

INVESTIGATIONS ON PHASE CHANGE MATERIALS FOR ENHANCEMENT OF THERMAL CONDUCTIVITY

by

***Emeema JANUMALA^a, Murali GOVINDARAJAN^{a*},
Venkateswara Reddi BOMMA REDDI^b, and Sivakandhan CHINNASAMY^c***

^aDepartment of Mechanical Engineering, Koneru Lakshmaiah Education Foundation,
Vaddeswaram, Guntur, Andhra Pradesh, India

^bDepartment of Mechanical Engineering, Vidya Jyothi Institute of Technology,
Hyderabad, Telangana, India

^cDepartment of Mechanical Engineering,
Nadar Saraswathi College of Engineering and Technology, Theni, Tamilnadu, India

Original scientific paper
<https://doi.org/10.2298/TSCI201113219J>

Experimental work has been undertaken to improve the thermal conductivity of the phase change material (PCM), paraffin wax (PW) by adding Al₂O₃ and Cu particles in increased mass fractions to elevate thermal energy storage efficiency. Composite PCM of PW-Al₂O₃ and PW-Cu with 5%, 10%, and 15% mass fractions were prepared by sonication. Morphology of micro-structures of PW and composite PCM were examined using SEM. Thermophysical properties were measured using standard testing methods. Latent heat and specific heat were recorded with differential scanning calorimeter. Thermal conductivity was tested using two slab guarded hot plate apparatus. The results showed an improvement in thermal conductivity and latent heat of the composite PCM. The enhancement ratio of thermal conductivity was 10% and 80% for PW-Al₂O₃ and PW-Cu composite PCM respectively at 15 wt.%.

Key words: Al₂O₃, composite PCM, Cu, mass fraction, PW,
PCM, thermal conductivity

Introduction

The growing global demand for energy is phenomenal and needs to be urgently addressed. Depletion of fossil fuels and their harmful effect on the environment creates the necessity to explore RES like solar energy which is abundantly available in nature. But the intermittent nature of its availability calls for storage of energy [1]. The technology used for storing thermal energy is garnering immense attention in contemporary times because of its potential for widespread application. Storage of thermal energy can be in the form of sensible, latent and thermo-chemical heat. Latent heat storage (LHS) technique utilizing PCM is very popular and widely used because of the superior characteristics exhibited [2].

*Corresponding author, e-mail: drmurali@kluniversity.in

A PCM absorbs, stores, and releases enormous quantum of energy called latent heat of fusion as it changes phase, while it melts and solidifies at the phase change temperature. Therefore, PCM are also known as LHS materials. Absorption or release of heat also occurs when change of state happens to the material *i.e.*, when changes occur in the internal structure of the material. The PCM find widespread usage in areas like domestic refrigerators, thermal regulation in buildings, air conditioning systems, applications involving energy from the Sun, cooling electronic gadgets, waste heat recovery systems, *etc* [3]. The PCM are classified as organic, inorganic, and eutectic materials. Many experiments have been conducted using PW as PCM, an organic material, because of the attributes it possesses, like high latent heat, small volume change, safe, eco-friendly, non-reactive, non-toxic, no phase segregation, low cost, no supercooling, low vapor pressure in the melt, good thermal and chemical stability, self-nucleating behaviour, *etc.*, and can be assimilated into thermal energy storage systems without much problem [2, 4]. However, low thermal conductivity, 0.2-0.24 W/mK, is a major limitation for PW. This reduces the rate at which it stores or releases heat during phase change (*i.e.* solid to liquid and vice-versa) and limits its effective use in practical applications. Various techniques for improving the PCM thermal conductivity are being adopted [5]. This will help improve the rate of transfer of heat in latent heat thermal energy storage systems (LHTESS) thereby improving their thermal performance [6].

Dhandayuthapani *et al.* [7] gathered extensive information that can help in finding suitable PCM for various applications in LHTESS. Ho and Gao [8] investigated the thermo-physical properties of paraffin PCM embedded with 5 wt.% and 10 wt.% Al_2O_3 nanoparticles and found that with 10 wt.%, the values of thermal conductivity increased by 6%. Jesumathy *et al.* [9] conducted experiments on PW combined with copper oxide, CuO, nanoparticles with 1, 2, 5, and 10 wt.% concentration and noted an increase in the values of thermal conductivity. Experiments by Wang *et al.* [10] on paraffin-based composites containing nanocopper particles with 0.1, 0.5, 1, and 5 wt.% concentration indicated a rise in thermal conductivity by 26% with 5 wt.%. Jagadheeswaran and Pohekar [11] experimented on a shell and tube heat exchanger embedded with Cu particles. The elevated conductivity of Cu enhanced the system performance and resulted in a significant reduction in the discharge time – about 28% and 85% with 0.1 and 0.6 volume fractions, respectively. Wu *et al.* [12] added 1 wt.% Cu particles to paraffin and the result showed a reduction in melting rate by 13%. Miqdam *et al.* [13] studied PW thermal conductivity enhancements with the addition of Al_2O_3 and TiO_2 nanoparticles with 1, 2, 3, 4, and 5 wt.%. The relative increase in thermal conductivity was recorded to be 65 for 5% mass fraction for Al_2O_3 and 40 for 5% mass fraction addition of TiO_2 . Sakthivel *et al.* [14] conducted experiments on PW and Al_2O_3 nanoparticles with mass fractions of 0% and 3%. Their results indicated that the increase of thermal conductivity of PW was 18.6% with 3 wt.% of Al_2O_3 . Saw *et al.* [15] experimented on the thermal properties of Cu-PW nanocomposite PCM by dispersing 20 nm Cu particles into PW with 0.5, 1.0, 1.5, and 2.0 wt.%. It was found that thermal conductivity of the nanocomposites showed a respective enhancement of 14.0%, 23.9%, 42.5%, and 46.3%. The goal of this study is to tackle the challenges of low thermal conductivity of PW by adding metal (Cu) and metal oxide (Al_2O_3) with increased mass fractions (up to 15 wt.%) and investigate improvements in thermal conductivity.

Experimentation

The PW ($T_m = 54\text{-}56\text{ }^\circ\text{C}$) with thermal conductivity 0.2 [$\text{Wm}^{-1}\text{K}^{-1}$], and additives, Al_2O_3 and Cu powders have been considered for this study. Stable composite PCM of PW- Al_2O_3 and PW-Cu were prepared with 5, 10, and 15 wt.%. Thermophysical properties like

thermal conductivity, specific heat, density, and latent heat of fusion of the composite PCM have been tested using standard testing methods.

Composite PCM – preparation

Probe Sonication was used to prepare composite PCM. The PW was heated to about 70 °C (above its melting temperature). The Al₂O₃ particles were then added to the melted PW in mass fractions of 5, 10, and 15 wt.%. A magnetic stirrer was used to prepare suspensions by shear mixing at 1000 rpm for 20 minutes. The resultant mixture was probe sonicated for 30 minutes and left to cool till it reaches room temperature. The PW- Al₂O₃ composite PCM thus prepared is used for further study. The same procedure was followed to prepare PW-Cu composite PCM.

Result and discussion

Morphology

Morphology of the micro-structure of Al₂O₃, Cu, and composite PCM has been studied with SEM. The images on morphology of Al₂O₃ and Cu, captured by SEM are shown in figs. 1 and 2. The Al₂O₃ particles appear to be irregular in shape. Average size of the Al₂O₃ particles is around 28 microns. The Cu particles appear to be circular in shape. Average size of the Cu particles is around 40 microns.

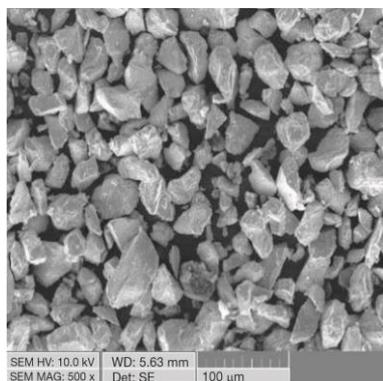


Figure 1. The SEM image of Cu powder

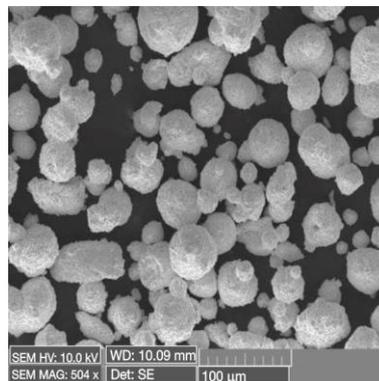


Figure 2. The SEM image of Al₂O₃ powder

Thermal conductivity

Thermal conductivity of samples has been tested following the standard guarded hot plate method under steady-state conditions. The following equation has been used for calculating the thermal conductivity of samples:

$$k = \frac{ivl}{2A(T_h - T_c)} \quad (1)$$

Specific heat and latent heat

Differential scanning calorimetry (DSC) method, which is generally used with thermally stable solids, was employed on the sample PCM, to test the specific heat capacity and latent heat. The normal operating temperature range is from -120 °C to 600 °C.

Latent Heat

Enthalpy or specifically enthalpy of fusion, H_o , is calculated:

$$H = \frac{EH_o}{W} \quad (2)$$

Specific heat

The calculation of specific heat capacity is done using eq. (3), assuming that the specimen, sapphire standard, and empty specimen holders are weight matched to within 0.1% of the sample weight:

$$C_{p(s)} = C_{p(st)} \frac{D_s W_{st}}{D_{st} W_s} \quad (3)$$

Heat flow into the sample to cause a phase change, the endotherm of PW is shown in fig. 3. Two separate endothermic peaks indicate two separate crystal structures for the same material.

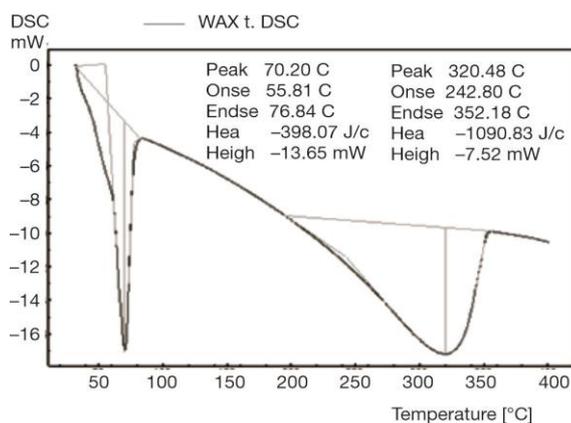


Figure 3. The DSC thermogram of PW

Termophysical properties in tabular form

Test results of thermophysical properties of PW and composite PCM have been arranged in tab. 1. The results reveal that the PCM show an increasing pattern of thermal conductivity and latent heat as mass fractions of the particles increase. The latent heat increase may be due to the inter molecular interaction between Al_2O_3 , Cu particles, and PW [16].

Table 1. Thermophysical properties of PW

No.	Parameter	Density [kgm ⁻³]	Thermal conductivity [Wm ⁻¹ K ⁻¹]	Latent heat [kJkg ⁻¹]	Specific heat [kJkg ⁻¹ K ⁻¹]
1	Paraffin wax	810	0.20	166	1.8
2	Paraffin wax + 5 wt.% Al_2O_3	835	0.21	172	1.8
3	Paraffin wax + 10 wt.% Al_2O_3	844	0.21	186	1.8
4	Paraffin wax + 15 wt.% Al_2O_3	859	0.22	210	1.7
5	Paraffin wax + 5 wt.% Cu	908	0.28	177	1.7
6	Paraffin wax + 10 wt.% Cu	922	0.31	191	1.7
7	Paraffin wax + 15 wt.% Cu	934	0.36	224	1.6

Enhancement ratio of thermal conductivity

The thermal conductivity enhancement ratio, ψ , of composite PCM has been calculated:

$$\psi = \left[\frac{k_{com} - k_p}{k_p} \right] \times 100 \tag{4}$$

The enhancement ratios of thermal conductivity for 5, 10, and 15 wt.% of composite PCM have been listed in tab. 2. A significant increase in enhancement ratio of 80% is achieved at 15 wt.% for PW-Cu composite PCM.

Table 2. Enhancement ratios of thermal conductivity of composite PCM

No.	Mass fractions	PW- Al ₂ O ₃ composite PCM ψ	PW-Cu composite PCM ψ
1	5 wt.%	5%	40%
2	10 wt.%	5%	55%
3	15 wt.%	10%	80%

Thermal conductivity variation with temperature

Thermal conductivity in PCM is a property that is widely studied and experimented with, since it impacts the process of charging and discharging during change of phase. Thermal conductivity changes with respect to temperature plays a crucial role in bettering the performance of LHTESS and therefore, a matter of significant interest for this study. Changes to the thermal conductivity of PW with respect to temperature can be observed in fig. 4. Thermal conductivity of PW increases gradually from room temperature in the solid state. It reaches a maximum of 0.2 [Wm⁻¹°C⁻¹] at 55 °C (phase-change temperature) and suddenly decreases thereafter with increase in temperature, as paraffin turns into liquid state. Figure 5 shows thermal conductivity variation of PW- Al₂O₃ composite PCM with temperature, from room temperature to 55 °C, at various mass fractions of Al₂O₃ – with 5 wt.%, 10 wt.%, and 15 wt.%. Thermal conductivity of the composite PCM increases gradually from room temperature in the solid state and reaches a maximum at 55 °C (phase-change temperature) and suddenly decreases when the composite turns into liquid state for all mass fractions. The increasing trend of thermal conductivity as mass fractions of Al₂O₃ increase can also be noted. Maximum thermal conductivity is 0.22 [Wm⁻¹°C⁻¹] at 15 wt.%.

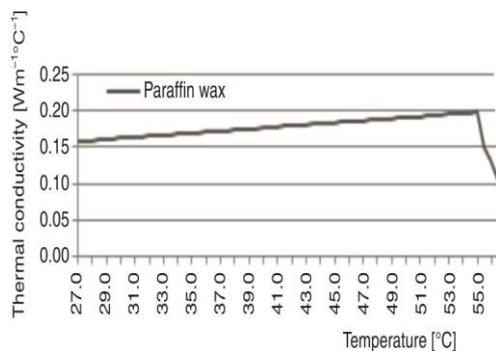


Figure 4. Changes to thermal conductivity of PW with temperature

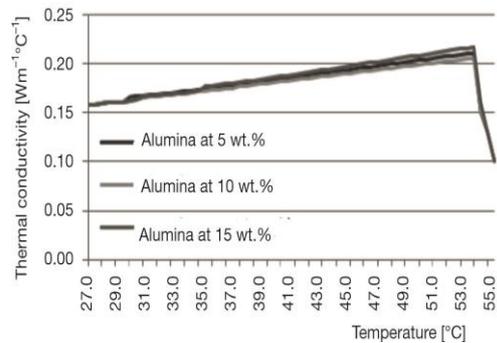


Figure 5. Variation of thermal conductivity with temperature of PW-Al₂O₃ composite PCM

Figure 6 shows the thermal conductivity variation of PW-Cu Composite PCM with temperature, for 5, 10, and 15 wt.% of Cu. The same pattern as in PW- Al_2O_3 composite PCM can be observed here. A significant achievement is that thermal conductivity touches $0.36 \text{ [Wm}^{-1}\text{C}^{-1}\text{]}$ for 15 wt.%. It can be observed that thermal conductivity increases with temperature, reaching a maximum at phase change temperature. This can be attributed to increase in molecular vibrations in the ordered lattice structure of the solid resulting in a rise in thermal conductivity [17]. Thermal conductivity decreases with temperature after phase change because the ordered lattice structure of the solid breaks down and becomes disordered when the solid changes to liquid.

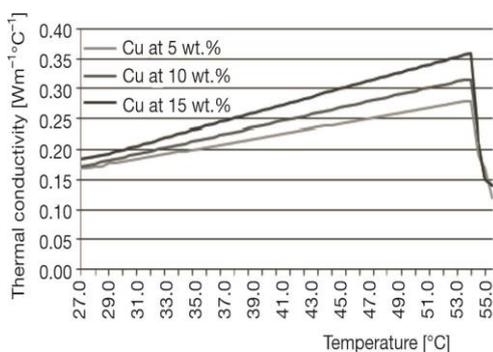


Figure 6. Variation of thermal conductivity with temperature of PW-Cu composite PCM

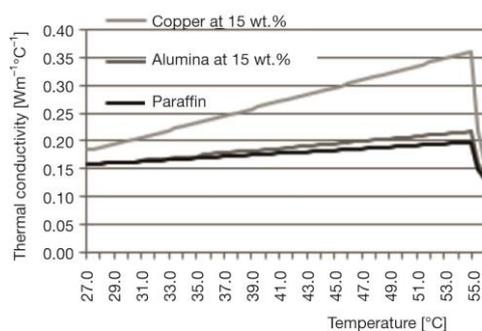


Figure 7. Comparison of thermal conductivity for PW, PW- Al_2O_3 and PW-Cu composite PCM

Comparison of thermal conductivity

Thermal conductivity variation with temperature of PW and composite PCM can be easily compared when they are plotted on a single graph. Figure 7 shows the graph of PW and composite PCM at 15 wt.% as the values of thermal conductivity are highest at that mass fraction. It can be noted that PW-Cu composite PCM acquires maximum thermal conductivity compared to PW- Al_2O_3 composite PCM owing to the fact that Cu thermal conductivity is superior to Al_2O_3 .

Conclusions

- Thermal conductivity increases as temperature increases and maximizes near the phase change temperature ($55 \text{ }^\circ\text{C}$) for PW as well as the composite PCM.
- As the mass fractions of additives are increased, composite PCM show increase in their thermal conductivity. Maximum thermal conductivity is observed at the highest mass fraction of 15 wt.%.
- Thermal conductivity enhancement ratio at 15 wt.% is 10% for PW- Al_2O_3 composite PCM and 80% for PW-Cu composite PCM.
- Latent heat of composite PCM is maximum at 15 wt.%, gradually increasing as the mass fractions of additives is increased.
- This study unequivocally demonstrates that PW-Cu composite PCM is a suitable material for LHTESS applications.

Nomenclature

A – specimen area enclosed by the boundary running midway through

the air gap between the central and the guard heater, [m^2]

$C_{p(s)}$	– specific heat capacity of the specimen, [$\text{Jkg}^{-1}\text{K}^{-1}$]	k	– thermal conductivity, [$\text{Wm}^{-1}\text{K}^{-1}$]
$C_{p(st)}$	– specific heat capacity of the sapphire standard, [$\text{Jkg}^{-1}\text{K}^{-1}$]	k_{com}	– thermal conductivity of composite PCM, [$\text{Wm}^{-1}\text{K}^{-1}$]
D_s	– vertical displacement between the specimen holder and the specimen DSC thermal curves at a given temperature, [m]	k_p	– thermal conductivity of PW, [$\text{Wm}^{-1}\text{K}^{-1}$]
D_{st}	– vertical displacement between the specimen holder and the sapphire DSC thermal curves at a given temperature, [m]	l	– thickness of specimen during test, [m]
E	– dimensionless calibration constant	T	– temperature, [K]
H	– enthalpy of fusion (or crystallization), [Jg^{-1}]	T_h	– temperature of hot plate, [K]
H_o	– observed enthalpy of fusion (or crystallization), [mJ]	T_c	– temperature of cold plate, [K]
i	– current through the central heater, [A]	T_m	– melting temperature, [K]
		v	– potential drop, [V]
		W	– mass of the specimen, [mg]
		W_s	– mass of specimen, [mg]
		W_{st}	– mass of sapphire standard, [mg]
		<i>Greek symbol</i>	
		ψ	thermal conductivity enhancement ratio, [%]

References

- [1] Naidu, P. V. K., Nair, A. M., Analysis of Paraffin Wax as a Phase Change Material, *International Journal of Current Engineering and Technology*, 8 (2018), 1, pp. 52-55
- [2] Ponnuraj, S. J., *Latent Heat Thermal Energy Storage System*, IntechOpen Ltd., London, UK, 2018
- [3] Kun Du, *et al.*, A Review of the Applications of Phase Change Materials in Cooling, Heating and Power Generation in Different Temperature Ranges, *Applied Energy*, 220 (2018), June, pp. 242-273
- [4] Bose, P., Amirtham, V. A., A Review on Thermal Conductivity Enhancement of Paraffin Wax as Latent Heat Energy Storage Material, *Renewable and Sustainable Energy Reviews*, 65 (2016), Nov., pp. 81-100
- [5] Qureshi, Z. A., *et al.*, Recent Advances on Thermal Conductivity Enhancement of Phase Change Materials for Energy Storage System: A Review, *Int. J. of Heat and Mass Transfer*, 127 (2018), Dec., pp. 838-856
- [6] Nasiru, I. Ibrahim, *et al.*, Heat Transfer Enhancement of Phase Change Materials for Thermal Energy Storage Applications: A Critical Review, *Ren. and Sustainable Energy Reviews*, 74 (2017), July, pp. 26-50
- [7] Dhandayuthabani, M., *et al.*, Investigation of Latent Heat Storage System Using Graphite Micro-Particle Enhancement, *Journal of Thermal Analysis and Calorimetry*, 139 (2020), 3, pp. 2181-2186
- [8] Ho, C. J., Gao, J. Y., Preparation and Thermophysical Properties of Nanoparticles in Paraffin Emulsions Phase Change Material, *Int. Communications in Heat and Mass Transfer*, 36 (2009), 5, pp. 467-470
- [9] Ponnuraj, S. J., *et al.*, Experimental Study of Enhanced Heat Transfer by Addition of CuO Nanoparticle. *Int. J. Heat Mass Transf.*, 48 (2012), 6, pp. 965-78
- [10] Wang, N., *et al.*, Preparation And Heat Transfer Behavior Of Paraffin-based composites containing nano-copper particles, *Proceedings*, 7th Int. Conference on Multiphase Flow (ICMF). Tampa, Fla., USA, 2010
- [11] Jegadheeswaran, S., Pohekar, S. D., Exergy Analysis of Particle Dispersed Latent Heat Thermal Storage System for Solar Water Heaters, *Renewable Sustainable Energy Reviews*, 13 (2009), 2, pp. 2225-2244
- [12] Wu, S., *et al.*, Numerical Simulation on Thermal Energy Storage Behavior of Cu/Paraffin Nanofluids PCMs, *Procedia Engineering*, 31 (2012), Dec., pp. 240-244
- [13] Miqdam, T. Chaichan., *et al.*, Thermal Conductivity Enhancement by Using Nanomaterial in Phase Change Material for Latent Heat Thermal Energy Storage Systems, *Saussurea*, 5 (2015), 6, pp. 48-55
- [14] Sakthivel, P., *et al.*, Experimental Study About Thermal Resistance of Windows with Air Gap Between Two Glasses Used in Single Houses, *Thermal Sciences*, 20 (2020), 1B, pp. 515-518
- [15] Saw, C. Lin., Hussain, H. Al-Kayiem., Evaluation of Copper Nanoparticles – Paraffin Wax Compositions for Solar Thermal Energy Storage, *Solar Energy*, 132 (2016), July, pp. 267-278
- [16] Colla, L., *et al.*, Nano-PCMs for Enhanced Energy Storage and Passive Cooling Applications, *Applied Thermal Engineering*, 110 (2017), Jan., pp. 584-589
- [17] Wang, J. *et al.*, Enhancing Thermal Conductivity of Palmitic Acid-Based Phase Change Materials with Carbon Nanotubes as Fillers, *Solar Energy*, 84 (2010), 2, pp. 339-344