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Thermo-physical studies and corrosion analysis of organic binary eutectic phase change material for cooling application

Chosun University Graduate School

Department of Mechanical Engineering

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저온냉동 적용을 위한 유기 공융 상변화 혼합물의 열물성 및 부식성 연구

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Nomenclature

CR	Corrosion rate (mg/cm^2.year)
CTES	Cold thermal energy storage
CA	Caprylic acid
C_p	Specific heat of the compound (kJ/(K·kg)
DSC	Differential scanning calorimetry
FT-IR	Fourier transform infrared spectroscopy
HDPE	High-density polyethylene
LHTES	Latent heat thermal energy storage
MP	Melting point
ΔH_f	Latent heat of fusion during freezing (J/g)
ΔH_m	Latent heat of fusion during melting (J/g)
PCM	Phase change material
RPD	Relative percentage difference
SA	Stearyl alcohol
T_{Onset}	Onset phase change temperature
T_m	Melting point temperature (°C)
TGA	Thermogravimetric analysis
TES	Thermal energy storage
T_{Peak}	Peak melting/freezing point temperature
T_f	Freezing point temperature (°C)
X_a	Molar mass fraction

Abstract

Thermo-physical studies and corrosion analysis of organic binary eutectic phase change material for cooling application

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The rapid increase in energy demand due to high living standards has resulted in wildly excessive exploitation of carbon-based energy resources. Excessive use of these energy resources is a serious threat to the environment, and it is imperative to move to sustainable energy sources. The ever-increasing need for energy necessitates innovative approaches to its production as well as storage. To effectively use ample energy sources available such as solar energy, a crucial component is required: a proficient and economical heat storage system to compensate for its intermittent nature. Different thermal energy storage (TES) technologies are utilized to reduce the peak load energy and augment system energy efficiency. Among various thermal storage techniques, latent heat thermal energy storage (LHTES) with phase change materials (PCMs) is put forward due to its high energy storage capacity and isothermal storage operation. Commercially available organic PCM has fixed phase transition temperature, an

imperative parameter for any specific application. To overcome the limitation of application temperature ranges, binary phase change material mixtures are introduced and prepared with the desired melting point temperature for any required application.

This work provides a detailed discussion on developing organic binary mixture as a phase change material for cold thermal energy storage applications. In this study, two novel organic binary mixtures as phase change material, namely caprylic acid-cetyl alcohol and caprylic acid-stearyl alcohol were used. Prior to utilization in a real-time application, the prepared binary mixture was examined for all the necessary and important factors. As a result, the caprylic acid-cetyl alcohol has a eutectic point at 85:15 molar mass ratio and the thermal properties determined with differential scanning calorimetry (DSC) have an onset melting point temperature of 10 °C with the latent heat of fusion of 154.1 $J.g^{-1}$. In addition, the onset freezing point temperature was 8.9 °C with the latent heat of fusion of 153.3 $J.g^{-1}$. The eutectic point for caprylic acid-stearyl was for 90:10 molar mass ratio and shows an onset melting point temperature and latent heat of fusion 11.4 °C and 154.4 $J.g^{-1}$ Caprylic acid-stearyl alcohol has onset freezing point temperature of 11.8 °C with the latent heat of fusion 150.5 $J.g^{-1}$. In addition, the thermal conductivity of the binary mixtures was measured for caprylic acid-cetyl alcohol in the solid phase (0.288 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 0 °C), liquid phase (0.160 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 20 °C), and caprylic acid-stearyl alcohol solid phase (0.267 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 0 °C), liquid phase (0.165 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 20 °C) which is in the convincing range for organic PCMs.

Thermogravimetric analysis was performed to investigate the thermal stability for the prepared binary mixture. The results showed a higher decomposition temperature compared to its melting point temperature, which will not affect its performance due to thermal fluctuation in real-time applications. Thermal properties reliability was examined with accelerated thermal cycling for 200 melting/freezing cycles, which did not show much variation, and was in the acceptable range. The FT–IR results showed that after 200 thermal cycles, no structural change was evidenced and the binary mixtures were chemically stable. Corrosion test was performed with different metals, namely (aluminum, copper, stainless steel (SS 316)) for a total of 12 weeks, and the metal strips were examined after 1 week, 4 weeks, and 12 weeks. Based on calculating the corrosion rate, the metals can be recommended for its use with a binary mixture prepared. The result confirmed that the binary mixtures were stable up to 200 thermal cycles and have potential as a eutectic phase change material for cooling applications.

국 문 초 록

저온냉동 적용을 위한 유기 공융 상변화 혼합물의 열물성 및 부식성 연구

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높은 생활수준으로 인한 에너지 수요의 급격한 증가는 탄소 기반 에너지 자원의 과도한 이용을 초래하였다. 이러한 에너지 자원의 과도한 사용은 심각한 환경 문제를 야기하며, 지속 가능한 에너지원의 전환이 필수적이다. 에너지에 대한 요구가 계속 증가함에 따라 에너지의 생산 및 저장에 대한 혁신적인 접근 방식이 필요하다. 태양 에너지와 같이 사용 가능한 풍부한 에너지원을 효과적으로 사용하기 위해서는 중요한 구성 요소, 즉 간헐적 특성을 보완할 수 있는 효율적이고 경제적인 열 저장 시스템이 필요하다. 다양한 열 에너지 저장(TES; thermal energy storage) 기술은 최대 부하 에너지를 줄이고 시스템 에너지 효율을 높이기 위해 사용된다. 다양한 열 저장 기술 중에서 상변화 물질(PCM; phase change materials)을 이용한 잠열 에너지 저장(LHTES; latent heat thermal energy storage)은 높은 에너지 저장 용량과 등온 저장 작동의 특성이 있다. 시중에서 판매되고 있는 유기 PCM은 특정 응용 분야에 필수

적인 매개변수인 고정된 상전이 온도를 가진다. 적용 온도 범위의 한계를 극복하기 위해 이원 상변화 물질 혼합물을 도입하여 필요한 응용분야에서 원하는 융점 온도로 변경할 수 있다.

본 연구에서는 저온 열에너지 저장 응용을 위한 상변화 물질로서 유기 이원 혼합물의 개발에 대한 연구를 수행하였다. 이에 따라 상변화 물질인 카프릴산-세틸 알코올 및 카프릴산-스테아릴 알코올에 대한 두 가지 새로운 유기 이원 혼합물에 대한 열물리학적 특성을 분석하였다. 실시간 응용에 활용하기 전에 준비된 이원 혼합물에 대한 모든 필요 요소 및 중요 요소를 조사하였다. 그 결과 카프릴산-세틸알코올은 85:15 몰 질량비에서 공융점을 가지며 시차주사 열량측정법(DSC; differential scanning calorimetry)로 측정되는 열적 특성은 154.1 J.g-1의 융해 잠열에서 함께 10 °C의 개시 융점 온도를 가진다. 또한, 개시 빙점 온도는 8.9 °C이며 융해 잠열은 153.3 $J.g^{-1}$로 나타났다. 카프릴산-스테아릴의 공융점은 90:10 몰 질량비이며 개시 융점 온도 및 융해 잠열은 11.4 °C와 154.4 $J.g^{-1}$로 나타났다. 카프릴산-스테아릴 알코올의 개시 빙점 온도는 11.8 °C이며, 융해 잠열은 150.5 $J.g^{-1}$로 나타났다. 또한 이원 혼합물의 열전도율은 PCM에 대한 사용 범위에 있는 고체상(0 °C에서 0.288 $W{\cdot}m^{-1}{\cdot}K^{-1}$), 액체상(20 °C에서 0.160 $W{\cdot}m^{-1}{\cdot}K^{-1}$)에서 카프릴산-세틸 알코올과 고체상(0 °C에서 0.267 $W{\cdot}m^{-1}{\cdot}K^{-1}$), 액체상(20 °C에서 0.165 $W{\cdot}m^{-1}{\cdot}K^{-1}$)에서 카프릴산-스테아릴 알코올을 측정하였다.

제조된 이원 혼합물의 열 안정성을 조사하기 위해 열중량 분석을 수행하였다. 그 결과, 융점 온도에 비해 분해 온도가 더 높아 실시간 적용 시 열변동으로 인해 성능에 영향을 미치지 않는 것으로 나타났다. 열 물성 신뢰성은 200번의 용융/동결 사이클 동안 가속 열 사이클

링으로 조사하였으며, 이는 큰 변화를 보이지 않았으며 허용 범위 내에 있었다. FT-IR 결과, 200번의 열 사이클 후에 구조적 변화가 나타나지 않았으며, 이원 혼합물은 화학적으로 안정적이었음을 확인하였다. 부식 시험은 알루미늄, 구리, 스테인리스강(SS 316) 등 다양한 금속으로 총 12주 동안 수행하였으며, 금속 스트립은 1주, 4주, 12주 후에 검사하였다. 부식률 계산을 기반으로 이원 혼합물에 대하여 스테인리스강(SS 316) 과 알루미늄에서 내부식성이 우수한 결과를 나타내었다. 이에 따라 종합적으로 모든 이원 혼합물은 최대 200번의 열 사이클까지 안정적이었으며 냉각 응용 분야에서 공융 상변화 물질로서 잠재력이 있음을 확인하였다..

1. Introduction

This thesis reports two novel organic binary mixtures as phase change materials for cooling applications. In-depth characterization of the prepared binary mixture was performed with a focus on its thermal and chemical stability. Thermophysical properties reliability was examined for 200 melting/freezing thermal cycles. In addition, the corrosion test was performed to investigate its compatibility with different metals utilized for the manufacturing of cold thermal energy storage vessels. The results revealed the binary mixtures could be potential candidates for cold thermal energy storage systems.

1.1. Background and previous studies

The substantial rise in global temperature over the last few decades owing to increased energy consumption is alarming and has negative global ramifications. Reports on future energy demand forecast an increase of 18% for developed countries and 71% for developing countries until 2040, which is a great concern. Long-term utilization of fossil fuels for energy production threatens human life and the ecosystem. These factors have motivated the stakeholders to reduce their dependence on traditional non-renewable energy sources [1,2]. The cognizance of people's role in climate change is the primary driver of environmentally friendly energy production and utilization [3]. Eco-friendly energy resources are abundant and

safe for the future. Therefore, it is essential to explore sustainable sources, such as wind energy, solar energy, and biomass energy, which have sufficient potential to fulfill the energy demands [4]. Thermal heat storage (TES) is getting more attention due to its supply and demand differences, shaving peak load, or enhancing the system performance. TES system stores energy during charging when an excess amount of heat is available and retrieves energy during discharging for utilization. The steps involved in utilizing thermal energy include charging, storing, and discharging, which together are termed a cycle. During charging, energy is supplied to the system to be stored and retrieved during the discharging. The main variations involve the amount of energy stored and the selection of storage methods utilized [5,6].

Based on the TES mechanism, three different techniques are commonly used, which was sensible heat storage, latent heat storage, and thermochemical heat storage. Among various thermal storage techniques, latent heat thermal energy storage (LHTES) with phase change materials (PCMs) is put forward due to its high energy storage capacity and isothermal storage operation. These are depicted in Fig. 1.1. The latent heat storage represented in Fig 1.1 (b) shows the different steps involved in storing the heat energy; charging step shown in the pictorial view were absorbing the heat that increase the temperature of phase change material which is termed as sensible heat storage and the constant temperature line shows the phase change of the material and for further increase, the temperature is increased as sensible heat,

and follow the reverse for discharging.

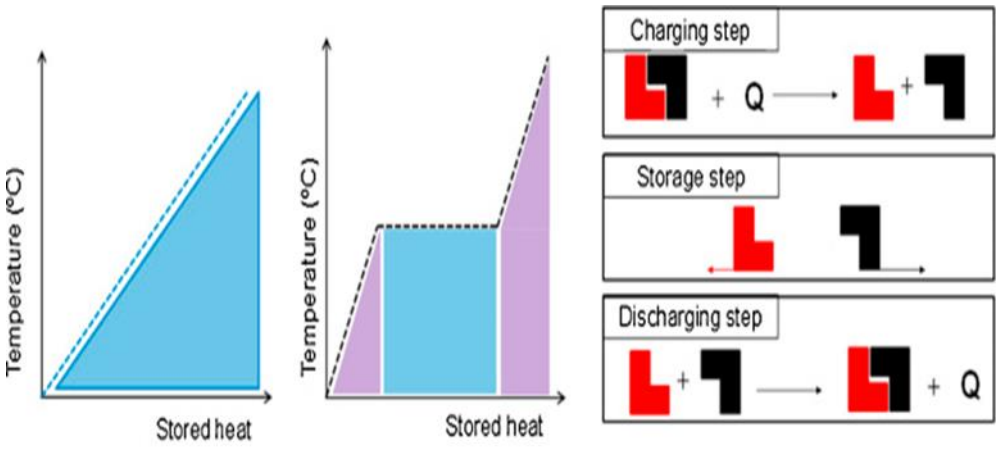


Fig. 1.1. Different approaches for TES: (a) Sensible heat storage; (b) Latent heat storage; (c) Thermochemical heat storage [7].

Latent heat storage employs a phase transition at a constant temperature to accumulate or retrieve thermal energy by the latent heat of fusion of the storage medium, as shown in Fig. 1.1 (b). Phase change materials (PCMs) have a high energy density and they can increase the energy storage capacity of the system; however, they have a low thermal conductivity. The latent heat of fusion, melting point, and chemical stability of the material are essential properties to be utilized in real-time applications [8–10]. The amount of heat stored in such a storage system can be calculated using Eq. (1).

$$Q = \int_{T_i}^{T_m} mc_p dT + ma_m H + \int_{T_m}^{T_f} m\, c_p dT \quad (1)$$

Where Q is the amount of latent heat energy stored (J), m mass of the storage material (kg), c_p specific heat capacity ($kJ \cdot kg^{-1} \cdot K^{-1}$), dT temperature difference (°C), am amount of fraction melted (kg), T_f final temperature (°C), T_i initial temperature (°C), T_m melting temperature (°C), and T_f is the freezing temperature (°C).

PCM incorporated into available systems, experimental investigations, and numerical simulations significantly improve thermal energy storage capacity. A recent study concluded that a TES system for a solar flat-plate collector with PCM could store 20% more thermal energy than the water storage system [11]. Latent heat thermal storage (LHTES) has various applications and was previously utilized for floor heating [12], cold energy recovery in storage plants [13], solar energy storage systems [14], and cooling applications [15]. The latent heat thermal energy storage is classified as cold thermal energy storage and hot thermal energy storage (CTES). The energy retrieved for solid-liquid PCM in cold thermal energy storage during discharging is from solid-liquid phase change, whereas conversely for hot thermal energy storage [16]. The discharging characteristics of PCM decide the type of latent heat for any application.

Recently CTES system with PCMs is getting more attention and utilized for air conditioning indoor application (18 °C–22 °C) [17], refrigeration system (0 °C–10 °C) [18], and pharmaceutical transport (sub-zero applications) [19]. The CTES integrated into these systems helps shift electrical energy demand during peak/off-peak hours and reduces CO_2 emission [20,21].

Therefore, CTES with PCM will augment the system performance and give more operational flexibility. PCMs, which are classified as organic and inorganic based on their chemical composition, play a key role in designing the CTES system for any application. Many researchers have performed a detailed study on different types of PCMs for CTES systems [22]. Based on the chemical composition of PCM, they are classified as organic (paraffin, non-paraffin) and inorganic (salt hydrates). The organic PCM has potential properties such as congruent phase change, non-toxic nature, lower supercooling, good nucleation rate, and economical. Moreover, some organic PCM as fatty acids can be prepared from sustainable or reused raw materials like animal fat, palm oil, coconut oil, and animal milk [23].

Naturally available organic PCM has a fixed phase change temperature, which limits their applications. Therefore, a new class of phase change materials was introduced, namely eutectic PCM (binary/ternary mixture), which can be developed with desired phase change temperature for any specific application. Eutectic PCM is a combination of two or more naturally available PCM blended with a specific mass proportion of each to have a congruent phase change [24]. Progress in the binary mixture has received more attention due to the limited number of potential PCMs for the CTES system. Detailed literature consisting of the binary mixture as a phase change material for different cooling applications is presented. Veerakumar et al. [25] studied the thermophysical characteristics of a new binary combination of a fatty acid and a

fatty alcohol namely capric acid–cetyl alcohol with a 70:30 molar ratio for the CTES, as well as their compatibility with other metals. Thermal cycling and Fourier-transform infrared spectroscopy (FT-IR) were used to determine the binary mixture's thermal and chemical stability. The peak melting point temperature and freezing point temperature during phase transition were 22.8 °C and 11.97 °C, respectively, with latent heats of fusion during melting (ΔH_m) and freezing (ΔH_f) of 144.92 and 145.85 $J.g^{-1}$. After 1,000 cycles of accelerated thermal cycling, the melting point temperature changed by 6.37%, while the latent heat of fusion dropped by 18.35%. The author also reported a binary mixture of lauric acid–myristyl alcohol combined with a 40:60 molar ratio. The melting and freezing points were determined to be 18.7 °C and 22.46 °C, with (ΔH_m) and (ΔH_f) of 151.5 and 151.6 $J.g^{-1}$, respectively [26]. The novel binary mixture reported was stable and a good addition to indoor thermal comfort phase change materials.

Zuo et al. [27] reported caprylic acid and 1-dodecanol in a 70:30 molar ratio to make an organic binary combination for the CTES system. The thermophysical characteristics of the binary mixture were determined using the differential scanning calorimetry (DSC) technique, which revealed a phase transition temperature of 6.52 °C during melting, a degree of supercooling of 2 °C, and a latent heat of fusion (ΔH_m) of 171.06 $J.g^{-1}$. The binary mixture's thermal stability was tested for 60 and 120 melting/freezing cycles, and no significant changes

in thermophysical characteristics were found. For cooling purposes, a binary combination of capric acid and lauric acid was prepared by Dimano et al. [28] with the addition of pentadecane. To attain the eutectic point, the capric acid and lauric acid (CA–LA) combination was initially mixed in a 65:35 molar ratio, and the melting point temperature was determined to be 18 °C with a phase enthalpy of 140.8 $J.g^{-1}$. To lower the melting temperature even further, three different combinations of pentadecane with 0.1, 0.3, and 0.5 mole fractions were mixed into a CA–LA mixture and the energy storage performance was evaluated in a shell and tube heat exchanger. The CA–LA combination containing a 0.1 mole percentage of pentadecane outperformed the others, with a phase transition temperature of 13.2 °C and a phase enthalpy of 142.2 J/g. According to the authors, the binary combination was also evaluated with a 0.1 mole proportion of different organic chemical additives. Methyl salicylate, cineole, and eugenol have narrow melting point ranges and a high capacity for energy storage. The melting points of these additions were 12.2 °C, 12.3 °C, and 13.9 °C, respectively, with latent heats of fusion of 126.7, 111.6, and 117.8 $J.g^{-1}$, respectively [29].

Wang et al. [30] prepared a binary combination of caprylic acid-nonanoic acid for cooling purposes with an 81.4:18.6 molar ratio. The DSC method yielded a H_m of 171.06 $J.g^{-1}$ and a melting point temperature of 7.6 °C. Furthermore, they studied the change in melting point temperature and latent heat of fusion by completing 100 melting/freezing cycles, which

revealed no discernible change. Nadiya et al. [31] developed an efficient binary combination of lauryl–cetyl alcohol with an 80:20 molar ratio and examined its efficency in the refrigeration system chamber. The peak phase transition temperature during melting and freezing was 20.01 °C and 12.04 °C, respectively, with latent heats of fusion of 191.63 and 189.51 $J.g^{-1}$. The binary mixture discharge characteristics to reach the ambient temperature for 1 kg PCM (343 min), 2 kg (372 min), and 3kg (402 min) which indicates it is a good fit for the CTES system. Xing et al [32] prepared a binary mixture with a 90:10 molar mass proportion of caprylic acid-palmitic acid and studied thermophysical properties using the DSC technique. The melting onset/peak phase change temperature was 6.53 °C/11.33 °C, whereas the freezing phase was 4.31 °C/1.79 °C. The melting and freezing phase enthalpies obtained were 116.47 and 116.23 $J.g^{-1}$, respectively.

Gao [33] developed a binary PCM combination of capric acid and dodecanol with a molar mass ratio of 60:40 for refrigeration application. The DSC method was initially employed to study the thermal characteristics of the prepared binary mixture. The phase change temperature was 8.9 °C, with a phase change enthalpy of 156.6 $J.g^{-1}$. Eutectic PCM for building energy storage at low temperature is reported where the PCM is infiltered into the supporting building material. Wang et al. [34] prepared a new eutectic PCM of tetradecanol-lauric acid with the addition of expanded perlite-aluminum for building heat storage. The thermal properties of

composite PCM were T_m=24.9 °C with ΔH_m=78.2 J.g^{-1} and T_f=25.2 °C with ΔH_f=81.3 J.g^{-1}, respectively. The thermal reliability was analyzed for 2000 thermal cycles, which did not show any significant variation in the thermal properties.

Huang et al. [35] reported three different eutectic mixtures with HDPE-EVA supporting structures for building energy storage applications. DSC was performed for the determination of thermal properties for tetradecanol (TD)–capric acid (CA), TD–lauric acid (LA), and TD–myristic acid (MA) for five weight concentrations of HDPE-EVA. The result showed 70 wt% (TD-CA), 65 wt% (TD-LA), and 60 wt% (TD-MA) have negligible leakage with melting/freezing point temperature of 9.13 °C/13.32 °C (TD-CA), 24.53 °C/24.92 °C (TD-LA), 33.15 °C/30.72 °C (TD-MA) and latent heat of fusion 90.20 J.g^{-1}/88.70 J.g^{-1}, 100.50 J.g^{-1}/99.70 J.g^{-1}, and 128.60 J.g^{-1}/125.70 J.g^{-1} respectively. The material put forward to 1000 accelerated thermal cycles, which shows good stability in thermal properties. The summary of the previously reported eutectic phase change materials and the present study is presented in Table 1.1. The previous study reported give less attention on phase change materials for cooling application in the range 10–15 ℃ which has plenty of application and consumes plethora of energy to operate.

Table 1.1 Summary of the PCM binary mixture reported for cold thermal energy storage.

PCM binary mixture	Eutectic composition	Melting point temperature (℃)	Latent heat of fusion ($J.g^{-1}$)	Ref.
Capric acid-cetyl alcohol	70:30	22.89	144.92	[25]
Lauric acid-myristyl alcohol	40:60	22.46	151.5	[26]
Lauryl-cetyl alcohol	80:20	20.01	191.63	[31]
Caprylic acid-1-dodecanol	70:30	6.52	171.06	[27]
Capric acid-dodecanol	60:40	8.9	156.6	[33]
Caprylic-palmitic acid	90:10	11.33	116.47	[32]
Capric-lauric acid	65:35	18	140.8	[28]
Caprylic-nonanoic acid	81.4:18.6	7.6	123	[30]
Caprylic acid-cetyl alcohol	85:15	10	154.1	Present study
Caprylic acid-stearyl alcohol	90:10	11.4	154.4	Present study

1.2. The objective for the present research

Phase change materials to maintain the temperature at 10 – 15℃ to store food items, pharmaceutical transport, or in supermarket display cabinets are limited, which motivates to the exploration of more potential PCM in this range. This work reports a novel organic PCM

binary mixture of caprylic acid-stearyl alcohol and caprylic acid-cetyl alcohol with a eutectic point at 90:10 and 85:15 molar mass ratios. The binary mixture prepared is not presented in the open literature, and it is essential to uncover related information before utilizing it in real-time application. The thermophysical properties, including melting point temperature, latent heat of fusion, and thermal conductivity, were investigated experimentally and their results are presented. The thermal conductivity of the prepared binary mixture was measured in the solid and liquid phases. In addition, the thermal and chemical stability was analyzed with thermogravimetric analysis and Fourier transform infrared spectroscopy (FT–IR). Thermal properties reliability was determined for 200 melting/freezing thermal cycles. In addition, the compatibility of the binary mixture was tested with different metals used for the manufacturing of the CTES container. This work will be pioneering in developing an effective CTES system for cooling applications.

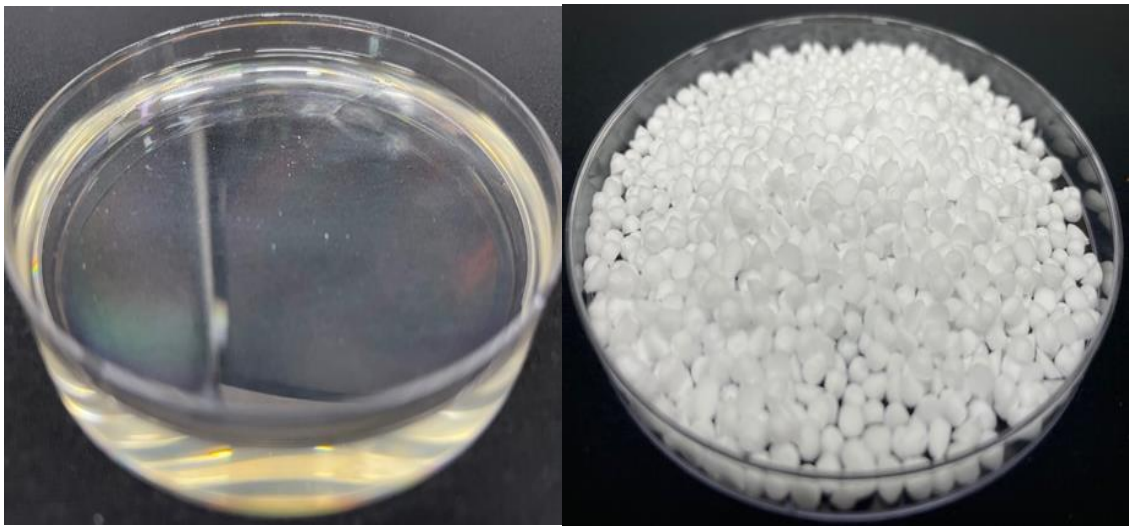
2. Materials and Methodology

This section briefly describes the common peripheral devices used in all of our characterizations for the binary mixture prepared. It includes differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and KD2PRO. Thereafter, a brief description of the binary mixture prepared and corrosion test is presented.

2.1. Materials

In this study, two binary mixture preparation and their characterization techniques are explained precisely. Based on the gap identified by the literature as having limited phase change materials available for cold thermal energy storage. This study is performed to identify potential candidates for thermal cold thermal storage. One fatty acid and two fatty alcohols were selected to develop two organic binary mixtures as phase change materials for cold thermal storage were prepared. The materials for this work were provided by Daejung Chemicals and Metals, Republic of Korea. Caprylic acid (98% pure) is a straight medium-chain fatty acid with eight carbon and is represented by ($CH_3(CH)_6COOH$). At room temperature (RT 27 °C), it is a colorless to yellow saturated liquid. Cetyl alcohol (99% pure) is fatty alcohol obtained from the reduction of palm oil and has the chemical composition ($CH_3(CH_2)_{14}CH_2OH$).

Stearyl alcohol (99%) ($C_{18}H_{38}O$) is saturated fatty alcohol that appears to be small white granules at temperatures < 30 °C. At room temperature, it is a white spherical solid. Fig. 2.1. shows the pristine materials, while Table 2.1 presents their thermophysical properties and it was utilized to develop the eutectic phase change materials. These pristine materials were employed to develop eutectic phase change materials and in-depth characterization prior to real-time application was performed. The thermal properties of the eutectic PCM were determined with a focus on thermal and chemical stability. DSC determined the thermal properties of the pure and prepared eutectic PCM. Thermal and chemical stability was examined by using TGA analysis and FT-IR spectroscopy. The thermal conductivity of the phase prepared phase change material was measured in the liquid and solid phase with the KD2 PRO. The compatibility of the eutectic PCM was examined with different metals utilized for the manufacturing of cold thermal energy storage.



(a) (b)

(c)

Fig. 2.1. Pure materials at 27 °C; (a) Caprylic acid, (b) Cetyl alcohol, and (c) Stearyl alcohol.

Table 2.1. Thermophysical properties of pristine materials.

Materials	IUPAC name	Melting		Solidification	
		T_{Peak} (°C)	ΔH_m (J.g^{-1})	T_{Peak} (°C)	ΔH_f (J.g^{-1})
Caprylic acid	Octanoic acid	18.4	142.6	4.1	154.6
Cetyl alcohol	1-Hexadecanol	52.2	232.3	43.6 38.8	245.3
Stearyl alcohol	Octadecanol	61.4	240.7	52.4 48.1	257.9

2.1.1. Preparation of caprylic acid/cetyl alcohol binary mixture

To investigate the thermo-physical properties, the eutectic point of the binary mixture must be found. Based on the theoretical estimation of the eutectic point, the pristine materials were blended in 55%-100% mass proportion, with a 5% rise for each mixture. The pure materials were first weighed with precision balance (FZ-300iWP, Japan) with a precision of 0.001 g. The individual base material was heated to 75 °C and blended appropriately with a hot plate and magnetic stirrer. Eventually, the binary mixture prepared was cooled to room temperature.

2.1.2. Preparation of caprylic acid/stearyl alcohol binary mixture

The eutectic point of the binary mixture has to deduce firstly to analyze the thermal properties. The theoretical estimations were first hand to initiate forming various binary solutions of different mass ratios of the pure materials. Based on the calculations mass proportion of 60%-100% of the pure materials was amalgamated with an increment of 10% for

each mixture. The pure materials were first weighed with a precision balance (FZ-300iWP, USA) with an accuracy of ±0.001 g to add the accurate mass proportion of each material. Then, the binary mixture was heated to 80 °C and mixed properly with a hot plate and magnetic stirrer (GLHPS-C12, Korea). Finally, the binary mixture was cooled to room temperature.

2.2. Differential scanning calorimetry (DSC)

The thermophysical properties of the pristine materials and binary mixture were investigated using DSC (204 F1 Phoenix, Netzsch, Germany). The DSC analysis was based on the heat flux principle by holding 5 mg of the sample. Samples were subjected to a temperature range of -20 °C to 80 °C for endothermic and exothermic heat flow. The heating rate of 10 °C/min was fixed for this analysis. The phase transition temperature during melting/freezing together with its latent heat of fusion was obtained. The utilized instrument for DSC analysis is shown in Fig. 2.2.

Fig. 2.2. Picture of DSC.

2.3. Thermogravimetric analysis

The thermal stability of the fatty acid/fatty alcohol mixture was examined by a Thermogravimetric analyzer (SHIMADZU TGA-50, USA) with weight readability of 0.001 mg, as shown in Fig. 2.3. Thermogravimetric analysis (TGA) reports the variation in the mass of the materials by increasing the temperature. An aluminum macro pan inside the furnace holds the material subjected for analysis with incremental heating of 10 °C/min for 21 °C–350 °C. In addition, argon gas with a 50 mL/min flow rate was circulated in the environment to detect the reaction during decomposition. By analyzing the TGA curve, the decomposition temperature of the materials can be determined with a radical mass variation of the sample.

Fig. 2.3. Thermogravimetric analyzer.

2.4. Fourier transform infrared spectroscopy (FT-IR)

The chemical properties of the prepared binary mixture were examined by FTIR Spectrometry (Vertex 70v/Hyperion 2000) shown in Fig. 2.4. Attenuated total reflectance mode was utilized for infrared (IR) spectroscopy, a drop of the binary mixture prepared was spilled on the Kbr crystal, and a force of 8 tonnes was applied. The Kbr pellet was allowed to dry, and the spectral data was attained for an IR range of 4,000–450 cm-1 with 32 scans. The spectral data depicts the chemical composition of the binary mixture prepared.

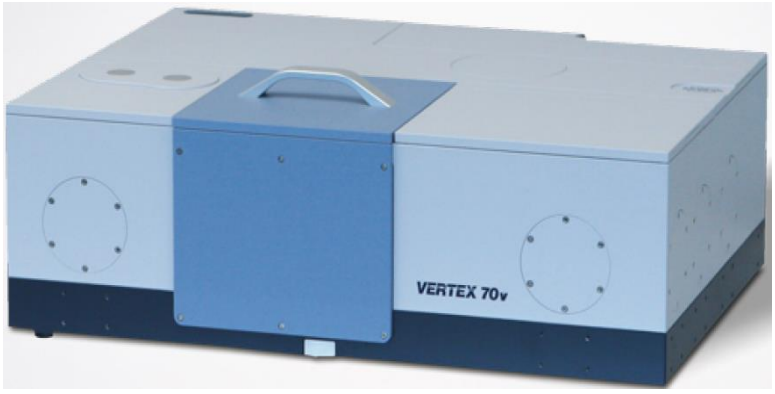


Fig. 2.4. FT-IR Spectrometer.

2.5. Thermal analyzer for measuring thermal conductivity

Thermal conductivity investigation of the binary mixtures was performed using a transient hot-wire technique KD2 Pro (Decagon Devices, USA) with an accuracy of ±5% for the liquid phase and ±10% for the solid phase, as shown in Fig. 2.5. The device comes with an ultra-low-power 16-bit microcontroller to process the data, and an A/D converter with a probe, consisting of a heater and sensor. The KD2 Pro analyzer waits 30 seconds for temperature equilibrium and records the temperature variation for a consecutive 30 seconds by every second. The KD2 pro analyzer with the single-needle (KS-1) and double-needle (SH-1) sensors were separately employed to measure the thermal conductivity in liquid and solid states. The sensor was set upside down in a glass container holding 50 mL of the binary mixture to be analyzed. The measured response by the sensor was processed by the microcontroller and converted to digital data with an analog-to-digital converter and displayed the measured thermal

conductivity.

Fig. 2.5. KD2 PRO thermal property analyzer.

2.6. Corrosion test

The compatibility of the binary mixture was examined with three different metals utilized for the fabrication of thermal energy storage. Three different metals, namely aluminum (Al), copper (Cu), and stainless (SS 316), were selected for the corrosion test of the binary mixture. The standard procedure recommended by American Standard for Testing and Materials (ASTM G1-03) [36] was adopted. Firstly, the metal strips were cut into a rectangle shape with dimensions 5×1 cm height and width, respectively, as shown in Fig. 2.6. Next, the metals strips were clean

with acetone and kept to dry. After preparing the metal strips, it was weighed with the precision balance before subjecting to the binary mixture. Finally, the metals were put into a binary mixture and conducted corrosion test for a total of 12 weeks, followed by calculating the corrosion rate for the 1st week, 4th week, and 12th week. The glass container was enclosed to have minimal contact with the surrounding.

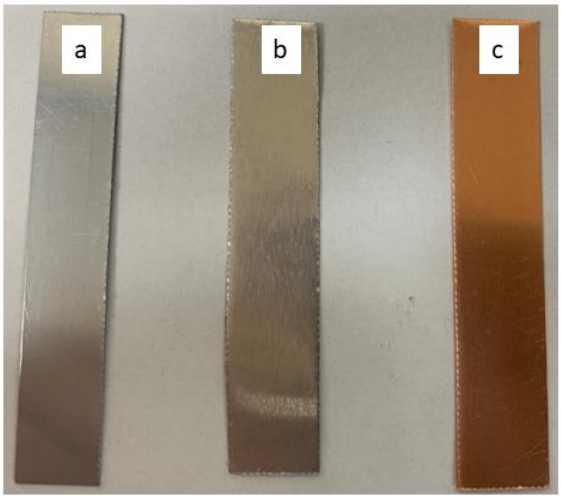


Fig. 2.6. (a) Stainless steel (SS 316), (b) Aluminum (Al), and (c) Copper (Cu), before corrosion test.

3. Results and Discussions

This section presents the results determined in this study and is discussed in detail. The section is divided into two subsections, the first portion consists of the results attained for caprylic acid-cetyl alcohol, and the last portion presents the results for caprylic acid-stearyl alcohol.

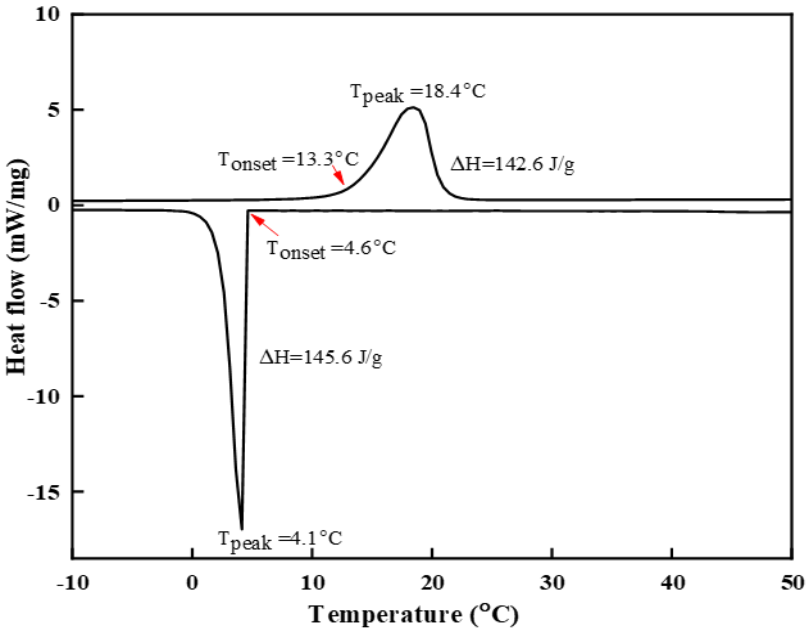
3.1. Characterization of caprylic acid-cetyl alcohol

Preparing different molar mass ratios of caprylic acid-cetyl alcohol first eutectic point was determined to investigate other thermophysical properties. This section presents the detailed result of caprylic acid-cetyl alcohol.

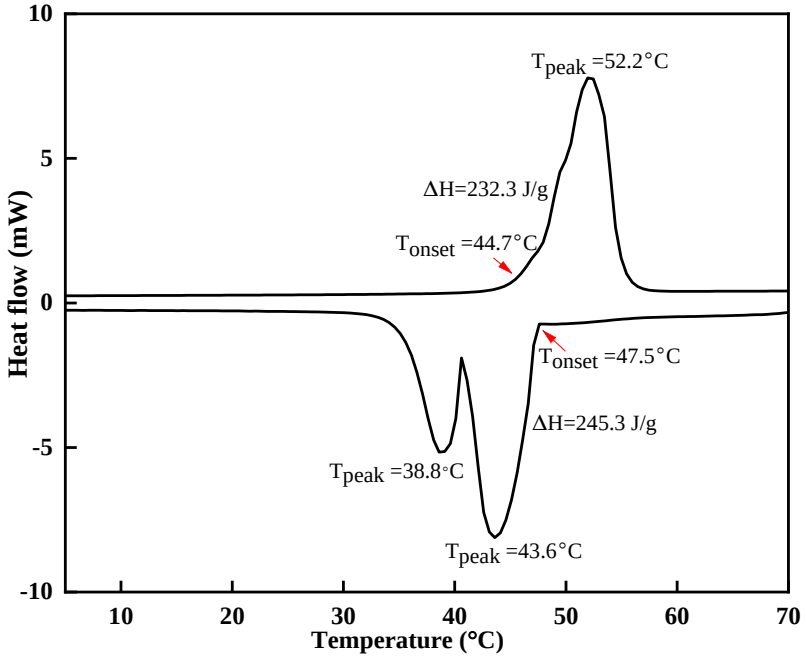
3.1.1. Thermal and structural analysis of the caprylic acid–cetyl alcohol binary mixture

Fig. 3.1 (a) and (b) illustrate the thermograph determined from the DSC analysis for the pristine caprylic acid and cetyl alcohol with its peak melting/freezing point temperatures with the latent heat of fusion in both phases. The line trace corresponding to the positive heat flow is termed the endotherm curve related to the melting phase of the material; conversely, the second curve represents the solidification of the material with an exotherm curve. The DSC

curve for pure caprylic acid depicts its onset/peak melting point temperature of 13.3 °C/18.4 °C with phase enthalpy of 142.6 $J.g^{-1}$, whereas, during solidification, it possesses a peak freezing point temperature of 4.6 °C/4.1 °C with phase enthalpy of 145.6 $J.g^{-1}$. The onset melting temperature of the pure cetyl alcohol determined was 44.7 °C and 47.5 °C with the latent heat of fusion of 232.3 and 245.3 $J.g^{-1}$, respectively. In addition, the peak melting and freezing temperatures determined were 52.2 °C and 43.6 °C, respectively. During cooling, cetyl alcohol has two exotherm peaks; the first peak at 43.6 °C shows the liquid-to-solid phase transition. The second peak at 38.8 °C illustrates the crystalline change from hexagonal to an orthorhombic structure [37]. The degree of supercooling for caprylic acid and cetyl alcohol was 8.7 °C and 2.8 °C, respectively.



(b) Caprylic acid



(a) Cetyl alcohol

Fig. 3.1. DSC curves for caprylic acid and cetyl alcohol.

The mass proportion for the eutectic point was theoretically evaluated with Schröder's van Laar equation, and it can be expressed by Eq. (2):

$$lnX_A = \frac{\Delta H_A}{R}\left(\frac{1}{T_A} - \frac{1}{T}\right) \quad (2)$$

Where X_A is the molar mass of the base material, R is the general gas constant (8.31 $J.mol^{-1}.K^{-1}$), ΔH_A is the latent heat of fusion ($J.g^{-1}$), T_A is the melting point of the base material (K), and T is the melting point (K) calculated for different proportion.

The onset melting point temperature for the caprylic acid/cetyl alcohol was calculated using Eq. (2), which temperature was 12.3 °C for an 85:15 molar mass ratio and less than the melting point of the individual material. Fig. 3.2 illustrates the heating curve of caprylic acid/cetyl alcohol with different mass concentrations from DSC analysis. The presented thermographs have two peaks for all the mass concentrations, except for the pure materials and eutectic point composition. In the binary mixture heating curves, the first peak, known as the solidus temperature, occurs at an almost constant temperature of around 10 °C, while the second peak (the liquidus temperature) moves towards the solidus temperature with different concentrations of the mixture. For the 85:15 molar ratio, only one peak was observed, having simultaneous melting for both the materials, which was marked as the eutectic point. Both the materials present in the eutectic material melt concurrently at this composition. Therefore, the binary

mixture will have a similar melting point temperature for both of the materials, which is a function of the eutectic mixture.

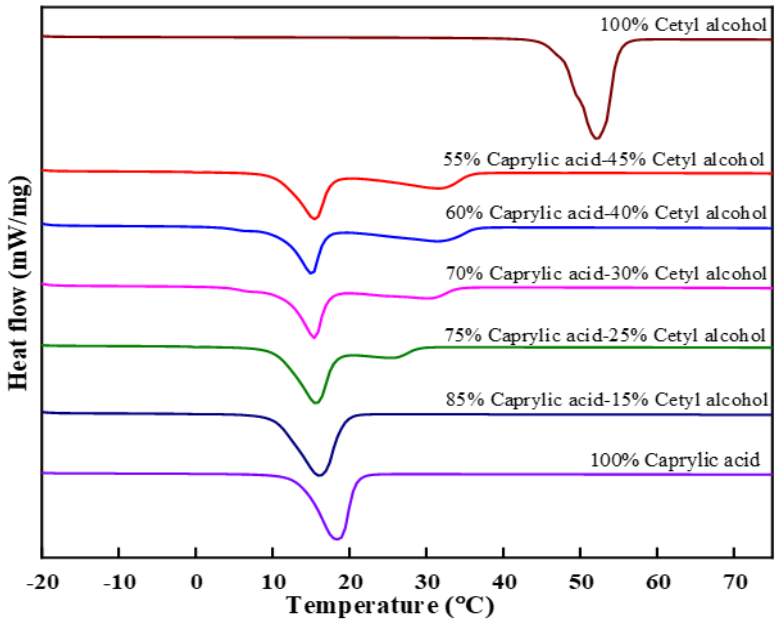


Fig. 3.2. Heating curve of caprylic acid/cetyl alcohol different mass concentration.

The thermophysical properties during the melting/freezing phase for the binary mixture determined from DSC are depicted in Fig. 3.3. The onset/peak melting point temperature during phase transition was 10 °C/16.1 °C with a phase transition enthalpy of 154.1 $J.g^{-1}$. The onset/peak freezing point temperature determined was 8.9 °C/6.2 °C with a phase change enthalpy of 153.3 $J.g^{-1}$. Supercooling degree is an undesirable attribute of PCM, where the nucleation is not triggered, even below the freezing point temperature. The factors responsible for the supercooling degree are the cooling rate, material purity, size, and experimental parameter. The degree of supercooling can be calculated from the difference between T_m(onset)

and T_f(onset) [38]. The degree of supercooling for the binary mixture (caprylic acid–cetyl alcohol) prepared was 6.9 °C, which was considerably less than the base materials of the binary mixture. The supercooling was reduced by the addition of cetyl alcohol to the caprylic acid, and this enabled efficient thermal energy storage and retrieval. The low degree of supercooling indicates better performance of the binary mixture in real-time cooling applications.

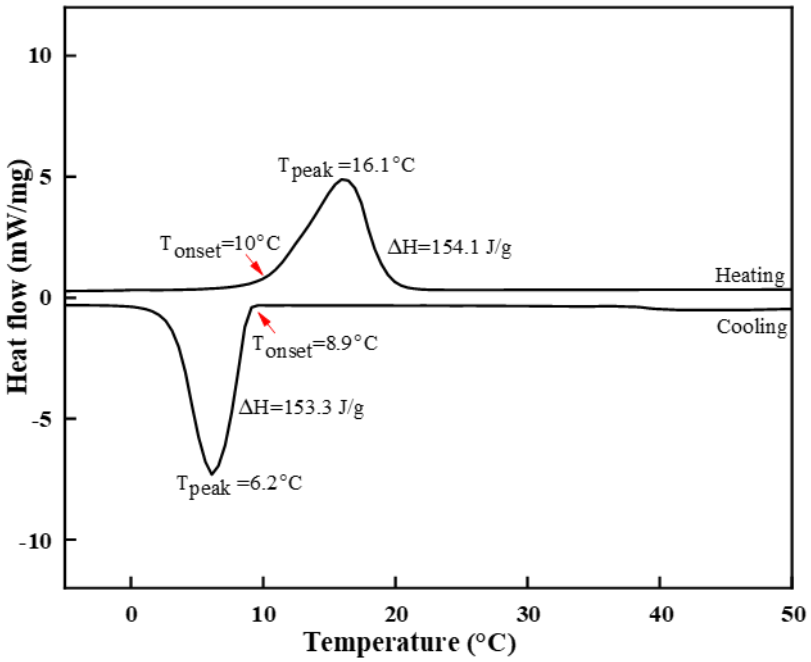


Fig. 3.3. Thermophysical properties of caprylic acid/cetyl alcohol.

The measured melting point temperature from the DSC was plotted for different mass concentrations of the caprylic acid is depicted in Fig. 3.4. The drop in melting point temperature can be seen with the addition of cetyl alcohol. The minimum melting point temperature from the phase diagram for both the materials of the binary mixtures can be regarded as the eutectic point. The eutectic point for caprylic acid–cetyl alcohol is shown at an 85:15 molar mass fraction with the onset melting point of 10 °C. Both the materials are in solid phase below the solidus line, and in the liquid phase above the liquidus line. The phase diagram can be drawn theoretically with Schröder's van Laar equation (Eq. (1)) by calculating the melting point temperature for different concentrations [39]. The caprylic acid–cetyl alcohol has an appropriate phase transition temperature for cooling applications.

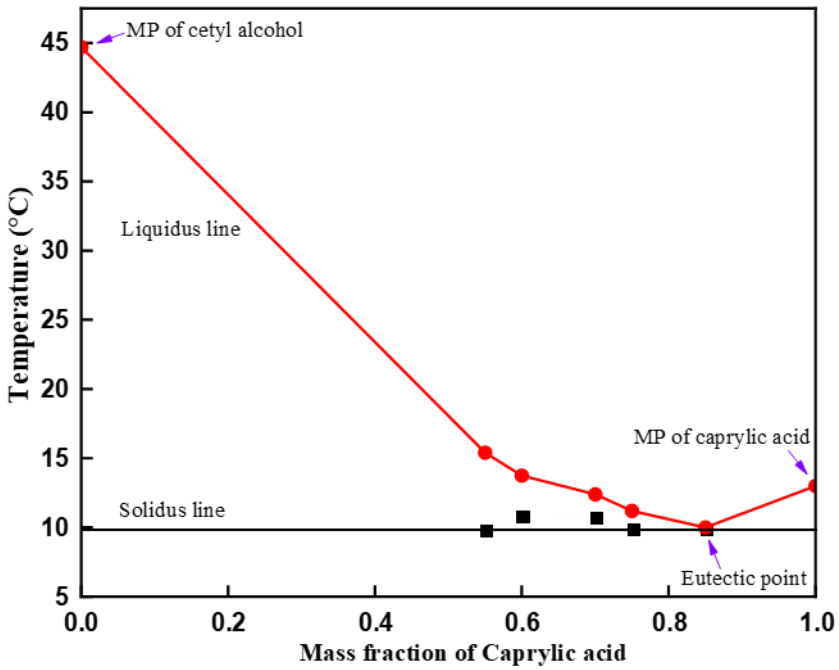


Fig. 3.4. Phase diagram of caprylic acid/cetyl alcohol.

Thermogravimetric analysis (TGA) was performed to examine the thermal stability of the binary mixture prepared as shown in Fig. 3.5. The rate of mass loss in percentage is plotted with respect to temperature variation. The decomposition temperature of the pure materials and binary mixture was determined, and if the temperature is increased due to thermal fluctuation, it shows no compromise of the thermal stability. To recommend a new binary mixture, it is vital to examine its thermal stability; it should have a high decomposition temperature. By the addition of cetyl alcohol to the caprylic acid, the decomposition temperature slightly improved. The decomposition temperature for the binary mixture is 161 °C, comparatively high enough compared to its melting point temperature, and thus safe to recommend for a cold thermal energy storage system.

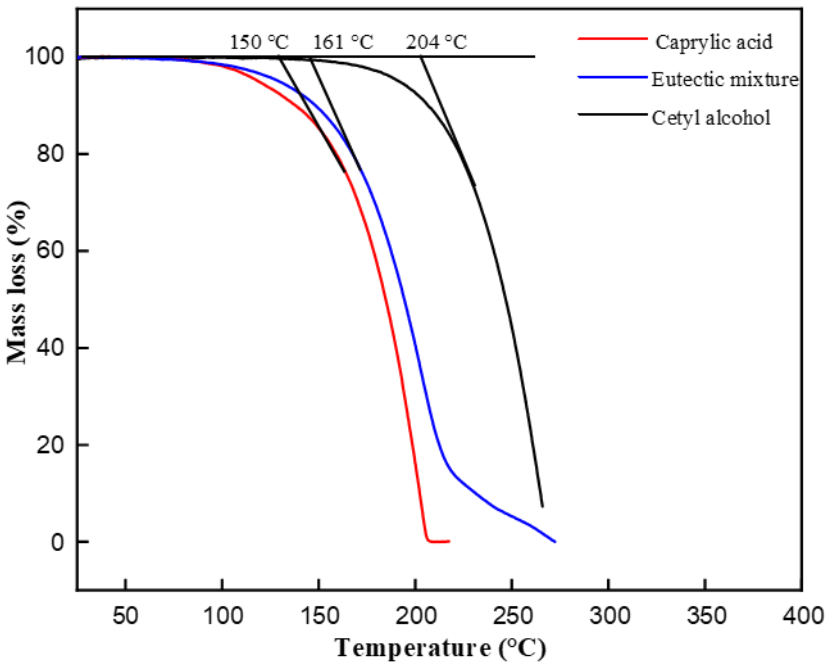


Fig. 3.5. TGA result of different pure materials and binary mixtures.

The Fourier-transform infrared spectroscopy (FTIR) spectral data of caprylic acid, cetyl alcohol, caprylic acid/cetyl alcohol binary mixture, and binary mixture after 200 thermal cycles are shown in Fig. 3.6. The spectral data attained was similar to the reported data in the literature [25]. The spectral peaks at 2,931 and 2,855 cm^{-1} of the caprylic acid and binary mixture belong to the O–H and C–H stretching, respectively. The 1,712 and 1,228 cm^{-1} peaks represent the carbonyl functional groups. The absorption peaks at 1,417, 929, and 725 cm^{-1} represent the bending trend of the saturated fatty acid. For cetyl alcohol, the 3,324 cm^{-1} peaks portray intermolecular H bonds. The peaks at 1,468, 1,060, and 724 cm^{-1} represent the CH2 stretch and secondary cycle alcohols. The FT–IR spectrum of the binary mixture consists of combined peaks of both the caprylic acid and cetyl alcohol. This shows that the base materials were not reacted together, and the same functional groups exist in the mixture. The binary mixture after 200 cycles did not show any variation in the structure, making it a stable binary mixture that can be utilized for a long duration in the storage system.

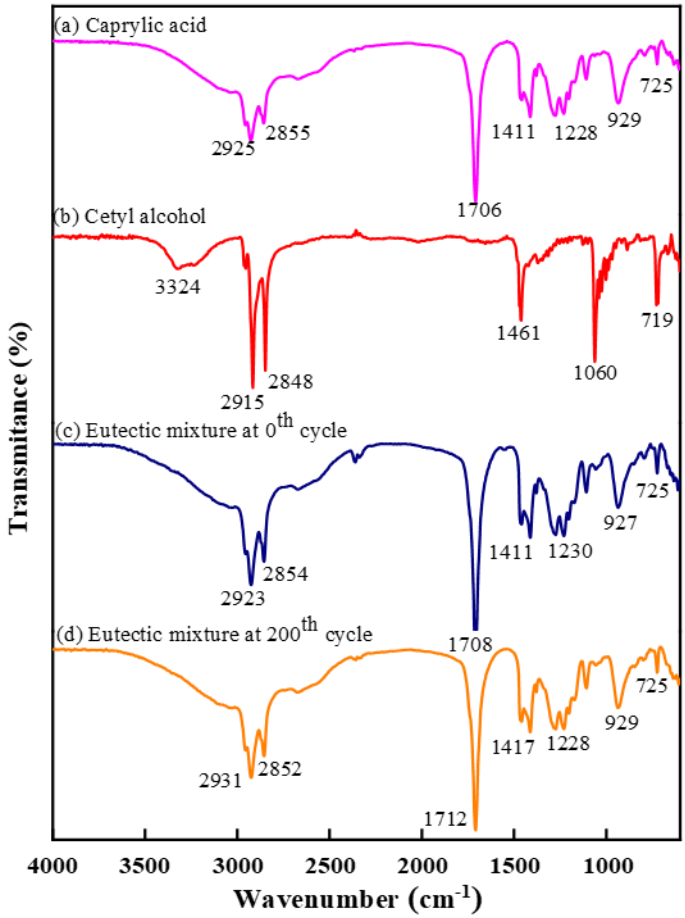


Fig. 3.6. FT-IR results for the pure and binary mixture.

Thermal conductivity is an important factor of PCMs because it has a direct influence on their performance. The rate of the heat stored and retrieved depends on the value of thermal conductivity. Fig. 3.7 illustrates the thermal conductivity of the binary mixture. The thermal conductivity of the caprylic acid–cetyl alcohol binary mixture was in the range of 0.154 – 0.288. $W.m.K^{-1}$. The thermal conductivity was measured in the temperature range -5 °C–30 °C for the solid and liquid phases. The thermal conductivity in the solid phase (0.288 $W.m.K^{-1}$) more pronounced due to the tightly-packed molecules than in the liquid phase (0.154 $W.m.K^{-1}$). The obtained thermal conductivity from the measurement was in good range compared to other organic PCM [40]. The results showed the binary mixture prepared is well suited for application to the cold thermal energy system.

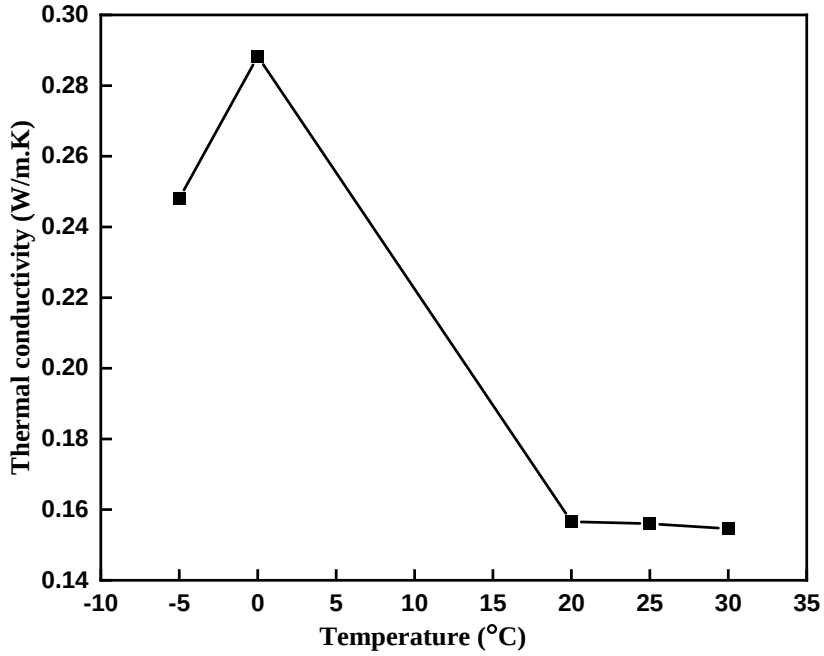


Fig. 3.7. Thermal conductivity of the binary mixture.

3.1.2. Accelerated thermal cycling for caprylic acid-cetyl alcohol

Fig. 3.8. shows the thermal cycling that was performed to investigate the thermophysical properties of the binary PCM after 100 and 200 melting/freezing cycles. The melting point temperature and latent heat of fusion for the 0th cycle were marked to examine the deviation after the 100 and 200 cycles. The caprylic acid/cetyl alcohol binary mixture during heating after 200 cycles showed a decrease in onset melting point temperature by 2.16 °C and 5.9 $J.g^{-1}$ of phase change enthalpy. During freezing, the onset freezing temperature was decreased by 2.4 °C and 3.8 $J.g^{-1}$ of phase change enthalpy. The deviation of the thermophysical properties can be quantified by the relative percentage difference (RPD), and it is expressed by Eq. (2) [41]:

$$RPD = \frac{X_{n,i} - X_{o,i}}{X_{o,i}} \times 100 \quad (2)$$

Where $X_{n,i}$ represents the thermal properties for the nth cycle and $X_{o,i}$ for the referenced cycle. The subscript i is the property of eutectic PCM melting/freezing point temperature and latent heat of fusion. The variation in the thermophysical properties for 200 thermal cycles is measured by using Eq. 2 and presented in Table 3.1. After the 200 cycles, not much variation was observed in the thermophysical properties compared to the uncycled properties, which also makes it a potential thermal energy storage material. A maximum variation of 20% was shown in the freezing temperature, and the changes in latent heat values were minimal.

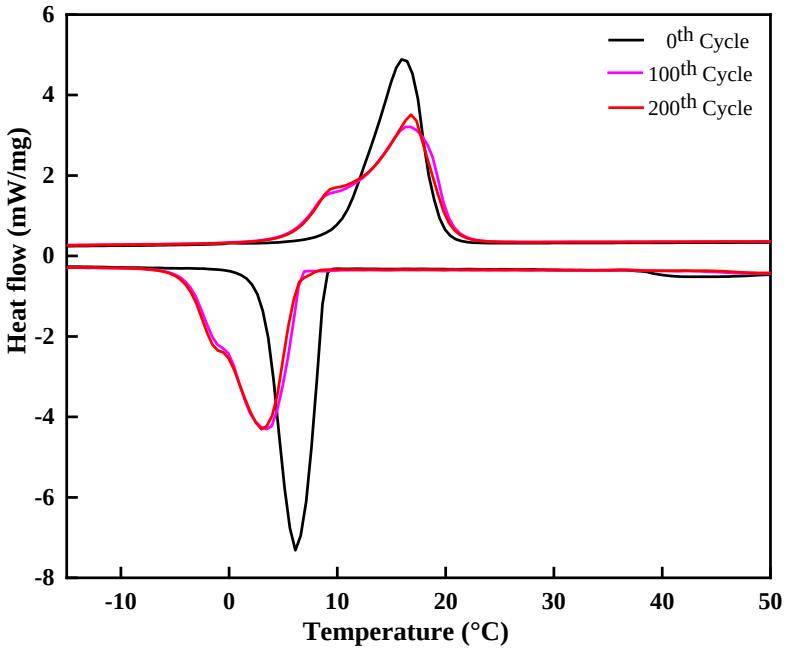


Fig. 3.8. Accelerated thermal cycling of the prepared binary mixture.

Table 3.1 Thermal cycling RPD for the thermophysical properties.

No. of cycles	T_m °C	T_f °C	ΔH_m J.g^{-1}	ΔH_f J.g^{-1}	RPD of T_m %	RPD of T_f %	RPD of ΔH_m %	RPD of ΔH_m %
0	10	8.9	154.1	153.3				
100	8.3	7.2	149.1	149	-17	-19.1	-3.2	-2.8
200	8.2	7.1	148.2	149.5	-18	-20.2	-3.8	-2.4

3.1.3 Corrosion analysis for caprylic acid-cetyl alcohol

It is important to investigate the compatibility of the binary mixture with the different metals used to manufacture the cold thermal storage system. The corrosion test results were determined for 1, 4, and 12 weeks. Fig. 3.9. shows the metal strips stainless steel (SS 316), aluminum (Al), copper (Cu) for the corrosion test immersed in the caprylic acid-cetyl alcohol (CA-CA) for 12 weeks and the corrosion rate is shown in Fig. 3.10. The metal strips used for the corrosion test followed the same trend by reducing the corrosion rate with respect to time. The corrosion rate for the metal samples immersed in caprylic acid-cetyl alcohol is presented in Table 3.2. The corrosion rate at the first week for SS 316, Al, and Cu was 3.12, 8.34, and 15.64 $mg.cm^{-2}.year^{-1}$, respectively, which was initially in effect to the dirt particles on the metal strips and reduced by forming an oxidizing layer in-between the metal strip and binary mixture. For aluminum and stainless steel, no visible surface variation was observed, while yellowish deposition was seen in the case of copper. The calculated corrosion rate after 12 weeks was 0, 1.73, and 11.29 $mg.cm^{-2}.year^{-1}$ for stainless steel, aluminum, and copper, respectively. The results indicate copper can be used for short-term applications, and the corrosion rate of aluminum and stainless steel is less than 9 $mg.cm^{-2}.year^{-1}$ and can be utilized for a longer duration [42]. It is confirmed that aluminum and stainless steel are recommended for long-term use in cold energy storage applications using the caprylic acid–cetyl alcohol binary mixture.

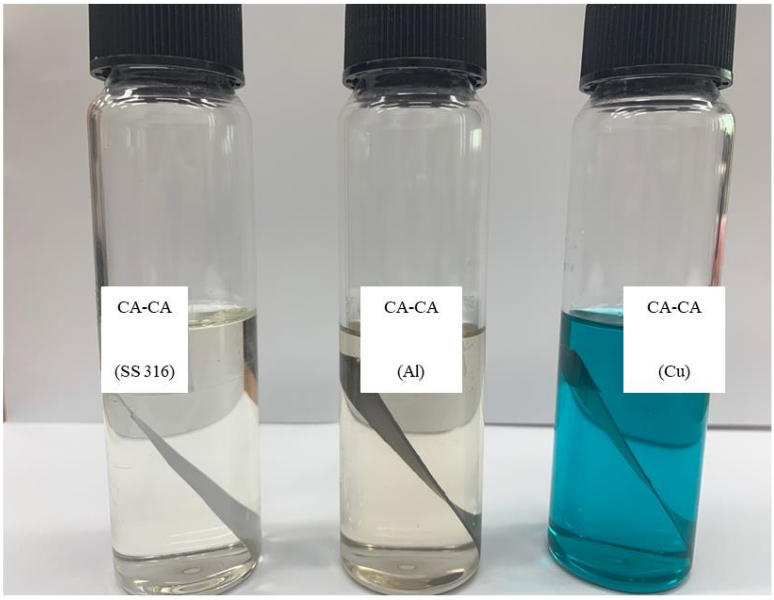


Fig. 3.9. Stainless steel (SS 3116), aluminum (Al), and copper (Cu) after 12 weeks of corrosion test.

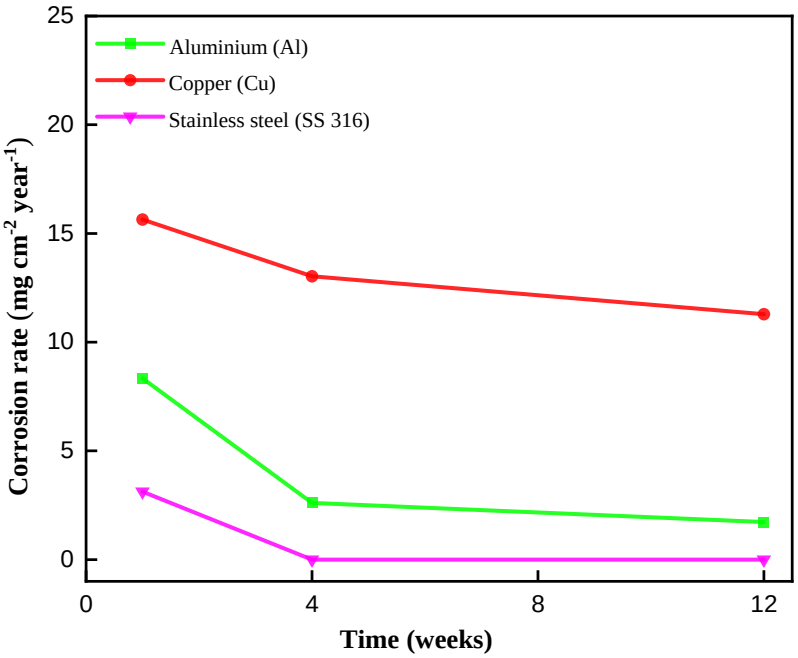


Fig. 3.10. The corrosion rate for different metals after 1 week, 4 weeks, and 12 weeks.

Table 3.2 The corrosion rate of metal strips immersed in caprylic acid-cetyl alcohol.

Material	Corrosion rate $mg.cm^{-2}.year^{-1}$		
	After 1 week	After 4 week	After 12 week
SS 316	3.12	0	0
AL	8.34	2.60	1.73
Cu	15.64	13.03	11.29

3.2. Characterization of caprylic acid-stearyl alcohol

This section presents the detailed thermophysical study of the prepared caprylic acid-stearyl alcohol. The thermal properties of the caprylic acid-stearyl alcohol binary mixture were determined at the eutectic point. Also, the thermal and chemical stability of caprylic acid-stearyl alcohol was analyzed. The thermal properties reliability is presented for 200 thermal cycles. In addition, a corrosion test was performed to investigate the compatibility of the binary mixture.

3.2.1. Thermal properties, thermal and chemical stability of the caprylic acid-stearyl alcohol

The thermograph from the DSC analysis represents heat stored/retrieved with the onset/peak melting points temperature and enthalpy change on the fusion of the pure materials, as shown in Fig. 3.11. The two thermographs depict the heating and cooling curves of the materials with positive and negative heat flow, showing the phase transition and energy storage/retrieval. The measured onset/peak melting point temperature and latent heat of fusion for stearyl alcohol were 54.4 °C/61.4 °C and 240 $J.g^{-1}$ respectively. The cooling curve represents the onset/peak freezing point temperature with enthalpy change on fusion of 56.66 °C/52.4 °C with 257.9 $J.g^{-1}$ [24]. The thermograph of caprylic acid was already discussed in section 3.1. The endotherm of the even number of straight-chain fatty alcohols transforms into 3 different polymorphisms

having different thermodynamic stability over the temperature and pressure range.

The two peaks in the exothermic curve and a small bump in the endothermic curve of stearyl alcohol can be resolved by peak separation. In the heating curve, the transition occurs between the ordered phase γ and rotator phase α, the melting point of the γ and α is very close, which results in a small shoulder on the heating curve. The two peaks represent the liquid-solid phase and solid-solid transformation $\alpha \rightarrow \gamma$ prior to stable crystal shape in the cooling curve. The degree of supercooling is more pronounced in a solid-solid phase transition, whereas from liquid to α is quite low. The supercooling degree is a detrimental factor linked to PCM, which has a negative effect on overall heat storage/retrieval performance. The supercooling degree can be calculated by using difference in the melting and freezing point temperature. The degree of supercooling is attributed to cooling rate, material purity, and operating conditions. In this study, the degree of supercooling for stearyl alcohol was 6.28 °C.

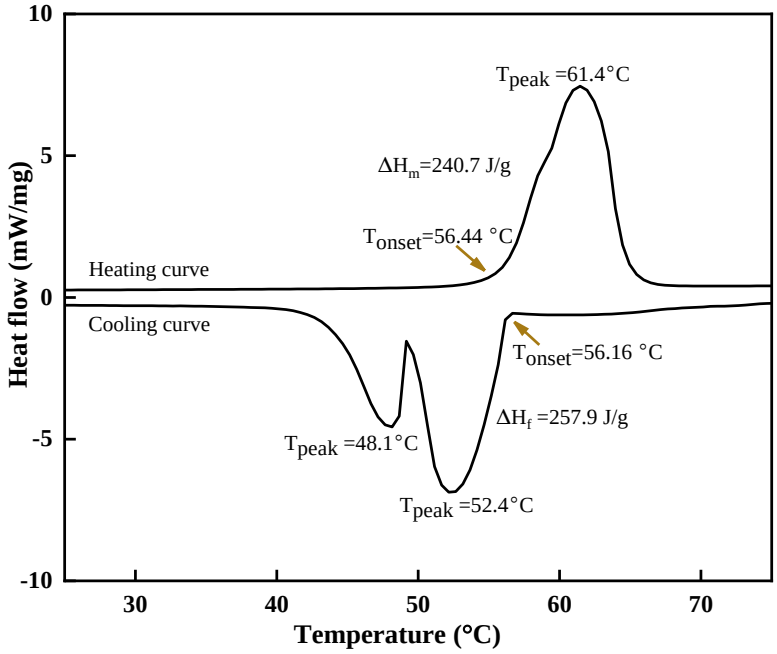


Fig. 3.11. DSC result of the stearyl alcohol.

The DSC analysis was performed for binary mixture at the theoretical eutectic point and nearby other mass proportions. The heating curve for the mass proportion 60%-100% of caprylic acid-stearyl alcohol is graphically presented in Fig. 3.12. It is observed from the endotherm presented for all the binary mixture proportion is having first onset melting point temperature almost fixed as known the solidus temperature. In contrast, the second melting point temperature (liquidus temperature) varies with reducing the mass proportion of stearyl alcohol. The binary mixture having a 90% mass proportion of caprylic acid and 10% stearyl alcohol shows one melting point temperature of 11.4 °C by the DSC analysis, which is similar to the theoretical estimated eutectic point for the prepared binary mixture.

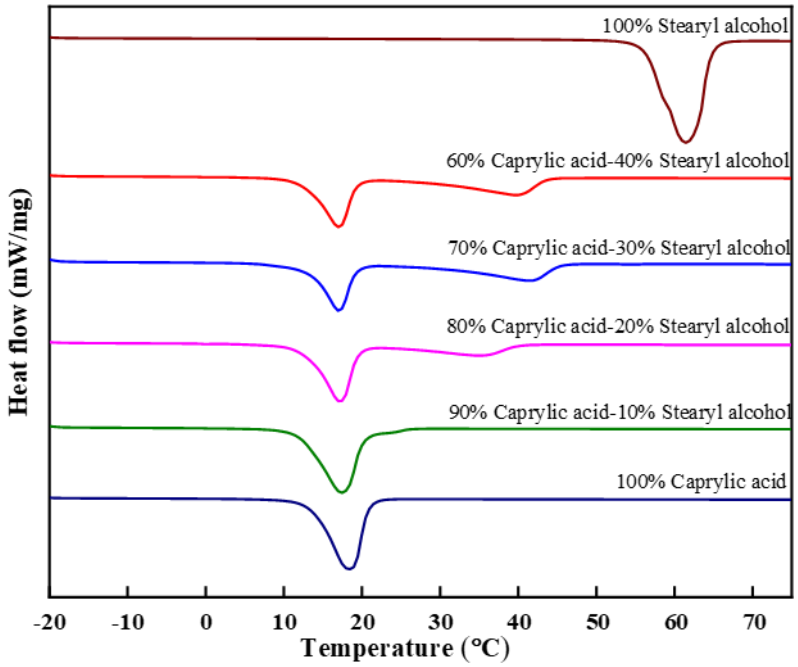


Fig. 3.12. Heating curves of the different mass proportions of the binary mixture.

The phase diagram of the eutectic binary mixture was plotted based on the onset melting point temperature measured with the DSC for different mass proportions. The onset melting point temperature of the binary mixture plotted against the mole fraction of the caprylic acid is shown in Fig. 3.13. The solidus temperature remained approximately invariant while the liquidus line varied with the incremental mole fractions of the caprylic acid. The second peak diminished slowly with the increase of caprylic acid; a minimum onset melting point in the curve was marked at 0.9 and 0.1 mole fraction of caprylic acid and stearyl alcohol, respectively. Thus, the minimum onset melting point of 11.4 °C was confirmed as the eutectic point for the binary mixture.

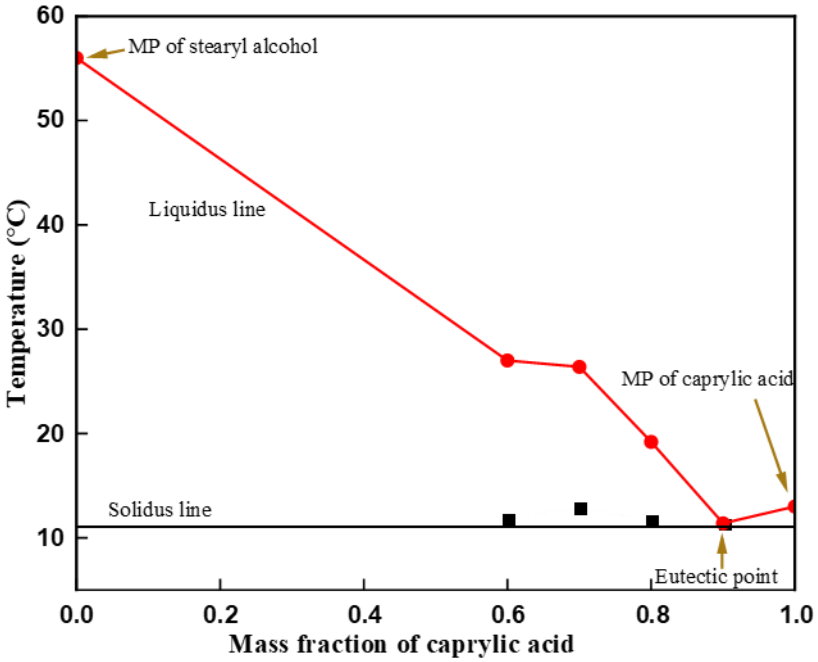


Fig. 3.13. Phase diagram of the caprylic acid-stearyl alcohol eutectic binary mixture.

The DSC heating and cooling curve for the eutectic caprylic acid-stearyl alcohol is shown in Fig. 3.14. The endotherm for the binary mixture prepared shows the onset/peak melting point temperature of 11.4/17.4 °C with the latent heat of fusion ΔH_m 154.4 $J.g^{-1}$. The exotherm presents an onset/peak freezing point temperature of 11.8/8.7 °C with ΔH_f 150.5 $J.g^{-1}$. The degree of supercooling is an undesirable factor linked to the PCM and was higher for the pure materials utilized to prepare the binary mixture. The befitting thermal properties and lower degree of supercooling make the novel eutectic mixture suitable for cooling applications. The onset melting point temperature of the binary mixture prepared makes it a potential candidate for CTES because few PCM exists in this range of temperature.

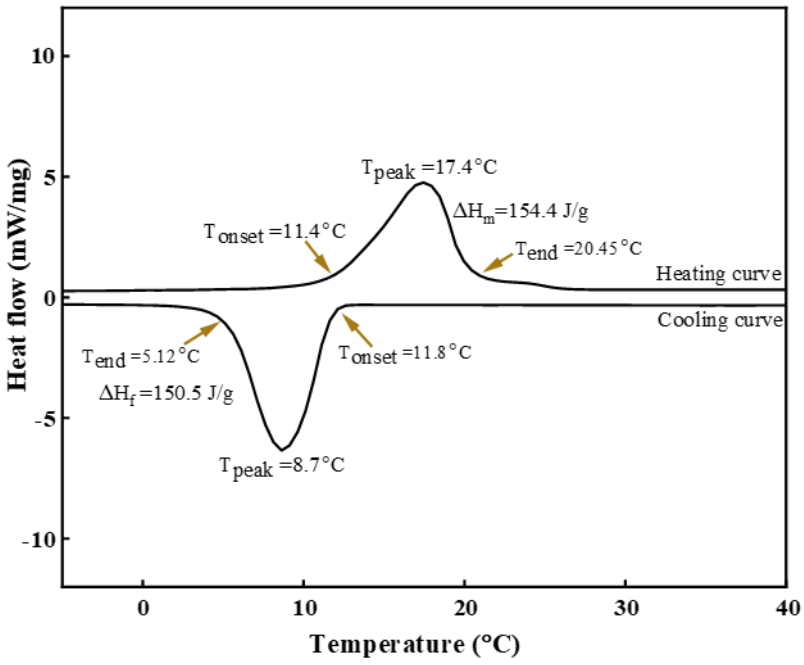


Fig. 3.14. DSC of the caprylic acid-stearyl alcohol binary mixture prepared.

The thermal conductivity is a significant property of PCM for enhanced performance of the heat transfer during phase transition. The thermal conductivity of the prepared binary mixture was measured in the solid and liquid phases, as shown in Fig. 3.15. The organic liquids have a lower thermal conductivity with the range of 0.1 – 0.2 $W{\cdot}m^{-1}{\cdot}K^{-1}$ [40]. The measured thermal conductivity in the solid phase was 0.242 $W{\cdot}m^{-1}{\cdot}K^{-1}$ and 0.267 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at -5 °C and 0 °C, whereas in the liquid phase it was 0.165 $W{\cdot}m^{-1}{\cdot}K^{-1}$ (20 °C), 0.160 $W{\cdot}m^{-1}{\cdot}K^{-1}$ (25 °C), and 0.157 $W{\cdot}m^{-1}{\cdot}K^{-1}$ (30 °C), respectively. The thermal conductivity in the solid phase was more pronounced due to the tightly packed molecules [24]. Therefore, the thermal conductivity of the eutectic mixture is higher than the organic PCM reported in the literature, which will enhance its performance for the cooling application.

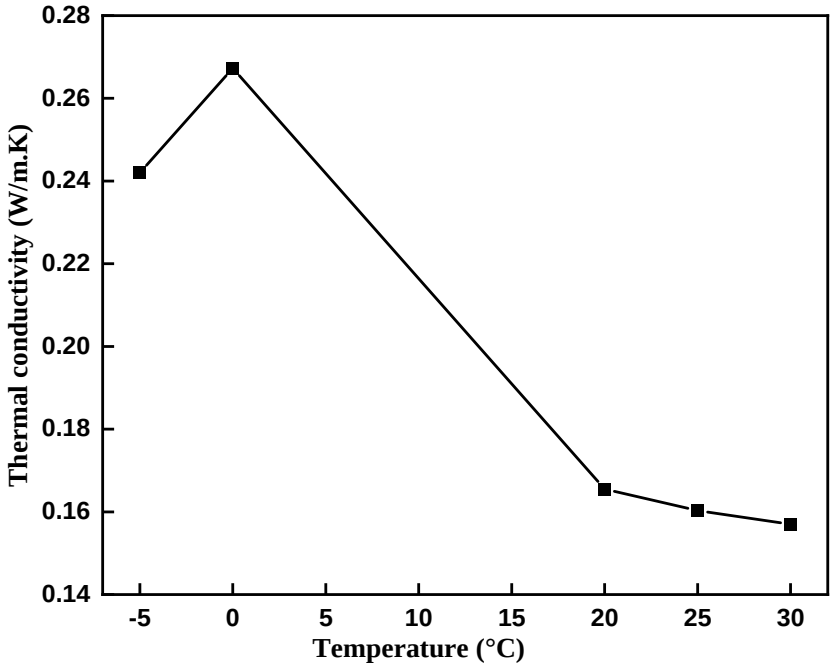


Fig. 3.15. Thermal conductivity of the binary mixture at solid and liquid phase.

The TGA analysis depicts the mass loss (%) with incremental temperature, as shown in Fig. 3.16. The thermal stability of the eutectic PCM was analyzed with TGA study. The decomposition temperature of the eutectic PCM was in between the caprylic acid and stearyl alcohol utilized, starting at 159.8 °C. However, the decomposition temperature was higher than its melting point temperature, which did not affect its performance during temperature increase due to thermal fluctuation. Therefore, the caprylic acid-stearyl alcohol holds good thermal stability and is safe to utilize for real-time applications.

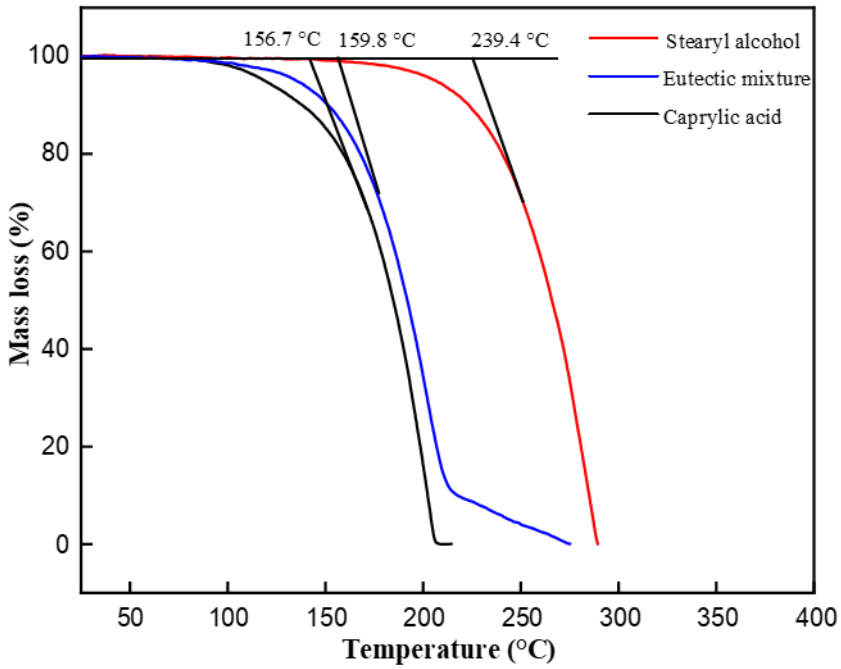


Fig. 3.16. TGA result of pure materials and eutectic PCM.

FT-IR spectroscopy gives insight into the chemical structure of the eutectic PCM to indicate its chemical stability. The FT-IR spectral data for caprylic acid, stearyl alcohol, Eutectic PCM at 0 cycle and 200 cycles are shown in Fig. 3.17. The spectral data for the pristine materials were similar to the results reported in the previous studies [43,44]. The spectral peaks of caprylic acid at 2935 cm^{-1} and 2863 cm^{-1} indicate the O–H and C–H vibration stretching. The spectral peaks at 1712 cm^{-1} and 1417 cm^{-1} represent the C=O and –CH2 stretching, respectively. The 1239 cm^{-1} and 727 cm^{-1} show the C–O stretching. The absorption peak 3340 cm^{-1} for stearyl alcohol signifies the –OH stretching vibration. The –CH2 is represented by 1463 cm^{-1}, and C–O appears by 1064 cm^{-1} and 727 cm^{-1}. The FT-IR results for the pure materials and eutectic PCM present that the materials are neither chemically mingled nor the chemical structure is varied. The chemical structure of the eutectic PCM was analyzed for 200 thermal cycles, which did not show any variation, and deduced the eutectic PCM is chemically stable. The chemical stability of the material is a vital factor in deciding its utilization for real systems; the eutectic PCM prepared with good chemical stability can be a potential candidate for cooling applications.

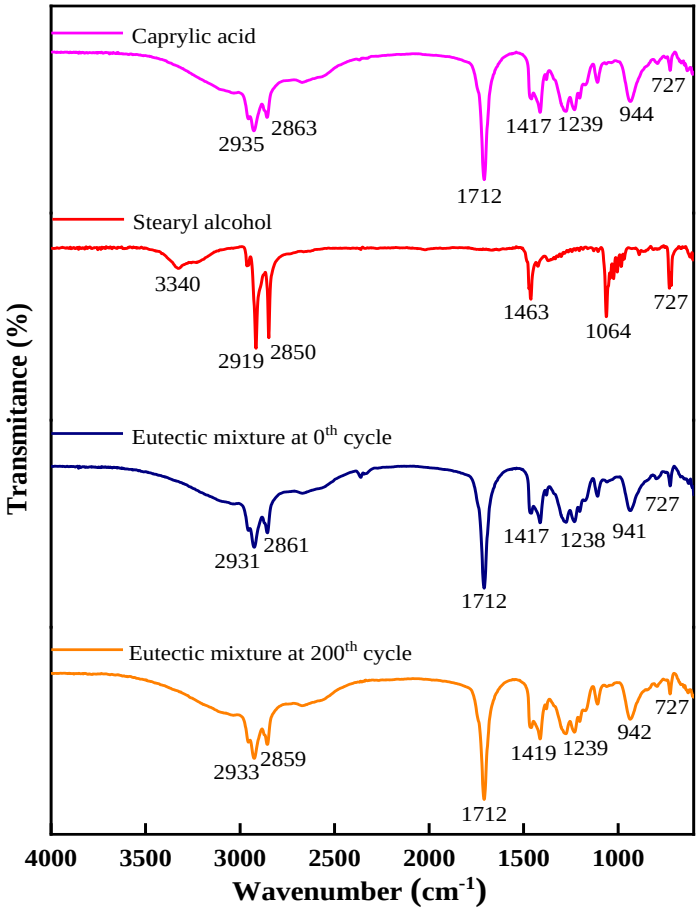


Fig. 3.17. FT-IR of the pure materials and eutectic mixture prepared.

3.2.2. Accelerated thermal cycling of caprylic acid-stearyl alcohol

The thermal properties of the prepared eutectic PCM are essential to be investigated for various melting/freezing thermal cycles to conclude its performance for long-term applications. In this study, 200 melting/freezing thermal cycles were employed with a regular interval of 100 cycles. DSC thermographs were attained for 0, 100, and 200 thermal cycles to predict the variation in melting/freezing point temperature and latent heat of fusion, as shown in Fig. 3.18. The results showed that the variation in the onset melting/freezing point temperature and latent heat of fusion after 100 cycles was varied by 2.2/1.9 °C and 4.7/0.2 $J.g^{-1}$, respectively. The variation in the thermophysical properties for 200 thermal cycles is measured using Eq. 2 and is presented in Table 3.3. The positive sign shows an increase, while a negative sign represents a decrease in the thermal properties compared to the reference values. The maximal variation observed for phase change temperature and latent heat of fusion was -16.1% and -18.9%, respectively. Thus, the change in the thermal properties of the prepared eutectic PCM was in good range and made the material a good fit for its utilization in cold thermal energy storage applications.

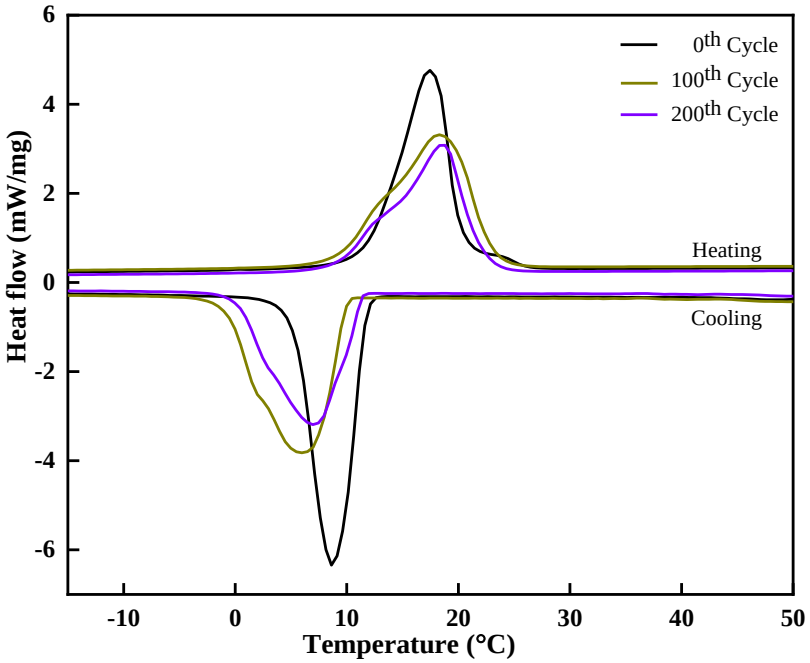


Fig. 3.18. DSC thermographs of the eutectic PCM for 0, 100, and 200 thermal cycles.

Table 3.3 Relative percentage difference of thermophysical properties after thermal cycling.

No. of cycles	T_m	T_f	ΔH_m	ΔH_f	RPD of T_m	RPD of T_f	RPD of ΔH_m	RPD of ΔH_m
	℃	℃	J/g	J/g	%	%	%	%
0	11.4	11.8	154.4	150.5				
100	9.8	9.9	149.7	150.3	-14.03	-16.1	-3.04	-0.13
200	10.8	11.4	125.2	124.3	-5.2	-3.3	-18.9	-17.4

3.2.3. Corrosion test of caprylic acid-stearyl alcohol

The different kinds of metals, namely aluminum, copper, and carbon steel, which are utilized for the manufacturing of thermal energy storage components, were analyzed for compatibility of the prepared eutectic PCM. The metal strips in the eutectic PCM are shown in Fig. 3.19. The color of the solution was observed for the copper and carbon steel changed to bluish-green and dark brown color, respectively. The bluish-green color of copper immersion indicates corrosion which is due to the formation of hydrated metal chloride salts, and dark brown for carbon steel was by iron oxide formed. The aluminum immersed in the eutectic PCM did not show any color change after 12 weeks of corrosion. The metals strip after 12 weeks of corrosion test is shown in Fig. 3.20. The copper strip shows slight black deposition on its surface, a mild brown layer was seen on the carbon steel surface, and minute white deposition was formed for aluminum which indicates the corrosion.

The corrosion rate from the mass loss was measured for 1, 4, and 12 weeks of a time interval presented in Table 3.4. From Fig. 3.21, it is deduced that the corrosion rate for stainless steel, copper, and aluminum was decreased with an increase in the exposure duration of the metal strips in the eutectic PCM. The decremental corrosion rate was due to the formation of an oxidized layer in-between the metal strip and eutectic PCM, which limits the direct contact of the metal strip. A general guide used in the industries for the corrosion rate and weight loss

is presented in table 3.5. Following the guidelines, copper can be utilized based on caution for specific applications but is not recommended for the manufacturing of cold thermal energy storage components. Aluminum and stainless steel are safe due to their low corrosion rate, which can be used for long-term applications and utilized to manufacture cold thermal energy storage.

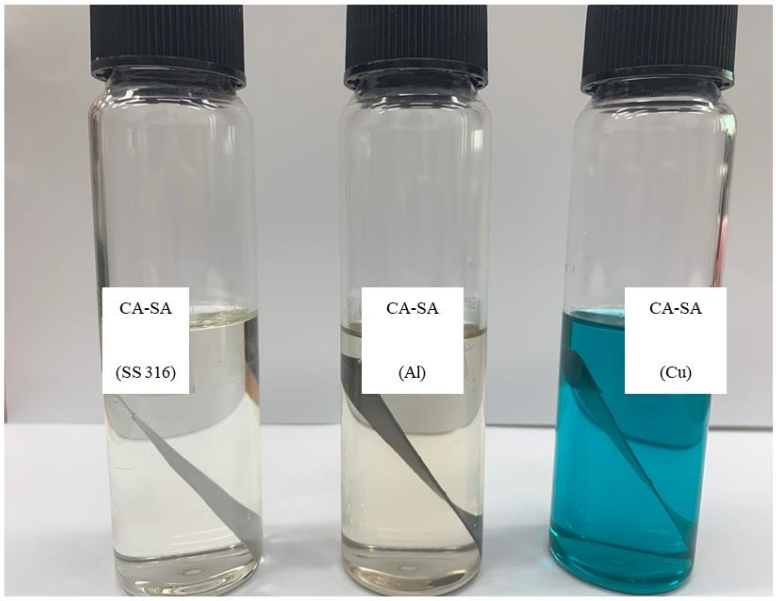


Fig. 3.19. Metal samples in eutectic PCM after 12 weeks.

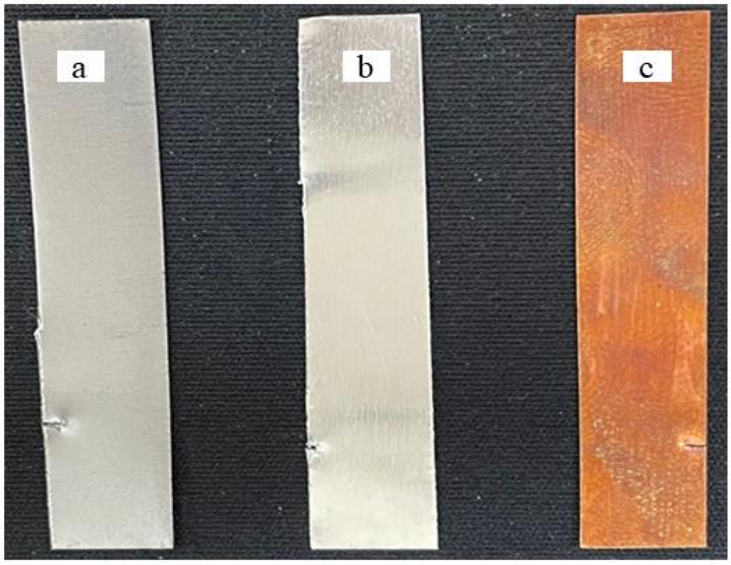


Fig. 3.20. .Metal strips (a) stainless, (b) aluminum, and (c) copper after 12 weeks of corrosion test.

Table 3.4 Corrosion rate for metal strips for 1, 4, and 12 weeks.

Material	Corrosion rate (mg/cm^2.year)		
	After 1 week	After 4 week	After 12 week
Aluminum	5.214	2.607	1.738
Copper	15.642	13.035	10.863
Stainless steel	2.085	0	0

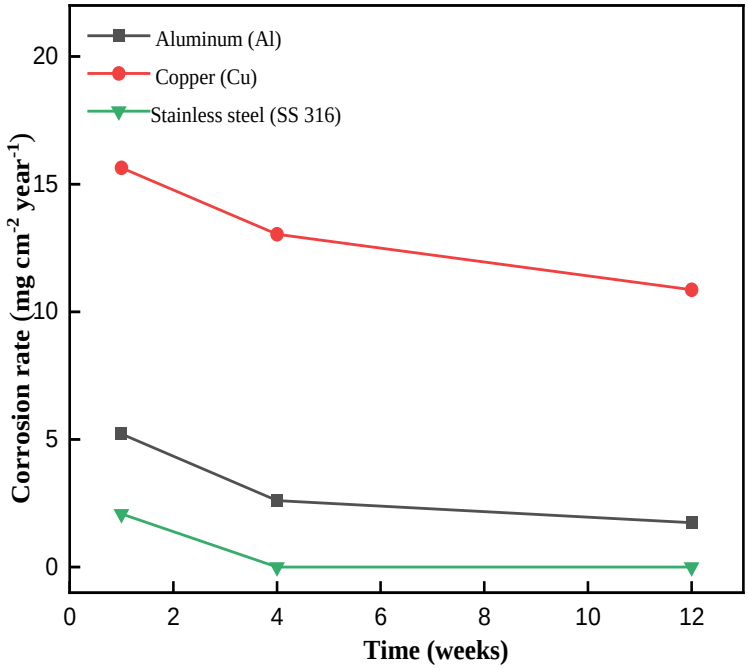


Fig. 3.21. Corrosion rate of aluminum, copper, and stainless steel in a eutectic mixture.

Table 3.5 Guide for corrosion and weight loss in industries [25]

mg/cm year	mm/year	Recommendation
>1000	2	Completely destroyed within days
100-999	0.1-1.99	Not recommended for service greater than a month
50-99	0.1-0.19	Not recommended for service greater than one year
10-49	0.02-0.09	Caution recommended, based on the specific application
0.3-9.9	-	Recommended for long term service
<0.2	-	Recommended for long term service; no corrosion, other than as a result of surface cleaning was evidenced

4. Conclusion

In this study, organic binary mixture as phase change materials is presented for cold thermal energy storage applications. The thermophysical study of the binary mixtures were investigated by determining the thermal properties, analyzing the thermal and chemical stability, performing accelerated thermal cycling to observe the thermal properties reliability. In addition, a corrosion test showed the compatibility of the prepared binary mixture with various metals utilized for manufacturing CTES vessels. Firstly, a binary mixture of caprylic acid-cetyl alcohol is presented with a eutectic point at an 85:15 molar mass ratio. The onset phase transition temperature during melting and freezing was 10 °C and 8.9 °C, whereas the latent heat of fusion was 154.1 and 153.3 $J.g^{-1}$, respectively. In addition, the thermal conductivity of the binary mixture was measured in the solid phase (0.288 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 0 °C) and liquid phase (0.160 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 20 °C) which is in the convincing range for organic PCMs. Thermogravimetric analysis was performed to investigate the thermal stability for the prepared binary mixture. The results showed a decomposition temperature of 161 °C for caprylic acid – cetyl alcohol which was higher compare to its melting point temperature which will not affect its performance due to thermal fluctuation in real-time applications.

Next the caprylic acid and stearyl alcohol presented in the second section with the eutectic composition of 90:10 was investigated. As a result, it has the onset melting and freezing

temperature was 11.4 °C and 11.8 °C with the latent heat of fusion 154.4 $J.g^{-1}$ and 150.5 $J.g^{-1}$, respectively. Thermogravimetric analysis shows the decomposition temperature was 159.8 °C which will not affect its performance by thermal fluctuation. The accelerated thermal cycling and FT-IR show convincing thermal and chemical stability of the eutectic PCM. No significant change was evidenced in the thermal properties and chemical structure of the prepared eutectic mixtures after 200 thermal cycles. The measured thermal conductivity in the solid and liquid phase was in a good range, which will positively impact energy storage/retrieval. A corrosion test was carried out for three different metals, among which aluminum and stainless steel showed less corrosion and was recommended for long-term use with prepared binary mixture. The thermophysical properties were studied and presented in this work and it will facilitate the use of the binary mixture while developing an efficient thermal energy storage system using a caprylic acid–cetyl alcohol and caprylic acid-stearyl alcohol binary mixture as PCM.

REFERENCE

[1] A. Narayanan, K. Mets, M. Strobbe, and C. Develder, "Feasibility of 100% renewable energy-based electricity production for cities with storage and flexibility," *Renew. Energy*, vol. 134, 2018, doi: 10.1016/j.renene.2018.11.049.

[2] Energy Information Administration, "Future Global Energy Demand: Up, Up, and Away!," 2016. https://www.globalenergyinstitute.org/future-global-energy-demand-and-away.

[3] A. De Matteis, "Decomposing the anthropogenic causes of climate change," *Environ. Dev. Sustain.*, 2017, doi: 10.1007/s10668-017-0028-4.

[4] D. Larcher and J. M. Tarascon, "Towards greener and more sustainable batteries for electrical energy storage," *Nat. Chem.*, vol. 7, no. 1, pp. 19–29, 2015, doi: 10.1038/nchem.2085.

[5] I. Sarbu and C. Sebarchievici, "A Comprehensive Review of Thermal Energy Storage," *Sustainability*, vol. 10, no. 1, p. 191, 2018, [Online]. Available: https://www.mdpi.com/2071-1050/10/1/191.

[6] L. F. Cabeza, I. Martorell, L. Miró, A. I. Fernández, and C. Barreneche, "1 - Introduction to thermal energy storage (TES) systems," in *Advances in Thermal Energy Storage Systems*, L. F. Cabeza, Ed. Woodhead Publishing, 2015, pp. 1–28.

[7] A. de Gracia and L. F. Cabeza, "Phase change materials and thermal energy storage for buildings," *Energy Build.*, vol. 103, pp. 414–419, 2015, doi: https://doi.org/10.1016/j.enbuild.2015.06.007.

[8] M. Khan, S. Rahman, and F. Al-Sulaiman, "A review for phase change materials (PCMs) in solar absorption refrigeration systems," *Renew. Sustain. Energy Rev.*, vol. 76, pp. 105–137, 2017, doi: 10.1016/j.rser.2017.03.070.

[9] M. Mofijur *et al.*, "Phase Change Materials (PCM) for Solar Energy Usages and Storage: An Overview," *Energies* , vol. 12, no. 16. 2019, doi: 10.3390/en12163167.

[10] C. Veerakumar and A. Sreekumar, "Phase change material based cold thermal energy storage: Materials, techniques and applications – A review," *Int. J. Refrig.*, vol. 67, pp. 271–289, 2016, doi: https://doi.org/10.1016/j.ijrefrig.2015.12.005.

[11] A. Joseph, M. Kabbara, D. Groulx, P. Allred, and M. A. White, "Characterization and real-time testing of phase-change materials for solar thermal energy storage," *Int. J. Energy Res.*, vol. 40, no. 1, pp. 61–70, Jan. 2016, doi: https://doi.org/10.1002/er.3336.

[12] B. Y. Yun, S. Yang, H. M. Cho, S. J. Chang, and S. Kim, "Design and analysis of phase change material based floor heating system for thermal energy storage," *Environ. Res.*, vol. 173, pp. 480–488, 2019, doi: https://doi.org/10.1016/j.envres.2019.03.049.

[13] P. Dhamodharan and A. K. Bakthavatsalam, "Experimental investigation on thermophysical properties of coconut oil and lauryl alcohol for energy recovery from cold condensate," *J. Energy Storage*, vol. 31, p. 101639, 2020, doi: https://doi.org/10.1016/j.est.2020.101639.

[14] B. Ghorbani and M. Mehrpooya, "Concentrated solar energy system and cold thermal energy storage (process development and energy analysis)," *Sustain. Energy Technol. Assessments*, vol. 37, p. 100607, 2020, doi: https://doi.org/10.1016/j.seta.2019.100607.

[15] S. Lu, B. Liang, X. Li, X. Kong, W. Jia, and L. Wang, "Performance Analysis of PCM Ceiling Coupling with Earth-Air Heat Exchanger for Building Cooling," *Materials* , vol. 13, no. 13. 2020, doi: 10.3390/ma13132890.

[16] H. Selvnes, Y. Allouche, R. I. Manescu, and A. Hafner, "Review on cold thermal energy storage applied to refrigeration systems using phase change materials," *Therm. Sci. Eng. Prog.*, vol. 22, p. 100807, 2021, doi: https://doi.org/10.1016/j.tsep.2020.100807.

[17] B. Nie, X. She, B. Zou, Y. Li, Y. Li, and Y. Ding, "Discharging performance enhancement of a phase change material based thermal energy storage device for transport air-conditioning applications," *Appl. Therm. Eng.*, vol. 165, p. 114582, 2020, doi: https://doi.org/10.1016/j.applthermaleng.2019.114582.

[18] A. Maiorino, M. G. Del Duca, A. Mota-Babiloni, A. Greco, and C. Aprea, "The thermal

performances of a refrigerator incorporating a phase change material," *Int. J. Refrig.*, vol. 100, pp. 255–264, 2019, doi: https://doi.org/10.1016/j.ijrefrig.2019.02.005.

[19] E. Borri, J. Y. Sze, A. Tafone, A. Romagnoli, Y. Li, and G. Comodi, "Experimental and numerical characterization of sub-zero phase change materials for cold thermal energy storage," *Appl. Energy*, vol. 275, p. 115131, 2020, doi: https://doi.org/10.1016/j.apenergy.2020.115131.

[20] E. Oró, L. Miró, M. M. Farid, V. Martin, and L. F. Cabeza, "Energy management and CO2 mitigation using phase change materials (PCM) for thermal energy storage (TES) in cold storage and transport," *Int. J. Refrig.*, vol. 42, pp. 26–35, 2014, doi: 10.1016/j.ijrefrig.2014.03.002.

[21] A. Maiorino, M. G. Del Duca, A. Mota-Babiloni, and C. Aprea, "Achieving a running cost saving with a cabinet refrigerator incorporating a phase change material by the scheduling optimisation of its cyclic operations," *Int. J. Refrig.*, vol. 117, pp. 237–246, 2020, doi: https://doi.org/10.1016/j.ijrefrig.2020.05.017.

[22] L. Yang *et al.*, "A comprehensive review on sub-zero temperature cold thermal energy storage materials, technologies, and applications: State of the art and recent developments," *Appl. Energy*, vol. 288, p. 116555, 2021, doi: https://doi.org/10.1016/j.apenergy.2021.116555.

[23] D. Rozanna, T. G. Chuah, A. Salmiah, T. S. Y. Choong, and M. Sa'ari, "Fatty Acids as Phase Change Materials (PCMs) for Thermal Energy Storage: A Review," *Int. J. Green Energy*, vol. 1, no. 4, pp. 495–513, Jan. 2005, doi: 10.1081/GE-200038722.

[24] N. Philip, C. Veerakumar, and A. Sreekumar, "Lauryl alcohol and stearyl alcohol eutectic for cold thermal energy storage in buildings: Preparation, thermophysical studies and performance analysis," *J. Energy Storage*, vol. 31, p. 101600, 2020, doi: https://doi.org/10.1016/j.est.2020.101600.

[25] C. Veerakumar and A. Sreekumar, "Preparation, Thermophysical Studies, and Corrosion Analysis of a Stable Capric Acid/Cetyl Alcohol Binary Eutectic Phase Change Material for Cold Thermal Energy Storage," *Energy Technol.*, vol. 6, no. 2, pp. 397–405, Feb. 2018, doi:

https://doi.org/10.1002/ente.201700540.

[26] V. Chinnasamy and S. Appukuttan, “Preparation and thermal properties of lauric acid/myristyl alcohol as a novel binary eutectic phase change material for indoor thermal comfort,” *Energy Storage*, vol. 1, no. 5, p. e80, Oct. 2019, doi: https://doi.org/10.1002/est2.80.

[27] J. Zuo, W. Li, and L. Weng, “Thermal performance of caprylic acid/1-dodecanol eutectic mixture as phase change material (PCM),” *Energy Build.*, vol. 43, no. 1, pp. 207–210, 2011, doi: https://doi.org/10.1016/j.enbuild.2010.09.008.

[28] M. N. R. Dimaano and T. Watanabe, “The capric–lauric acid and pentadecane combination as phase change material for cooling applications,” *Appl. Therm. Eng.*, vol. 22, no. 4, pp. 365–377, 2002, doi: https://doi.org/10.1016/S1359-4311(01)00095-3.

[29] M. N. Roxas-Dimaano and T. Watanabe, “The capric and lauric acid mixture with chemical additives as latent heat storage materials for cooling application,” *Energy*, vol. 27, no. 9, pp. 869–888, 2002, doi: https://doi.org/10.1016/S0360-5442(02)00024-5.

[30] Z. Wang, G. Ma, S. Liu, Y. Jing, J. Sun, and Y. Jia, “A novel binary mixture of caprylic acid/nonanoic acid as latent heat storage for air conditioning and cooling,” *Energy Build.*, vol. 145, pp. 259–266, 2017, doi: https://doi.org/10.1016/j.enbuild.2017.04.018.

[31] N. Philip, G. Raam Dheep, and A. Sreekumar, “Cold thermal energy storage with lauryl alcohol and cetyl alcohol eutectic mixture: Thermophysical studies and experimental investigation,” *J. Energy Storage*, vol. 27, p. 101060, 2020, doi: https://doi.org/10.1016/j.est.2019.101060.

[32] L. Xing, G. Fang, and F. Yang, “Preparation and thermal performance analysis of cold storage material for air conditioning system,” *China Appl. Technol.*, 2006.

[33] H. T. Gao, “Investigation on organic phase transition materials in Energy Storage Air Conditioning system,” *ICMREE2011 - Proc. 2011 Int. Conf. Mater. Renew. Energy Environ.*, vol. 1, pp. 669–672, 2011, doi: 10.1109/ICMREE.2011.5930898.

[34] E. Wang, X. Kong, X. Rong, C. Yao, H. Yang, and C. Qi, “A Study on a Novel Phase Change Material Panel Based on Tetradecanol/Lauric Acid/Expanded Perlite/Aluminium Powder for

Building Heat Storage," *Materials* , vol. 9, no. 11. 2016, doi: 10.3390/ma9110896.

[35] J. Huang, S. Lu, X. Kong, S. Liu, and Y. Li, "Form-Stable Phase Change Materials Based on Eutectic Mixture of Tetradecanol and Fatty Acids for Building Energy Storage: Preparation and Performance Analysis," *Materials* , vol. 6, no. 10. 2013, doi: 10.3390/ma6104758.

[36] ASTM, "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens," 2011. https://www.astm.org/DATABASE.CART/HISTORICAL/G1-03R11.htm.

[37] T. S. Awad, E. S. Johnson, A. Bureiko, and U. Olsson, "Colloidal Structure and Physical Properties of Gel Networks Containing Anionic Surfactant and Fatty Alcohol Mixture," *J. Dispers. Sci. Technol.*, vol. 32, no. 6, pp. 807–815, Jun. 2011, doi: 10.1080/01932691.2010.488134.

[38] N. Beaupere, U. Soupremanien, and L. Zalewski, "Nucleation triggering methods in supercooled phase change materials (PCM), a review," *Thermochim. Acta*, vol. 670, pp. 184–201, 2018, doi: https://doi.org/10.1016/j.tca.2018.10.009.

[39] F. Liu, L. Zargarzadeh, H.-J. Chung, and J. A. W. Elliott, "Thermodynamic Investigation of the Effect of Interface Curvature on the Solid–Liquid Equilibrium and Eutectic Point of Binary Mixtures," *J. Phys. Chem. B*, vol. 121, no. 40, pp. 9452–9462, Oct. 2017, doi: 10.1021/acs.jpcb.7b07271.

[40] G. Latini and M. Pacetti, "The Thermal Conductivity of Liquids — A Critical Survey BT - Thermal Conductivity 15," V. V Mirkovich, Ed. Boston, MA: Springer US, 1978, pp. 245–253.

[41] G. Raam Dheep and A. Sreekumar, "Influence of accelerated thermal charging and discharging cycles on thermo-physical properties of organic phase change materials for solar thermal energy storage applications," *Energy Convers. Manag.*, vol. 105, pp. 13–19, 2015, doi: https://doi.org/10.1016/j.enconman.2015.07.040.

[42] J. R. Davis, *Corrosion: Understanding the basics*. Asm International, 2000.

[43] Y. Tang, Y. Lin, Y. Jia, and G. Fang, "Improved thermal properties of stearyl alcohol/high density polyethylene/expanded graphite composite phase change materials for building thermal

energy storage," *Energy Build.*, vol. 153, pp. 41–49, 2017, doi: https://doi.org/10.1016/j.enbuild.2017.08.005.

[44] S. Tanwar and R. Kaur, "Development and investigation of microencapsulated caprylic acid-based phase change materials for thermal energy storage applications," *Int. J. Energy Res.*, vol. n/a, no. n/a, Mar. 2021, doi: https://doi.org/10.1002/er.6611.

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