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THERMAL PERFORMANCE ANALYSIS OF TiO_2 AND PARAFFIN AS PHASE CHANGE MATERIALS

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Abstract. Phase change materials (PCMs) are materials that can store and release thermal energy through phase changes from solid to liquid at specific temperatures. This study aims to analyze the effect of TiO_2 concentration in paraffin as a phase change material for thermal energy storage applications. TiO_2 is used as an additive to paraffin to enhance thermal conductivity and accelerate heat transfer, thus improving the performance of the phase change material (PCM). This research investigates the thermal characteristics of the paraffin and TiO_2 mixture by measuring thermal properties such as melting point, heat capacity, thermal stability, and the energy storage capability of the material using techniques such as Differential Scanning Calorimetry (DSC). The results show that the addition of TiO_2 can enhance the thermal performance of pure paraffin as a phase change material. A concentration of 10% TiO_2 can absorb thermal energy up to 94.58 kJ/kg. This study is expected to contribute to the development of more efficient energy storage materials.

Keywords: Latent Heat Phase, Change Material Composite, Thermal Conductivity, Thermal Energy Storage, Thermal Performance Analysis.

1. INTRODUCTION

Phase change materials (PCMs) are capable of absorbing and releasing heat energy in the form of latent heat during phase transition processes. Paraffin is one of the most commonly used types of PCM due to its several advantages, such as chemical stability, non-corrosiveness, and relatively low cost [1-3]. However, paraffin has a limitation in its low thermal conductivity, which hinders the efficiency of heat transfer during the melting and solidifying processes [4-6].

To address the limitation of low thermal conductivity in paraffin, various PCM composites have been developed by incorporating high-conductivity materials such as expanded graphite, aluminium, TiO_2, and coconut-shell carbon. Previous studies have reported significant enhancements; for example, the addition of 10–20 wt% expanded graphite increased the thermal conductivity of paraffin from approximately 0.25 W/m·K to 2–5 W/m·K [7–9]. Aluminium particles at concentrations of 5–15 wt% have been shown to improve thermal conductivity by 50–200% [10–11], while 5–10 wt% coconut-shell carbon resulted in an increase of around 30–70% [12–13].

The use of TiO_2 as an additive in PCM has also been widely investigated. Studies conducted in [14–18] demonstrated that incorporating 1–15 wt% TiO_2 can enhance the thermal conductivity of paraffin by approximately 20–90%, depending on particle size and dispersion quality. In addition to improving thermal conductivity, TiO_2 contributes to thermal stability; for instance, the addition of 10 wt% TiO_2 has been reported to reduce the rate of temperature fluctuation during heating and cooling cycles by up to 25%, thereby improving resistance to thermal degradation and enhancing stability during repeated operational cycles [19].

TiO_2 particles typically have a nanometres size, ranging from approximately 20 nm to 180 nm, depending on the synthesis method and thermal treatment [20]. The small particle size and almost homogeneous distribution can increase the surface area and interaction between TiO_2 and the PCM matrix, enhancing thermal conductivity and mechanical stability of the PCM. TiO_2 has a surface morphology that can be in the form of spherical particles or other steric shapes with a tendency to agglomerate when the concentration is too high. A uniformly distributed morphology and slightly surface roughness can enhance the heat transfer efficiency and energy circulation during the phase change process [21-22].

The use of TiO_2 as a thermal energy storage material combined with paraffin wax is expected to provide a good solution for the development of thermal energy storage (TES). The concentration of TiO_2 in paraffin wax is studied to determine the optimum concentration for the development of thermal energy storage materials.

2. METHODS

2.1 Material

The materials used in this study are paraffin wax, titanium iso-propoxide ($TiOR_4$), ethanol (EtOH), and distilled water (H_2O). The paraffin wax utilised in this study was obtained from PT. Aneka Kimia Inti (Indonesia) to ensure material traceability and reproducibility. Its detailed specifications are provided in Table 1 [23].

Table 1. Characterization of Paraffin Wax.

Temp. Melting (ºC)	Heat of Fusion (kJ/kg)	Thermal Conductivity (W/mK)	Density (kg/m3)
64	266	0,339 (solid 45,70C)	916 (solid 24^0C)

2.2 TiO_2 Synthesis

The TiO_2 material used in the experiment was obtained from titanium iso-propoxide via the sol-gel method. The sol–gel method was chosen for this study because it enables a more homogeneous dispersion of particles within the paraffin matrix, allows better control over particle morphology and size, and facilitates the formation of a stable porous structure that helps to prevent PCM leakage during phase transitions. In addition, the sol–gel process can be carried out at relatively low temperatures, thereby minimising paraffin degradation and enhancing the thermal stability of the composite. These advantages make the sol–gel method more suitable than conventional synthesis techniques for producing PCM composites with improved thermal performance. The initial step involved performing hydrolysis and condensation processes. In the hydrolysis stage, titanium iso-propoxide was dissolved in ethanol (EtOH) and hydrolyzed by the addition of distilled water (H_2O) with the following reaction:

$$Ti\,(OR)_4 + H_2O \longrightarrow Ti\,(OH)_4 + ROH$$

The titanium hydroxide formed will precipitate as a solid in the solution, marking the initial step in the Sol-Gel process. The next step is the condensation process, where a transition occurs from sol to gel. The hydroxide ions (OH) produced from the hydrolysis of the metal precursor with alcohol (ROH) undergo a condensation reaction, forming bonds between the oxygen (O) atoms in the hydroxide. The result of this condensation process is the formation of a three-dimensional network (gel) from the oxygen particles that begin to form solid material. The reaction that occurs is:

$$Ti\,(OH)_4 \longrightarrow TiO_2 + H_2O$$

In this reaction, the Titanium Hydroxide molecules undergo condensation to form Titanium Dioxide (TiO_2) and water molecules (H2O). This process involves the bonding of oxygen atoms within the hydroxide, resulting in the formation of a solid material in the form of a gel consisting of TiO_2.

2.3 Preparation Composite PCM (Paraffin Wax-TiO_2)

The PCM composite was synthesised through a three-step preparation process, as illustrated in Figure 1. In Step 1, the raw materials—paraffin wax and TiO_2 derived from the sol–gel process—were prepared and weighed according to the desired composition. In Step 2, the paraffin was placed into a beaker and heated on a magnetic stirrer until fully melted at 100 °C. The temperature was then reduced to 70 °C, and the mixture was stirred at 60 rpm while TiO_2 powder was gradually introduced to ensure uniform dispersion. The mixing process was continued for 2 hours to obtain a homogeneous paraffin-TiO_2 (PCM PT) composite. In Step 3, the molten mixture was cast into a mould and allowed to solidify before being subjected to thermal characterisation tests.

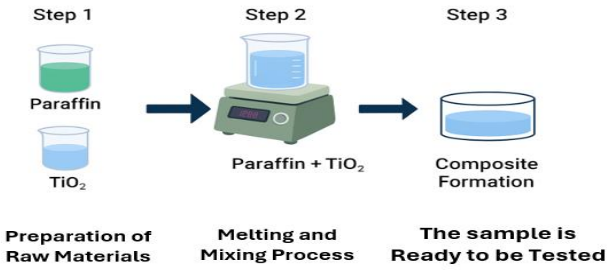

Figure 1. Schematic Diagram of PCM Composite Preparation

The testing process of the samples was carried out at various concentrations of TiO_2 in paraffin wax. The composition of the samples is presented in Table 2.

Table 2. Composition of TiO_2 and paraffin wax mixture for PCM.

Sample Code	Sample Description	Paraffin (%)	TiO_2 (%)
PCM PP	Pure paraffin	100	0
PCM PT 5%	Paraffin composite with 5 wt.% TiO_2	95	5
PCM PT 10%	Paraffin composite with 10 wt.% TiO_2	90	10
PCM PT 15%	Paraffin composite with 15 wt.% TiO_2	85	15

2.4 Research Variables

The variables in this study consist of independent and dependent variables. The independent variable in this study is the PCM material, which is the concentration of TiO_2 in paraffin, while the dependent variable is the thermal characteristics of the PCM material.

2.5 Material Characterization

The characterisation of the PCM material was conducted to determine the physical and thermal properties of each prepared sample. The thermal behaviour of pure paraffin and the composite PCM was analysed using Differential Scanning Calorimetry (DSC), performed at a heating/cooling rate of 10 °C/min within a temperature range of 20–80 °C under a nitrogen atmosphere (100 mL/min). Thermal stability was assessed using Thermogravimetric Analysis (TGA, Q50) with a heating rate of 10 °C/min from 30 to 550 °C, also under nitrogen flow. The rate of mass loss with increasing temperature was further evaluated using Derivative Thermogravimetry (DTG) to identify decomposition stages.

3. RESULTS AND DISCUSSION

3.1 Thermal Energy Absorption Capacity of PCM

The DSC test results showed that the addition of TiO_2 into paraffin altered the thermal properties of the PCM, as demonstrated in Figure 2.

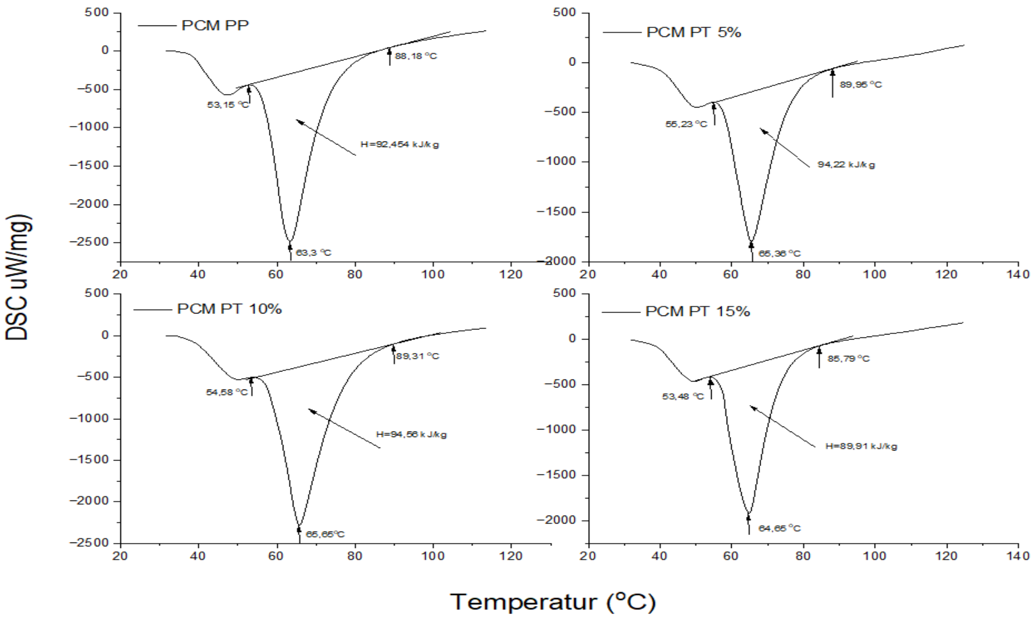

Figure 2. DSC test results of PCM material with various TiO_2 concentrations in paraffin

Figure 2 shows the DSC test results of PCM materials, which include paraffin wax (pure PCM) and a mixture of paraffin wax and TiO_2 (PCM PT). For pure PCM, an endothermic peak (heat absorption) occurs around 53.15-89.18 °C. The area under the curve for this peak is 92.45 kJ/kg, indicating the melting enthalpy (ΔH), which is the energy required to melt the paraffin. For the PCM with a 95% paraffin wax and 5% TiO_2 mixture, the endothermic peak occurs at temperatures between 55.23-89.95°C, and the area under the curve for this peak is 94.22 kJ/kg, showing the melting enthalpy (ΔH), which is the energy required to melt the PCM PT 5%. In this condition, the melting point occurs at 65.36°C. For the PCM with a 90% paraffin wax and 10% TiO_2 mixture, the onset of melting occurs at 54.58°C, and the end-set of melting occurs at 89.31°C. The melting point of this PCM PT 10% is 65.65°C. The total heat absorbed during the endothermic process reaches 94.56 kJ/kg. At a TiO_2 concentration of 15%, the initial melting process begins at 53.48°C, the melting point occurs at 64.65°C, and the endset of melting occurs at 85.79°C. The total heat required for this PCM to change from solid to liquid is 89.91 kJ/kg. The detailed results are presented in Table 3.

Table 3. Thermal transition parameters of PCM

Sample	Onset (°C)	Melting point (°C)	Endset (°C)	ΔH (kJ/kg)
PCM PP	53.15	63.30	89.18	92.45
PCM PT 5%	55.23	65.36	89.95	94.22
PCM PT 10%	54.58	65.65	89.31	94.56
PCM PT 15%	53.48	64.65	85.79	89.91

The results of these tests show a shift in the on-set melting and end set melting when TiO_2 is added to pure PCM. The addition of TiO_2 into paraffin increases the on-set melting and end-set melting of the PCM material, except for the addition of 15% TiO_2 into paraffin. The on-set and end-set melting shift because TiO_2 particles interact with the paraffin molecular chains, limiting the free movement of the molecules during the melting process, which results in either an increase or decrease in the initial melting temperature. The on-set melting depends on how well TiO_2 is dispersed in the paraffin matrix. At 5% and 10% TiO_2 compositions, both the on-set and end-set slightly increase, indicating enhanced local thermal stability. However, at 15%, the values slightly decrease due to possible agglomeration. TiO_2 increases the thermal conductivity of the mixture, leading to more uniform heat distribution during heating. This can cause a more uniform melting process but also affects the on-set and end-set temperatures depending on the heat distribution and particle size. If the TiO_2 particles are evenly distributed, they can act as nucleation centers that stabilize the melting process, increasing the on-set /end-set temperatures. However, if particle agglomeration occurs, as may happen with 15% TiO_2, it can disrupt the paraffin crystal structure, lowering the on-set /end-set melting temperatures. From Figure 2, the optimal composition in terms of thermal stability and enthalpy occurs in the PCM with 5%–10% TiO_2 content, while 15% TiO_2 tends to cause a decrease in performance.

Looking at the specific heat capacity (Cp) of the PCM produced, it is observed that the higher the TiO_2 concentration in the PCM, the greater the specific heat capacity of the material, as shown in Figure 3.

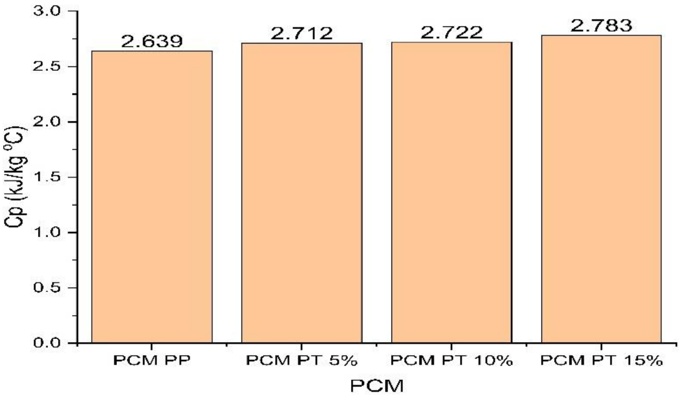

Figure 3. Specific heat capacity of PCM material with TiO_2 concentrations

Specific heat capacity (Cp) is the amount of heat energy required to raise the temperature of one unit mass of a substance by one degree Celsius (°C) or one Kelvin (K) without a phase change. Compared to Figure 2, there is a phenomenon where, at a TiO_2 concentration of 15% in paraffin, the amount of heat energy that can be absorbed by the PCM is the lowest compared to the other PCMs. However, the specific heat capacity at 15% TiO_2 concentration is the highest. This phenomenon contradicts the equation $Q = m.Cp.\Delta T$, where an increase in Cp should result in a higher Q. In Figure 2, when the TiO_2 concentration reaches 15%, a portion of the paraffin fraction decreases due to the dispersion of more TiO_2 particles, which, by volume, do not contribute to the latent heat release/absorption like paraffin. This reduces the amount of material actively undergoing phase changes, resulting in a lower total ΔH. At TiO_2 concentrations of 5%-10%, TiO_2 helps improve heat distribution without significantly disrupting the phase change of paraffin. However, at a TiO_2 concentration of 15%, aggregation or saturation of TiO_2 particles can occur, leading to a hindrance in the movement of paraffin molecules during melting or freezing, and a reduction in the effective paraffin mass fraction capable of contributing to the phase change. At a 15% TiO_2 concentration, interactions between TiO_2 particles can form more efficient thermal pathways (increasing Cp), but on the other hand, they create a microstructure that limits the crystallization or perfect melting of paraffin, which impacts the melting enthalpy.

3.2 Thermal Stability of PCM

The thermal stability of the PCM can be observed from the TGA and DTG test results, as shown in Figures 4 and 5. The thermal stability of the PCM material, as shown in Figure 4, indicates that all PCMs demonstrate good thermal stability below 250°C, as evidenced by the lack of significant mass reduction up to 250°C. Figure 5, which presents the DTG test results of various PCM materials consisting of paraffin and TiO_2, shows that all samples exhibit a melting peak in the same temperature range, between 50–70°C, which corresponds to the characteristics of paraffin. The addition of TiO_2 to paraffin modifies the peak intensity and thermal stability. At a 15% TiO_2 concentration, a significant change is observed with a much larger peak, which may indicate a catalytic effect or chemical interaction between TiO_2 and paraffin. The addition of TiO_2 particles to paraffin-based PCM affects the phase transition process and the thermal stability of the material. Although the melting point remains similar, the intensity and mass change profile vary, indicating thermal modification and changes in the melting kinetics.

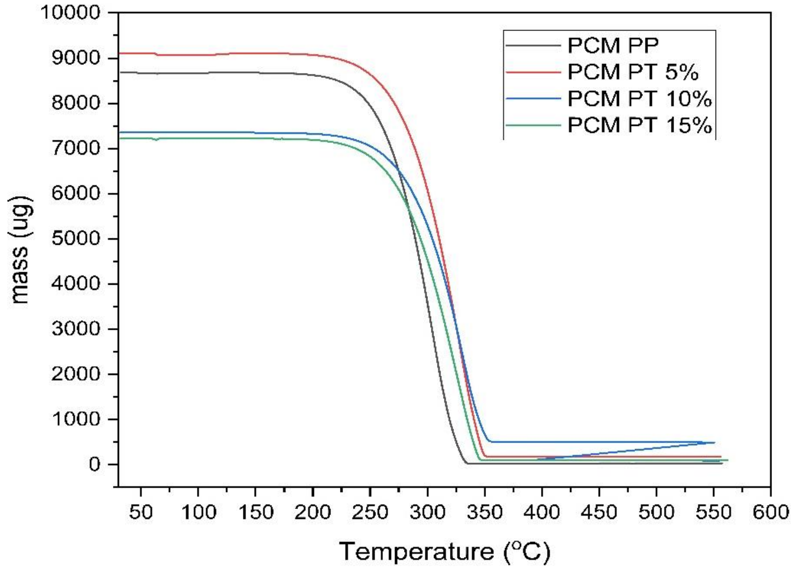

Figure 4. TGA test results of PCM PP and PCM with a mixture of paraffin wax and TiO_2

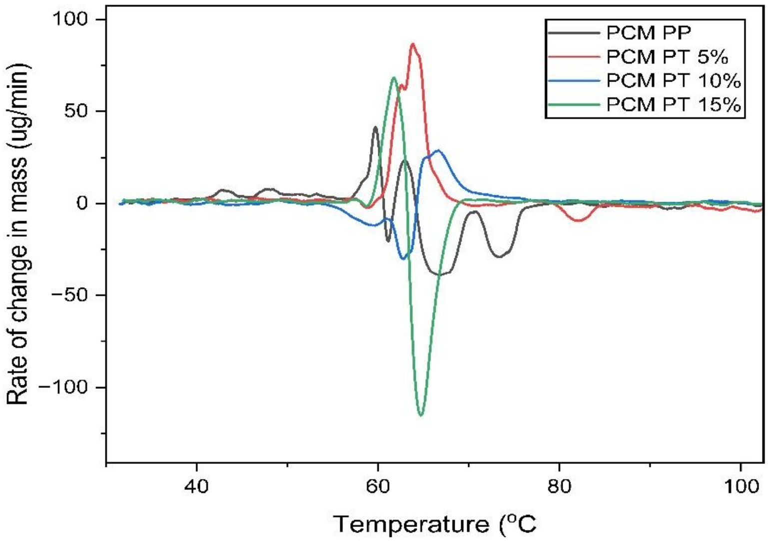

Figure 5. DTG test results of PCM PP and PCM with a mixture of paraffin wax and TiO_2

The DTG curves provide a more detailed representation of the thermal degradation mechanism Figure 5. The incorporation of TiO_2 causes a slight shift in the DTG peak temperature and broadening of the decomposition profile. This phenomenon suggests an interaction between paraffin molecules and the surface of TiO_2 particles, which restricts molecular mobility. As a result, a higher amount of energy is required for chain scission, thereby enhancing the thermal stability of the composite.

At a TiO_2 concentration of 15 wt%, the DTG peak becomes sharper and more pronounced. This may indicate a catalytic effect or specific chemical interactions between TiO_2 and paraffin. A sharper peak implies a more uniform degradation process, suggesting stronger interfacial interactions or a more homogeneous dispersion of TiO_2 within the paraffin matrix. Variations in DTG peak intensity and temperature confirm that TiO_2 acts not merely as an inert filler, but actively modifies the thermal decomposition mechanism. These kinetic changes are associated with enhanced heat-transfer pathways, alterations in crystallisation behaviour, and a possible partial confinement effect induced by the TiO_2 surface. Although TiO_2 affects the degradation characteristics, the melting peak remains within the range of 50–70 °C, indicating that the phase-change mechanism is not disrupted. This is crucial, as the performance of PCMs depends heavily on consistent melting–solidification temperatures. Overall, the DTG analysis demonstrates that TiO_2 improves the thermal resistance of paraffin-based PCMs by regulating molecular mobility, modifying decomposition kinetics, and strengthening interfacial interactions. These enhancements are most pronounced at higher TiO_2 concentrations, highlighting its strong potential as an effective thermal stabiliser in PCM composites.

4. CONCLUSION

The thermal analysis results demonstrate that the incorporation of TiO_2 into pure paraffin induces notable changes in the thermal behaviour of the PCM. The addition of TiO_2 enhances the specific heat capacity of the material, indicating improved heat-storage ability. Among the tested samples, the PCM containing 10 wt% TiO_2 exhibits the highest latent heat absorption, reaching 94.56 kJ/kg. Furthermore, the presence of TiO_2 particles significantly influences both the phase-transition characteristics and the thermal stability of paraffin-based PCM, indicating that TiO_2 acts not only as a filler but also as a functional additive capable of modifying the thermal performance of the composite.

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