



Increasing the rating performance of paraffin up to 5000 cycles for active latent heat storage by adding high-density polyethylene to form shape-stabilized phase change material

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ABSTRACT

The unstable phase transition of pure paraffin limits its application, particularly for active latent heat storage (ALHS). In passive latent heat storage, the addition of high-density polyethylene (HDPE) can decrease paraffin's leakage rate, which is associated with unstable phase transition and increase its durability after a large thermal number. This study aims to discover the possibility to use HDPE as a shape-stabilizer to increase the paraffin's performance for the ALHS system. Pure paraffin and composite paraffin/HDPE (80:20 wt%) are prepared as the reference material. The evaluation is focused on thermal properties, stability and performance during charging and discharging under different thermal cycles. Thermal cycle treatment uses temperature as a working boundary where the sample is heated from 30°C to 150°C, then cooled back to 30°C and repeated until 5000 cycles. Three different cycle references are chosen (1, 1000 and 5000 cycles) for each evaluation. The melting temperature of paraffin is decreased from 61.6°C to 59.8°C after 5000 cycles where Paraffin/HDPE slightly decreased from 60.4°C to 60.1°C. The heat fusion is decreased by 8.7% and 2.9% for paraffin and Paraffin/HDPE, respectively. The isothermal phase change is observed for paraffin/HDPE even after 5000 cycles with a higher rating performance by 30% faster to complete one cycle than pure paraffin. The other thermal performance is discussed in detail within the article, including the phase transition model during charging and discharging for the sample.

1. Introduction

Latent heat storage has a unique character as thermal energy storage because it utilizes the phase change of the storage material to provide a better storage capacity without experiencing a high-temperature gradient. In the actual application for a latent heat storage system, the phase change properties are often combined with the sensible properties of the same material, allowing to store more thermal energy under the given working temperature. Paraffin is a good example of a phase change material that is widely used for latent heat storage. Its main features are high latent heat fusion, inexpensive and suitable for low temperatures (< 200°C).

The application of paraffin as thermal energy storage is divided into two methods: passive and active latent heat storage. Passive latent heat storage, in general, is used in building applications to decrease heating and cooling energy consumption [1]. It is defined as passive technology because it works based on the temperature difference between the

storage and surrounding without using a heat exchanger or mechanical system [2]. Paraffin as passive latent heat storage is applied for ceiling and floor, attached to windows and combined with buildings' wall material [3]. In contrast, active latent heat storage requires extensive components and a complex control system, such as a heat exchanger and mechanical system, to provide a heat transfer process for thermal source, load and storage [4]. The storage capacity and working temperature for active latent heat storage are higher and can be applied for broader applications than passive latent heat storage [5].

The utilization of paraffin as a storage material both in passive and active latent heat storage systems has an identical problem related to the nature of paraffin as a heat storage material [6]. Particularly, for passive latent heat storage system in building application, leakage issue during the melting process of paraffin is the main problem [7]. In general, paraffin is charged into a particular container to encounter the issue, but it decreases the storage capacity substantially and increases the cost of storage [8]. Another alternative is proposed by embedding paraffin into

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supporting materials to produce shape-stabilized phase change material (SSPCM) [9]. For example, adding high-density polyethylene (HDPE)-based polymer gives a remarkable effect for shape-stabilized paraffin-based phase change material, where the leakage is decreased during phase transition [10]. Moreover, the addition of high-density polyethylene into paraffin as a supporting matrix can prevent significant deformation after repeating the thermal cycle during the usage and maintain its thermal performance [11]. The addition of high-density polyethylene to form shape-stabilized paraffin-based phase change material is considered an effective method to improve the phase transition properties, increasing the durability and maintaining the thermal performance without requiring special treatment, making this method is considerably inexpensive and easy to perform.

For active latent heat storage, the application of paraffin as a storage material is troublesome due to the presence of supercooling and unstable phase change transition, which decreases the heat transfer rate from the material [12]. To reduce the drawbacks for active latent heat storage, some efforts have been made by using fins-based heat exchangers [13] as well as thermal conductivity enrichment by adding high thermal conductivity materials such as metal foam and expanded graphite (EG) [14]. Improving the heat transfer rate by modifying the heat exchanger and adding high thermal conductivity materials might be working successfully for the latent heat storage unit. However, the main problem from the paraffin as storage material remains, particularly for unstable phase transition during charging and discharging.

Unstable phase transition of paraffin during phase transition brings the difficulty to estimate the phase change during charging and discharging [15] and forms a mushy region which decreases the heat transfer rate [16]. Numerous efforts have been taken to minimize the unstable phase transition of the paraffin. For example, Farsani et al. used a rotational cavity, which increased the melting and heat transfer rate by 8 % compared to a fixed cavity [17]. Adding nanoparticles (Al_2O_3) into the paraffin in the fins heat exchanger changes the rate of melting and solidification by 17 and 44.2 % [18]. A suitable phase transition during charging and discharging can be achieved by using graphene-carbon nanotubes aerogel. Unfortunately, it is highly dependent on the quantity of graphene-carbon nanotubes aerogel which reduces the paraffin content and decreases the latent heat energy [19]. These efforts show a significant improvement for stabilizing the phase transition of paraffin. Nevertheless, an alternative method that might be feasible to stabilize the phase transition of paraffin should be considered by using the cost-effective method and widely available materials.

Considering the outstanding improvement for shape-stabilized paraffin-based phase change material with high-density polyethylene as passive latent heat storage, it is possible to use the same method for active latent heat storage to minimize the effect of unstable phase transition that decrease the rating performance of the storage system. Shape-stabilized paraffin-based phase change material is conceivable for further development in active latent heat storage by using a heat exchanger as the storage container [20]. It can be combined with the improved heat exchanger for paraffin storage [21] and deliver better active latent heat storage [22]. Unfortunately, no study explicitly discussed the application of shape-stabilized paraffin-based phase change material for active latent heat storage. Therefore, the study explores the possibility of improving the performance of active latent heat storage by using shape-stabilized paraffin-based phase change material with high-density polyethylene. High-density polyethylene is chosen as a supporting matrix to form shape-stabilized phase change material since it has good compatibility with paraffin, is economically feasible and widely available.

The idea of shape-stabilized paraffin-based phase change material with high-density polyethylene from passive latent heat storage to active latent heat storage should be further studied, particularly for the life cycle as a storage material. It is based on the differences between the operational characteristic of a passive and active latent heat storage system. Passive latent heat storage works with relatively small

temperature changes, making it suitable for many thermal cycles. Oppositely, active latent heat storage works with a relatively large temperature range (i.e., from room temperature to over a hundred degrees), which is highly possible to reduce its durability due to a large thermal cycle under a high-temperature gradient. Thus, the effect of thermal cycling for shape-stabilized paraffin-based phase change material with high-density polyethylene must be studied and compared to pure paraffin through life cycle assessment.

Life cycle assessment for material storage, particularly for novel storage material, is essential to be studied at first place since it relates to the aging effect, which causes a significant drop in the storage performance due to repeated cycles [23]. A. Vasu et al. conducted a thermal cycling assessment for pure paraffin and found the latent heat capacity decreased by 25.71% after 200 cycles [24]. Wang et al. reported that latent heat capacity and phase transition temperature for paraffin/EG was decreased between 1–3% after 100 cycles [25]. Another study related to life cycles assessment was conducted by Long et al. and showed that the heat fusion of pure paraffin was reduced by 9.1% after 10,000 thermal cycles where there was no substantial effect on the melting temperature of paraffin [26]. The present study conducts a life cycle assessment for pure paraffin and shape-stabilized paraffin-based phase change material, composite paraffin/high-density polyethylene (HDPE). The thermal cycling of the prepared samples is done by using the actual heating and cooling process under a specific temperature reference. Even though the actual thermal cycling requires an extended time, it provides a more accurate assessment of the material performance compared to the accelerated aging method [27]. After thermal cycling, the sample will be characterized for its thermal properties, including the charging and discharging rate according to the thermal performance assessment by using a heat exchanger.

2. Materials and method

2.1. Sample preparation and characterization

Commercial paraffin and high-density polyethylene/HDPE (granule) were purchased from the marketplace. Since this study is related to material development and life cycle assessment for thermal storage material, the material's initial properties are essential to be obtained at the beginning of the study. Pure paraffin and HDPE were tested to obtain its fundamental properties, particularly thermophysical and flashpoint. The results are summarized in Table 1.

The properties of pure paraffin and HDPE, as shown in Table 1, is essential to be used as an initial reference before further characterization. It is important to set the maximal working temperature of the sample for safety measurement since paraffin is considered a flammable material [28]. Since paraffin has the lowest flashpoint, it is taken to determine the maximum working temperature for the test. The maximum working temperature for this study is set at 150°C (~ 75% from flash point temperature of paraffin). The thermal conductivity measurements were done by using Hot Disk Thermal Constant Analyzer TPS-3500. A transient plane source (TPS) is a convenient method to determine the thermal properties of materials, particularly for thermal conductivity. The Hot Disk, which works as the heat source and temperature sensor, is placed between the measured sample. The sample is

Table 1
The initial properties of pure paraffin and HDPE.

Parameter	Unit	Paraffin	HDPE
Flashpoint (T_f)	°C	198	314
Melting temperature (T_m)	°C	61.5	110.1
Freezing Temperature (T_f)	°C	74.3	121.6
Heat Fusion (ΔH)	J/g	188.7	120.6
Thermal conductivity (K) @30°C	W/m•K	0.214	0.415
Thermal conductivity (K) @100°C		0.169	0.348
Thermal conductivity (K) @150°C		0.151	0.278

heated by the Hot Disk, which at the same time measure temperature increment with respect to time. By comparing the temperature differences between samples, heat transfer rate, and the sample's dimension, the measured sample's thermal conductivity can be estimated precisely. The measurements were taken at three different temperatures regarding the minimum and maximum working temperature of the study, 30°C and 150°C, respectively, where the temperature of 100°C is taken as median working temperature. The measurement of thermal conductivity at three different temperatures was also intended to obtain the average conductivity of the material at different phases (solid phase at 30°C and liquid phase at 150°C).

The ratio of composite paraffin/HDPE is set at 80/20 wt%. According to the recommendation from a previous study, the HDPE content is limited by 20 wt% because adding HDPE more than 20 wt% will reduce the storage capacity significantly [29]. The composite was prepared by melting the paraffin at a temperature of 70°C by using an oil bath heater while HDPE is melted in an electric oven at a temperature of 150°C. Liquid paraffin was mixed into liquid HDPE. The mixture was stirred manually until the HDPE dispersed adequately in the composite. The mixture is cooled at room temperature and then reheated for 1 h using an electric oven while stirring every 10 min. After one hour, the mixture is cooled at room temperature for 5 h. The two samples (P for paraffin and P/H for paraffin/HDPE) were introduced to thermal cycle treatments before characterization. The thermal cycle is taken at 1, 1000 and 5000 cycles. Differential scanning calorimetry (Mettler Toledo TGA/DSC 1) was used to obtain each sample's heat fusion, melting and freezing temperature under different thermal cycles. The same apparatus was also used to observe the thermal reliabilities using a thermogravimetric analyzer from 30°C to 600°C. A thermal performance assessment was conducted to evaluate each sample's charging and discharging rate using a regenerator-type heat exchanger.

2.2. Thermal cycle treatment

Mostly, the life cycle assessment is done by using accelerated thermal cycling. The method is excellent to determine the overall performance of the tested sample, which can be done within a short time. Unfortunately, the deviation of the results is remarkably high and less accurate since it uses some mathematical modeling. To minimize the risk of high uncertainty from thermal cycling, this works used an actual thermal cycle for the tested sample. Actual thermal cycling is done by heating the sample until the preferred maximum temperature and cooling back to its preferred minimum temperature [30]. Although it takes more time for the treatment, the actual thermal cycle method is highly recommended since the tested sample is experiencing an actual thermal cycle like the

existing thermal storage system.

The state of charge (SoC) for a storage system is essential since it indicates the storage capacity based on its working boundary [31]. Thermal energy storage works based on the temperature difference between the storage materials and thermal load. Therefore, the minimum and maximum temperature can be used as a working boundary to indicate the state of charge of the storage materials [32]. The state of charge percentage can be obtained by monitoring the amount of heat absorbed during charging and released during discharging [33]. There are three targeted thermal cycles for sample characterization: 1, 1,000 and 5,000 cycles. The temperature was used as a working boundary for the state of charge (SoC) and taken as a thermal cycling reference. The minimum working temperature is set at 30°C and taken as 0% SoC, and the final temperature is 150°C which is indicated as 100% SoC. One complete thermal cycle is measured from the charging process of 0% SoC (30°C) to 100% SoC (150°C) and discharged from 150°C (100% SoC) to 30°C (0% SoC). The Loop line in Fig. 1 shows the schematic model to describe one thermal cycle used in this study (0% → 100% → 0% SoC).

Fig. 1 shows the schematic model of the thermal cycle treatment of the sample. The sample was placed into a low relative roughness copper tube as a container and media for conduction heat transfer during the thermal treatment. A low relative roughness copper tube was used to minimize the sediment of the treated sample inside the tube. The thermal cycle treatment was done as follows: chilled sample ($T_{\min} = 30^\circ\text{C}$) was heated using a multi-pan oil bath heater.

Thermal paste was used at the second pan to accelerate the heating process. A thermocouple (type K) was attached to the body sample holder to monitor the body temperature to estimate the sample temperature. When the sample holder reached the targeted temperature, the sample was measured using an infrared thermometer (Fluke 572-2). When the sample has reached the targeted temperature ($T_{\max} = 150^\circ\text{C}$), the sample holder is moved to the icebox briefly to remove the heat on the body sample holder. Afterwards, the sample holder is moved into a controlled temperature water-cooling bath. Once the sample reaches its minimum temperature (30°C), the cycle is repeated. The mass of each treated sample is 13.0 grams. According to the first thermal cycle treatment, the heating process was done within 50 s, the cooling process was 40 s and the transition time to move the sample holder was around 30 s. Therefore, it takes around 167 h to complete 5000 thermal cycle treatments for the sample.

2.3. Thermal performance assessment

The thermal performance assessment is done by observing the

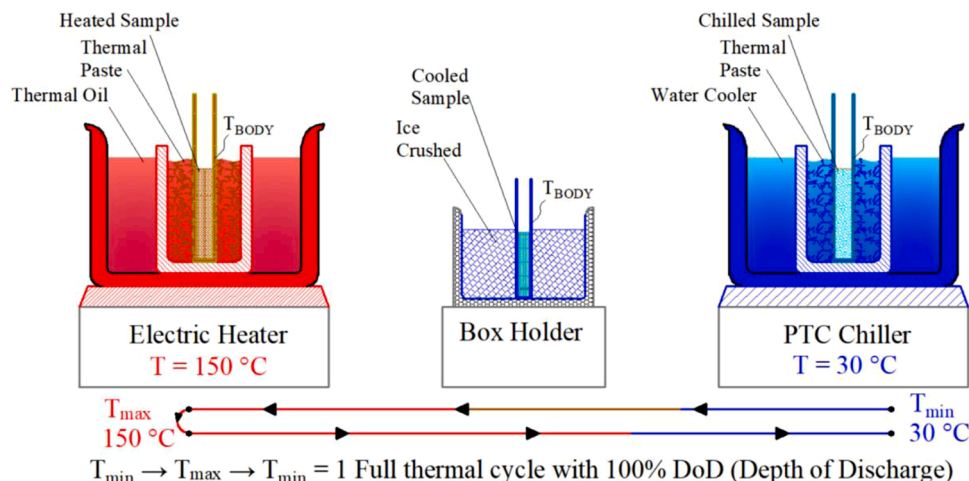


Fig. 1. The schematic design for thermal cycle treatment.

charging and discharging characteristics of the storage material to evaluate the effect of the cycling process on the rating performance of the material. The charging and discharging process for active latent heat storage requires interaction between the external heat source, thermal load and the storage material. Thermal performance assessment was done by modeling the heat exchange process between storage material and external heat source [34]. By setting a specific working temperature of the storage material, the rating performance of the storage material can be obtained by measuring the duration of each process to achieve the targeted temperature. Fig. 2 shows the schematic design of the apparatus for thermal performance assessment. The model was developed according to the NBSIR 74–634 recommendation for thermal performance assessment of active sensible/latent heat storage.

Heat Transfer Fluid (HTF) was used as a heat transfer medium for the charging and discharging process of the tested sample inside the heat exchanger. During the charging test, the inlet temperature of the HTF (Smooth Fluid–05, with boiling point 251–255°C and density 1.031 g/cm³ @ 40°C) was kept constant at 170°C. Three thermocouples monitored the temperature of the tested sample to ensure the reliability of the measurement. Once the sample reaches the targeted temperature, the discharging test is started. During discharging test, the inlet temperature of the HTF was kept constant at 25°C. The result of each test was plotted in a Temperature-time graph to observe the phase change transition of the tested sample. The void volume of the shell side is 14 cm³. The mass of the sample inside the shell side is 12.6 grams, approximately 90% of the shell's void volume, to give space for the tested sample during phase transition. Before running the actual test, the apparatus was tested by using water as storage material. From the initial test, the overall heat transfer coefficient of the heat exchanger is estimated at around 84.1 W/m²·K.

3. Results and discussion

3.1. Thermal properties

Fig. 3 presents the Differential Scanning Calorimetry (DSC) curve for each sample under different thermal cycling where the melting temperature (T_m), freezing temperature (T_f), and melting enthalpy (ΔH) are summarized in Table 2. As seen in Fig 3a and 3b, pure paraffin has two peaks, where the first peak is indicated as solid-solid transition caused by the initial change in the crystalline structure of solid paraffin. The second peak indicates the melting point of pure paraffin. Composite paraffin and HDPE (P/H) have three different peaks, where the first peak indicates the solid-solid transition for the paraffin (Fig.3c and d). The second peak marks the melting point for the composite, and the last peak, which is quite apart from the second peak, expresses the second melting point for the HDPE. The last peak for P/H is indicated that a

small portion of HDPE melts at this point, and most of it melts together with paraffin (second peak).

The effect of thermal cycling for each sample are observed clearly according to the DSC curve. As shown in Fig. 3a, the melting temperature (T_m) of pure paraffin (P) decreases as the cycle increases. It happens as the effect of thermal stress on the material as the repeated phase change along with the thermal cycle. The first melting temperature of composite Paraffin and HDPE (P/H) is lower than pure paraffin (Fig. 3b). As the cycling increases, sample P/H only experiences a slight decrease in melting temperature. The polymer network of HDPE can maintain the melting temperature of the composite, which is relatively constant since it minimizes the effect of thermal stress from repeating the cycle for the paraffin. It is a noticeable outcome that makes HDPE highly recommended to improve paraffin's thermal properties and reliabilities as passive latent heat storage [35].

The cooling curve shows that the freezing temperature (T_f) for pure paraffin is started earlier than its melting temperature (Fig. 3c). Rapid solidification for pure paraffin is highly related to the supercooling effect as the nature of pure paraffin. The effect of thermal cycling also accelerates the freezing temperature of pure paraffin, which makes the difference between melting and freezing temperature enlarge significantly. In contrast, sample P/H shows a better freezing temperature with only slight differences between melting and freezing temperature, even after 5,000 thermal cycles (Fig. 3d). It is a distinct advantage since the supercooling effect can be minimized on sample P/H. The addition of HDPE helps the crystal growth of paraffin to be more stable and occurs close to its melting temperature. According to those achievements, the addition of HDPE as a shape-stabilizer is proven to promote a better phase change transition for pure paraffin and minimize the effect of thermal cycling on its thermal properties.

The addition of HDPE reduces the melting enthalpy of the composite paraffin/HDPE (Table 2). The main drawback of adding HDPE for latent heat storage is that the melting enthalpy is an essential parameter for latent heat storage as it is associated with the amount of stored energy during phase transition on the storage material. It enhances the recommendation to limit the addition of HDPE by a maximum of 20 wt% to prevent significant loss of the storage capacity for the composite paraffin/HDPE. However, the effect of thermal cycling for the melting enthalpy of composite paraffin/HDPE is relatively low. The melting enthalpy for pure paraffin drops significantly along with the increase in cycling. Still, the melting enthalpy of pure paraffin is much higher than composite paraffin/HDPE, which can be said that the storage capacity of pure paraffin is still higher than the composite.

3.2. Thermal performance

The energy storage system works under a specific repeated cycle during charging and discharging. The working boundary of each cycle depends on the type and working principle of the storage system. For thermal energy storage (particularly for sensible and latent heat storage), the temperature is an important indicator to set the system's minimum and maximum working boundary. The thermal cycle treatment done in the first place is used temperature as a working reference, so the change in storage performance as the results of a repeated thermal cycle can be analyzed appropriately. The first performance assessment compares the temperature versus time change during the charging process of pure paraffin and composite paraffin/HDPE. Fig. 4 presents the charging characteristic for pure paraffin (a) and composite paraffin/HDPE (b).

It can be seen that both graphics have distinguished patterns along with temperature increments with respect to time. First, both samples experience multi-step transition, which can be described as solid-sensible phase, solid-liquid phase transition and liquid-sensible phase. As seen in Fig. 4a, the first step is denoted as a solid-sensible phase for pure paraffin, indicated by a sharp temperature increment. It is mainly affected by high-thermal conductivity for solid paraffin compared to the

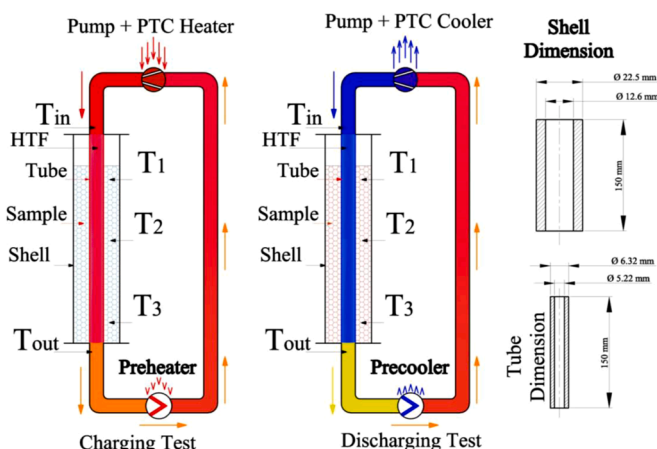


Fig. 2. Schematic design for thermal performance assessment.

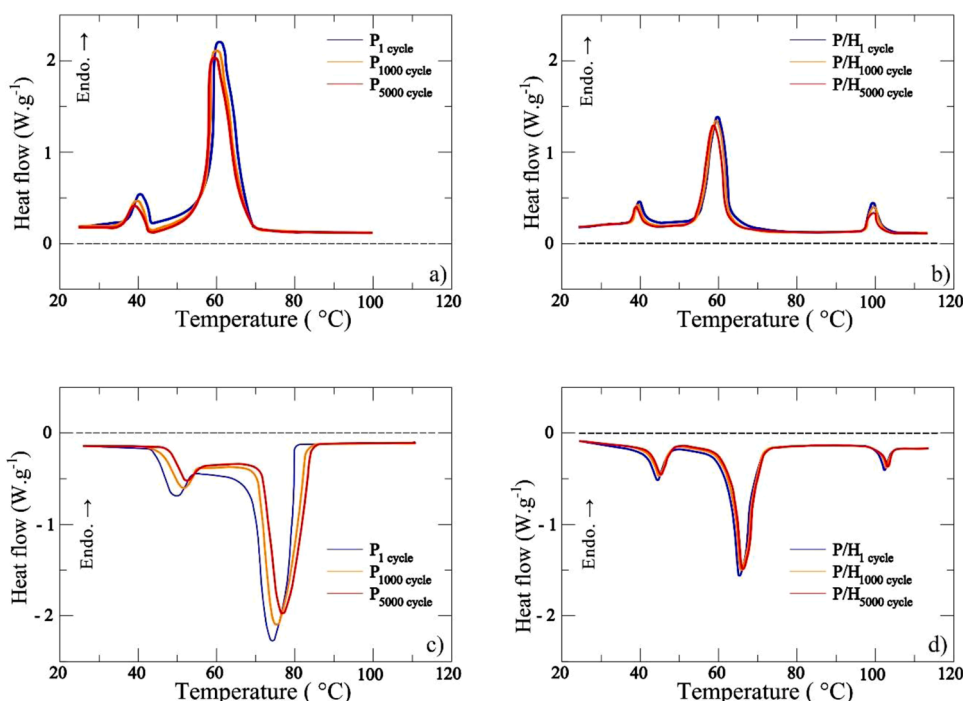


Fig. 3. DSC results: (a) heating curve paraffin, (b) heating curve paraffin/HDPE, (c) cooling curve paraffin, (d) cooling curve paraffin/HDPE.

Table 2
Thermal properties from DSC characterization.

Properties	P ₁	P ₁₀₀₀	P ₅₀₀₀	P/H ₁	P/H ₁₀₀₀	P/H ₅₀₀₀
T _m (°C)	61.6	60.9	59.8	60.4	60.2	60.1
T _f (°C)	74.2	74.8	75.2	66.3	66.5	66.8
ΔH _m (J/g)	188.4	178.2	172.1	132.5	130.4	128.7

liquid phase (Table 1.). The next step is non-isothermal phase transition which ranges from 59.3–78.6°C. Unstable phase transition can be observed distinctly where the phase transition takes place with significant temperature increments. The final step is the liquid-sensible phase, where temperature rises slower than the solid-sensible phase during the initial liquid phase. Once the temperature is close to 100°C, it rises at a greater rate, attributed to a better temperature distribution in molten paraffin. The effect of thermal cycling is shown by a longer period of charging time. The solid-sensible phase has a minor effect regarding thermal cycling. The solid-sensible phase has good stability, which is associated with strong molecular bonding within the material. In contrast, the repeated phase transition from solid to liquid (vice versa)

due to thermal cycling treatment caused internal thermal stress for the material, decreasing the heat transfer rate. It can be observed based on the duration required for the material to reach the maximum temperature. The charging rate for pure paraffin is decreased somewhat between the first and 1,000 cycles and reduced significantly after 5000 cycles.

Stable phase transition for paraffin/HDPE can be observed noticeably from Fig. 4b, where phase transition occurs with slight temperature change. Accordingly, the almost perfect isothermal phase change is achieved. It demonstrates the effect of HDPE as a shape-stabilizer, which promotes a more stable phase transition for pure paraffin. The temperature gradient during the phase transition of paraffin/HDPE is relatively low, only 7.9–8.4°C. A slight temperature gradient is advantageous during the phase transition since the energy can be absorbed substantially without experiencing temperature rise. It is desirable for active latent heat storage, which works under a specific temperature range, i.e., a thermal management system [36]. The cycling effect is observed during the liquid phase, where the temperature increment becomes slower after 1,000 and 5,000 thermal cycles. Even though there is deceleration during the liquid phase, the effect of HDPE makes the deceleration during the liquid phase still lower than pure paraffin. The thermal conductivity of liquid HDPE (Table 1) is higher than pure

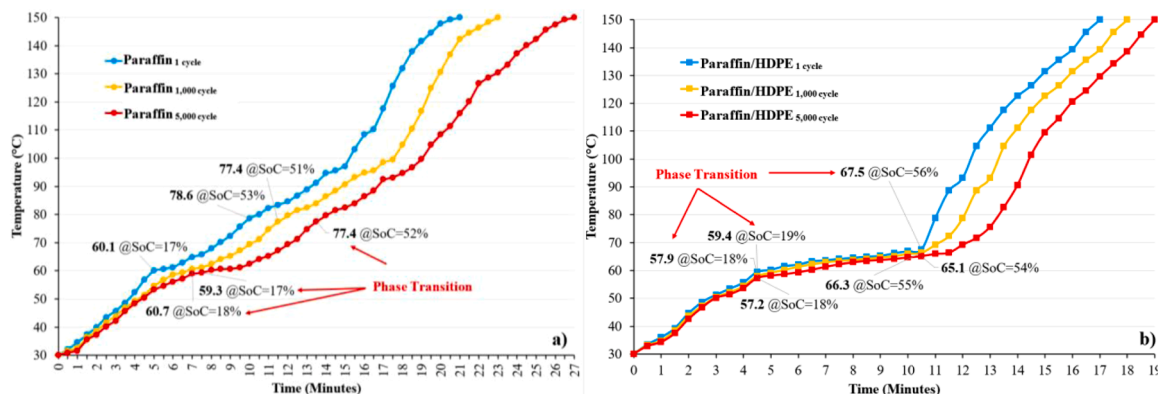


Fig. 4. Charging profile for (a) pure paraffin, (b) paraffin/HDPE.

paraffin, which helps to reduce slow heat absorption from pure paraffin, especially after repeated thermal cycling.

The amount of heat absorbed from heat transfer fluid and temperature rise from the storage materials are taken to define the State of Charge (SoC) with respect to time. As plotted in Fig. 5a, SoC evolution during the solid-sensible phase is relatively low and then sharp increment occurs as the phase change takes place. It is the critical parameter for a latent heat storage system where most of the absorbed heat is stored as the heat of fusion. Unfortunately, since pure paraffin has non-isothermal phase change, the heat absorption during phase transition is followed by significant temperature increment, which in some applications is not desirable. As the heat is kept supplied to the paraffin, SoC keeps rising at a slower rate since now paraffin is in the liquid state. Although temperature increases greatly after 100°C (Fig. 4a), the SoC evolution does not significantly affect the amount of absorbed heat from heat transfer fluid decreases during the liquid-sensible phase. Based on SoC evolution, thermal cycling mainly reduces the charging rate, particularly for the solid-sensible phase.

A remarkable performance regarding the SoC evolution is shown by paraffin/HDPE (Fig. 5b). First, it can maintain the SoC evolution after repeated thermal cycling, especially during solid-sensible and phase-transition. The SoC evolution for 1, 1,000 and 5,000 cycles is relatively close at almost identical duration and temperature. The presence of HDPE in the composite can protect the paraffin from thermal stress and hysteresis losses because of the plasticizing effect. It is also explaining why a relatively significant drop in the SoC evolution occurred during the liquid-sensible phase. During the liquid-sensible phase, a small portion of HDPE remains solid (indicates the third peak in Fig. 3b), which hinders the heat absorption within the material.

As seen in Fig. 6a, the discharging profile for pure paraffin occurs at two distinguished steps. First, a sharp temperature drop along with sensible-liquid phase, followed by a slower temperature decreased during phase-transition until solid-sensible phase. An intense temperature drop in the liquid-sensible phase can be considered as a desirable effect where the stored energy can be discharged quickly during the liquid phase, but it also indicates the material cannot store the heat effectively and tends to experience heat losses during storing mode. There is a notable temperature difference between phase transition during discharging and charging. It indicates the supercooling phenomenon takes place where solidification started earlier and occurred at a longer duration. It is caused by poor nucleation and crystal growth for pure paraffin. The results support the fact that unstable phase transition is unfavorable for actual latent heat storage, making it difficult to estimate the phase transition for pure paraffin, especially for designing the control system for the storage system. The effect of thermal cycling also increases the supercooling degree. It can be seen by comparing temperature differences along with phase transition during charging and discharging, where after 5,000 cycles, the final solidification

temperature falls substantially. It leads to a sluggish temperature drop during the solid-sensible phase, making the discharging duration much longer.

The addition of HDPE as a shape-stabilizer does not affect significantly during the discharging process. It can be seen from Fig. 6b that during the discharging process, the phase transition occurs as the non-isothermal phase change with a higher temperature gradient compared to the charging process. The heat releasing process, along with the liquid-sensible phase, is relatively slower than pure paraffin. Regarding this, the presence of HDPE helps to maintain the heat exchange rate, which is highly associated with the co-crystallization process with paraffin. The composite paraffin/HDPE still experiences supercooling at a relatively small temperature gradient compared to pure paraffin. The effect of thermal cycling also affects the discharging performance for composite paraffin/HDPE, especially for the discharging duration. Despite that, the temperature change for the phase transition between the charging and discharging process of composite paraffin/HDPE and the discharging duration is relatively similar to the charging process.

Fig. 7 shows the changes in the state of charge during the discharging process where all samples demonstrate an identical pattern where the rate of SoC reduction is relatively stable until it reaches the solid-sensible phase. For pure paraffin, the effect of thermal cycling makes the rate of SoC reduction change. It shows a slower SoC reduction between the first and 1000 cycles, and the rate of SoC reduction is accelerated after 5000 cycles. Even though the SoC falls considerably after 5000 cycles, it shows a poor heat releasing process during the solid-sensible phase. It can also be found for paraffin/HDPE at the same cycles, where the heat releasing becomes slower during the solid-sensible phase. In addition, between the first and 1000 cycles for paraffin/HDPE, the heat release is relatively stable without significant changes, except for the solid-sensible phase.

Fig. 8 compares the charging time between pure paraffin and paraffin/HDPE at different thermal cycles. The charging time for all samples becomes slower as the thermal cycling increase. It proves that the charging rate is decreased along with repeated use. Pure paraffin has the lowest charging rate after 5000 thermal cycles. The addition of HDPE helps to maintain the charging rate with only minor deterioration, especially for the first 1000 cycles. After 5000 cycles for paraffin/HDPE, the charging rate is decreased by 11.3%, much lower than pure paraffin by 15.3%. From this perspective, the presence of HDPE helps to maintain the charging rate of the paraffin substantially and reduce the effect of thermal cycling on the deterioration of the charging rate.

As seen in Fig. 9, the discharging rate for all samples is slower than the charging rate, which is a normal phenomenon for latent thermal energy storage material [37]. The critical aspect is the differences between charging and discharging duration. The difference between charging and discharging duration can be used to determine the

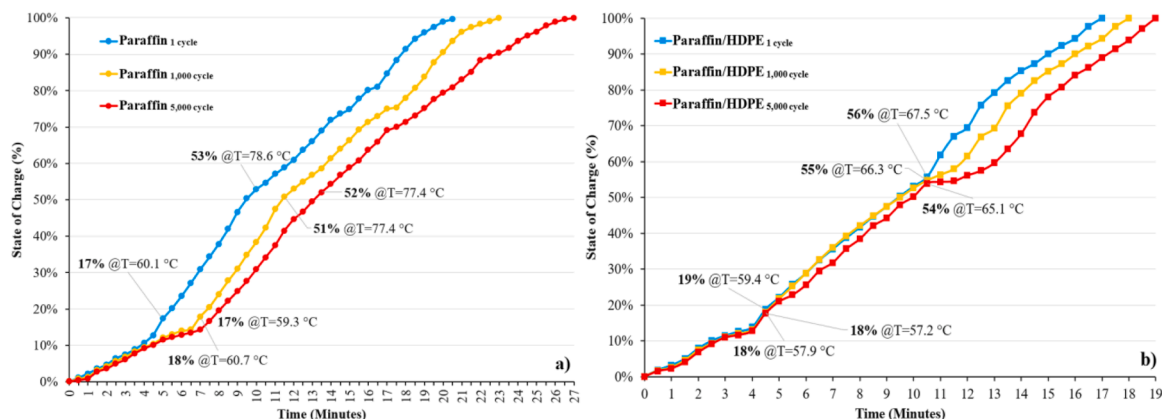


Fig. 5. State of Charge evolution during charging for: (a) pure paraffin, (b) paraffin/HDPE.

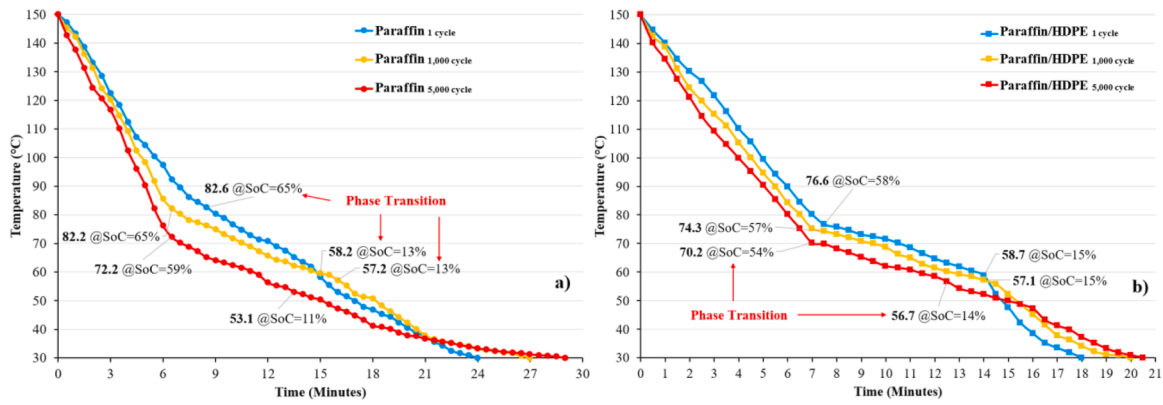


Fig. 6. Discharging profile for (a) pure paraffin, (b) paraffin/HDPE.

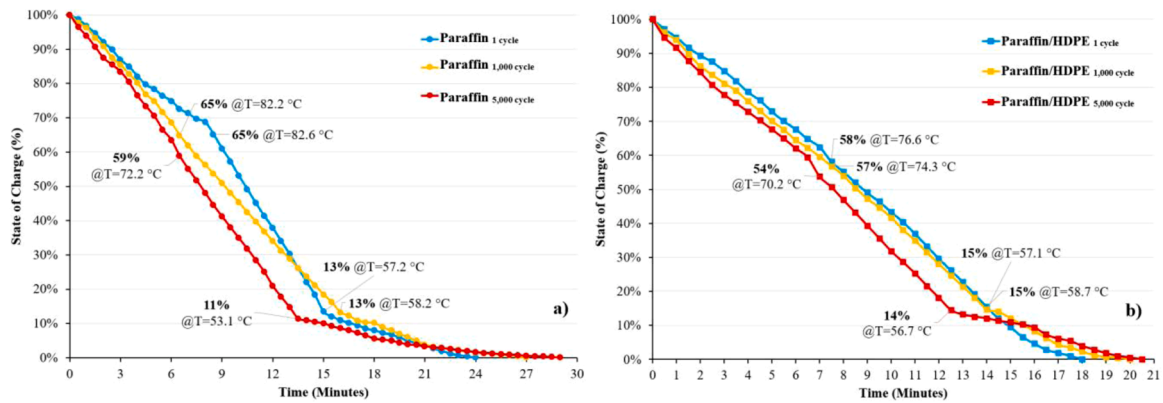


Fig. 7. State of Charge reduction during discharging for: (a) pure paraffin, (b) paraffin/HDPE.

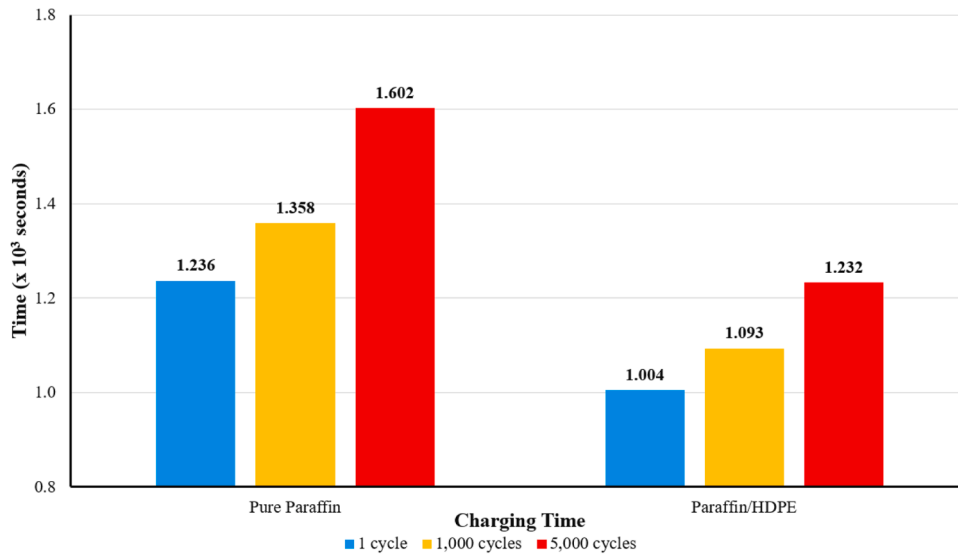


Fig. 8. Charging time comparison for paraffin and paraffin/HDPE.

performance of the storage material, which high differences indicate the storage material is not suitable to be used in a storage system. The discharging rate of pure paraffin is much higher than its charging rate, which can be said that the performance of pure paraffin is low. In contrast, paraffin/HDPE can maintain slight differences between charging and discharging rates, making it suitable for storage material. Furthermore, the effect of thermal cycling can be seen clearly for pure

paraffin, which decreases the discharging rate at 1000 and 5000 thermal cycles. The discharging rate is decreased by 12.6% and 18.2% for pure paraffin, while paraffin/HDPE only decreased by 8.3% and 11.5%.

Fig. 10 summarizes the total duration for each sample to complete one thermal cycle under different thermal cycling. Pure paraffin takes more time to complete one thermal cycle than composite paraffin/HDPE. The effect of thermal cycling is also shown clearly for pure

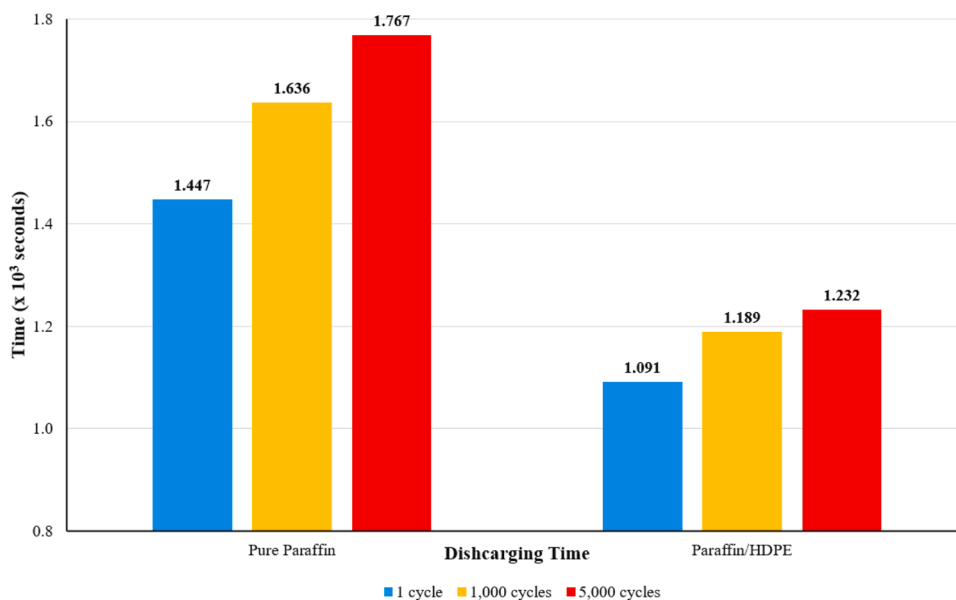


Fig. 9. Discharging time comparison for paraffin and paraffin/HDPE.

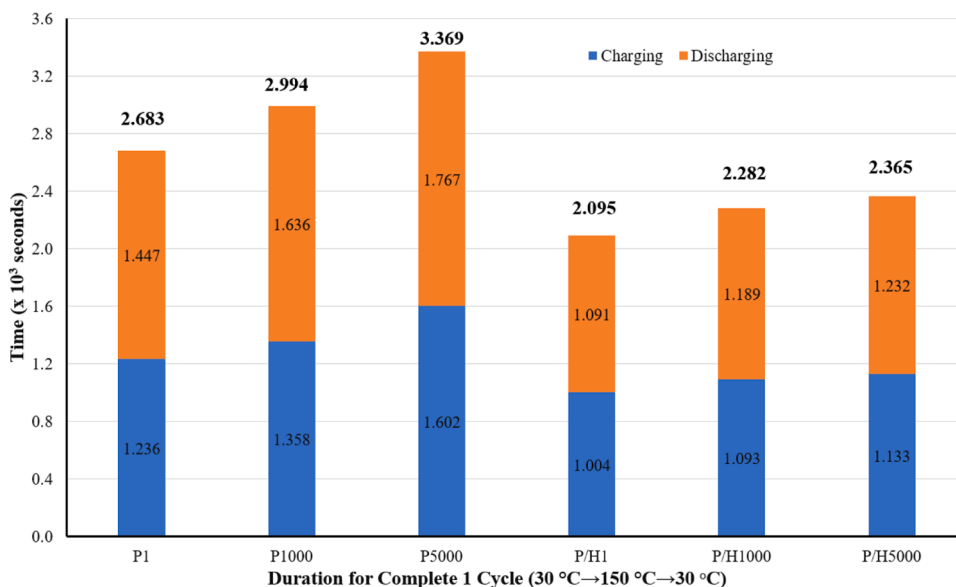


Fig. 10. Duration for complete one cycle for each sample at different cycling.

paraffin, which makes the duration to complete one thermal cycle is increased after a large number of thermal cycles.

It makes the rating performance of pure paraffin decrease significantly after repeated use. Thus, it has to consider the actual storage system, which uses paraffin as a storage material to maintain its performance. The decrease in rating performance is also observed for composite paraffin/HDPE but only a small portion compared to pure paraffin. It can be said that paraffin/HDPE can maintain its performance after repeated use, which is advantageous for the existing storage system. The reliability based on the charging and discharging time of paraffin/HDPE is better than pure paraffin. Thus, the performance of the storage system can be extended after a large number of thermal cycles.

3.3. Thermal stability

Thermal stability is crucial for thermal storage since it relates to the materials' reliability and durability during the operation. Thermal

properties and performance assessment show noticeable change for each sample after different thermal cycling. The decomposition process for each sample by mean TGA (thermal gravimetric analysis) curves is shown in Fig. 11.

First, pure paraffin starts to evaporate around 188°C and decompose with one-step degradation until 402°C. The effect of thermal cycling for paraffin can be observed distinctly after 5,000 cycles, where it starts to evaporate around 182°C and continue to decompose until 398°C. Composite paraffin/HDPE shows a different curve. In order to give a clear explanation, the TGA curve for HDPE is also plotted. HDPE starts to evaporate around 452°C and continue with a single go decomposition until 544°C. It is clear that paraffin and HDPE have different temperature degradation, which can be addressed as the reason for paraffin/HDPE, which have two-step degradation. For paraffin/HDPE, the first degradation is related to paraffin degradation, where the second step is the decomposition of HDPE. The change in decomposition rate is highly attributed to the paraffin, while HDPE can maintain its degradation rate

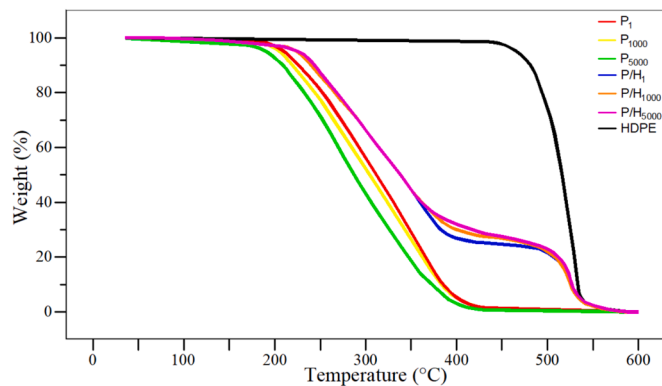


Fig. 11. TGA diagram for HDPE, Paraffin and composite paraffin/HDPE at 1, 1000 and 5000 cycles.

after many thermal cycles. Since the maximum temperature during the thermal cycling treatment is 150°C, far from the first temperature degradation of HDPE, it has no impact on the degradation rate of HDPE.

4. Conclusion

The present work shows the possibility to improve the performance of paraffin as a storage material in an active latent heat storage system by adding 20 wt% of high-density polyethylene/HDPE to form shape-stabilized phase change material. The use of the actual thermal cycle for life cycle assessment of the paraffin and paraffin/HDPE reveals the influence of thermal cycle treatment on the rating performance for both samples. The effect of the thermal cycle for pure paraffin can be observed according to the DSC curve where the melting temperature decreases and the freezing temperature increases, which enlarges the supercooling effect. The heat fusion of pure paraffin is also decreased after 1,000 and 5,000 thermal cycles by values 5.5% and 8.7%, respectively. The addition of HDPE has positive influences where it can maintain the differences between melting and freezing temperature relatively low, minimizing the supercooling effect of the paraffin. The decrease of heat fusion for paraffin/HDPE is much lower than pure paraffin, which only decreased by 1.6% and 2.9% after 1000 and 5000 cycles.

The amount of stored and released heat during each process is derived from temperature differences of heat transfer fluid and material's temperature and taken to determine the State of Charge (SoC). According to the thermal performance assessment, the effect of thermal cycling for all samples is noticeable, which reduces the charging and discharging rate. Pure paraffin requires a longer duration to complete one thermal cycle compared to paraffin/HDPE. The effect of thermal cycling for pure paraffin is substantial, both for charging and discharging. The duration to complete one thermal cycle for paraffin is increased by 10.4% and 20.4% after 1000 and 5000 cycles. In contrast, paraffin/HDPE maintained its rating performance which only increased by 8.2% and 11.5% after 1000 and 5000 cycles. The non-isothermal phase change caused by unstable phase transition is found for pure paraffin both for charging and discharging. Composite paraffin/HDPE shows almost perfect isothermal phase change with a slight temperature gradient during charging, proving that stable phase transition occurs for the composite. It emphasizes the effect of HDPE as a shape-stabilizer for paraffin which promotes a better phase transition. Stable phase transition is desirable since the temperature during phase transition can be estimated precisely, suitable for temperature-sensitive storage systems. The thermal reliability for pure paraffin is relatively lower than paraffin/HDPE since HDPE has a higher decomposition temperature than pure paraffin.

There is still, however, a limitation in this study. The presence of HDPE does not affect significantly during the discharging process where

non-isothermal phase change still occurs. Even though the temperature gradient for paraffin/HDPE during liquid-solid transition is smaller than pure paraffin, still it shows supercooling effect. Also, the addition of HDPE reduces the heat fusion of pure paraffin, which can be associated with the decrease in thermal storage capacity. Further studies are highly encouraged to evaluate the thermal capacity of paraffin/HDPE, including further characterization by using Scanning Electron Microscope and Fourier transform infrared spectroscopy to understand the effect of thermal cycling on the structure and chemical composition of the sample, which might be helped to improve its discharging performances.

CRedit authorship contribution statement

Dwi Rahmalina: Conceptualization, Methodology, Resources. **Reza Abdu Rahman:** Data curation, Investigation, Writing – review & editing. : Formal analysis, Supervision.

Declaration of Competing Interest

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

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