1. INTRODUCTION

The rise in energy demand requires extensive effort to maximize energy mix from renewable sources [1]. The approach can be taken by improving renewable energy sources in wind farms by addressing suitable configurations and producing a more effective power coefficient [2]. However, wind energy and photovoltaic systems depend on electric batteries considered uneconomical. Different actions can be done by utilizing solar thermal conversion. The method is favorable since it utilizes thermal energy storage (TES), which is considered low cost compared to electric battery. Also, TES offers a higher flexibility which make it suitable for numerous applications [3].

TES utilization of sensible material is proven to be a suitable method to store heat energy and is already used in many applications, particularly for hot water supply [4]. Thus, it has achieved a commercial-stage which makes the system’s cost highly affordable. Improvement in the storage capacity for the TES can be taken by using phase change material (PCM) [5]. It allows the system to store a better energy capacity than the sensible system [6-8]. The PCM has a higher storage capacity in terms of volumetric and gravimetric. It can be achieved since the system uses latent heat that stores better thermal energy during phase transition. Therefore, the operation of latent heat storage (LHS) as thermal energy storage can meet the merit of storage requirements, promoting a higher level with a better storage capacity that potentially significantly reduces the cost of storage [9].

Paraffin wax (PW) is one of the ideal PCM in TES for low to medium temperatures. The operation of PW can be used for temperatures above 100°C, combining the latent heat of fusion and liquid sensible of the PW. Thus, the system’s overall capacity and operational consideration can be appropriately adjusted. Low thermal conductivity can be modified by adding solid additives as thermal enrichment to provide sufficient heat transfer [10]. The solid additives can be taken from volcanic ash, which improves the thermal conductivity up to 200% [11]. Another solid additive based on nanocarbon is also suitable for thermal conductivity improvement [12].

Acceleration on the heat transfer rate can be combined by modifying the heat exchanger within the storage tank [13]. It is affected by a higher surface area between the storage material and heat exchanger which makes the average heat transfer rate can be improved. Different approach also can be taken by adjusting the inclination angle [14], modified the storage tank with fin [15], and using nanofluid as heat transfer fluid (HTF) [16]. Therefore, the system can provide excellent heat transfere, which utilizes high thermal conductivity additives, a proper heat exchanger and suitable working fluid in the storage tank.

The material storage in energy storage system experiences repeating cycle during the operation [17]. It potentially reduces the overall performance of the system until certain cycles. The condition is generally found for the high charging rate electrical battery which causes a higher aging rate and reduces the state of health after a specific cycle [18]. The high heat transfer rate for TES leads to a high cycling process, which potentially reduce the performance of the storage material, especially for long-term operation.

Long-term operation is essential to ensure the system works appropriately as storage material [19]. It becomes one particular aspect vital for PW as TES material. Performance degradation occurs as the direct effect of repeating the
operation. The study by Wang et al. [20] showed that thermal capacity decreases after 100 thermal operations. The decrement ranges between 1-3% of the total enthalpy of fusion. Another study indicates a significant decrement in thermal capacity up to 25.2% for PW after 200 thermal cycles. The highest cycling operation was set at 10,000 thermal cycles. It implies the same pattern where the thermal capacity of the storage material decreases around 9.1% [21] and 12.7% [22]. Despite the different results from various studies, it signifies the tendency of thermal capacity decrement after thermal treatment, which is a high risk to the storage system's operation.

A practical method to protect the PW from degradation after repeating thermal cycles is done by using polymer to form composite PCM (cPCM) [23-25]. It is also advantageous since the thermal stability of PW can be improved where cPCM has a lower supercooling degree compared to pure PW. The supercooling degree occurs due to the rapid freezing process, which enlarges the PCM's deviation of melting/freezing temperature [26]. The phenomenon is caused by mushy region formation that disrupts the heat release process during solidification [27]. Adding high-density polyethylene (HDPE) for the cPCM reduces the impact since it maintains the freezing temperature relatively close to its melting temperature. Hence the supercooling degree is reduced [28]. The method is preferable to ensure the operation of PW in a latent heat system (LHS) and protect the storage material from thermal degradation. However, the main drawback for adding HDPE is a lower enthalpy which make the proper ratio for HDPE should be evaluated for the cPCM.

The critical performance for TES system is thermal capacity, including its ability to absorb/release heat during the heating and cooling stage [29-31]. Thus, it can be used as specific reference for evaluating the long-term performance of cPCM. Despite that, the proper ratio of HDPE needs to be examined to provide sufficient thermal capacity and protection to the PW as TES material. The assessment was performed on 10,000 heating cycles at 55-65°C. The proposed temperature is aimed to provide a repeating melting and solidification process for the cPCM. After thermal treatment, the aged sample was evaluated through differential scanning calorimetry (DSC), which can be used as the basic information on the thermal properties of the evaluated samples. Moreover, performance assessments through heating and cooling tests were conducted before and after thermal treatment. Therefore, the impact of the heating cycle can be observed more thoroughly, which can be used as an essential consideration for the application of LHS.

2. MATERIALS AND METHOD

2.1 Sample detail and characterization

Table 1 displays the detailed sample and ratio used in this study. The industrial grade PW and HDPE were used in this work. According to the study [32], the HDPE content is limited to reduce significant decrement on the storage capacity. Thus, the work used 15wt% as maximum reference with interval 5 wt% HDPE as variation for evaluating more in detail HDPE role within the composite.

The mixing process for the cPCM was performed in the liquid state by first melting the HDPE and then pouring the liquid PW gradually. The mixture was stirred slowly for about half an hour. Then, the mixture was rested at room temperature for solidification. After that, the mixture was heated in the electric oven for remelting and repeating the mixing process. It aimed to ensure the proper distribution between the HDPE and PW. Finally, the sample was cooled in the container for thermal treatment. The total mass of the sample was set to 10 grams.

<table>
<thead>
<tr>
<th>Identifier</th>
<th>Wax</th>
<th>HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>cPCM1</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>cPCM2</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>cPCM3</td>
<td>85</td>
<td>15</td>
</tr>
</tbody>
</table>

The sample in Table 1 were characterized for its thermal properties using calorimetry method. To provide a clear basis reference, the samples were compared before and after cycling treatment. Thus, the effect of HDPE content, including the impact of cycling treatment can be evaluated notable. Also, charge/discharge behavior was also evaluated through static heating/cooling scheme.

2.2 Cycling treatment

The thermal treatment was conducted by heating/cooling samples repeatedly. The sample temperature was set as a cycle indicator to ensure a valid reference for the thermal treatment [33]. Figure 1 presents the schematic of thermal treatment as the cycling process. The initial temperature of the sample was set at 55°C. The heating process was performed by introducing heat into the sample until it reached 65°C. At this point, the sample undergoes half cycle. The sample was then moved to the cooling bath. It aimed to remove the heat from the sample until it reached 55°C. After completing the cooling process, the sample has taken one full cycle. The process was repeated up to 10,000 times.

![Figure 1. Temperature-based thermal cycling treatment](image)

The temperature of sample was monitored using thermocouple at three different positions. The oil and water temperature were also monitored to ensure steady heating/cooling process during the treatment. The process was performed manually for heating/cooling the sample, which
require several adjustments during treatment such as changing the oil and water after 500 cycles. Despite that, the effective duration to complete the treatment process was approximately 420 hours (without counting for the adjustment during the process).

2.3 Heating/Charging evaluation

The characteristic of the thermal behavior from the tested sample was examined using the static charge/discharge scheme. The examination was performed using a circular charging/discharging process, which promotes convective heat transfer [34]. It is suitable for the actual implementation of passive and active TES. Figure 2 presents the illustration for the circular charging/discharging test. The process was started by heating the sample from room temperature (30°C) to the final temperature (110°C). The sample temperature was recorded simultaneously at three locations (Figure 2) using multiple thermocouples. The oil temperature was maintained steadily at 150°C using an electric heater during this process.

![Figure 2. Circular charging/discharging evaluation](image)

Once the sample reached the final temperature of 110°C, the container was switched into the cooling bath. The cooling bath was filled with water (at a temperature of 15°C). The volume of water was set at 500 ml to avoid temperature increment during the heat release from the high-temperature sample. From the examination, performance characteristics of the sample can be analyzed for the condition before and after thermal treatment.

3. RESULTS AND DISCUSSION

Figure 3a shows the typical profile curve of the PCM before thermal treatment. The identical pattern of PW consists of two distinct peaks, which are identified as solid transition and melting process (second peak). The temperature of the melting process for PW is obtained at 60.22°C. The addition of polymer for the cPCM causes a small transformation for the region under the first and second peaks. The decrement is observed notably in the second peak. It can be observed from the change in the cPCM melting point, which varies between 58.42-59.74°C. In addition, the third peak appears for the cPCM at a temperature of 98°C. It is close to the melting point of HDPE. Since the peak at this area is relatively small, it can be assumed that most HDPE melts in the second peak along with PW, which is in good agreement from previous studies [35-37].

The change of the curve pattern is observed distinctively after thermal treatment (Figure 3b). It changes the enthalpy of fusion and critical temperature of the tested sample. As seen in Figure 4a, both values are shifted for the PW and cPCM.

![Figure 3. DSC pattern for the tested sample](image)

The PW has the highest decrement in the enthalpy of fusion, around 5.1%. It affects the total thermal capacity of the PW, which is undesirable for the actual operation of the LHS system. The degradation of the thermal capacity causes the deterioration of the operational aspect, particularly for the power performance, which is extremely important for the active system (using a heat exchanger) [38]. Compared to PW, the composites demonstrate suitable performance without experiencing significant degradation on the enthalpy of fusion. The decrement is unsubstantially, which proves the good thermal stability of the cPCM due to the addition of HDPE.

The variation of HDPE can be observed based on the change of melting enthalpy. The melting enthalpy of cPCM has the highest decrement of the melting enthalpy (2%) after thermal treatment. The addition of higher HDPE content (10 wt% and 15 wt%) maintains sufficient melting enthalpy of the PW where the decrement is less than 1%. The effect of thermal treatment is also indicated by the change in supercooling degree (Figure 4b). PW has the highest supercooling degree of 8.01°C. After 10,000 thermal treatments, it gets higher where
the supercooling degree increases by 9.65°C. Repeating the heating process amplifies the hysteresis effect, which alters the melting and freezing temperature of PW [39]. The composite PCM demonstrates a lower supercooling, particularly for cPCM with HDPE content of 15 wt%. It signifies the role of HDPE, which act as a shape stabilizer that maintains the solid-liquid transition of PW.

Further observation is performed using a scanning electron microscope (SEM), as presented in Figure 5, by comparing the PW and cPCM before and after thermal treatment. The morphological change for PW is observed notable after 10,000 thermal treatments (Figure 5c). There is void formation (blue square) which is affected by the shrinkage effect that appear after repeating the cycling process [40]. It is highly related to the nature of the melting and solidification process of PW, which generally forms a mushy region. In contrast, the cPCM indicates different morphology since the local agglomeration is observed (red square in Figure 5b).

The effect of thermal treatment is found as phase segregation (green arrow in Figure 5d). It is caused by the differences in thermophysical properties between PW and HPDE which causes separation after repeating the melting process. In addition, the treatment was performed without inert gas which may causes oxygen molecules diffuse into the sample during the treatment. It is possibly to cause chemical crystallization which make migration on the molecular structure of PW and HDPE [41]. Despite that, it confirms the positive influence of HDPE, which protects PW from the void formation. As a result, the melting/freezing temperature of cPCM can be maintained effectively after 10,000 thermal treatments.

(a) Latent heat
(b) Supercooling degree

Figure 4. The change of thermal properties for the tested sample

(a) Paraffin Wax before thermal treatment
(b) cPCM before thermal treatment
(c) Paraffin Wax after thermal treatment
(d) cPCM before thermal treatment

Figure 5. SEM images for the paraffin wax and cPCM
Figure 6a compares the heating rate obtained from the circular charging test. It seems the composite has a higher heating rate compared to PW. Two factors contribute to this phenomenon. The relative thermal conductivity of HDPE is generally higher than paraffin, and the decrement on the thermal capacity of the composite (Figure 4a). It accelerates the heating process for the composite. However, the critical point is the heating rate change after thermal treatment. The heating rate of PW is decelerated at around 13.4\%, while the composite cPCM experiences deceleration at around 6.2\%. It indicates that HDPE should be added at the proper ratio to maintain a sufficient heating rate after thermal treatment.

![Graph](image1)

**Figure 6.** Comparison of the charging/discharging rate

The thermal treatment also affects the cooling rate during the annular discharging process. As seen in Figure 6b, the cooling rate for the aged samples is increased. It confirms the change in the supercooling degree, which indicates the sample experiences a rapid solidification process (Figure 4b). It can be observed clearly for the cPCMs, which experiences a higher increment on the cooling rate around 7.05\%. Interestingly, the cooling rate for pure PW only increases around 6.42\%. It implies that adding 5 wt\% HDPE has a drawback, promoting a higher cooling rate and rapid solidification after thermal treatment. Adding a suitable ratio of HPDE (10 wt\% and 15 wt\%) contribute positively where the cooling rate can be maintained at a relatively smaller deviation after thermal treatment. Therefore, the minimum ratio of HDPE for PW is recommended at 10 wt\% to provide suitable thermal reliability that can maintain the heating and cooling rate at the desired level. It protects the PW from thermal stress and contributes positively to maintaining PCM's long-term operation in the LHS system.

The key finding shows the proper ratio of HDPE protect the PW from extreme thermal degradation. It ensures the operation of LHS can be managed effectively. The recent trend in LHS development uses multiple storage tank [42-44] to provide a higher storage capacity. Thus, using cPCM for the system reduces the drawback of high thermal cycling which promote a better charge/discharge condition of the system. Moreover, combined storage system which operates at elevated temperature require a more stable PCM. Thus, the approach to use cPCM can be considered as suitable method to maintain long-term operation of the high temperature system.

### 4. CONCLUSIONS

The long-term operation of PW as PCM for thermal storage applications was evaluated intensively. The cycle treatment of the PCM was repeated up to 10,000 times and showed significant influences on the thermal behavior, which altered its performance. The change in storage capacity with respect to the enthalpy of fusion and increment on the supercooling is found for the aged samples. Adding polymer (HDPE) at a suitable ratio is proven to maintain the long-term performance of PW. It can be seen from the average enthalpy of fusion, which only slightly decreases around 0.5 J/g for the composite with 15 wt\% HDPE compared to pure PW. It is caused by the presence of HDPE, which generally has better thermal reliability than PW. It protects the PW from significant degradation due to the repeating cycling process. According to the finding, the minimum ratio of HDPE is 10 wt\%.

Further research can be conducted to explore new method for reduce the thermal aging and synthesize new PCM that able to withstand from extreme thermal degradation. In addition, the proposed method which using HPDE can be evaluated for sensitive temperature application and high cycling TES system such as solar dryer. Also, designing new cycling apparatus that can operate autonomously is desirable to reduce the uncertainty and time for conducting thermal treatment. It makes the devopment of stable and durable PCM can be extended in a higher level which lead tp a high quality material for thermal storage application in the future.

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### REFERENCES


