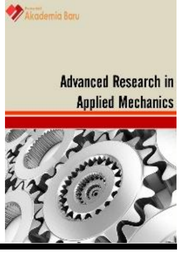
Penerbit
Akademia Baru

Journal of Advanced Research in
Applied Mechanics

Journal homepage: www.akademiabaru.com/aram.html
ISSN: 2289-7895



Thermo Physical Enhancement of Advanced Nano-Composite Phase Change Material

Open Access

Ahmad Tajuddin Mohamad[1], Nor Azwadi Che Sidik[1,*], M'hamed Beriache[2]

[1] Malaysia – Japan International Institute of Technology (MJIIT), University Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra (Jalan Semarak), 54100 Kuala Lumpur, Malaysia
[2] Department of Mechanical Engineering, Faculty of Technology, University of Hassiba Benbouali, Algeria

ARTICLE INFO

Article history:
Received 17 January 2019
Received in revised form 27 February 2019
Accepted 20 March 2019
Available online 24 March 2019

ABSTRACT

In this study inorganic salt hydrated phase-change material (PCM) based on calcium chloride hexahydrate ($CaCl_2{\cdot}6H_2O$) is employed to characterize phase change behavior such as the supercooling degree and phase change temperature. The $CaCl_2{\cdot}6H_2O$ nanocomposite PCM contained with different volume fraction wt.% of graphene nanoplatelets (GNP) are verified by heating-cooling curves resulted in enhancing thermal behavior. Results demonstrate the validation phase change temperature of the $CaCl_2{\cdot}6H_2O$ pure PCM are significantly referenced, supercooling of $CaCl_2{\cdot}6H_2O$/GNP nanocomposite PCM are studied. The degree of supercooling is within the range of 6.0-15.2°C, with the maximum reductions of 68% and no phase segregation was observed. The $CaCl_2{\cdot}6H_2O$/GNP nanocomposite PCM presented acceptable thermal reliability, chemical stability, and heat transfer characteristics, thereby reflecting its acceptability for low-temperature thermal energy storage applications.

Keywords:
Phase change material (PCM), calcium chloride hexahydrate, supercooling degree, graphene

1. Introduction

Advanced energy technologies have such a great demand in improving the efficiency of renewable energy sources utilization as well as to promote the green technologies toward protecting the environment. Thermal energy storage technique based on phase change material (PCM) has been recognized as one of advanced energy technologies. The inorganic salt hydrates PCM have a great attention of exploring due to their high-energy storage density, greater phase change enthalpy, rational price, non-flammable, multiple sources and relatively good thermal conductivity to be implemented in the field of energy storage technology. Commonly, $CaCl_2{\cdot}6H_2O$ [1], $MgCl_2{\cdot}6H_2O$ [2], $NaSO_4{\cdot}10H_2O$ [3,4], $CH_3COONa{\cdot}3H2O$ [5], $Na_2HPO_4{\cdot}12H_2O$ [4,6] and $Mg(NO_3)_2{\cdot}6H_2O$ [7] are employed as the base material of PCM storage media. Among various types of inorganic PCMs, the $CaCl_2{\cdot}6H_2O$ PCM is the most preferred inorganic salt hydrate PCM as their low cost, accessibility, and high thermal

---

[*] *Corresponding author.*
E-mail address: azwadi@utm.my (Nor Azwadi Che Sidik)

storage performance [8]. The potential inorganic PCMs substances in recent studies are shown as in Table 1 below as overview reported by Mohamad and Nor Azwadi [9]. The substances are suit in class of low and high temperature applications. Mainly, the thermophysical properties are summarized in order to review the substances performance and accuracy according to the related application.

Table 1
Thermo-physical properties of salt hydrates [9]

Salt Hydrates	Melting Temperature (°C)	Heat of Fusion (J/g)	Density (Solid) (10^3 kg/m^3)	Thermal Conductivity (Solid) (W/mK)	Specific Heat (Solid) (J/g.°C)	Reference
$LiClO_3.3H_2O$	8	253				[10]
$KF.4H_2O$	19	231	1.45		1.84	[11,12]
$Mn(NO_3)_2.6H_2O$	25.8	125.9	1.60			[10]
$CaCl_2.6H_2O$	28	174	1.80	1.088	1.42	[15,10]
$LiNO_3.3H_2O$	30	256	1.58	0.820	1.80	[10,13]
$Na_2SO_4.10H_2O$	32.4	248	1.49			[14]
$Na_2CO_3.10H_2O$	33	247			1.88	[14]
$CaBr_2.4H_2O$	34	115.5	1.52			[16]
$LiBr_2.2H_2O$	34	124				[16]
$Na_2HPO_4.12H_2O$	35-44	280		0.514	1.7	[11,12]
$Zn(NO_3)_2.6H_2O$	36	149.6	1.94		1.34	[16]
$KF.2H_2O$	42	162				[16,14]
$MgI_2.2H_2O$	42	133				[11,12]
$Ca(NO_3)_2.4H_2O$	42.4				1.46	[14]
$Fe(NO_3)_2.9H_2O$	47	155				[14]
$Na_2SiO_3.4H_2O$	48	168				[14]
$K_2HPO_4.7H_2O$	48	99				[14]
$MgSO_4.7H_2O$	48.5	202				[15]
$Na_2S_2O_3.5H_2O$	49	220	1.75	1.46		[15]

Inorganic salts containing water of crystallization is known as salt hydrates. It is formulated generally as $AB.nH_2O$, where number of water molecules and salt composition represented. The phase transformation dehydration of the salt can be expressed as

$$AB.nH_2O = AB + nH_2O - Q \tag{1}$$

$$AB.nH_2O = AB.mH_2O + (n-m)H_2O - Q \tag{2}$$

Nevertheless, $CaCl_2{\cdot}6H_2O$ as inorganic PCM exhibits some drawbacks such as supercooling, low heat transfer and so on which reflects to the long period cycles of thermal energy storage application. Thus, the performance of thermal energy storage systems is enhanced with the employment of nanomaterials which has recently been acknowledged. The study as well recognize the effect on PCM thermal properties. Many of researchers have started to study the phase change performance and other thermal physical properties of nanocomposite PCM by adding the nanoparticles into the PCM [17,18,19]. According to the overview by Yaxue *et al.,* [20] as shown in Table 2, many studies have been reported on graphene/graphite related nanoparticles were implemented in the base PCMs and fluids to enhance their thermal conductivity. Recent cases overviewed by Mohamad *et al.,* [21] and Zik *et al.,* [22] also support the hypothesis that the employment of nanoparticles in which related to the size and surface area effect towards enhancement the thermal conductivity of advanced nanocomposite PCM. However, study on the combination of inorganic $CaCl_2{\cdot}6H_2O$/GNP nanocomposite PCMs system has been minimally reported.

Table 2
PCM-Graphene based nanoparticles combination [20]

Phase Change Material	Carbon Material Additive	Fraction of Additive	Thermal Conductivity of Composite PCM kc (W/m.K)
Palmitic Acid	Graphene nanoplatelets	5 wt%	2.75/2.54 (solid/liquid) (300 m2/g)
Beeswax	Graphene nanoplatelets	0.3 wt%	2.89
Paraffin	Graphene	2.0 wt%	0.46
Binary carbonate eutectic salts	Graphene	1.5 wt%	-
Eutectic mixture (adipic acid and sebacic acid)	Graphite nanoplates	0.5 wt%	0.131
OP10E/water emulsions	Graphite nanoparticles	4 wt%	0.648

In the present study, the GNP nanoparticles were embedded into the $CaCl_2{\cdot}6H_2O$ as base PCM to develop advanced $CaCl_2{\cdot}6H_2O$/GNP nanocomposite PCM. The study was further conducted to characterize their phase change behaviour such as the supercooling degree, phase change temperature and thermal conductivity. Furthermore, this study was comprehensively to identify the mechanism that efficiently optimized the thermal properties of $CaCl_2{\cdot}6H_2O$/GNP nanocomposite PCM to be utilized in any thermal energy storage applications.

2. Experimental

2.1 Materials

Inorganic salt hydrate calcium chloride hexahydrate ($CaCl_2.6H_2O$, extra pure >98.5%, Fisher) as based PCM was purchased. Grade 4 carboxyl graphene nanoplatelets (GNP, purity >99.9%) nanoparticles were purchased from Biotek Abadi Sdn Bhd.

2.2 Preparation of Advanced Nano-Composite PCM

The two-step method is one of the more practical and effective way in preparing the $CaCl_2.6H_2O$ nanocomposite PCM [9]. The $CaCl_2{\cdot}6H_2O$ material was produced by dissolved and crystallized of industrial grade $CaCl_2$. The homogeneously advanced nanocomposite PCM was prepared initially using a magnetic stirrer at a constant temperature, 50°C in 10 minutes. The graphene nanoparticle was then added to the $CaCl_2{\cdot}6H_2O$-based PCM to mix into the solution and continuously stirred for extra 20 minutes. Finally, in order to improve the dispersion stability of the mixture and minimize nanoparticle aggregation, ultrasonic vibration was applied to the preparation processes for another 30 minutes. The importance of preserve liquidity is the factor to constant the vibrator temperature above the $CaCl_2{\cdot}6H_2O$ melting point during the preparation processes. The volume fractions of the nanoparticle were 0.1, 0.5 and 1.0 wt.% of GNP. The used preparation method is schematized in Figure 1.

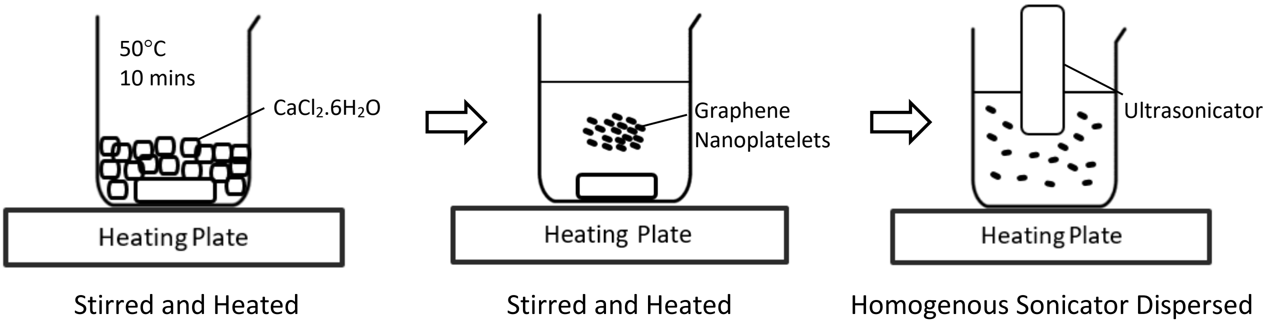


Fig. 1. Nano enhanced PCM sample preparation

2.3 Phase Change Temperature

In this study, the phase change temperature of advanced nanocomposite PCM was conducted through heat storage method. The set-up consists of a water bath and data acquisition system. The values of the $CaCl_2.6H_2O$/GNP nanocomposites PCM phase change temperature was determined under rapid heating rate using the DAIHAN-digital precise water bath set-up with fixed operating temperature as shown in Figure 2. The water bath had a temperature resolution of 0.1°C, with ±0.1°C temperature accuracy in range of ambient +5°C to 100°C operating temperature.

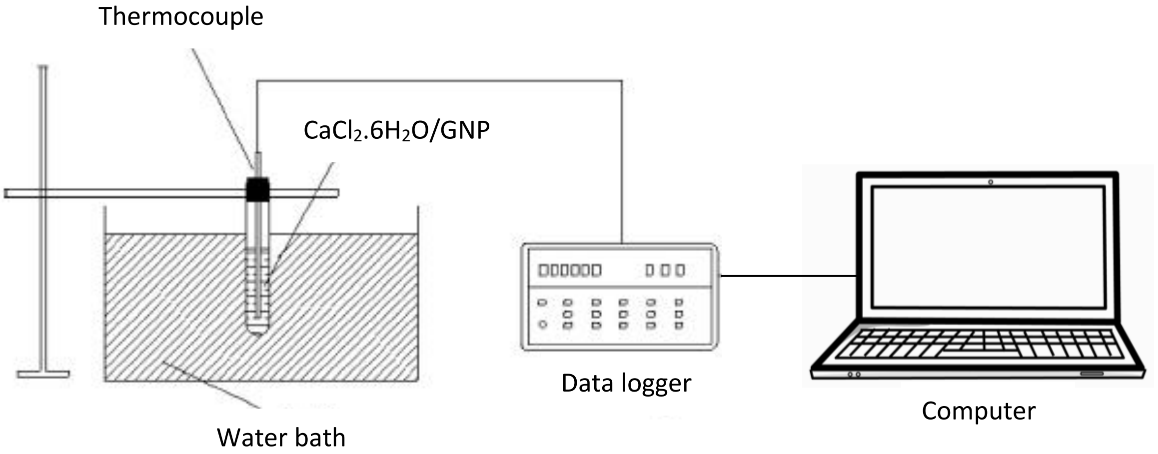


Fig. 2. Heating curve experimental set-up

2.4 Supercooling Degree

The correlation between the GNP nanoparticles concentration and the supercooling degree of the nanocomposite PCM is shown as experimental set-up diagram in Figure 3. The set-up consists of a refrigerated circulator and a data acquisition system. The data acquisition system consists of a data collecting instrument (HIOKI-MEMORY HiLOGGER LR8431-20), a computer and a copper-constantan Omega thermocouple (T type). Temperature of the nanofluids inside the glass test tube is measured by the thermocouple which is set in the test tube. The volume of the solution was fixed at 50ml in the 30mm diameter of test tube. The average relative error was 0.75% when the temperature above 0°C. The results indicate that the supercooling degree of the $CaCl_2{\cdot}6H_2O$/GNP nanocomposite PCM is indicative of the additional latent heat released by the nanocomposite PCM.

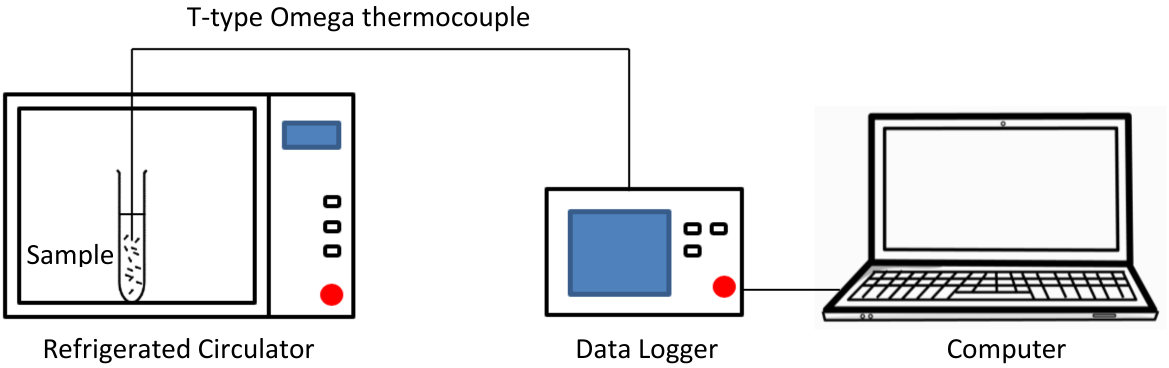


Fig. 3. Supercooling degree experimental set-up

3. Results and Discussion

Figure 4 shows the heating curve of $CaCl_2.6H_2O$/GNP advanced nanocomposite PCM respected to time of phase change. The phase change temperature obtained was 28.9°C. The aim of the temperature is for the verification and validation of the melting/freezing point while completed solidification/melting was observed. The time for completed melting under rapid heating rate was 13.8 minutes which indicated equilibrium the total amount of latent heat stored. The latent heat of phase change is calculated Eq. (3) below.

$$\Delta H = \int \rho cp(T)dT \tag{3}$$

where ρ is the density, *C* is the specific heat capacity, *T* is the temperature. The correlation of latent heat of phase change was proportional with the specific heat capacity, while the other conditions remain unchanged.

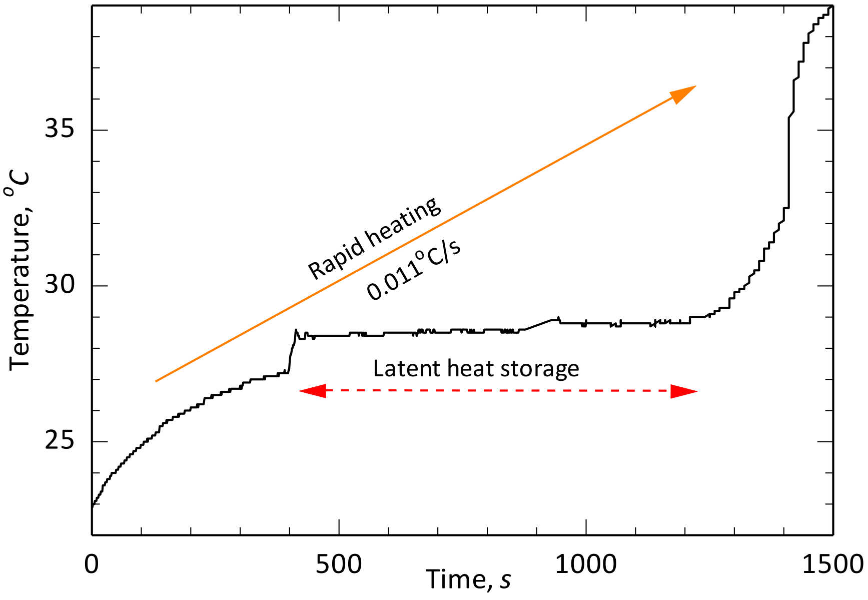


Fig. 4. Heat storage curve of $CalCl_2.6H_2O$/GNP

A heating-cooling curve is a main criterion in this study to ensure the effectiveness of GNP nanoparticle in $CaCl_2{\cdot}6H_2O$ based PCM. The improved thermal physical properties of the advanced nano-composite are the key factors in this research. The GNP nanoparticle was fixed at 0.1, 0.5 and 1.0 wt.% respectively. Figure 5 shows the heat release/freezing curve of $CaCl_2{\cdot}6H_2O$ advanced nanocomposites PCM under rapid cooling condition. It was slightly displayed that the $CaCl_2{\cdot}6H_2O$ with 0.5 and 1.0 wt.% GNP nanoparticle concentration exhibited a significant supercooling degree about 5.4°C and 9.2°C compared to 0.1wt.% of GNP nanoparticle. The degree of supercooling is within the range of 6.0-15.2°C, with the maximum reductions of 68% and no phase segregation was observed. The supercooling degree calculation of the 0.1, 0.5 and 1.0 wt.% $CaCl_2{\cdot}6H_2O$ with GNP nanoparticle applied the uncertainty formula, which was established by Moffat [23] as presented in the Eq. (4) below.

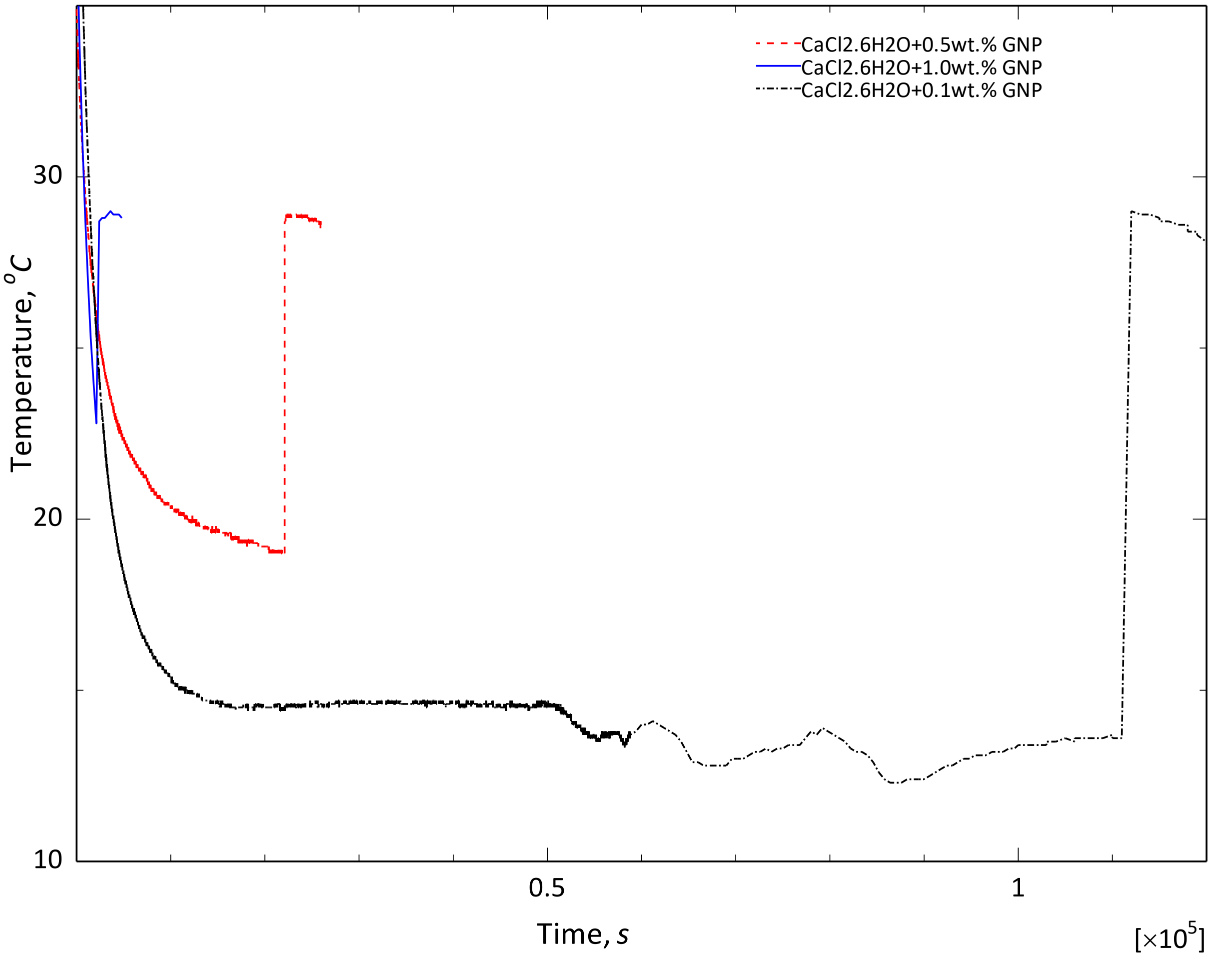


Fig. 5. Heat release curves of the pure $CaCl_2.6H_2O$ PCM and with 0.1, 0.5 and 1.0wt% GNP nanoparticle

$$\frac{\delta\Delta T}{\Delta T}=\left[\left(\frac{\delta T_n}{T_n}\right)^2+\left(\frac{\delta T_m}{T_m}\right)^2\right]^x \tag{4}$$

where, *x* is volume fraction, *Tn* is the supercooling temperature; *Tm* is the temperature of the plateau during crystallization; and Δ*T* is the supercooling degree, such that Δ*T* = *Tm* - *Tn*.

4. Conclusion and Recommendations

In view of this study, a new nanocomposite phase change material $CaCl_2{\cdot}6H_2O$/GNP nanocomposite PCM was prepared and phase change behavior were systematically studied. The addition of graphene nanoplatelets act as a nucleating agent in reducing the supercooling degree. The supercooling degree of $CaCl_2.6H_2O$/GNP was 6.0°C after the present of 1.0 wt.% GNP nanoparticles, while the complete solidification times of $CaCl_2{\cdot}6H_2O$/GNP nanocomposites PCMs slightly reduced.

Further investigation is designed to determine the effect of the GNP to the thermal conductivity of PCM with respected to different temperature. The addition of GNP nanoparticles is expected to enhance the thermal conductivity of PCM.

In addition, experimentation in suppressing more supercooling degree of inorganic salt hydrate PCM is strongly recommended. In the next section, the study will further present some of the findings of empirical research on the impact of the addition of nucleating agent in the advanced nanocomposite PCM. Furthermore, the implications of invented synthesis method will be a route to the properties study of specific thermal characterization techniques which should be considered for further studies.

Acknowledgement

This research was funded by a grant from International - Takasago Thermal Engineering Co. Ltd. (Takasago Grant R.K130000.7343.4B314).

References

[1] Li, Xiang, Yuan Zhou, Hongen Nian, Xiufeng Ren, Ouyang Dong, Chunxi Hai, Yue Shen, and Jinbo Zeng. "Phase change behavior of latent heat storage media based on calcium chloride hexahydrate composites containing strontium chloride hexahydrate and oxidation expandable graphite." *Applied Thermal Engineering* 102 (2016): 38-44.

[2] Li, Gang, Binbin Zhang, Xiang Li, Yuan Zhou, Qingguo Sun, and Qiang Yun. "The preparation, characterization and modification of a new phase change material: CaCl2· 6H2O–MgCl2· 6H2O eutectic hydrate salt." *Solar Energy Materials and Solar Cells* 126 (2014): 51-55.

[3] Zhang, J., S. S. Wang, S. D. Zhang, Q. H. Tao, L. Pan, Z. Y. Wang, Z. P. Zhang, Y. Lei, S. K. Yang, and H. P. Zhao. "In situ synthesis and phase change properties of Na2SO4· 10H2O@ SiO2 solid nanobowls toward smart heat storage." *The Journal of Physical Chemistry C* 115, no. 41 (2011): 20061-20066.

[4] Wu, Yuping, and Tao Wang. "Hydrated salts/expanded graphite composite with high thermal conductivity as a shape-stabilized phase change material for thermal energy storage." *Energy Conversion and Management* 101 (2015): 164-171.

[5] Li, Xiang, Yuan Zhou, Hongen Nian, Fayan Zhu, Xiufeng Ren, Ouyang Dong, Chunxi Hai, Yue Shen, and Jinbo Zeng. "Preparation and thermal energy storage studies of CH3COONa· 3H2O–KCl composites salt system with enhanced phase change performance." *Applied Thermal Engineering* 102 (2016): 708-715.

[6] Liu, Yushi, and Yingzi Yang. "Preparation and thermal properties of Na2CO3· 10H2O-Na2HPO4· 12H2O eutectic hydrate salt as a novel phase change material for energy storage." *Applied Thermal Engineering* 112 (2017): 606-609.

[7] Frusteri, F., V. Leonardi, and G. Maggio. "Numerical approach to describe the phase change of an inorganic PCM containing carbon fibres." *Applied Thermal Engineering* 26, no. 16 (2006): 1883-1892.

[8] N'Tsoukpoe, Kokouvi Edem, Holger Urs Rammelberg, Armand Fopah Lele, Kathrin Korhammer, Beatriz Amanda Watts, Thomas Schmidt, and Wolfgang KL Ruck. "A review on the use of calcium chloride in applied thermal engineering." *Applied Thermal Engineering* 75 (2015): 513-531.

[9] Mohamad, Ahmad Tajuddin, and Nor Azwadi Che Sidik. "Nano-enhanced phase change material effects on the supercooling degree improvement: A review." In *IOP Conference Series: Materials Science and Engineering*, vol. 469, no. 1, p. 012036. IOP Publishing, 2019.

[10] Pielichowska, Kinga, and Krzysztof Pielichowski. "Phase change materials for thermal energy storage." *Progress in materials science* 65 (2014): 67-123.

[11] Kenisarin, Murat, and Khamid Mahkamov. "Salt hydrates as latent heat storage materials: Thermophysical properties and costs." *Solar Energy Materials and Solar Cells* 145 (2016): 255-286.

[12] Mohamed, Shamseldin A., Fahad A. Al-Sulaiman, Nasiru I. Ibrahim, Md Hasan Zahir, Amir Al-Ahmed, R. Saidur, B. S. Yılbaş, and A. Z. Sahin. "A review on current status and challenges of inorganic phase change materials for thermal energy storage systems." *Renewable and Sustainable Energy Reviews* 70 (2017): 1072-1089.

[13] Shamberger, Patrick J., and Timothy Reid. "Thermophysical properties of lithium nitrate trihydrate from (253 to 353) K." *Journal of Chemical & Engineering Data* 57, no. 5 (2012): 1404-1411.

[14] Khan, Zakir, Zulfiqar Khan, and Abdul Ghafoor. "A review of performance enhancement of PCM based latent heat storage system within the context of materials, thermal stability and compatibility." *Energy Conversion and Management* 115 (2016): 132-158.

[15] Cabeza, Luisa F., Albert Castell, C. de Barreneche, A. De Gracia, and A. I. Fernández. "Materials used as PCM in thermal energy storage in buildings: a review." *Renewable and Sustainable Energy Reviews* 15, no. 3 (2011): 1675-1695.

[16] Zalba, Belen, Jose Ma Marın, Luisa F. Cabeza, and Harald Mehling. "Review on thermal energy storage with phase change: materials, heat transfer analysis and applications." *Applied thermal engineering* 23, no. 3 (2003): 251-283.

[17] Fang, Yutang, Hao Wei, Xianghui Liang, Shuangfeng Wang, Xin Liu, Xuenong Gao, and Zhengguo Zhang. "Preparation and thermal performance of silica/n-tetradecane microencapsulated phase change material for cold energy storage." *Energy & Fuels* 30, no. 11 (2016): 9652-9657.

[18] Geng, Lixia, Shuangfeng Wang, Tingyu Wang, and Ruilian Luo. "Facile synthesis and thermal properties of nanoencapsulated n-dodecanol with SiO2 shell as shape-formed thermal energy storage material." *Energy & Fuels* 30, no. 7 (2016): 6153-6160.

[19] Fang, Xin, Li-Wu Fan, Qing Ding, Xiao Wang, Xiao-Li Yao, Jian-Feng Hou, Zi-Tao Yu, Guan-Hua Cheng, Ya-Cai Hu, and Ke-Fa Cen. "Increased thermal conductivity of eicosane-based composite phase change materials in the presence of graphene nanoplatelets." *Energy & Fuels* 27, no. 7 (2013): 4041-4047.

[20] Lin, Yaxue, Yuting Jia, Guruprasad Alva, and Guiyin Fang. "Review on thermal conductivity enhancement, thermal properties and applications of phase change materials in thermal energy storage." *Renewable and sustainable energy reviews* 82 (2018): 2730-2742.

[21] Mohamad, Ahmad Tajuddin, Jesbains Kaur, Nor Azwadi Che Sidik, and Saidur Rahman. "Nanoparticles: A review on their synthesis, characterization and physicochemical properties for energy technology industry." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 46, no. 1 (2018): 1-10.

[22] Zik, Nor Azyan Farrah Adila, Sarina Sulaiman, and Parveen Jamal. "Thermally Produced Nano Catalyst for Biodiesel Production: A Review." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 52, no. 2 (2018): 139-147.

[23] Moffat, Robert J. "Using uncertainty analysis in the planning of an experiment." *Journal of Fluids Engineering* 107, no. 2 (1985): 173-178.