C/min, 240 °C for 1 min). The first MS detection was performed at 70 eV from *m/z* 20 to 449. A Multi Ion monitoring method was established with the previous results to enhance the signal-noise ratio. A schematic overview of the workflow is presented in Fig. 3.

3. Results and discussion

The long-term stability of capric acid was assessed using an accelerated thermal cycling test (see Section 2.2.1. Accelerated thermal cycling). Following the test, a variety of characterization techniques were used to determine its thermal and chemical stability. The cycled capric acid thermal properties and chemical features were then compared to those of an uncycled sample.

3.1. DSC characterization of uncycled capric acid and accelerated thermal cycling

3.1.1. DSC of capric acid before thermal cycling

Before the thermal cycling experiment, the thermogram of the capric acid was acquired. The thermal properties (phase change equilibrium temperature and latent heat) will be utilized as the reference for the analysis of the thermal reliability of the properties during the accelerated thermal cycling test [22]. The thermal cycles performed in the DSC with the thermogram of the uncycled capric acid are shown in Fig. 4. All the samples tested in the DSC undergo four thermal cycles. In contrast, only the thermal properties of the three last cycles are presented for discussion. During the melting process, the onset phase change equilibrium temperature T_{m(onset)} is 31.2 ± 0.4 °C, whereas the latent heat of fusion is Δ_{fus}H is 156 ± 2 J/g. These results are in good agreement with the open literature data [23,24].

3.1.2. Benchmark experiment for accelerated thermal cycling of capric acid

In the benchmark experiment for accelerated thermal cycling, two parameters were investigated in order to optimize the long-term accelerated thermal cycling experiment (see Section 3.1.3. long-term accelerated thermal cycling of capric acid). In the scope of this study, different heating/cooling rates (0.5, 1, and 2 °C/min) and sample sizes

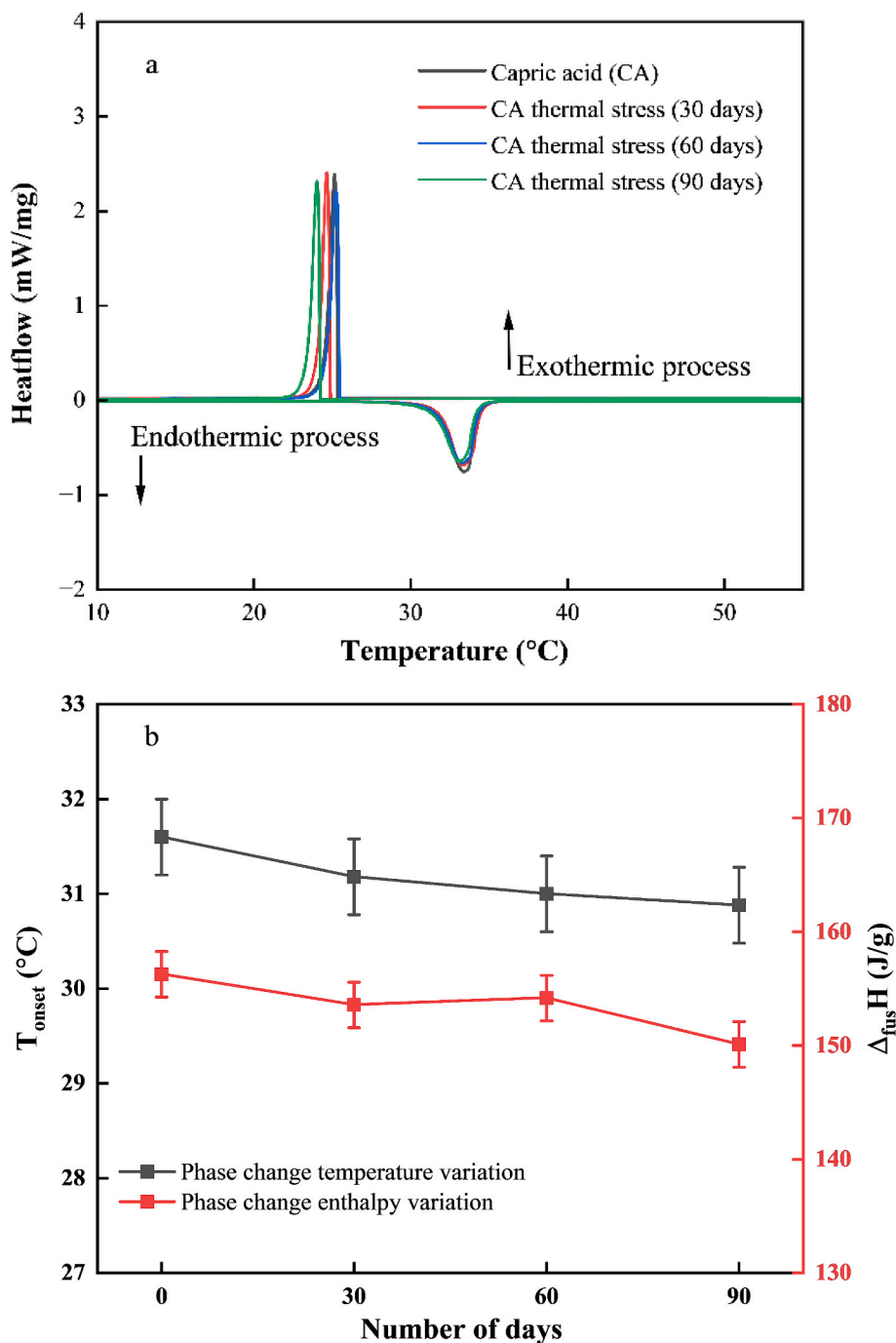


Fig. 7. Thermal properties variation after thermal stress test, a) thermograph of the samples and b) thermal properties variation.

(5.6 and 56 mL) were investigated and the results are shown in Fig. 5. The impact of these parameters was presented based on the variation of the PCM thermal properties (latent heat and solid-liquid equilibrium temperature) determined using the DSC. The different heating/cooling rates did not show any significant change in the thermal properties, as shown in Fig. 5(a). The same tendency was confirmed in the results for different volumes shown in Fig. 5(b). As the uncertainty bars overlap, it was deduced from the results that the different heating/cooling rates and the different volumes of samples analyzed during accelerated thermal cycling had no impact on thermal properties for the first 50 thermal cycles. Because the results are the same for the different heating/cooling rates and volumes, the higher rate with the lower volume (2 °C/min and 5.6 mL) is selected in order to perform the experiments

for long-term accelerated thermal cycling as quickly as possible using a minimal amount of PCM.

3.1.3. Long-term accelerated thermal cycling of capric acid

A heating/cooling rate of 2 °C/min and 5.6 mL of the sample volume were selected for long-term accelerated thermal cycling. The results for uncycled and cycled capric acid are shown in Fig. 6. During accelerated thermal cycling, each sample was extracted at an interval of 100 thermal cycles for DSC analysis. Fig. 6(a) shows the thermogram that represents the melting process for all the samples. The crystallization process was excluded from the analysis due to the erratic behavior caused by the supercooling of the PCM. The thermal properties of the PCM throughout the long-term thermal cycling experiment are shown in Fig. 6(b). Fig. 6

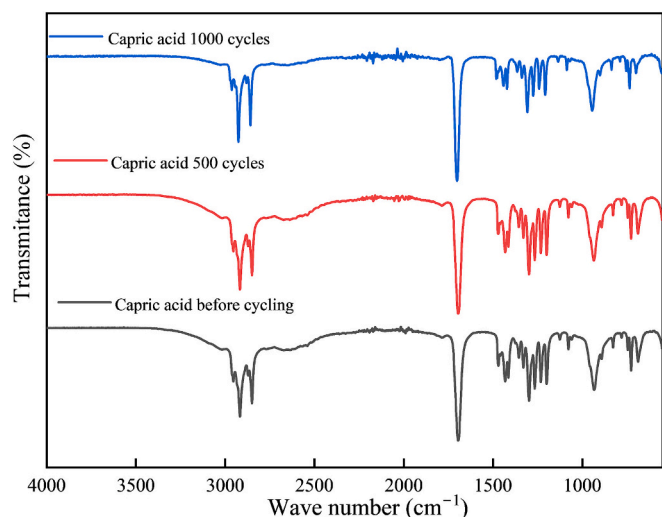


Fig. 8. FT-IR absorption spectrum for uncycled and cycled samples after 500 and 1000 thermal cycles.

focuses on two important properties of the PCM, phase change temperature and latent heat. The results obtained after 1500 thermal cycles of capric acid were compared with the open literature data [14,15] presented in Table 2. The variation in the result compared to the open literature data is attributed to the different experimental parameters (sample size and temperature ramp) utilized during accelerated thermal cycling, which can directly influence the reaction kinetics and potential degradation of the sample. Martin et al. [15] utilized a sample of 0.5 mL with a cooling/heating rate of 240/300 °C/min where no degradation was evidenced. On the contrary, Majo et al. [14] employed a lower heating/cooling rate of 0.5 °C/min and saw a small reduction in the latent heat without giving information on sample size. Our experimental campaign with a 2 °C/min heating/cooling rate and 5.6 mL volume of the sample led to a significant decrease in the latent heat. From the comparison, it is confirmed that a small sample size and higher heating/cooling rate may not trigger the degradation phenomenon in the PCM.

The results displayed in Fig. 6b show that after the first 100 thermal cycles, a decrease in the latent heat was observed, whereas the variation in phase change equilibrium temperature was generally within the uncertainty bars. The change in $T_{m(\text{onset})}$ was 3.2 % and 10.45 % in $\Delta_{\text{fus}}H$ after 1500 thermal cycles. The graph depicts a temporary decrease in T_m (onset) at 1300 thermal cycles. This change is a fluctuation rather than a permanent change. However, the observed variation in the latent heat can be attributed to capric acid degradation, which could be due to a chemical degradation of the PCM. Quant et al. [25] investigated the long-term stability of a binary mixture PCM containing urea and sodium nitrate. Their findings revealed that changes in thermal properties were associated with urea degradation, leading to the formation of byproducts such as biuret and cyanuric acid. This section will be followed by thermal stress and a detailed chemical stability investigation of the capric acid.

3.1.4. Thermal stress test of capric acid

The thermal properties measured after the thermal stress test are shown in Fig. 7. The results show a small variation in the phase change equilibrium temperature, but the uncertainty bar overlaps, which leads to the conclusion that no variation occurred. The latent heat was quite stable, and nothing significant was evidenced in terms of thermal properties variation compared to the results obtained during the accelerated thermal cycling when a decrease in the latent heat was observed. Based on the results of both tests (thermal stress and accelerated thermal cycling), it seems that the degradation in capric acid was not caused only by the upper temperature (50 °C) during accelerated thermal cycling:

the phase change process may have assisted the degradation of the PCM. During the thermal stress test, the capric acid was kept for more time at 50 °C, when compared to the experiment where the sample undergoes 1500 thermal cycles. Therefore, capric acid is stable if the temperature in the thermal energy storage system rises to 50 °C due to thermal fluctuation.

3.2. Capric acid chemical stability

The chemical stability of capric acid was followed by different techniques to explain the thermal behavior revealed by DSC.

3.2.1. Capric acid FT-IR

FT-IR was first performed, and the spectra are reported in Fig. 8. As mentioned in the introduction, FT-IR was widely used to study the chemical stability of PCM, often with limited success [4,6,26]. The different absorption peaks show information on the functional group within the sample. The capric acid FT-IR spectra present first an overlap of two stretching signals in the 3400–2400 cm^{-1} region, with a large underlying $\nu\text{-O-H}$ band and sharp $\nu\text{-C-H}$ peaks (from 3000 to 2800 cm^{-1}) characteristic of carboxylic acid and aliphatic chains respectively. The carboxylic acid function is confirmed by several other signals such as $\nu\text{C=O}$ and $\nu\text{-C-O}$ at 1693.03 cm^{-1} and 1295.37 cm^{-1} , but also peaks revealing bond bending at 1420.02 cm^{-1} $\delta\text{O-H}_{\text{in-plane}}$ and 930 cm^{-1} $\delta\text{O-H}_{\text{on-plane}}$. This spectral data for capric acid aligns with the open literature data [27]. The spectra of the sample after 500 and 1000 thermal cycles exhibit identical absorption peaks. However, due to the subtle nature of possible degradations, it is difficult to draw firm conclusions.

3.2.2. NMR of capric acid

The NMR spectra for both uncycled and cycled samples are presented in Fig. 9. The spectrum of the uncycled sample corresponds to previously reported data for capric acid in the scientific literature [28]. The peak at 7.26 ppm is due to the solvent (CDCl_3) utilized in this analysis. Then the different protons of the molecule can be found at 0.9 ppm (triplet CH_3 , proton a in Fig. 9a), 1.3 ppm (multiplet, $6\times\text{CH}_2$, b), 1.6 ppm (multiplet, CH_2 , c), 2.4 ppm (triplet, CH_2 , d) and finally the exchangeable carboxylic acid proton can classically be observed in the zoom Fig. 9b in a large peak around 11 ppm (singlet, COOH , e).

If Fig. 9(a) does not show any differences between capric acid before and after thermal treatment, a zoom, reported in Fig. 9(b), reveals the formation of by-products. Indeed, several new peaks appear but also grow in time in the range of 3.6–4.4 ppm and at 8.1 ppm. ^1H NMR peaks around 4 ppm could be classically attributed to ester ($\text{CH}_2\text{-O-C=O}$) or lactones (cyclic esters) that could result from the reaction of the carboxylic acid function of capric acid with an unknown material, often an alcohol [29]. It could also be due to the formation of an anhydride ($\text{CH}_2\text{-COOOC-R}$), product of two capric acid condensation with the release of a water subproduct. The peak at 8.1 ppm [30], in the context of this study, could be related to formic acid (HCOOH) or another formate ester (HCOOR) that could result from two capric acid coupling and decarboxylation. Quantitative analysis of the by-product, performed by comparing the 3.6–4.4 ppm and 8.1 ppm peak intensity, to the one of the capric acid CH_3 at 0.9 ppm, indicated a formation of less than 1 % of degradation after 1500 thermal cycles. However, at such a low concentration, the ^1H NMR spectroscopy reaches its quantitative limits, and other analytic techniques should be used. While ^1H NMR spectroscopy confirms the progressive degradation of capric acid during the thermal treatment, determining the exact nature of the products and the reaction mechanism wasn't possible, and further investigation was needed.

3.2.3. GC chromatograms of capric acid

The chromatograms for the uncycled and cycled samples, obtained via the GC-FID are presented in Fig. 10. The figure shows multiple peaks were detected for the samples, reflecting that the capric acid is not the only molecule detected. The analysis revealed that the purity of capric

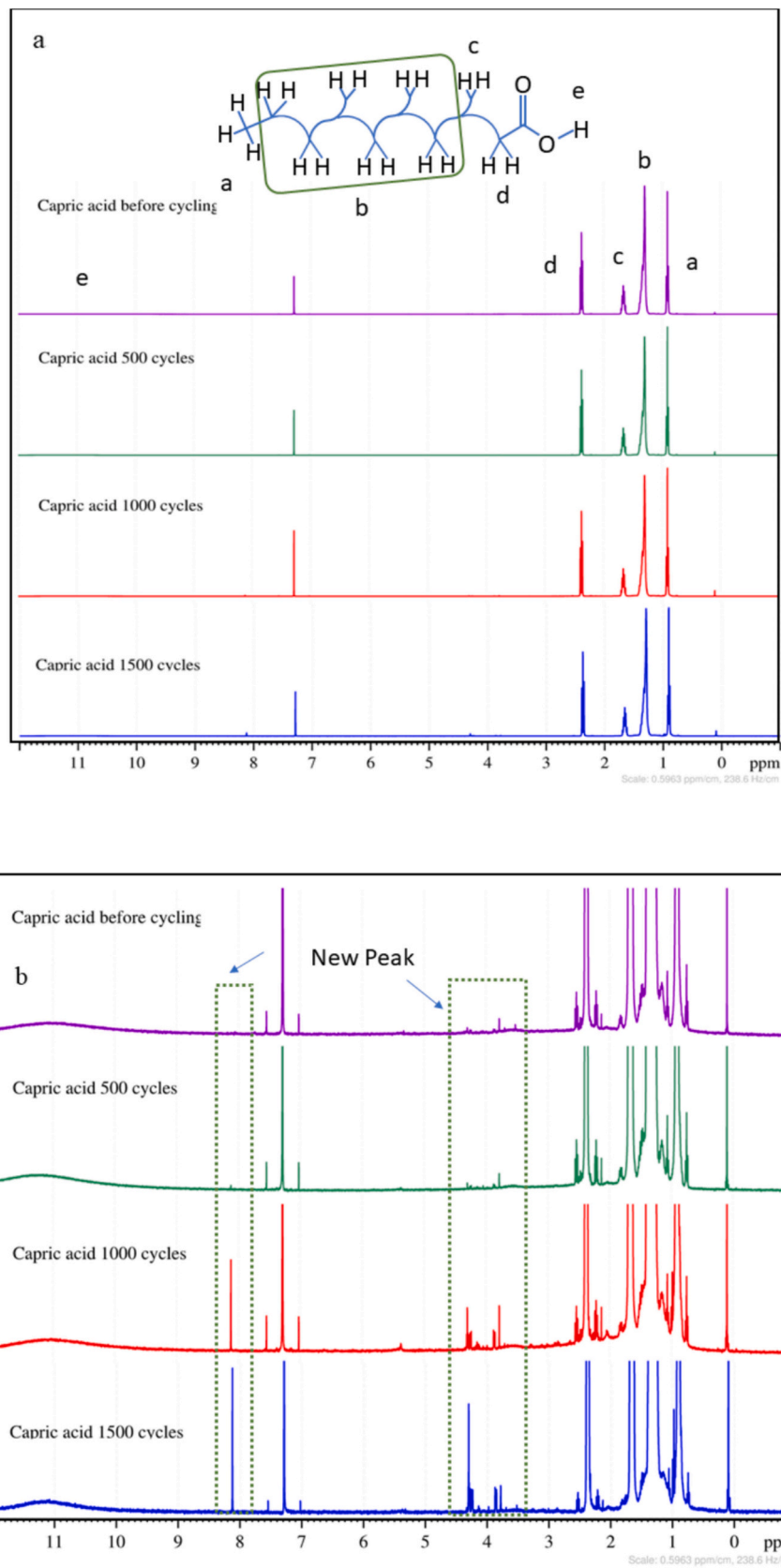


Fig. 9. NMR spectra for various samples of capric acid, a) full spectrum and b) zoom to reveal the products formed by degradation.

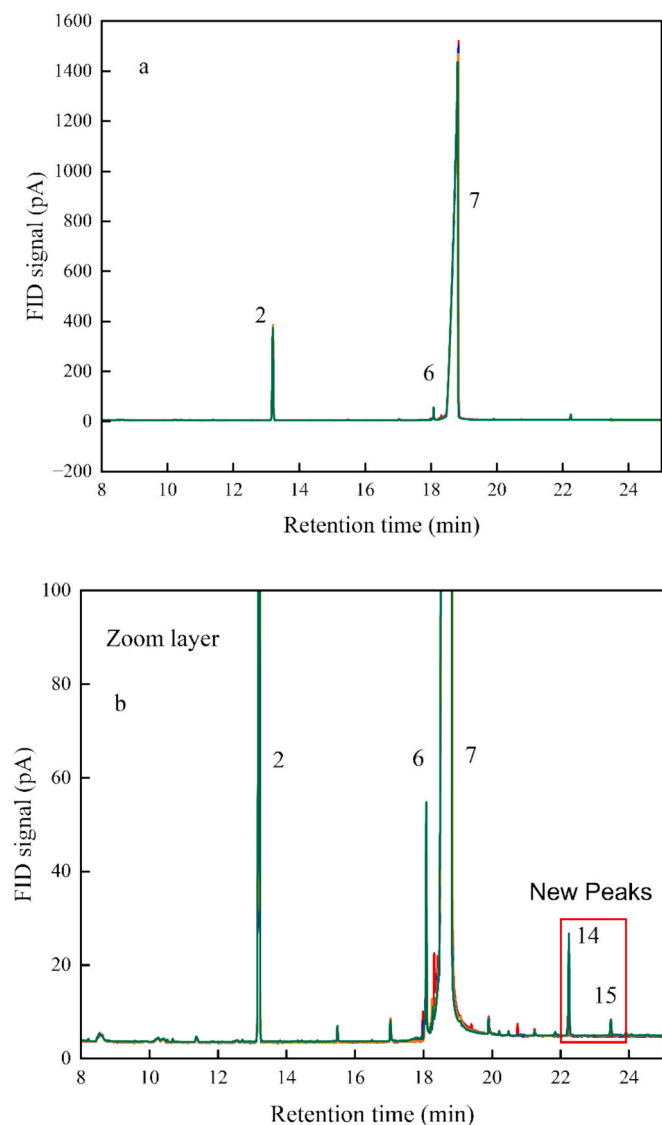


Fig. 10. Chromatograms of the capric acid, a) uncycled and cycled capric acid samples (GC-FID) and b) zoom layer to reveal the by-products formed.

Table 3

Kovats retention index for the comparison of GC-FID experiments. Identification according to NIST database.

Compound number	Retention time	Retention index	ID
2	13,21	1000,4	Decane (internal standard)
6	18,09	1306,6	decanoic acid, methyl ester
7	18,85	1358,2	n-Decanoic acid
10	20,08	1447,8	γ -Decalactone
11	20,50	1480,4	δ -Decalactone
13	22,22	1596,0	Dodecanoic acid, ethyl ester
14	23,31	1641,2	Octanoic acid, heptyl ester
15	23,93	1665,9	Heptadecane

acid was estimated at between 97 and 98.5 %. The result shows a similar trend to that observed in the work of Majo et al. [14] where multiple peaks were found after GC analysis for capric acid after 1000 thermal cycles. However, contrary to the work of Majo et al. [14], the by-

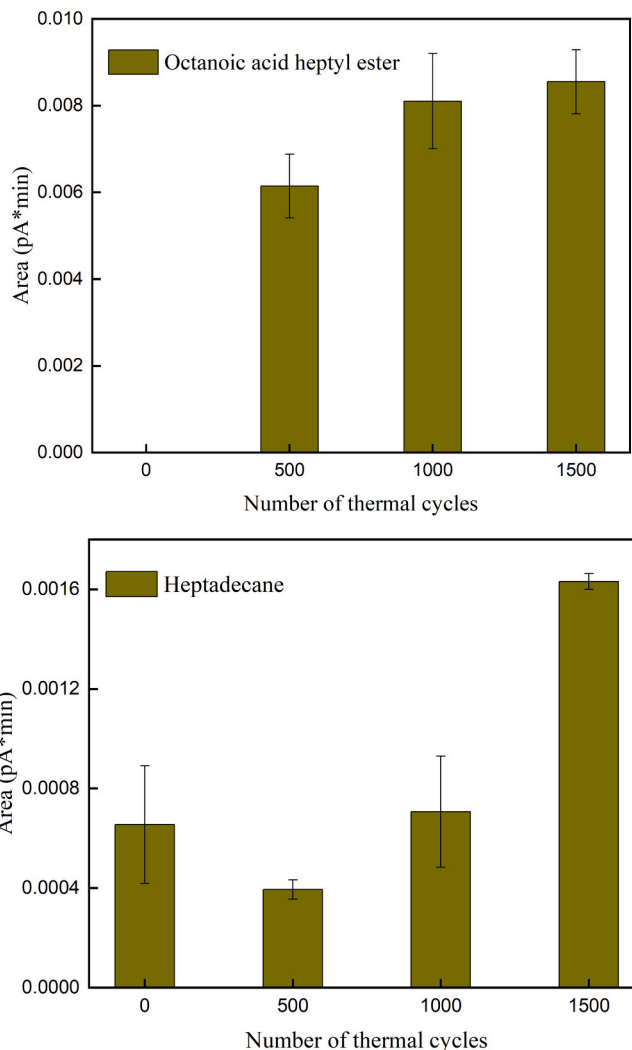


Fig. 11. Evolution of the peaks representing by-products formed during accelerated thermal cycling.

products observed were identified. The main one was decanoic acid, methyl ester. This compound corresponds to the esterification reaction between capric acid and the solvent (methanol) during injection into the GC. This was confirmed by changing the temperature of the injector and replacing the solvent with ethanol. Twelve other minor peaks were observed on the GC-FID chromatograms for a total amount of 0,01 % of capric acid. Five of these compounds have been identified with GC-MS, by comparison to the NIST database and the Kovats retention index (Table 3): two lactones: γ -Decalactone and δ -Decalactone, two esters: Dodecanoic acid, ethyl ester and Octanoic acid, heptyl ester and one alkane: Heptadecane (shown in Fig. 10 zoom). The other peaks were too small to be observed and identified with GC-MS. The evolution of the two main byproducts Octanoic acid, heptyl ester and Heptadecane was observed with the cycling, suggesting to be responsible for the variation in the thermal properties of capric acid (Fig. 11). The chemical pathways of capric acid degradation leading to these byproducts are not completely understood.

Although the mechanism could not be determined at this stage, ^1H NMR and GC-FID converged on the fact that capric acid was degraded during thermal treatment, producing esters and lactones. Heptadecane could not be confirmed by ^1H NMR because the proton signals are hidden below the capric acid ones. Formic acid was not confirmed by GC-FID because of the solvent delay applied in the methods, which hides its potential peak.

4. Conclusion

Capric acid thermal and chemical stability was studied. The initial results presented in this work will help to develop a standard procedure for stability investigation. The protocol suggests performing a benchmark experiment. This experiment will optimize the key parameters utilized for accelerated thermal cycling. It will be followed by long-term accelerated thermal cycling experiments. Along with accelerated thermal cycling impact of thermal stress should be investigated. In addition, the PCMs chemical stability should be investigated at atomic and molecular levels rather than utilizing a single characterization technique without respecting its limit.

In this work, the benchmark experiment deduces the optimal value of key parameters (2 °C/min and 5.6 mL) for long-term accelerated thermal cycling. Among the two thermal treatments (accelerated thermal cycling and thermal stress) performed, accelerated thermal cycling led to more degradation, which can be due to the combined effect of temperature and the phase change process. The thermal reliability of thermophysical properties was assessed using DSC after subjecting capric acid samples to 1500 accelerated thermal cycles from 0 to 50 °C. The variation in the thermal properties after 1500 thermal cycles were 3.2 % in $T_{m(\text{onset})}$ and 10.45 % in $\Delta_{\text{fus}}H$. The results and their comparison to literature data indicate that high heating/cooling rates and small sample volumes may fail to trigger degradation in the PCMs during accelerated thermal cycling. A significant reduction of 16.3 J/g was evident in the results for latent heat. Chemical stability was studied using various characterization techniques. FT-IR was initially employed to examine the chemical structure changes during thermal cycling, but proved insufficient for accurate insights. ^1H NMR spectroscopy confirmed capric acid degradation and by-product formation but was not able to reveal the nature or the amount of the product formed.

Gas Chromatography-Mass Spectrometry (GC-MS) and Gas Chromatography with Flame Ionization Detection (GC-FID) offered the most comprehensive chemical structure analysis. Chromatograms confirmed sample degradation and allowed for by-product quantification. Two primary by-products were identified: Octanoic acid, heptyl ester and heptadecane, with peak intensities increasing over successive thermal cycles. The chemical degradation could be responsible for the variation in thermal properties. However, this work gathered more information about the chemical changes in the PCM during its degradation. Nevertheless, this did not establish the precise mechanism of by-product formation, and further experiments should be performed. These findings will contribute valuable insights to the research community regarding the stability analysis of PCMs for thermal energy storage applications.

4.1. Recommendations and future work

The protocol proposed in this study emphasizes the importance of conducting a benchmark experiment to identify optimal parameters for long-term thermal cycling. Furthermore, when assessing the chemical stability of PCMs, the selection of appropriate characterization techniques is critical. While FT-IR analysis is commonly employed, its limitations often result in no observable spectral changes, potentially leading to misleading conclusions regarding chemical stability. A comprehensive evaluation should involve multiple complementary techniques. To ensure broader applicability, the protocol should be validated across different groups of PCM. As part of future work, the degradation mechanism of capric acid will be further investigated through two approaches. First set of experiments will be performed using high purity capric acid to rule out effects from initial impurities, and secondly repeating the same experiments as reported in this work under an oxygen-free environment.

CRedit authorship contribution statement

Hamza Ayaz: Writing – original draft, Visualization, Validation,

Methodology, Investigation, Conceptualization. **José Lara Cruz:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. **Marie-Hélène Alvès:** Investigation, Formal analysis. **Antoine Bousquet:** Writing – review & editing, Visualization, Formal analysis. **Mickaël Le Bechec:** Writing – review & editing, Investigation, Formal analysis. **Jean-Pierre Bédécarrats:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Formal analysis.

Declaration of competing interest

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

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Data availability

Data will be made available on request.

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