The role of particle dopant to the thermal conductivities of PCM coconut oil by means of the T-history method

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Abstract. We described in this paper the role of chemical dopant to the thermal conductivity of organic phase change material (PCM) of coconut oil (co_oil) based on T-history method. We used the nanoparticle dopant, namely graphite, CuO, and ZnO. Each kind of dopant was added to co_oil in a certain amount of 1 wt% and 2 wt%. For comparison, the data of pure co_oil was also taken and compared to the data from direct measurement. Because of the smaller diameter to height ratio, the lumped capacitance method is applicable here. Hence, the heat transfer between PCM and water during solidification or melting process is one dimensional, so that the one-dimensional transient heat diffusion equation for cylindrical geometry is applicable. Analysis of the data for solidification and melting processes led to the values of solid and liquid thermal conductivities. We note that in general 1 wt% dopants have effectively increased the thermal conductivities of co_oil, which is important for the effective heat transport of the material in response to the heat from the environment. More increase of dopant concentration has resulted in the reduction of thermal conductivities, which might be due to the agglomeration of particle dopant due to van der Waals interaction between particles.

Keywords: Phase Change Material (PCM), co_oil, T-history method, one dimensional transient heat diffusion, solid thermal conductivity and liquid thermal conductivity.

1. Introduction

One of many strategies for energy conservation in the future is thermal energy storage (TES) technology based on the phase change material (PCM) [1-2]. Besides temperature regulator for building application, low-temperature applications of this technology such as for food storage, chemical container, and medicine transportation need low melting temperature PCM [3]. Among many candidate materials, coconut oil (co_oil) is a very promising organic PCM, due to the fact of its abundant amount in tropical areas, human and environmentally friendly and relatively low price. Besides that, from the physical viewpoint, co_oil has a melting temperature of around 26°C and heat of fusion about 80 kJ/kg and relatively small supercooling degree [4-5]. In addition, the thermophysical parameters values of co_oil are expected to depend on the type and dopant concentration, which enable one to choose and optimize the dopant to get the maximum performance of the material for the certain application.
The thermal conductivity of a material is a very important parameter for PCM due to the fact that it measures the effectiveness of heat exchange between material and its’ environment [6]. This is particularly important for co_oil that consist of many kinds of fatty acids with only carbon, hydrogen, and oxygen atoms as the building blocks of its chain. Various experimental studies show that nanoparticle dopant is an effective agent to increase the thermal conductivity of the base fluid material, and several models have been developed to fit the experimental data [7-8]. It is to be noted that thermal conductivity models depend on some factors, including static and dynamic conditions of nanoparticles such as particle size, shape, and volume fraction, temperature, particle movement, particle surface chemistry and interaction potential. Among many types of material, some dopants that are commonly used to effectively increase the thermal conductivity are powders of metals or metal oxides such as graphite, Al2O3, SiO, TiO2, CuO, or Fe3O4, and they are directly added to the base fluid to form a suspension.

In this paper, we describe solid and liquid thermal conductivities of co_oil added by some nanoparticle dopants, i.e. graphite, CuO, and ZnO, derived from the analysis of the T-history data. The dopant concentrations are 1 wt% and 2 wt%, with the data of pure co_oil is taken as reference. It is to be noted that T-history method introduced firstly by Zhang et al. [9] is a simple and indirect method to determine the thermophysical parameters of PCM, namely solid and liquid specific heats, the heat of fusion, as well as solid and liquid thermal conductivities. Compared to other technique, T-history offer some advantages such as relatively cheap measurement and reliable data due to the fact that it used a substantial amount of sample and can be applied directly to some samples as dependent on the number of temperature sensor used in a measurement. In particular for thermal conductivity, very less data reported in the reference, while some available data reported only the final value for some PCM without any detailed analysis [9-10]. We note, however, that larger increase of solid and liquid thermal conductivities added with micro-particle dopant compared to nano-particle dopant was reported in reference [10].

The T-history method is based on the lumped capacitance method. Hence, the heat transfer from PCM to water during solidification is one dimensional (1D) and the 1D transient heat diffusion equation for cylindrical geometry can be written as [9],

\[
\frac{\kappa_s}{\rho_sc_{p,s}} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T(r,t)}{\partial r} \right) = \frac{\partial T(r,t)}{\partial t} \quad (r_{\text{int}} < r < R, \ t > 0)
\]

with \(\kappa_s\) is the solid thermal conductivity, \(\rho_s\) is the solid density, and \(c_{p,s}\) is the solid specific heat of PCM and \(T(r,t)\) is the temperature of the PCM sample at radius \(r\) and instant \(t\). The boundary and initial conditions are

\[
\kappa_s \left. \frac{\partial T}{\partial r} \right|_{r=r_{\text{int}}} = h_w (T_w - T(r,t)) \quad ; \quad t > 0
\]

\[
T(r_{\text{int}} = R) = T_m \quad ; \quad t = 0
\]

where \(T_m\) is the melting temperature of PCM, \(r_{\text{int}}\) is the radius of the interface between the solid and liquid phases of the PCM, \(R\) is the radius of the tube, and \(h_w\) is the coefficient for convective heat transfer from the tube to the stirred cool water. At any time, the conditions for the solid/liquid interface are,

\[
T(r = r_{\text{int}}) = T_m
\]

\[
\frac{\kappa_s}{\rho_s h_m} \left. \frac{\partial T}{\partial r} \right|_{r=r_{\text{int}}} = \frac{\partial T}{\partial t} \quad ; \quad t = 0
\]
with $h_m$ is the heat of fusion of the PCM. Thus using the perturbation theory, the solid thermal conductivity of PCM can be expressed as

$$k_s = \frac{1 + \text{Ste}}{4\frac{t_f}{\rho_s R^2 h_m}} \left(\frac{T_m - T_w}{\rho_s R^2 h_m} - 1\right)$$

with $t_f$ is the time taken for complete solidification and Stefan number is defined as $\text{Ste} = c_{p,s}(T_m - T_w)/h_m$. To simplify the formula, we may assume to neglect the second term in the denominator as it is valid for most experiments so that the solid thermal conductivity formula becomes

$$k_s = \frac{1 + \text{Ste}}{4\frac{t_f}{\rho_s R^2 h_m}} \left(\frac{T_m - T_w}{\rho_s R^2 h_m}\right)$$

Similarly, if the tube containing solid PCM is dipped into a hot water bath, which is at a temperature higher than the melting point of PCM, once the time taken for the complete melting ($t_m$) is known, the expression for thermal conductivity of liquid PCM can be achieved following a similar procedure described above,

$$k_l = \frac{1 + \text{Ste}}{4\frac{t_m}{\rho_l R^2 h_m}} \left(\frac{T_m - T_w}{\rho_l R^2 h_m}\right)$$

with $\text{Ste} = c_{p,l}(T_w - T_m)/h_m$, $c_{p,l}$ is the liquid specific heat and $\rho_l$ is the liquid density of PCM.

2. Methods

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 powder dopants have the purities of higher than 99.9%. Prior to the usage, the dopants were milled with Pulverisette 7 classic line for 20 hours. After the milling, the powders are characterized by means of Scanning Electron Microscopy (SEM) to analyze the particle size and distribution. The SEM instrument is JEOL JSM 6063LA from Japan.

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.

For T-history measurement, the sample of pure co_oil and co_oil+ dopant are placed in some chemical reaction tubes with a dimension of length 15 cm and 14 mm inside diameter to fulfill the 1D heat transfer along cylindrical axis as measured by the Biot number ($Bi = h_w R/2k$ with $h_w$ is the natural convective heat-transfer coefficient of air outside the tube, $R$ the radius of the tube and $k$ the thermal conductivity of material). Prior to the measurement of solid thermal conductivity, the test tube containing molten PCM with temperature is suddenly put into the cool water with temperature value ($T_w$) lower than the melting temperature of PCM so that solidification process can be initiated. For liquid thermal conductivity, on the other hand, the test tube containing solid PCM is suddenly put into the warm water with temperature value ($T_w$) just above the melting temperature of PCM so that melting process can be initiated.
3. Results and Discussion

Figure 1 shows the result of SEM analysis for particle dopant of (a) graphite, (b) CuO, and (c) ZnO for the same magnification. From that figure, 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 particle distribution of all chemical dopant samples is quite homogeneous.

![Figure 1. Scanning electron microscope of (a) graphite, (b) CuO, (c) and ZnO to be used as dopant material to PCM co_oil.](image)

The typical T-history graphs to determine the solid thermal conductivity of co_oil and co_oil + dopant are shown in figure 2(a) that show the solidification curves from a high temperature above melting to low temperature in a cool water environment. From this figure, one can see that from a high temperature about 55°C the sample undergo supercooling signify by the deep in the curve before the temperature rises to reach the solidification temperature due to dominant of latent heat release. Finally the temperature decrease monotonously due to heat exchange with the environment.

![Graphs of T-history](image)
Figure 2. (a) Illustration for the temperature-time dependent of co_oil and co_oil+graphite dopant in a cool water environment for solid thermal conductivity and (b) Illustration for data analysis to determine the time for the end of solidification $t_f$.

For liquid thermal conductivity, on the other hand, the melting curves of co_oil and co_oil+dopant in a warm water environment are shown in Figure 3(a). Start from a low temperature of about $-5^\circ$C, the sensible heat absorption is marked by a steep increase of temperature before it reduces the slope which is expected for latent heat period. Finally, the temperature of the sample is increased again to reach the thermal equilibrium with the environment.

Figure 3 (a) Illustration for the temperature-time dependent of co_oil and co_oil+CuO dopant in a warm water environment for liquid thermal conductivity and (b) Illustration for data analysis to determine the time for complete melting $t_m$.

To obtain the values of solid and liquid thermal conductivities from the experimental data, one has to determine the parameters of $t_f$ and $t_m$ for complete solidification and complete melting of co_oil. Figure 2(b) give the illustration for the determination of $t_f$ from the graph of temperature derivative towards time for solidification, as the time interval between $t_i$ and $t_s$, each of them signify the supercooling temperature and end of solidification where the slope value in temperature derivative is zero. In other side Figure 3(b) give the illustration for the determination of $t_m$ from the graph of temperature derivative towards time for melting process as the time interval between two peaks, each designates the times for initial and complete melting before the sample enter the region of sensible heat absorption. Thus, the values of solid and liquid thermal conductivities of co_oil and co_oil+dopant can be obtained by means of Equations 1 and 2 with the other thermophysical parameters are obtained from independent measurement data performed based on the same method in air environment [11].

The results for data analysis are shown in figure 4 for solid thermal conductivity and figure 5 for liquid thermal conductivities. We note that solid thermal conductivity of pure co_oil is higher than liquid thermal conductivity, although they are higher than reference values from direct measurement [12]. The difference with literature value might be due to the limitation of the model used in the data analysis. For example, the T-history model assumes a clear interface between solid and liquid phases during phase change process and neglection of the second-order term of the perturbation expansion. Besides that, the solid-liquid phase transition of co_oil is not sharp due to its mixture composition nature.
Figure 4 Normalized solid thermal conductivity ($k_s$) as a function of dopant concentration for dopant type of (a) graphite, (b) CuO, and (c) ZnO.
From figures 4 and 5 one can see that the variation of thermal conductivities depends on the dopant type and concentration. In particular, graphite dopant has resulted in the monotonous increase of liquid thermal conductivity with dopant concentration. For another type of dopant, the solid and liquid thermal conductivities have a maximum value at 1 wt%. It is interesting to note that the best enhancement of thermal conductivity for 1.0 wt% addition of nanoparticles is in agreement with specific heat results, see for example reference [13] and references therein. Different mechanisms were proposed to explain the enhancement of thermal conductivity. They are based on the Brownian motion of nanoparticles [14-16], aggregation of nanoparticles [17-19] and formation of a nanolayer [20-23].

An early study of the effective thermal conductivity of nanofluid is based on the classical analysis of Maxwell [24]. According to this effective medium theory, the effective thermal conductivity for two-phase solid-liquid mixtures is given by:

$$\kappa = \kappa_f \left[ \frac{\kappa_p + 2\kappa_f + 2\phi(\kappa_p - \kappa_f)}{\kappa_p + 2\kappa_f - \phi(\kappa_p - \kappa_f)} \right]$$  \hspace{1cm} (4)

where $\kappa_f$ and $\kappa_p$ are fluid’s and dopant particle’s thermal conductivity and $\phi$ is volume concentration of dopant that can be determined as

$$\phi = \frac{y/\rho_p}{y/\rho_p + 1/\rho_{liq}}$$  \hspace{1cm} (5)

with $y = M_p/M_{liq}$; hence $M_p$ and $M_{liq}$ denote the mass of dopant and co_oil as the base liquid. It is important to note that the model makes satisfactory predictions for randomly dispersed, and uniformly sized spherical shaped particles at low $\phi$ under ambient conditions.

The formula of thermal conductivity given in Eq (4) predicts the monotonous increase of $\kappa$ with particle dopant concentration. As shown in figures 4 and 5, this model is applicable to most data for 1 wt% dopant concentration. The exceptional is the liquid thermal conductivity of co_oil with graphite dopant, where it shows a monotonous increase of $\kappa$ with dopant concentration (figure 5(a)). In general, the decrease of thermal conductivities with further increase of particle dopant concentration to 2 wt% might be due to agglomeration of particle dopant which is usually ascribed to van der Waals interaction between particles. We note that the decrease of thermal conductivity with dopant particle size has been reported previously, see for example a review in references [25] and [26].

**Figure 5** Normalized liquid thermal conductivity ($k_l$) as a function of dopant concentration for dopant type of (a) graphite, (b) CuO, and (c) ZnO.
4. Conclusion
We have described in this paper the variation of solid and liquid thermal conductivities of coconut oil (co_oil) with a dopant by analysis the T-history data based on one-dimensional transient heat diffusion equation for cylindrical geometry. The solid thermal conductivity tends to have a maximum value for 1 wt% dopant concentration, for all type of dopant. The liquid thermal conductivity, on the other hand, has a strong variation with the dopant: it increases monotonously with dopant concentration for graphite dopant, while for another type of dopant it has the same variation like those of solid thermal conductivity. In general, the thermal conductivities data up to 1 wt% dopant concentration are consistent with two-phase solid-liquid mixtures based on effective medium theory from Maxwell.

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References
[1] Advances in Thermal Energy Storage Systems, Methods and Applications 2015 Edited by Luisa F. Cabeza, (Woodhead Publishing Copyright Elsevier Ltd.)
[2] Sharma A and Kar S K (Editors) 2015 Energy Sustainability Through Green Energy (Springer)
[3] Košny J 2015 An application of phase change materials in building envelopes and internal structures PCM-Enhanced Building Components (Springer)
[4] Tipvarakarmkoon T, Blochwitz R and Senge B 2008 Rheological properties and phase change behaviors of coconut fats and oils Annual Transactions of the Nordic Rheology Society 16
[5] Silalahi O Alfriska, Sukmawati N, Sutjahja I M, Kurnia D and Wonorahardjo S 2017 Thermophysical parameters of organic pcm coconut oil from t-history method and its potential as thermal energy storage in Indonesia Materials Science and Engineering 214 012034 (doi:10.1088/1757-899X/214/1/012034)
[6] Fleischer A S 2015 Thermal Energy storage using phase change materials fundamentals and applications (Springer)
[7] Kleinstreuer C, Feng Yu 2011 Experimental and theoretical studies of nanofluid thermal conductivity enhancement: a review Nanoscale Research Letters 6 229
[8] Kumar P M, Kumar J, Tamilarasan R, Sendhilnathan S and Sivan Suresh 2014 Review on nanofluids theoretical thermal conductivity models Engineering Journal 19 Issue 1 (doi:10.4186/ej.2015.19.1.67)
[9] Zhang Y, Yi J, Yi J 1999 A simple method, the T-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials Meas. Sci. Technol. 10 201–5
[10] Jegadeeswaran S, Pohekar S D, Kousksou T 2012 Matter Renew. Sustain Energy 1 5 (doi:10.1007/s40243-012-0005-7)
[11] Silalahi A O, Sukmawati N, Sutjahja I M, Kurnia D and Wonorahardjo S 2017 Thermophysical parameters of organic pcm coconut oil from t-history method and its variation with chemical dopant (presented in Asian Physics Symposium).
[12] Lane G A 1980 Low temperature heat storage with phase change materials Int. Journal of Ambient Energy 1 (2) 155-68
[13] Chieruzzi M, Cerritelli G F, Miliozzi A and Kenny J M 2013 Effect of nanoparticles on heat capacity of nanofluids based on molten salts as pcm for thermal energy storage Nanoscale Research Letters 8 448
[14] Jang S P and Choi S U S 2004 Role of brownian motion in the enhanced thermal conductivity of nanofluids Appl. Phys. Lett. 84 4316–18
[15] Prasher R, Bhattacharya P, Phelan P 2005 Thermal conductivity of nanoscale colloidal solutions (nanofluids) Phys. Rev. Lett. 94 025901
[16] Evans W, Fish J and Keblinski P 2006 Role of brownian motion hydrodynamics on nanofluid thermal conductivity App. J Phys. Lett. 88(9) 093116
[17] Evans W, Prasher R, Fish J, Meakin P, Phelan P and Keblinski P 2008 Effect of aggregation and interfacial thermal resistance on thermal conductivity of nanocomposites and colloidal nanofluids Int J Heat Mass Tran 51(5) 1431–38
[18] Zhu H, Zhang C, Liu S, Tang Y and Yin Y 2006 Effects of nanoparticle clustering and alignment on thermal conductivities of Fe3O4 aqueous nanofluids Appl. Phys Lett. 89 023123
[19] Xuan Y, Li Q and Hu W 2003 Aggregation structure and thermal conductivity of nanofluids AIChE Journal 49(4) 1038–43
[20] Shin D and Banerjee D 2011 Enhancement of specific heat capacity of high temperature silica-nanofluids synthesized in alkali chloride salt eutectics for solar thermal-energy storage applications Int. J. Heat Mass Tran 54 1064–70
[21] Li L, Zhang Y, Ma H and Yang M 2010 Molecular dynamics simulation of effect of liquid layering around the nanoparticle on the enhanced thermal conductivity of nanofluids J Nanopart Res. 12 811–821
[22] Oh SH, Kauffmann Y, Scheu C, Kaplan WD and Rühle M 2005 Ordered liquid aluminum at the interface with sapphire Science 310:661–663
[23] Yu W and Choi S U S 2003 The role of interfacial layers in the enhanced thermal conductivity of nanofluids: a renovated Maxwell model J. Nanopart Res. 5 167–71
[24] Maxwell J C 1973 A Treatise on Electricity And Magnetism (UK: Clarendon)
[25] Saterlie M, Sahin H, Kavlicoglu B, Liu Y and Graeve O 2011 Particle size effects in the thermal conductivity enhancement of copper-based nanofluids Nanoscale Research Letters 6 217
[26] Sharma K V, Suleiman A, Hassan S B. and Hegde G Considerations on the Thermophysical Properties of Nanofluids Engineering Applications of Nanotechnology from Energy to Drug Delivery (Springer) ed. Korada V S and Hamid N H (http://www.springer.com/978-3-319-29759-0)