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ORIGINAL ARTICLE

Development of Coconut Oil/Capric Acid Eutectic Phase Change Material with Graphene as Latent Thermal Energy Storage

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ABSTRACT – In this study, a eutectic mixture of coconut oil (CO)-capric acid (CA) was synthesised and investigated with the aim of producing newly eutectic phase change materials (PCMs) with improved thermal properties as thermal energy storage (TES). Although eutectic fatty acids have been widely studied, the information on the thermal properties of the CO-CA eutectic mixture is very limited to the authors' knowledge. Coconut oil offers good thermal and chemical stability with acceptable latent heat and melting temperature. The thermal properties of the eutectic mixture were enhanced by graphene addition at 1, 3, 5, and 7 wt% concentrations. The surfactant was added to the mixture to avoid the sedimentation of graphene. The material characterisation techniques include thermal conductivity measurement, Fourier Transform Infrared (FTIR) spectroscopy, Differential Scanning Calorimetry (DSC), and Thermal Gravimetric (TG) analysis. The results revealed that the pure eutectic CO-CA has a melting point of 23.5°C with a latent heat of 110 J/g. With the addition of graphene, the melting point of the mixture is 22.8°C, and the latent heat is 103 J/g. Overall, the findings showed that the thermal conductivity improved by 21.7% for 7wt% graphene concentration. The spectra from FTIR and TG analysis showed that the mixture offers thermal and chemical stability. The promising findings in this study showed that the newly developed eutectic mixture with improved thermal properties makes them favourable to be used as TES for low-temperature applications.

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INTRODUCTION

The last ten years have given us plenty of examples of the urgency of climate change and how it threatens the economic sector and societies. Recent unexpected floods in central Malaysia, extreme heatwaves in North America, and wildfires burning in Turkey are the manifestation of the effects of climate change that are happening at an alarming rate. Climate change modifies our energy generation and needs. The rise in temperature will likely intensify the electricity demand for cooling during summer, thus increasing our reliance on fossil fuels. The recent pandemic COVID-19 has dramatically affected the energy sector, and for the first time since Second World War, carbon emission is showing a decreasing trend due to the lockdown happening all around the world. Even though it seems like a cause to celebrate, it is pertinent to note that the economic scars from the pandemic will likely persist for years to come, resulting in economic turmoil. The fall in carbon emissions from energy use induced by COVID-19 is temporary as the world economy recovers, making it impossible to sustain emissions reduction without changing how we live.

Buildings are accountable for two-thirds of the energy used globally and are the most significant contributor to global warming [1]. Therefore, reducing energy usage during building's operation is vital to combat the effects of climate change. Thermal energy storage (TES) has been in the limelight as a solution that could save energy by incorporating phase change materials (PCMs). Basically, latent heat is stored in TES, which allows them to be used later. Taking advantage of PCMs that store energy during absorption and release energy during heat dissipation, TES assists in balancing the energy demand and supply, decreasing the peak demands, energy consumption, and carbon emissions. Latent thermal energy storage (LTES) offers advantages compared to sensible heat energy storage as it possesses excellent energy storage density, low mass density, and slight temperature fluctuation [2]. Essentially, all materials could be classified as phase change materials. However, corresponding temperature ranges, enthalpy energy storage, favourable phase equilibrium, high heat of fusion, and excellent heat transfer are among the crucial characteristics needed for the TES system [3]. Up until recently, bio-resourced phase change materials (BPCMs) have to come to the limelight in search of a renewable source and more environmentally friendly PCMs with a low carbon footprint.

Two common PCMs used are organic and inorganic. Paraffin which is an organic PCM, is the most common PCM use as it offers excellent latent heat, chemically and thermally stable, making it favourable for wide range of applications [4]. Organic PCMs can be categorised into paraffin and non-paraffin, while inorganic PCMs include salt, salt hydrates, alloys, and metals. Biobased and fatty acids are the non-paraffin organic PCMs. Biobased PCMs such as coconut oil, soybean oil, palm kernel oil and fatty acids are obtained from vegetable or animal fats which come from natural resources and mostly renewable. Non-paraffin organic PCMs attracted considerable research interest as they exhibit suitable melting

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temperatures, excellent latent heat, are non-corrosive, and are thermally and chemically stable. In addition, they usually could be recovered from abundant underused feedstock and are available at low cost [5]. Bio-resourced plant oil such as coconut oil[6], palm kernel oil, Allanblackia, shea butter[7], vegetable fat[5], and beef tallow [8] have also been used as PCMs. Kahwaji and White [9] reported that coconut oil is thermally and chemically stable with acceptable latent heat and melting temperature. Another study by Okogeri et al. [10] reiterated that coconut oil has been widely recognised as a suitable candidate for PCMs. Studies have been conducted using coconut oil for cooling passenger vehicles [11], air temperature control [12], underfloor heating [13], thermal energy storage [6], and thermo-regulating fabric [14].

PCMs are typically used for four types of applications which are shown in Figure 1. Practically, there are no existing PCMs that could meet all the requirements needed for TES application, which means that there is no one-size-fits-all. In the building sector, PCMs often integrated to control indoor temperature fluctuations. According to the Malaysian Standard MS 1525:2019 [15], the indoor temperature is suggested to be between 24 to 26°C. American Society of Heating, Cooling and Air Conditioning Engineers (ASHRAE) [16] recommended that the acceptable indoor temperatures range from 23.5 to 25.5°C and 21.0 to 23.0 °C for summer and winter, respectively. However, most PCMs have a specific temperature range [17]. A study by Du et al. [18] recommended that medium-low temperature range PCMs with melting temperature of 21°C are typically used for indoor climate cooling. Other than that, they are also incorporated in a building as building materials[19]–[21], for underfloor heating [13], and for free cooling[22].

Organic eutectic PCMs produced by mixing two or more PCMs have gained more attention due to their temperature adjustability. The organic eutectic mixture works as a component that freezes and melts the crystal mixture simultaneously without separation. Most of the transition temperatures of PCMs are not adjustable, and PCMs with specific melting temperatures are scarce, making them impossible to be used for specific applications, particularly in low-temperature applications [9], [23]. Most of fatty acids have a high melting temperature, which makes them unsuitable to be used for indoor comfort control where the required temperature is around 25 °C. In such cases, eutectic mixtures offer the possibility to modify the melting temperature to the required temperature for certain applications. By forming a eutectic mixture using more than one fatty acids, the melting point could be adjusted to the required temperature while at same time retaining its excellent latent heat and other desirable properties.

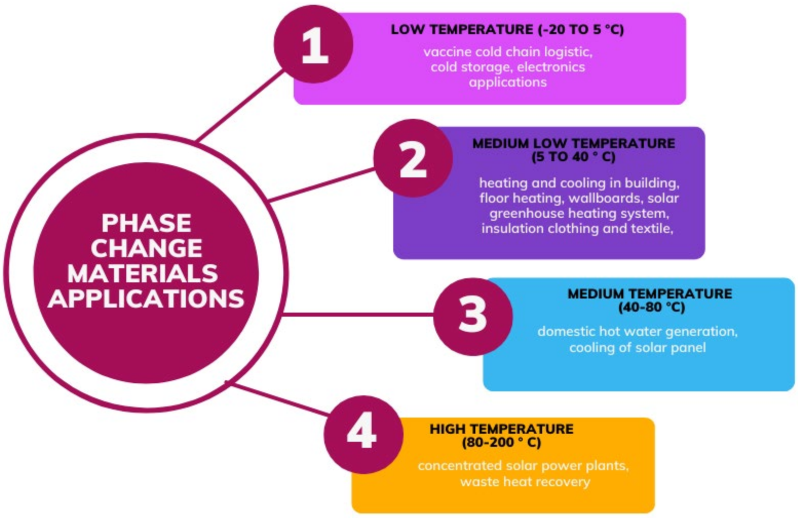


Figure 1. Phase change materials applications [10]

Numerous studies [24]–[28] have been carried out on eutectic PCMs with the aim of obtaining suitable melting temperatures for practical applications. The most common fatty acids that have gained research interest are fatty acids with carbon numbers of 10-18, which includes capric acid, myristic acid, palmitic acid, stearic acid and lauric acid [29]. However, based on literature [29], these fatty acids have high melting temperatures ranging from 32-70°C, which is impractical to be incorporated in the building to control the indoor climate. Thus, further studies have been conducted to develop a eutectic mixture with lower melting temperatures and enhanced thermal properties. Kaurane et al. [30] found that adding another fatty acid could modify the transition temperature of fatty acid. The eutectic mixture of fatty acids provides superior thermo-physical properties and reliability to pure fatty acids [31].

Recently, Doguscu et al. [32] synthesised capric acid and palmitic acid encapsulated as a eutectic mixture in a polystyrene capsule. The melting temperature was between 13.5 to 17.1 °C with 46.3 and 77.3 J/g latent heat capacity, which is appropriate for the building's heating and cooling. Eanest et al. [31] developed a eutectic mixture of capric acid and myristics acid with a mass ratio of 85:15 and found that the melting temperature is 20.86 °C with a latent heat capacity of 156.99 J/g and thermally stable after hundreds cycle. In another study, Mathis et al. [33] synthesised a eutectic mixture of capric acid and lauric acid, and the melting temperature was found to be 19.7°C with 128.7 kJ/kg latent heat fusion. Besides commonly used fatty acids, coconut oil, margarine, and beef tallow were also used to prepare a eutectic mixture.

Thiab et al. [8] in his study on thermal properties of coconut oil/beef tallow (BT), found that the latent heat ranged between 72.32-101.05 kJ/kg, which offers a high potential to be used in wall-building applications to control the indoor climate. All these studies indicated that the melting point of the eutectic mixture of fatty acids could be tailored to suit the required application.

Apart from suitable melting temperatures, the eutectic mixture needs to have high thermal conductivity to enable optimum absorption and release of energy storage. One of the most common problems of PCMs is liquid leakage during the transition from solid to liquid phase [32] which affects the efficiency during the charging and discharging process [33]. Most fatty acids exhibit low thermal conductivity, which hinders their applications due to the longer time needed for the releasing and storing energy process. Thus, researchers have put efforts into finding ways to increase the thermal conductivity of PCMs by dispersing high thermal nanofillers which include nanoparticles, nano-fibres and nano-sheets. Adding nanoparticles in PCMs alters the thermal properties of PCMs, particularly the thermal conductivity, latent heat, phase change temperature, the effectiveness of charging and discharging process, density and viscosity [4], making them an excellent candidate for numerous applications. Among the fillers that are typically used in studies of PCMs are graphene [6], [34], [35], graphite [36]–[39], carbon nanotubes [40], steel wool fibre [41], silica fume [42] and silicon oxide [37]. Other than that, bio-fillers such as pinecone biochar [43], mixed of spruce tree, rice husk, and miscanthus straw [44], rice husk [44], and chestnut biochar [45] have also been used to produce shape-stabilised PCMs, which possessed favorable thermal properties, outstanding thermal and chemical stability to be used as TES. Among all, graphene has been widely used in PCMs study as nanofiller since its discovery in 2004 as it offers excellent thermal and mechanical properties. Recently, Safira et al. [6] studied the thermal properties of coconut oil with graphene and discovered that the thermal conductivity of the sample improved by 69% with 0.3wt% graphene addition. Imran et al. [46] conducted another study using capric and lauric acid and found that adding 0.5wt% graphene increased its thermal conductivity by 41%, making it favourable to be used as TES.

Among all the studies that have been discussed, the potential of a eutectic mixture of coconut oil with capric acid has yet to be reported in the literature. Capric acid has low volume change on melting, is cheap, and is thermally stable, making it suitable to be used as TES [47]. However, capric acid has a higher melting temperature than the temperature needed for indoor climate control. Another rising candidate of PCMs is coconut oil, one of the favourable bio-based phase change materials due to their desirable thermophysical properties, low carbon footprint, cheapness, environmental friendly, and abundantly available in tropical countries. The melting temperature of coconut oil ranged between 24-27°C and thermally stable above room temperature [48]. The study carried out by Kahwaji, and White [28] found that coconut oil possessed higher latent heat, which is 105 J/g, than other edible oils, which makes it attractive to be integrated as PCMs. The high melting temperature of fatty acids makes them least favourable to be used for low-temperature applications such as for indoor comfort control where the required temperature is around 25°C. The eutectic mixture of coconut oil and capric acid is predicted to have a melting point that suits the temperature needed for the application and has superior thermal performance than pure PCMs. However, both selected fatty acids have low thermal conductivity, which hinders the effectiveness of the charging and discharging of TES. The addition of graphene as nanofillers is predicted to improve the thermal conductivity of the eutectic mixture. Therefore, this study aims to develop a eutectic PCM with appropriate phase change temperatures and high thermal conductivity than the individual PCMs for low-temperature applications such as indoor temperature control for buildings. The present work provides the thermal conductivity enhancement of eutectic phase change materials induced by graphene nanoparticles. Thermal properties characterisation, which includes thermal conductivity, latent heat, melting temperature, and thermal and chemical stability, were investigated in this study. The findings from this study will be useful in discovering environmentally friendly high thermal properties phase change materials for low-temperature TES applications.

EXPERIMENTAL

Materials

The eutectic mixtures of capric acid and coconut oil (CA-CO) were chosen for this study. Commercially available coconut oil was used in this study. A study found that the melting temperature of coconut oil ranges between 23 to 27°C [1]. Capric acid was purchased from Sigma Aldrich, with a melting temperature ranging between 27 to 32 °C. The typical properties of the PCMs are shown in Table 1. Sodium dodecylbenzenesulfonate (SDBS) purchased from Sigma Aldrich is used as the surfactant. Graphene of 12 nm average thickness and surface area of 80 m^2/g was used as nanofillers. It is reported that the thermal conductivity of graphene is approximately 4000 W/m.K [2].

Table 1. Phase change materials properties

Trade name	Scientific name	Formula	Melting temperature
Coconut Oil [1]	Cocos Nucifera	$C_{33}H_{62}O_6$	23-27 °C
Capric Acid [3]	Decanoic Acid	$C_{10}H_{20}O_2$	27-32 °C

Theoretical Prediction of Eutectic Mixture of CO-CA

Ideally, the eutectic mixture melting point is lower compared to its components. There are two ways to determine the eutectic point, either by using the prediction method or the proportioning method. For the proportioning method, a group of samples with different mass proportions are prepared, and the heat flow curves from the DSC test are evaluated to determine the eutectic point. While for the prediction method, the eutectic point and the ideal mass fraction are predicted using thermodynamic calculations. This method is preferable as it minimises the number of samples and cost for characterisation. Schrader equation in Eq. (1) was obtained from phase equilibrium, and the second law of thermodynamics was employed to determine the eutectic point [52].

$$T_M = \left[\frac{1}{T_i} - R\frac{lnX_i}{H_i}\right]^{-1}, i = A, B \tag{1}$$

where, T_M represents the melting point of the eutectic mixture of A and B in Kelvin (K), T_i represents the onset melting point of the i th component in Kelvin (K), X_i represents the mole fraction of the ith and H_i represents the molar latent heat in $Jmol^{-1}$. R is the general gas constant (8.314 $Jmol^{-1}$ K^{-1}). The latent heat fusion of the eutectic can be determined using Eq. (2) recommended by Zhang et al. [53] as follows;

$$H_m = T_m \sum_{i=0}^{n} \left[\frac{X_i H_i}{T_i} + X_i\left(C_{P,i}^{Liq} - C_{P,i}^{Sol}\right) ln\frac{T_m}{T_i}\right], i = A, B \tag{2}$$

where H_m represents the latent heat of fusion in J/mol, $C_{P,i}^{Liq}$ and $C_{P,i}^{Sol}$ represent the specific heat at a constant pressure of the "i" component for both liquid and solid in J/mol.K. In this study, the prediction method was employed, and 0.64:0.36 was found as the mass ratio for CO-CA mixture with a eutectic point of 21°C and latent heat of 128 J/g.

Synthesis of Samples

The synthesis of samples is illustrated in Figure 2 below. The eutectic mixture of CO-CA was weighed at 0.64:0.36 mass ratio using with a measuring uncertainty of ±0.001 and prepared by using the direct mixing method. The mixture was homogeneously stirred on a hot plate set at 40°C with a magnetic stirrer at 600 rpm for half an hour, followed by sonication for another half an hour. The mixture was poured into a bottle and then let cool to room temperature. Next, samples with filler were prepared by adding the graphene-based on concentration (1, 3,5, and 7wt %). The samples with filler were prepared with and without surfactant. The ratio of surfactant to graphene is 1:1. After the addition of filler and surfactant, the mixture was again stirred on the hot plate at the same temperature and speed for half an hour, sonicated for half an hour and let cool to room temperature. The sample labelling and composition were tabulated in Table 2.

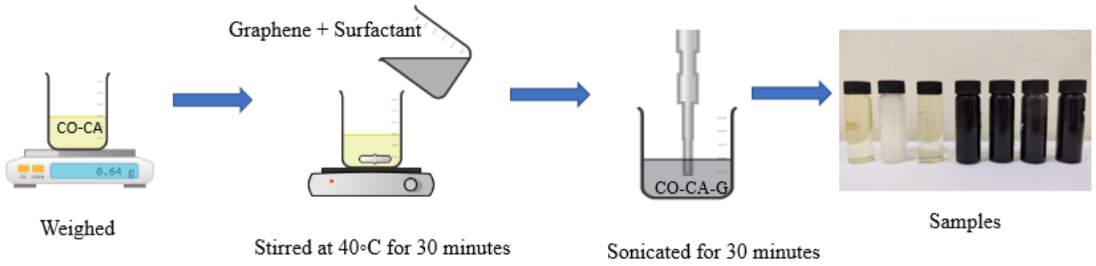


Figure 2. Synthesis of samples

Table 2. Samples labelling and composition

PCMs	Graphene concentration (wt%)	Samples label
Capric Acid	0	CA
Coconut Oil	0	CO
Coconut Oil-Capric Acid	0	CO-CA
Coconut Oil-Capric Acid	1	CO-CA-G1
Coconut Oil-Capric Acid	3	CO-CA-G3
Coconut Oil-Capric Acid	5	CO-CA-G5
Coconut Oil-Capric Acid	7	CO-CA-G7

Chemical and Thermal Properties Characterisation

Fourier transform infrared spectroscopy (FTIR, Perkin Elmer) was employed to observe the chemical structure by obtaining the spectra of the sample in the wavenumber range of 5000-400cm^{-1}. The chemical bonds in the organic compounds absorbed the electromagnetic radiation of frequencies from 4000-40 cm$^{-1,}$ and the absorption spectrum was analysed to determine the compatibility of the samples. The thermogravimetric (TG) analysis was conducted to determine the thermal stability of the samples by using Simultaneous Thermal Analyser (STA) set at 10 °C/min under nitrogen atmosphere with a temperature set from 30°C to 500°C.

Differential scanning calorimeter in nitrogen atmosphere (DSC, Netzsch, DSC 214 Polyma, accuracy ±0.1°C) at 50 ml/min with a scanning rate of 10°C/min from -20°C to 40°C is used to obtain the melting temperature and latent heat of the samples. The latent heat of melting (ΔH_m) was determined by calculating the area under phase change peaks by using PYRIS software.

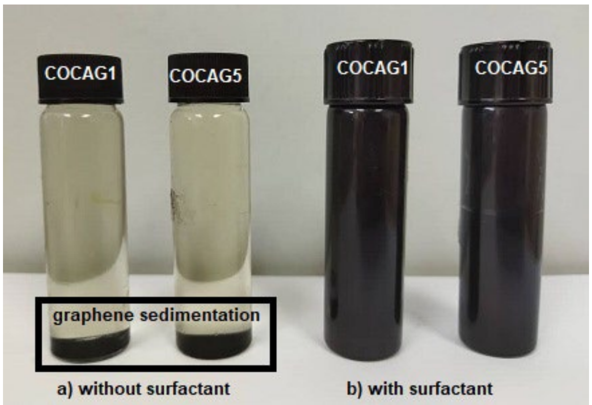
The thermal conductivity of the samples was obtained using the KD2-Pro (±5% accuracy), which consists of a probe that can measure thermal conductivity between 0.02 to 2 W/m.K. The device determines the thermal conductivity of samples by employing the transient line heat source approach. The sensor is ensured to immerse fully in the samples, and the readings were repeated three times at room temperature. For accuracy in reading, any movement and vibration that leads to convection in the sample were avoided during the measurement process.

EXPERIMENTAL RESULTS

This section is divided into a few sections that discuss dispersion stability, thermal conductivity, chemical stability, melting temperature and latent heat capacity, and thermal stability.

Dispersion Stability

Figure 3 shows the image of the dispersion study of the graphene in CO-CA eutectic mixture with and without surfactant after a 24-hours standby period and was evaluated with the naked eye. Graphene sedimentation was observed in samples without surfactant. The thermal conductivity measurement was conducted on two samples with 1 wt% and 5 wt% concentrations of graphene. For samples without surfactant, only a slight improvement of the thermal conductivity can be seen as sedimentation of the graphene was observed at the bottom of the eutectic mixture mostly due to the strong interlayer of van der Waals forces of graphene [4]. Graphene itself exhibits high thermal conductivity, which makes it attractive to be used as nanofillers to improve the thermal conductivity of the PCMs [5]. However, the agglomeration of graphene hindered the improvement of the thermal properties compared to expectations. Surfactant is typically used for carbon-based fillers to wrap the nanoparticles and prevent particle agglomeration caused by the van der Walls forces [6]. In this case, the synthesis of samples was then repeated with SDBS surfactant at a 1:1 surfactant-to-graphene ratio. After 24 hours standby period, less sedimentation was seen at the base of the mixture, which depicted better dispersion stability. The thermal conductivity of samples was measured, and a 15.9% thermal conductivity improvement for 5 wt% concentration of graphene was observed. The adsorbed surfactant produces strong electrostatic repulsion, which stabilises the graphene against the strong van der Waals interactions, which hindered the agglomeration of the graphene [7]. However, the surfactant may affect the thermal properties of the individual graphene particles as it produces a coating on the graphene sheet, which provides thermal boundary resistance at each graphene particle [4]. The thermal conductivity of samples at 1% and 5% concentrations were compared in Table 3. As evidently perceived, the samples with surfactant provide better stability compared to the samples without surfactant.



a) without surfactant
b) with surfactant

Figure 3. Samples with and without surfactant

Table 3. Comparison of thermal conductivity of samples with and without surfactant

Graphene concentration	Thermal conductivity without surfactant (W/m.K)	Thermal conductivity with surfactant 1:1 (W/m.K)
CO-CA-G1	0.156	0.162
CO-CA-G5	0.174	0.182

Thermal Conductivity

Thermal conductivity is phonon-based and often related to the molecular arrangement in the PCM matrix. It represents the rate of heat loading and releasing from the TES system. Thus, higher thermal conductivity manifests a higher rate of heat loading, which poses great interest in the low-temperature application. Generally, the thermal conductivity of fatty acids is low than other organic PCMs. The thermal conductivity for the sample is presented in Figure 4. As observed from Fig. 8, the thermal conductivity for CA, CO, CO-CA, CO-CA-G1, CO-CA-G3, CO-CA-G5, and CO-CA-G7 are 0.151, 0.161, 0.157, 0.162, 0.168, 0.182, and 0.196 W/m.K., correspondingly. The thermal conductivity of the eutectic mixture with 7% of graphene concentration was increased by 21.7% compared to the pure eutectic mixture. Compared to CO-CA eutectic PCMs, the increment in thermal conductivity of CO-CA-G varied from 3-21.7% with respect to the graphene content. The findings in this study are consistent with the findings by Safira et al. [8], which found that the thermal conductivity of coconut oil with graphene increased with the increase in graphene concentrations. The high thermal conductivity of graphene and Brownian motion contribute to the increase in the thermal conductivity of the eutectic mixture [9]. At higher concentrations, a denser percolation network of graphene was formed, which effectively transports heat, thus increasing the thermal conductivity [10]. Graphene addition enhanced the thermal conductivity of the eutectic mixture remarkably due to the covalent sp2 bonds between the carbon atoms and large specific surface area [11]. In addition, graphene possesses strong anisotropic bonding and a low mass of carbon atoms that boast its distinct thermal properties [12]. For chemical and thermal properties characterisation, only two samples were compared, the pure eutectic sample (CO-CA) and the sample with the highest thermal conductivity, which is the sample with 7 wt% graphene concentration (CO-CA-G7).

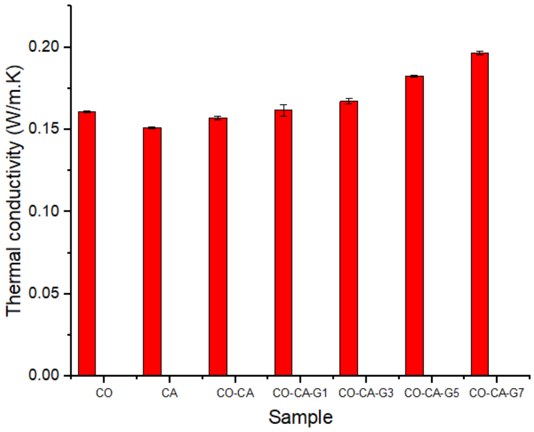
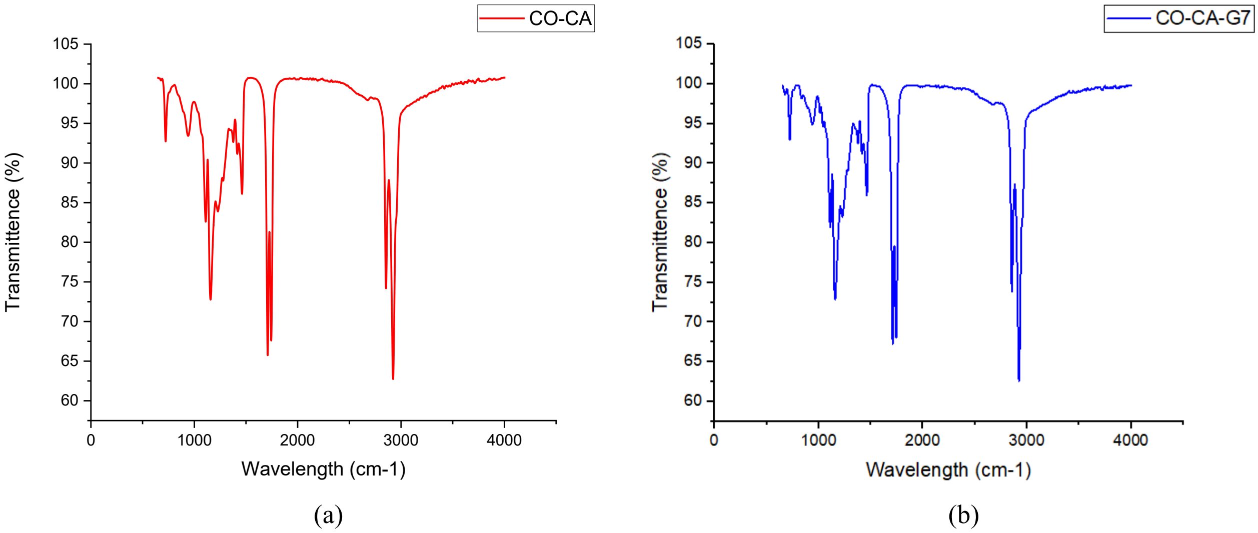


Figure 4. Thermal conductivity of samples

Chemical Stability

The reliability of PCM to be used in TES application depends on many factors; one of them is chemical stability. FTIR spectroscope was carried out to investigate the chemical structure and compatibility of the samples. The FTIR of the eutectic mixture CO-CA and CO-CA-G7 are shown in Figure 5(a) and 5(b). The addition of graphene did not display any new peaks. The FT-IR spectra of the CO-CA-G7 illustrated that the characterised absorption peaks at 723, 1161, 1710, 2854, and 2924 cm $^{-1,}$ which revealed that the eutectic mixture and graphene in the samples were physically mixed with no chemical action. The peaks at 2854 cm $^{-1}$ depicted the -CH_2 stretching vibration absorption band, 1710 cm $^{-1}$ depicted the C=O stretching vibration band, and 1161 cm $^{-1}$ depicted the C-O stretching vibration band. It is observed that there is no apparent change in the FTIR spectra of CO-CA and CO-CA-G7, which indicates that there are no structural changes in the CO-CA after the addition of graphene. This is in agreement with findings by [13]–[15], which found that the FTIR spectrum of fatty acids with carbon filler is the same as the pure PCMs.



(a) (b)

Figure 5. FTIR for (a) CO-CA and (b) CO-CA-G7

Melting Temperature and Latent Heat Capacity

Latent heat is another important parameter in determining the thermal energy storage capacity of PCMs at the required temperatures. The latent heat is obtained from the area under the DSC curve. The thermal energy storage properties of pure PCMs were measured from DSC curves during the melting cycle, as shown in Figure 6. The melting characteristics were evaluated to define the effectiveness during the charging process. Pure CO and CA have 95.2 and 150.5 kJ/kg of latent heat of melting. The newly developed eutectic mixture CO-CA had a latent heat of 110.5 kJ/kg and decreased by 6.8% to 103 kJ/kg when 7 wt% graphene was added. These findings are in line with a few studies [16]–[20] that have been conducted that saw a decrement trend of latent heat with the addition of nanoparticles. The higher composition of the PCMs results in higher heat storage and release, but the presence of graphene with low latent heat decreases the content of PCMs in the mixture, thus reducing the latent heat storage capability [21].

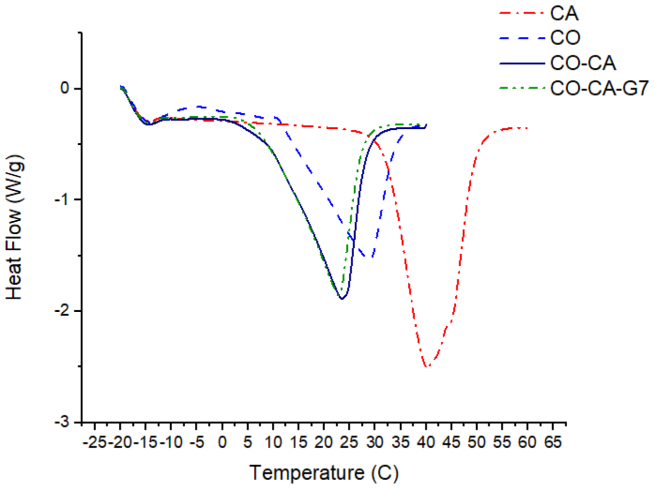


Figure 6. DSC of the samples

The corresponding onset melting temperature ($T_{m,onset}$), maximum melting peak temperature ($T_{m,peak}$), and latent heat of fusion (ΔH_m) are shown in Table 4. The melting temperature of CO and CA are 28.9 and 40.3 °C, respectively. The newly developed eutectic mixture, CO-CA had a melting temperature of 23.5 °C, slightly above the theoretical melting point which is 21°C, whereas the CO-CA-G mixture has a melting point of 22.8°C. The melting temperature of the eutectic mixture, CO-CA was 5.4°C and 16.8°C lower than pure CO and CA, respectively. The melting temperature depends highly on the molecule's length, which represents the strength of the crystal lattice and the amount of energy needed to break it [22]. The eutectic mixture has a lower melting temperature compared to the pure PCMs, as the mixture contains a high percentage of coconut oil. The average distance of the CO molecules is expanded once the lower compound of the mixture tries to break into the crystal lattice of the higher one, which in turn reduces the strength of the crystal lattice and the energy needed to break it [22].

Table 4. Melting temperature and latent heat of samples

Samples	$T_{melting,onset}$ (°C)	$T_{melting,peak}$ (°C)	$\Delta H_{melting}$ (kJ/kg)
CO	10.6	28.9	95.2
CA	32.2	40.3	150.5
CO-CA	10.3	23.5	110.5
CO-CA-G7	9.8	22.8	103.0

Table 5 compares the melting temperature and latent heat from current work with the literature. The melting temperature of eutectic mixtures that contained capric acid varied from 19.7 to 31.7 °C. In the current work, the melting temperature of the eutectic mixture of CO-CA manages to lower the melting temperature of pure capric acid from 40.3°C to 22.8°C, which makes it suitable for indoor thermal management application as the ideal indoor temperature range between 24-26°C based on MS1525:2019 [23]. However, the eutectic mixture of CO-CA has lower latent heat than other capric acid eutectic mixtures as it contains a high percentage of coconut oil which possesses low latent heat.

Thermal Reliability

Thermal gravimetric (TG) analysis is used to study the composition and thermal stability of a material as a function of temperature, time and atmosphere. The thermal stability of CO-CA and CO-CA-G was measured through TGA at the temperature of 30 to 500° C, and the TGA curves are illustrated in Figure 6. The thermal curves evidently observed that the eutectic mixture showed a two-step thermal degradation pattern since CO and CA react differently at high temperatures. Graphene doesn't decompose under 800 °C as it has high thermal durability [37]. Based on the literature review, decomposition of capric acid begins at 90 °C and stops at around 230 °C [38], and for coconut oil, the decomposition starts at approximately 257 °C [39].

Table 5. Eutectic PCMs melting temperature and latent heat

Fatty Acids and Binary Eutectics	Melting temperature (°C)	Latent heat (kJ/kg)	Reference
Capric acid (CA)	43.30	184	[24]
Capric acid (CA)	40.30	150.50	Current work
Palmitic acid (PA)	61.70	164.45	[25]
Mysrisctis acid (MA)	59.50	199.40	[26]
Coconut oil (CO)	22-24	103.25	[27]
Coconut oil (CO)	28.90	95.20	Current work
Coconut Oil-Beef Tallow (CO-BT)	33.53 - 35.07 °C	72.32 - 101.05	[28]
Capric acid-Lauric acid (CA-LA)	19.70	128.70	[29]
Capric acid-Myrisctis acid (CA-MA)	20.86	156.99	[30]
Capric acid-Palmitic acid (CA-PA)	21.85	171.22	[31]
Capric acid-Stearic acid (CA-SA)	31.70	197.20	[32]
Coconut oil-Capric acid (CO-CA)	23.50	110.50	Current work
Coconut oil fatty acids-Oleic-Linoleic Acid (CoFA-OA-LA)	18-25	40-100	[33]
Capric acid-Diatomite-Carbon Nanotube (CA-DT-CNT)	31.38	79.09	[34]
Capric acid- Palmitic acid-Expanded Graphite (CA-PA-EG)	23.50	131.8	[35]
Capric acid-Stearic acid-Graphite (CA-SA-G)	24.7	150.42	[36]
Coconut Oil-Capric acid- Graphene (CO-CA-G7)	22.8	103	Current work

Based on Figure 7, the weight of the sample was static before 100°C showing that no thermal decomposition took place and was stable at a temperature between 30°C to 100°C. The mass started to decrease in the approximate temperature of 100°c to 400°C, showing that the eutectic mixture was thermally decomposed. From the derivative weight curves in Figure 8, it can be seen that the first decomposition peak at T_1, is followed by the second step decomposition peak at T_2, as shown in Table 6. For the eutectic mixture CO-CA, the first decomposition peaks at 195 °C, and the second decomposition peaks at 353°C. With the addition of graphene, the decomposition shifted to the left, with first peaks at 174 °C and second peaks at 345°C, which depicted earlier decomposition occurred compared to the pure eutectic mixture. A similar TGA curve trend was observed in a study by Hua Fei et al. [39] where the eutectic mixture of capric acid with the addition of expanded graphite filler decomposed earlier than the pure eutectic mixture. This finding is in line with findings from another study by Lee et al. [40] that found the decomposition of 70/30 coconut oil/n-hexadecane eutectic mixture peak at 165.14°C and 363.68°C. Even though the decomposition of the CO-CA-G happened earlier than CO-CA, the weight loss in CO-CA-G happened at a wider temperature range compared to CO-CA. During the decomposition, the graphene offers a physical layer on the surface of the eutectic PCMs, delaying the decomposition of the eutectic mixture [41]. It can be concluded that the eutectic mixture showed thermal stability for low-temperature applications, particularly in regulating indoor temperature.

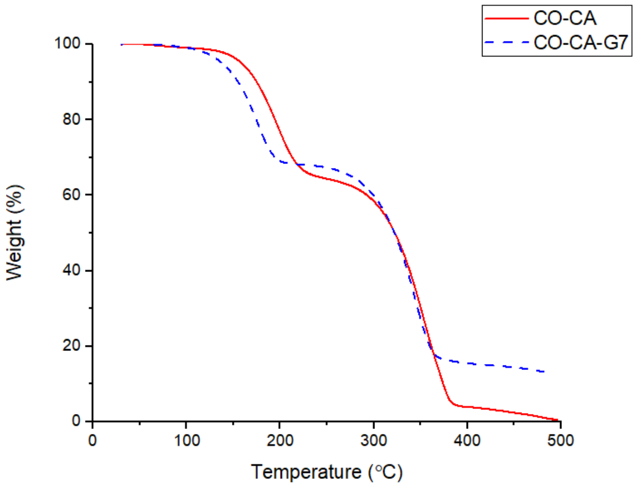


Figure 7. TGA analysis of samples

Table 6. Peak of derivative weight of the samples

Sample	First peak of derivative weight, T_1 (°C)	Second peak of derivative weight, T_2 (°C)
CO-CA	216	380
CO-CA-G7	193	368

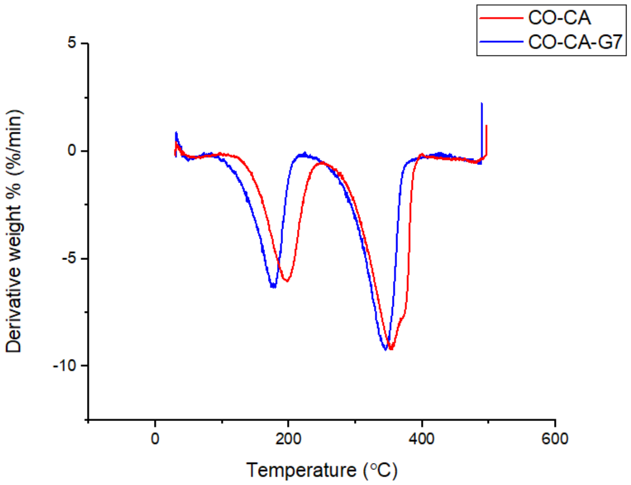


Figure 8. Derivative weight of the samples

CONCLUSIONS

In the current work, the newly developed CO-CA eutectic mixture was synthesised as a potential candidate for PCMs compared to other capric eutectic mixtures for LTHS to control the indoor temperature in the building. CO-CA eutectic mixture was synthesised by direct mixing method with the mass ratio of 64:36 using Schrader's equation. The newly developed eutectic mixture CO-CA-G7 had a melting point of 22.8°C, making them attractive for indoor cooling applications. The latent heat of CO-CA is 110.5 kJ/kg and decreased by 6.8% to 103 kJ/kg when 7wt% graphene was added. The addition of graphene as nanofillers at 1, 3, 5 and 7%wt concentrations greatly improved the thermal conductivity of the newly developed eutectic mixture. The improvement of the thermal conductivity with graphene is most significant at 7wt% concentration with a 21.7% increment due to the reduced inter-layer spacing between eutectic mixture molecules. The FTIR analysis proved no chemical structure changes in the eutectic mixture, and the TGA analysis evidently demonstrated that the eutectic mixture was thermally stable at a temperature below 100 °C. It is revealed that the thermal conductivity improved linearly with the increase in graphene concentrations. The newly eutectic mixture with improved thermophysical properties in terms of thermal conductivity and thermal stability makes it favourable to be used in numerous low-temperature applications. Due to their renewable and biodegradable nature, the mixture offers excellent potential as PCMs for LTHS as they are relatively cheap, non-toxic, and abundantly available. However, more work should be conducted to test the endurance of the eutectic mixture over cycles of charging and discharging. The integration of this eutectic mixture as PCMs should include long-term thermal reliability studies to ensure that the PCMs do not decompose at high temperatures. In addition, the incorporation of PCMs, particularly in buildings, is limited because of the leakage problems in the melted state and also degradation after numerous charging and discharging cycles. Future research should focus not only on the enhancement of the thermal properties of the PCMs but also on the incorporation of PCM in buildings by developing suitable encapsulation methods to increase the efficiency of PCMs.

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