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Thermophysical Properties of Inorganic Phase-Change Materials Based on MnCl$_2$·4H$_2$O

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Abstract: Manganese (II) chloride tetrahydrate, classified as an inorganic phase-change material (PCM), can be used as a thermal energy storage material, saving and releasing thermal energy during its phase transitions. In this study, thermophysical properties, such as phase change temperatures, latent heat, and thermal conductivities, of four types of MnCl$_2$·4H$_2$O PCMs were investigated under single and dual phases (liquid-, solid-, and dual-phase PCMs) using differential scanning calorimetry (DSC) and a heat flow meter. PCMs with a liquid or dual phases exhibited superheating issues, and their melting temperatures were 7 to 10 $^\circ$C higher than the reference melting temperatures. The PCMs had latent heats between 146 and 176 J/g in the temperature range of 23 to 45 $^\circ$C under the endothermic process. Severe supercooling during the exothermic process was observed in all as-received specimens, but was mitigated in the homogenization-treated specimen, which sustained an increase in solidification temperature of about 15 $^\circ$C compared with the as-received and treated PCMs. The diffusivities of the PCMs in the solid phase were higher than those in the liquid phase. During the initial holding time of the endothermic process, the PCM in the liquid phase could not be fully solidified due to an insufficient initial holding time and very low diffusivity, which caused superheating during the DSC measurement. Moreover, in the exothermic process, a fast cooling rate of 5 $^\circ$C/min and low thermal diffusivity caused supercooling. In particular, the diffusivity of the liquid PCM was lower than those of the solid PCM and other PCMs, which caused extremely high supercooling during the DSC measurement. This paper provides the thermophysical properties of MnCl$_2$·4H$_2$O PCMs, which are not available in the literature. The homogeneity of PCMs in their initial states and their heating/cooling rates were identified, and constitute important factors for accurately measuring the thermophysical properties of PCMs.

Keywords: phase-change material; MnCl$_2$·4H$_2$O; phase-change temperature; thermal diffusivity; supercooling

1. Introduction

According to a report from the U.S. Energy Information Administration, in 2021, 38% of worldwide energy was consumed in residential buildings. Specifically, 58% of residential energy consumption was used for heating and cooling buildings [1]. A thermal energy storage (TES) system is considered an ideal solution to reduce energy consumption in heating or cooling buildings. TES systems hold thermal energy in the form of hot or cold materials for later utilization [2].

TES systems can be classified by how energy is stored: sensible heat, latent heat, and chemical TES systems [2–4]. Latent heat TES systems can store 5–14 times more energy than sensible heat TES systems [5].

Phase-change materials (PCMs) are well-known TES materials, utilizing both sensible and latent heat to store energy. PCMs are classified according to raw materials: inorganic,
organic, and eutectic PCMs. Inorganic PCMs are formed from salt hydrates and metallic alloys [6,7].

Salt hydrate PCMs have a formula of AB·nH$_2$O, where AB is a working agent, and its material behavior can be determined from the binary phase diagram of the working agents AB and H$_2$O. Additionally, LiClO$_3$, KF, Mn(NO$_3$)$_2$, LiNO$_3$, Zn(NO$_3$)$_2$, and CaCl$_2$ are representative working agents for salt hydrates. The melting temperature of salt hydrate PCMs is increased by increasing the composition of the working agent in the hypereutectic region. Compared with organic and eutectic PCMs, low-cost inorganic PCMs have a high latent heat of fusion, high thermal conductivity, small volume change, and narrow phase-change temperature range. However, supercooling is one of the drawbacks of inorganic PCMs, leading to operating temperature delay and phase separation [5,7–10].

Accurate measurement of thermophysical properties is a prerequisite for the development and application of PCM-based TES systems because operating temperature and latent heat determine the performance of TES systems. In most studies, differential scanning calorimetry (DSC) methods under heating and cooling rates of 5–10 °C/min have been employed to measure thermal properties of PCMs, such as melting temperature, solidification temperature, and latent heat [11–17].

Many researchers have proposed the thermophysical properties of single-phase PCMs via DSC measurement. Prakash et al. [14] measured the thermophysical properties of a mixture of inorganic PCMs composed of Mg(NO$_3$)$_2$·6H$_2$O and Na$_2$SO$_4$·5H$_2$O. The properties were compared for three different weight ratios (70:30, 80:20, and 90:10) of Mg(NO$_3$)$_2$·6H$_2$O and Na$_2$SO$_4$·5H$_2$O, and the TES capacity increased with an increase in Mg(NO$_3$)$_2$·6H$_2$O composition. Wang et al. [15] evaluated the thermal performance of n-octadecane micro-encapsulated PCMs using DSC. The latent heat and melting temperature were 160 kJ/kg and 26.5 °C, respectively. The PCMs exhibited appropriate thermal energy storage capability over a temperature range between 5 and 45 °C at heating/cooling rates of 2–10 K/min. Drissi et al. [12] investigated the influence of damage on PCMs’ thermodynamic properties. The highlighted result was that the damaged PCMs suffered a loss of latent heat of about 12% compared with the nondamaged PCMs. Until now, many researchers have investigated properties of various PCM composites, including graphene, graphite, core shell, and nanocomposites, by DSC [18–27].

Supercooling and phase segregation are common issues in inorganic PCMs. They can cause loss of energy storage capacity and delay in phase-change temperature. Therefore, many researchers have studied how to solve these drawbacks. Atul Sharma et al. [5] suggested adding a nucleating agent, such as nucleon, which can easily initiate crystal formation. Sutjahja et al. [28] studied the effects of chemical nucleator additives such as SrCl$_2$·6H$_2$O, BaCO$_3$, and K$_2$CO$_3$ on the supercooling behavior of CaCl$_2$·6H$_2$O PCM. Among the additives, SrCl$_2$·6H$_2$O showed the best performance in preventing supercooling. Palittin [10] adopted sonocrystallization by using ultrasound radiation to crystallize CaCl$_2$·6H$_2$O. In order to minimize phase segregation, thickener agents have been used. Absorbent polymer [29], polyethylene glycol [30], silicon rubber [31], cellulose derivatives [27,29,32], and polyvinyl alcohol [29] have been added as thickening agents to inhibit or minimize phase segregation.

An inorganic PCM, MnCl$_2$·4H$_2$O, was confirmed to increase latent heat and decrease supercooling when it was used as an additive in Mn(NO$_3$)$_2$·6H$_2$O PCM [33]. However, there have been no previous studies regarding the properties of MnCl$_2$·4H$_2$O as a PCM rather than an additive. The objective of this study was to measure and investigate the thermophysical properties of inorganic MnCl$_2$·4H$_2$O PCMs. The specimens were delivered in liquid, solid, and dual phases. The scope of investigation comprised (1) superheating and supercooling analyses of the thermophysical properties (melting/solidification temperatures and latent heats) of single-phase PCMs under endo/exothermic processes using DSC; (2) in particular, analyzing the supercooling behavior of PCMs, which were treated to a homogeneous condition; and (3) determining thermal conductivities and thermal diffusivities analyses of single-phase PCMs.
2. Materials and Methods

2.1. Specimen Materials

Four macro-encapsulated inorganic PCMs based on MnCl\textsubscript{2}·4H\textsubscript{2}O were evaluated in this study. Specimens 1 to 4 were based on MnCl\textsubscript{2}·4H\textsubscript{2}O compositions, and an additive was added and modulated to control the melting temperatures. Table 1 lists the reference melting temperatures provided by the supplier and phases of the as-received and treated PCMs.

The spectra of the PCMs were collected using Fourier transform infrared spectroscopy (FTIR) and compared with the spectrum of pure MnCl\textsubscript{2}·4H\textsubscript{2}O on the Willey spectral DB [34] (Figure 1). The base PCM, MnCl\textsubscript{2}·4H\textsubscript{2}O, was confirmed by the molecular formula and spectrum data [35,36]. As shown in Figure 1, the modulations of MnCl\textsubscript{2}·4H\textsubscript{2}O compositions were between 3600 and 3100 cm\textsuperscript{−1} and between 1700 and 1600 cm\textsuperscript{−1}. The modulations of additives were between 1100 and 900 cm\textsuperscript{−1}. The specimens were delivered in different phases. As-received specimen 1 had fluidity, so it was marked as a liquid phase. Some parts of specimen 2 had a solid phase, while other parts had a dual solid and liquid phase. As-received specimens 3 and 4 had a solid phase. Specimen 2, with a dual phase, was homogenized through reheating in an oven at 50 °C for 15 min just before measurement.

Table 1. Phase of specimens at room temperature.

<table>
<thead>
<tr>
<th>PCM</th>
<th>Reference Melting Temperature</th>
<th>Phase</th>
<th>As-Received</th>
<th>Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen 1</td>
<td>21 °C</td>
<td>Liquid</td>
<td>Liquid</td>
<td>-</td>
</tr>
<tr>
<td>Specimen 2</td>
<td>23 °C</td>
<td>Solid</td>
<td>Solid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Specimen 3</td>
<td>26 °C</td>
<td>Solid</td>
<td>Solid</td>
<td>-</td>
</tr>
<tr>
<td>Specimen 4</td>
<td>30 °C</td>
<td>Solid</td>
<td>Solid</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 1. FTIR spectra of the PCMs: (a) reference MnCl\textsubscript{2}, (b) specimen 1, (c) specimen 2, (d) specimen 3, and (e) specimen 4.

2.2. Measurement

In this study, DSC measurements were conducted with a DSC Q 200 from TA Instruments (New Castle, DE, USA) with a temperature accuracy of 0.1 °C and an enthalpy precision of 0.1% [37,38]. The samples with weights between 6 and 7 mg were sealed in
aluminum pans and lids, and were measured in a chamber purged with nitrogen. The temperature profile for DSC temperature is given in Figure 2.

![Dynamic DSC testing temperature profile.](image)

The first step was a holding stage in which the sample was held for 1 min at 15 °C to stabilize the test chamber temperature. The second step was a heating stage in which the sample was heated from 15 to 105 °C with a heating rate of 5 °C/min. The third step was a holding stage in which the sample was held for 1 min at 105 °C to stabilize the chamber temperature. The last step was a cooling stage in which the sample was cooled from 105 to −40 °C with a cooling rate of 5 °C/min. The thermophysical properties of the PCMs were measured three times per condition. The phase change of PCMs occurs within a temperature range, but the peak temperature in a DSC thermogram was defined as the melting temperature under the endothermic process, or the solidification temperature under the exothermic process in this study.

The thermal conductivity of a PCM is an important factor in assessing the thermal performance of PCMs in the solid-state or liquid state [39]. In this study, a heat flow meter FOX 314 from TA Instruments was used to measure the thermal conductivities of the PCMs. The heat flow meter was designed to conform to the ASTM C 518-04 [40].

The thermal conductivities of PCMs having only single phase (either liquid or solid phase) were measured under the conditions in Table 2. The temperature of the lower plate was higher than that of the upper plate, and high sensitivity heat flow transducers and thermocouples were attached to both plates. Moreover, the heat flow equipment can measure thermal conductivity with a resolution of 0.6 µV and the thickness of the sample with an accuracy of 0.025 mm.

<table>
<thead>
<tr>
<th>PCMs</th>
<th>Temperature for Liquid Phase Conductivity (°C)</th>
<th>Temperature for Solid Phase Conductivity (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Upper Plate</td>
<td>Lower Plate</td>
</tr>
<tr>
<td>Specimen 1</td>
<td>21</td>
<td>35</td>
</tr>
<tr>
<td>Specimen 2</td>
<td>21</td>
<td>35</td>
</tr>
<tr>
<td>Specimen 3</td>
<td>33</td>
<td>43</td>
</tr>
<tr>
<td>Specimen 4</td>
<td>39</td>
<td>49</td>
</tr>
</tbody>
</table>

Thermal diffusivity indicates the ability of a material to transfer thermal energy. Accurate measurement of thermal diffusivity is necessary to make applications and control thermal energy for materials which have conduction, insulation, or have withstood temperature change.
The thermal diffusivity is given by

\[ \alpha = \frac{k}{\rho C_p} \]  

(1)

where \( \alpha \) is the thermal diffusivity, \( k \) is the thermal conductivity, \( \rho \) is the density, and \( C_p \) is the specific heat capacity.

3. Results and Discussion

3.1. Thermal Property of As-Received PCMs

The DSC results provided the onset temperature (\( T_o \)), peak temperature (\( T_p \)) as the melting temperature (\( T_m \)), end temperature (\( T_e \)), and latent heat (\( \Delta H \)) of the PCMs. Figure 3 shows thermograms of single-phase as-received PCMs using the test thermo-profile in Figure 2, and the measured thermophysical properties are summarized in Table 3.

During the endothermic process of liquid-phase specimen 1 and solid-phase specimen 2, hills with two peaks were observed: the first peak at the melting temperature and the second peak resulting from superheating. The observation of multiple peaks indicated the test material had a crystalline structure or was multiphase. Although specimens 1 and 2 were marked as liquid and solid phases, they would have dual phases in which the second phase was assumed to have only a small portion. Inferring by comparing the magnitude of the second peak, the proportion of the second phase in specimen 2 was smaller than that in specimen 1.

The observation of multiple peaks coincides well with Liu and Chung’s results [41], where DSC thermograms with multiple peaks were found under endothermic reaction.
The reason was that the PCM had multiphases because additives were partially unmelted during heating. On the other hand, specimens 3 and 4 showed a single peak under the endothermic process, which was evidence of a single phase.

Table 3. Thermophysical properties of PCMs under endothermic and exothermic processes.

<table>
<thead>
<tr>
<th>PCMs</th>
<th>Process</th>
<th>Onset Temp. (°C)</th>
<th>Peak Temp. (°C)</th>
<th>End Temp. (°C)</th>
<th>Latent Heat (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen 1</td>
<td>Endothermic</td>
<td>26.6</td>
<td>31.3</td>
<td>43</td>
<td>157.3</td>
</tr>
<tr>
<td>Specimen 2</td>
<td>Endothermic</td>
<td>27.2</td>
<td>31.1</td>
<td>43</td>
<td>176.8</td>
</tr>
<tr>
<td>Specimen 3</td>
<td>Endothermic</td>
<td>23.6</td>
<td>28.9</td>
<td>44</td>
<td>146.0</td>
</tr>
<tr>
<td>Specimen 4</td>
<td>Endothermic</td>
<td>28.9</td>
<td>33.8</td>
<td>45</td>
<td>161.0</td>
</tr>
<tr>
<td>Specimen 1</td>
<td>Exothermic</td>
<td>−1.8</td>
<td>−0.5</td>
<td>−7.6</td>
<td>135.4</td>
</tr>
<tr>
<td>Specimen 2</td>
<td>Exothermic</td>
<td>−5.7</td>
<td>−1.8</td>
<td>−10.3</td>
<td>152.5</td>
</tr>
<tr>
<td>Specimen 3</td>
<td>Exothermic</td>
<td>−4.0</td>
<td>−1.6</td>
<td>−9.5</td>
<td>131.0</td>
</tr>
<tr>
<td>Specimen 4</td>
<td>Exothermic</td>
<td>8.6</td>
<td>3.7</td>
<td>−6.4</td>
<td>50.7</td>
</tr>
</tbody>
</table>

All single-phase PCMs showed extreme supercooling under the endothermic process. Specimens 1 and 3 showed two connected peaks, whereas specimen 2 showed one peak, and specimen 4 showed two separated peaks, which occurred as a small eutectic impurity peak during the exothermic process and as a main peak for the supercooling issue [47]. In Kuznik and Vergone’s study on paraffin-based organic PCMs [48], the supercooling was only about −5 °C. However, their measured solidification temperatures were lower by 30–40 °C than their measured melting temperatures (Table 3).

In inorganic PCMs based on salt hydrates, supercooling is related to a slow rate of nucleation or nuclei growth [9,45]. In addition, DSC has a cooling rate much higher than field applications. A sufficiently slow cooling rate should be selected considering supercooling. Drissi [12] demonstrated that a much slower cooling rate, rather than a typical cooling rate between 5 and 10 K/min, was suitable for low-thermal-conductivity PCMs to avoid supercooling. However, low cooling rates can reduce the signal-to-noise ratio, which reduces the accuracy of measurement.

The latent heats of specimens 1 to 4 under the endothermic process were 157.3, 176.8, 146.0, and 161.0 J/g, respectively, at temperature ranges of 23 to 44 °C. The latent heats of fusion for specimens 1 to 4 under the exothermic process were 135.4, 152.5, 131.0, and 157.2 J/g, respectively. The latent heats of PCMs under the endothermic process were similar or higher values compared with the commercial products, having latent heats of 120 to 180 J/g at similar operating temperatures of 20 to 50 °C [49–52].

3.2. Thermal Property of Treated PCM

Dual-phase specimen 2 was homogenized into a liquid phase and evaluated by DSC. From the results in the previous section, single-phase specimen 2, marked as solid phase, contained a small amount of liquid phase.

The thermogram of treated specimen 2 (Figure 4) showed clear differences from that of the as-received-single-phase specimen 2 (Figure 3b) under endothermic and exothermic processes.

During the endothermic process, treated specimen 2 exhibited a distinct single peak, whereas as-received solid specimen 2 had two peaks (Figure 3b). The measured onset
temperature, melting temperature, and latent heat were 26.9 °C, 31.9 °C, and 149.8 J/g, respectively, which were similar to the measured properties of as-received specimen 2 under the endothermic process.

A similar degree of superheating was observed compared to the reference melting temperature. This implies that the degree of superheating is related to the state of the specimen at the first stage of DSC. Relatively high superheating was found in the following three specimens: specimen 1, which had a melting temperature lower than room temperature and was marked as liquid phase; as-received single-phase specimen 2, which was marked as solid phase and presumably had a small portion liquid; treated specimen 2, which had a homogeneous liquid phase. A liquid phase at the beginning could not be fully solidified in the first step of the DSC thermoprofile, as shown in Figure 2, which caused phase inhomogeneity during the endothermic process. This phenomenon is also related to the thermal diffusivity of the liquid phase, which is explained in the next section.

During the exothermic process, treated specimen 2 showed two exothermic peaks of onset temperatures of 15.8 and −9.5 °C, solidification temperatures of 13.5 and −10.7 °C, and latent heats of 36.6 and 12.6 J/g. The supercooling was mitigated via homogenization, but not fully prevented. The exothermic peak temperatures of treated specimen 2 were very similar to those of specimen 4, which had a melting temperature distinguishable from the room temperature.

Supercooling during the exothermic process can be caused by incongruent solidification behavior caused by phase segregation, low rate of nucleation, or the fast cooling rate of the DSC test. The multiple peaks that occurred under the exothermic process were also discussed by Vigo et al. [53]. They reported the thermophysical properties of fiber-containing PCM based on salt hydrates. The specimen was maintained at least 24 h at 293 K/45% relative humidity (RH) under full liquid phase prior to the DSC test at heating/cooling rates of 10 K/min. A single peak was observed under the endothermic process, but one major peak and two minor peaks were observed under the exothermic process. The incongruent solidification behavior of the materials based on salt hydrates was considered to be the cause of supercooling.

Figure 4. Dynamic DSC curve of treated specimen 2 in the liquid phase.

In this study, the solidification temperature of treated specimen 2 shifted toward a higher temperature compared with as-received specimen 2. From the results, we found that the homogenization treatment can affect nuclear distribution of the PCM under the exothermic process. Consequently, the measured solidification temperature increased, and the supercooling issue decreased. However, a slower cooling rate is preferable for accurate measurement of solidification temperature.
In some studies, supercooling was dependent on the cooling rate rather than the initial homogeneity. Nagano et al. [54] reported supercooling issues of PCMs (under solid phases) at a cooling rate of 5 °C/min. Even though additive materials were adopted to reduce supercooling, supercooling still occurred at 0 to −20 °C, while the melting temperature was 25 °C. A solution using a low cooling rate was verified by Kosny et al. [55]. They studied the thermophysical properties of an energy-storing building material under solid phase using DSC measurements with a heating/cooling rate of 0.3 °C/min, and the difference in melting and solidification temperatures was only 5 °C.

3.3. Thermal Conductivity and Thermal Diffusivity

The thermal conductivity and thermal diffusivity of a PCM are important factors in assessing the thermal performance of a PCM in the solid and liquid states [56]. Improving thermal performance is crucial to decreasing the energy consumption for heating and cooling. The thermal conductivities of the PCMs were evaluated under fully frozen conditions (in the solid state before the onset temperature) and fully melted conditions (in the liquid state after the melting temperature). The thermal conductivities were measured ten times per specimen. The thermal diffusivities under endothermic processes were investigated due to supercooling issues under exothermic processes.

Figure 5 shows the thermal conductivities of specimens 1 to 4. Specimens 1 to 4 under solid phases had thermal conductivities of 81, 79, 112, and 113 mW/mK, respectively. The specimens under liquid phases had thermal conductivities of 77, 75, 104, and 108 mW/mK, respectively. As shown in Figure 5, the thermal conductivities of the PCMs in the solid state were higher than those in the liquid state. This phenomenon occurs because of the effect of the microstructure changing from an orderly solid structure in the solid state to a disorderly liquid structure in the liquid state [57].

![Figure 5. Thermal conductivities of the PCMs.](image)

The thermal diffusivities of the PCMs were obtained using Equation (1). The calculated thermal diffusivities are listed in Table 4. The diffusivities are about one order of magnitude lower than those of the commercial product or those reported in other studies [3,42,49–52]. During the endothermic process, the PCMs under the solid phase showed less superheating due to the relatively high thermal diffusivity. On the other hand, the low thermal diffusivity in the liquid phase accelerated supercooling during the exothermic process. Low diffusivity in the liquid phase can cause nonuniform solidification and, resultantly, phase segregation and supercooling.
Table 4. Thermal diffusivities of the PCMs.

<table>
<thead>
<tr>
<th>PCM</th>
<th>$\alpha_{\text{solid}}$ (mm$^2$/s)</th>
<th>$\alpha_{\text{liquid}}$ (mm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen 1</td>
<td>$1.34 \times 10^{-5}$</td>
<td>$1.22 \times 10^{-5}$</td>
</tr>
<tr>
<td>Specimen 2</td>
<td>$1.40 \times 10^{-5}$</td>
<td>$9.76 \times 10^{-6}$</td>
</tr>
<tr>
<td>Specimen 3</td>
<td>$2.35 \times 10^{-5}$</td>
<td>$1.60 \times 10^{-5}$</td>
</tr>
<tr>
<td>Specimen 4</td>
<td>$1.56 \times 10^{-5}$</td>
<td>$1.07 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

In order to analyze the thermal behavior of the PCMs used in this study, the Fourier numbers, which denote the ratio of diffusive or conductive transport rate to the quantity storage rate, were compared with those of the references. In the DSC measurement for an organic PCM with a similar melting temperature \cite{58,59}, the Fourier number was 103.5 at a heating rate of 0.5 $^\circ$C/min. In the DSC for an inorganic PCM with a similar melting temperature \cite{42,60}, the Fourier number was 0.11 at a heating rate of 5 $^\circ$C/min, which is much lower than that of the organic PCM in references \cite{58,59}. However, the Fourier numbers of the PCMs used in this study were between 0.0036 and 0.0063 for the solid phase and between 0.0026 and 0.0043 for the liquid phase, which are much lower than the inorganic PCM in references \cite{42,60}. In the DSC measurement, a large enough Fourier number is necessary for uniform phase change, and the heating/cooling rate should be designed by considering the diffusivity and Fourier number.

4. Conclusions

We investigated the thermophysical properties of MnCl$_2$·4H$_2$O PCMs with various initial phases by using DSC and a heat flow meter, and the following conclusions were derived:

1. The melting/solidification temperature, latent heat, and thermal diffusivity were measured for MnCl$_2$·4H$_2$O PCMs, and the properties were provided. The melting temperatures of the PCMs under single phase were about 28 to 33 $^\circ$C. Specimens 1 and 2, having a dual or slurry phase, led to superheating issues. The latent heat of the PCMs under the endothermic process was 146 to 176 J/g with a temperature range of 23 to 45 $^\circ$C. The latent heats of as-received PCMs under the endothermic process were similar or higher than those of the commercial products with operating temperatures of 20 to 50 $^\circ$C.

2. In the endothermic process, the PCMs with a liquid or dual phase exhibited superheating because of the insufficient holding time in the initial stage until the PCMs were fully solidified. Another cause of this was the low thermal diffusivity of the PCMs based on the thermal diffusivity measurement in this study.

3. In the exothermic process, more severe supercooling was observed in the DSC measurement. The high cooling rate and low thermal diffusivity of the PCMs used in this study caused inhomogeneous solidification, phase segregation, and, consequently, supercooling. Homogenization treatment prior to DSC could mitigate the supercooling issue, such as an increase in solidification temperature of about 15 $^\circ$C compared with what was used for the as-received and treated PCMs. However, the treatment could not fully eliminate the supercooling issue.

4. The diffusivities of PCMs were measured as between $9.76 \times 10^{-6}$ and $2.35 \times 10^{-5}$ mm$^2$/s. The diffusivities of PCMs in the solid phase were higher than those in the liquid phase. The Fourier numbers of the PCMs were much lower than those in the references. The insufficient time for heat transfer resulted in high heating and cooling rates, and a very low level of thermal diffusivity was responsible for supercooling. Specimen 3 was the best PCM due to its high conductivity and high thermal diffusivity.

Accurate measurements of the thermophysical properties of PCMs were necessary prior to the design and application of PCMs. DSC was extensively used in the measurements, but homogeneity in the initial state, and proper heating and cooling rates considering diffusivity, were ensured to avoid superheating and supercooling.
Author Contributions: Conceptualization, K.-E.M., J.-W.J., J.-K.K., C.W. and S.Y.; methodology, K.-E.M., J.-W.J., J.-K.K., C.W. and S.Y.; investigation, K.-E.M., J.-W.J., J.-K.K., C.W. and S.Y.; writing—original draft preparation, K.-E.M.; writing—review and editing, C.W. and S.Y.; project administration, K.-E.M.; All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$</td>
<td>Specific heat capacity, J/g °C</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature, °C</td>
</tr>
</tbody>
</table>

**Acronym**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCM</td>
<td>Phase change material</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>TES</td>
<td>Thermal energy storage</td>
</tr>
</tbody>
</table>

**Greek Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Thermal diffusivity, mm$^2$/s</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity, mW/mK</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
</tbody>
</table>

References


52. PLUSS. Available online: https://pluss.co.in (accessed on 9 March 2022).


