Thermophysical parameters of organic PCM coconut oil from the T-history method and its variation with the chemical dopant

Alfriska O Silalahi¹, I M Sutjahja¹, D Kurnia¹ and S Wonorahardjo²

¹ Dept. of Physics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung
² Building Technology Research Division, School of Architecture, Planning and Policy Development, Institut Teknoologi Bandung
Jl. Ganesha No. 10, Bandung, Indonesia 40132

*) inge@fi.itb.ac.id, T. +62-22-2500834

Abstract. The thermophysical parameters of organic phase change material (PCM) of coconut oil (co_oil) with chemical dopant have been studied by analyzing the temperature vs time data during liquid-solid phase transition (solidification process) based on T-history method. The dopant consist of nanoparticles of graphite, CuO, and ZnO, each of them added separately to co_oil in 1 wt% and 2 wt%. The data of pure co_oil are taken as the comparison. Analysis of the data reveals the values of solid and liquid specific heats and the heat of fusion related to phase transition of co_oil+dopant. In general, we found that the solid specific heat tends to decrease with dopant concentration, while liquid specific heat tends to increase with dopant concentration with a rather small variation for all type of dopant. The heat of fusion, on the other hand, decreases with the increase of dopant concentration. The temperature dependent enthalpy shows that the solid-liquid phase transition of co_oil occurred with a temperature change, which might be due to its mixture composition.

Keywords: Phase Change Material (PCM), coconut oil (co_oil), T-history method, chemical dopant, solid and liquid specific heats, heat of fusion, temperature dependent enthalpy.

1. Introduction
Specific heat capacity and enthalpy are important thermophysical parameters for phase change material (PCM) as the thermal energy storage (TES) system, due to the fact that it measures the heat storage capacity of PCM in terms of sensible and latent heats [1-4]. For a low-temperature application, such as food storage during transportation and room temperature conditioning applications in building, one of potential organic PCM is coconut oil (co_oil). It has a melting temperature of around 26°C and a melting enthalpy of around 80 kJ/kg [5-6]. However, the result from the DSC study shows that a big storing capacity of co_oil in the temperature range of 12 to 35°C [7].

Like other materials such as molten salt that are commonly used as heat transfer fluid for energy transport and storage, the performance of PCM might be altered, in general, by adding the material with a chemical dopant. In particular case, nanoparticle dopant is experimentally shown to be an
effective agent to change the solid and liquid specific heat of nanofluids in general and PCM in particular [8-9]. Theoretically, at high temperatures the specific heat capacity of nanoparticles is somewhat larger than their bulk materials [10-11]. It is important to note, that although the change of specific heat or other thermophysical parameters of PCM in general still depends on the type of dopant, 1% dopant concentration is shown to be special due to the optimum stability of suspension [12].

We present in this paper the thermophysical parameters of co_oil with a dopant, consisted of liquid and solid specific heats (c_{p,l} and c_{p,s}) as well as the heat of fusion (h_m) for the solid-liquid transition. The chemical dopant consisted of nanoparticles graphite or metal oxide of CuO and ZnO, each of them has the concentrations of 1 wt% and 2 wt%. We note that the variation of thermophysical properties of co_oil along with dopant type and concentration are used to obtain the optimum condition of co_oil as the sensible and latent heat energy storages. These parameters are obtained by analyzing the T-history data during solidification process with data analysis follow the method proposed by Zhang et al. [13] combined with its modification by Hong et al. [14]. According to this method, the thermophysical parameters of PCM consist of liquid and solid specific heats of co_oil (c_{p,l} and c_{p,s}) and specific heat of fusion (Δh) are expressed as,

\[ c_{p,l} = \left( \frac{m_{l,w}c_{p,l} + m_wc_{p,w}}{m_p} \right) - \frac{m_{1,p}c_{p,t}}{A_1} \]  \tag{1}

\[ c_{p,s} = \left( \frac{m_{l,w}c_{p,l} + m_wc_{p,w}}{m_p} \right) - \frac{m_{1,p}c_{p,t}}{A'_1} \]  \tag{2}

\[ Δh = \left( \frac{m_{l,w}c_{p,l} + m_wc_{p,w}}{m_p} \right) \left( \frac{A_2}{A'_2} \right) \left( T_m - T_i \right) - \left( \frac{m_{1,p}c_{p,t}}{A_1} + \frac{c_{p,l} + c_{p,s}}{2} \right) \left( T_m - T_i \right) \]  \tag{3}

We note that in those above equations, m_p, m_w and m_{1,p}, m_{1,w} are the masses of the PCM, water, and tube used for PCM and water; c_{p,w} is the specific heat of water; c_{p,t} is the specific heat of tube material. The supercooling temperature and solidification temperature are each denoted by T_s and T_m, while T_i is the inflection temperature determined from inflection point in the temperature derivative curve. In addition, set values of \( \{A_1, A_2, A'_1\} \) and \( \{A'_2, A_2, A'_1\} \) correspond to the area calculation below the curve of PCM’s and water’s temperature towards air environment.

Besides that, the temperature-dependent enthalpy is also determined by means of a method proposed by Marín et al. [15]. Hence, evaluation for the energy absorption/release of PCM in small interval \( ΔT_j = T_{j+1} - T_j \) corresponds to time interval \( Δt_j = t_{j+1} - t_j \) has resulted in the temperature dependent specific enthalpy PCM as

\[ h(T) = \sum_{i=1}^{N} Δh(T_i) + h_0 \]  \tag{4}

with \( h_0 \) is a constant value of enthalpy that has been chosen by a criterion that enthalpy at the lowest temperature of measurement is equal to zero and specific enthalpy change

\[ Δh(T_j) = \left( \frac{m_{l,w}c_{p,l} + m_wc_{p,w}}{m_p} \right) \frac{A_j}{A'_j} ΔT_j + \frac{m_{1,p}c_{p,t}}{m_p} ΔT_j \]  \tag{5}
In that formula \( A_j = \int_{t_j}^{t_j+\Delta t_j} (T - T_a) dt \) and \( A'_j = \int_{t'_j}^{t'_j+\Delta t'_j} (T' - T_a) dt \) are the corresponding area for PCM and water towards air environment temperature.

2. **Experimental Procedures**

The coconut oil (co_oil) as PCM was provided from Indonesia, while the chemical dopant (graphite, CuO, and ZnO) were purchased from Sigma Aldrich. The graphite particles have the shape of plate-like with diameter is about 200nm, while CuO and ZnO particles have the spherical shape with diameter is around 100nm. The chemical dopants are added to pure CO in 2 different concentrations of 1 wt% and 2 wt%. We note that the T-history measurements were performed for each set of material: co_oil + graphite, co_oil + CuO, co_oil + ZnO, and for each measurement, we always include the pure sample of co_oil. Each measurement was repeated for 3 times to ensure the repeatability of the data. Prior to each measurement, the mixture of co_oil and dopants were mechanically stirred by using the ultrasonic bath for about 1 hour to reach the high stability of the suspension.

To characterize co_oil by this method, about 20gr reference sample (water) and 20g co_oil sample with dopant are each placed in 150mm long glass test tube with 14mm internal diameter and 1mm wall thickness. These tube dimensions were selected to ensure that the temperature distribution of the sample can be regarded as uniform and the lumped capacitance method can be applied [16]. This condition is fulfilled when the Biot number (\( Bi = \alpha R/2\kappa \) with \( \alpha \) is the natural convective heat-transfer coefficient of air outside the tube, \( R \) the radius of the tube and \( \kappa \) the thermal conductivity of material) is less than 0.1. Each tube is equipped with the temperature sensors (T-type thermocouple with a diameter about 1mm with an accuracy of 0.2%+1°C) that integrated to the multi-channel temperature meter from Applent (AT4508A from Applent Instruments Inc.).

Prior to the measurement, water and liquid co_oil (pure co_oil and co_oil+dopant) contained in the tube was heated to a high temperature (\( T_0 \)) above the melting point and stabilized for a few minutes to ensure the temperature homogeneity in the whole part of the sample. The tubes are then subsequently exposed to a cooler environment (\( T_a \)) provided by cooling bath (sizes: 100×50×45cm) to cool and solidify. During that process, the temperature of the water and co_oil/co_oil+dopant were recorded and plotted against time until the sample solidified.

3. **Results and Discussion**

For T-history measurement, when the tubes of PCM (co_oil) and water are suddenly exposed to cool air atmosphere whose temperature is \( T_a \) (which might be time-dependent), its temperature changes rapidly with time, as illustrated in figure 1. From this figure, the temperature of water decreases monotonously without any phase transition, while co_oil material experience a phase change from liquid to solid with non-monotonous temperature change signifying the supercooling effect.
Figure 1. Typical T-history curves of water and PCM (co_oil) with a dopant for graphite dopant. Each dopant has 2 different concentrations of 1 wt% and 2 wt%.

The results of the analysis for thermophysical parameters of co_oil+dopant for 3 set data are shown in the following figures, as the average values for solid specific heat (figure 2), liquid specific heat (figure 3) as well as for heat of fusion (figure 4). For easy comparison, the data for pure co_oil are also included, with standard deviation.

Figure 2. The average values of solid specific heat ($c_{p,s}$) of pure co_oil along with dopant concentration of 1 wt% and 2 wt% for dopant type of (a) graphite, (b) CuO, and (c) ZnO.
Figure 3. The average values of liquid specific heat \( (c_{p,l}) \) of pure co_oil along with dopant concentration of 1 wt\% and 2 wt\% for dopant type of (a) graphite, (b) CuO, and (c) ZnO.

Figure 4. The average values of specific heat of fusion (\( \Delta h \)) of pure co_oil along with dopant concentration of 1 wt\% and 2 wt\% for dopant type of (a) graphite, (b) CuO, and (c) ZnO.
From those above figures, one can see that the solid specific heat of co_oil ($c_{p,s}$) tend to decrease with dopant concentration for all type dopant type. The liquid specific heat of co_oil ($c_{p,l}$), on the other hand, tend to increase with the dopant, although with smaller variation compared to $c_{p,s}$. These variations of specific heat will be further analyzed with a simple model in the following paragraph. In addition, from figure 4 the heat of fusion tend to decrease with dopant concentration for all type of dopant.

Several models have been proposed to explain the variation of specific heat with the dopant (see, for example, a review paper in reference [8]). In a certain simple case, the dependence of the specific heat capacity of the nanofluid is well described by “simple mixing model” based on the assumption of thermal equilibrium between the particles and the surrounding fluid or the so-called the nanolayer concept [8, 17-18]

$$c_p = \frac{M_p c_{p,p} + M_{liq} c_{p,liq}}{M_p + M_{liq}} = \frac{\phi \rho_p c_{p,p} + (1-\phi) \rho_{liq} c_{p,liq}}{\phi \rho_p + (1-\phi) \rho_{liq}}$$  \hspace{1cm} (6)

where $M_{liq}$ is the mass of the base liquid, whereas $M_p$ is the total mass of the dopant particles, $c_{p,liq}$ and $c_{p,p}$ are the respective specific heat capacities of the two components. In another side, $\rho_{liq}$ and $\rho_p$ are the densities of base liquid and dopant particles, while $\phi$ is the volume fraction of the dopant defined by

$$\phi = \frac{y/\rho_p}{y/\rho_p + 1/\rho_{liq}}$$  \hspace{1cm} (7)

with $y = M_p/M_{liq}$. The equation (6) predicts the decrease of specific heat with dopant concentration. This reduction is mainly due to the low specific heat of oxide nanoparticles with respect to the base fluid, as shown in table 2. Taking into account the co_oil used in this study has a density value of about 910 kg/m$^3$ [19], one may conclude that equation (6) fit well the behavior of $c_{p,s}$ experimental data, as shown in figure 2.

| Table 1. Density and specific heat of dopant particles from references. |
|---|---|---|
| Dopant | Density, $\rho_p$ [kg/m$^3$] | Specific heat, $c_{p,p}$ [kJ/kg.K] |
| Graphite | 1.9–2.3×10$^3$ [20] | 0.71 [21] |
| CuO | 6500 [22] | 0.5356 [22] |
| ZnO | 5600 [23] | 0.514 [23] |

Moreover, the experimental value for the liquid specific heat of the co_oil with dopant tends to increase, and even higher than the base fluid. This different behavior was explained by admitting the existence of other mechanisms for nanofluids [24]. According to references [24-25], the most significative mechanism that led to an increment of $c_p$ could be considered the formation of a solid-like nanolayer on the surface of the nanoparticle, and this layer has higher thermal properties than the bulk liquid. In more detail, the enhancement of specific heat could be associated with the highly specific surface energies related to the high surface area of the nanoparticles per unit volume [10, 26]. Besides that, the nanoparticle diameter can play an important role related to the solid/liquid interface area and interfacial effects in the corresponding suspensions [27-28]. In this case, the solid-liquid interface may change the phonon vibration mode near the surface area of a nanoparticle and thus change the specific heat capacity of a nanofluid [18].

The T-history data of co_oil is then further analyzed following the method proposed by Marín et al. [15] to obtain the enthalpy-temperature curve, as shown in figure 5.
Figure 5. The temperature dependent-enthalpy of pure co_oil from 2 sets of measurement data.

From figure 5 one can see that the enthalpy curve of co_oil is different from other relatively pure fatty acids such as paraffin C\textsubscript{16} and alloy C\textsubscript{16} – C\textsubscript{18} [15]. It seems that the latent phase of co_oil comes together with sensible solid, or in other words, the latent phase occurs with a temperature change. This might be due to the fact of gradual nature for the phase transition of co_oil, due to its mixture composition that consists of many kinds of fatty acid, with the largest amount of lauric acid (about 50%).

**Conclusion**

We describe in this study the thermophysical parameters of co_oil as one of organic PCM and the role of dopant, by means of the T-history method based on the temperature vs time data during with water as the reference material. The data have been further analyzed based on the lumped capacitance method to obtain the solid and liquid specific heats and the specific heat of fusion (\(\Delta h\)) related to the phase transition of co_oil+dopant. The solid specific heat tends to decrease with dopant concentration for all type of dopant (graphite, CuO, and ZnO), in agreement with a simple mixing model. On the other hand, the liquid specific heat tends to increase with very small variation by the dopant concentration. On the other hand, the value of the heat of fusion tends to decreases by the dopant concentration. The enthalpy curve of co_oil is different from other relatively pure fatty acids. In this case the latent phase of co_oil with a temperature change, which might be due to the fact of gradual nature for the phase transition of co_oil due to its mixture composition.

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