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Nano-enhanced phase change material effects on the supercooling degree improvement: A review

Ahmad Tajuddin Mohamad and Nor Azwadi Che Sidik*

Malaysia – Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra (Jalan Semarak), 54100 Kuala Lumpur, Malaysia

*Corresponding author: azwadi@utm.my

Abstract. In this paper, an overview about experimental procedure of phase change material (PCM), in order to enhance its thermal properties is discussed. Enhancement of PCM needs the employment of nanoparticle that would affect the thermo-physical properties. The supercooling degree of PCM influenced by dispersion of nanoparticle which can be controlled by the nucleation process of nanoparticle. Hence, the best candidate material as nucleating agent is preferred in order to maximize the dispersion nanoparticle in PCM. In addition, the tiny structure will cause nanoparticle to have a large surface area that correlates with their physical and chemical properties that react to the thermal-physical properties of PCM. In this review, graphene-based nanoparticle is discussed. The surface area of graphene is the main characteristics used in determining the best thermal physical properties for nano-enhanced phase change material (NEPCM). Due to the best characteristics as base phase change material, inorganic salt hydrates material is reviewed in this paper. However, there have been limited research carried out about the employment of graphene nanoparticles synthesis, characterization and modification process of nanoparticle itself to enhance the thermal physical properties of inorganic PCM.

1. Introduction

Nowadays, the world primary energy demanding is keep increasing and projected to consume by 50% by 2040 compared to reference scenario in 2014 [1]. The energy sources are mainly contributed by 87% consumption of fossil fuel which includes gas, oil and coal energy. Recent study reported in Annual Energy Outlook also supports the hypothesis that the renewable energy consumes still low that can be conclude that the key policy priority should therefore be to plan for the long-term care of energy security, the harmful effect of non-renewable energy emissions and the increase of oil prices while support use of renewable energy [2]. The continuation consumption energy sources using fossil fuel currently would affect the level of greenhouse gas emission which will led to cause global warming due to increasing in atmosphere temperature. In addition, it would increase the world air pollution index (API). Therefore, it is an obligation to dig in alternative way for renewable energy as one of main energy source.

Current research is focusing on energy storage which is the most effective way to reuse the energy that stored in a device. This would be the new way of energy source in order to counter the energy supply and demand nowadays. Thermal energy storage would be among the best way of energy source. The thermal energy storage plays an important role in cost effective by reducing the wastage of energy and capital cost. Besides, it is the cleanest and inexhaustible renewable energy source. Therefore, the objective this review is to discuss and analyse the best method in enhancing the phase change material thermo-physical properties with the employment of nanoparticle.



2. Thermal Energy Storage

The basic principle of TES system is to store energy through absorbing process and release it to use at a later time. A complete storage process involves at least three steps: charging, storing and discharging as shown in Figure 1 [3]. The temperature range and application are led to the selection criteria of varieties existing thermal energy storage media. The mechanism for thermal energy storage is either by elevating the temperature of a substance which known as sensible heat storage (SHS) or by changing the phase of a substance which known as latent heat storage (LHS) or by the combination of these two types of heat storage methods.

Sensible heat storage, latent heat storage and chemical heat storage are the three common materials for heat storage employed nowadays. However, since SHS have variable in discharging temperatures and low energy density, this method is not efficient compared to latent or thermo-chemical thermal heat energy storage. Therefore, LHS is the preferred method for thermal energy storage in this study.

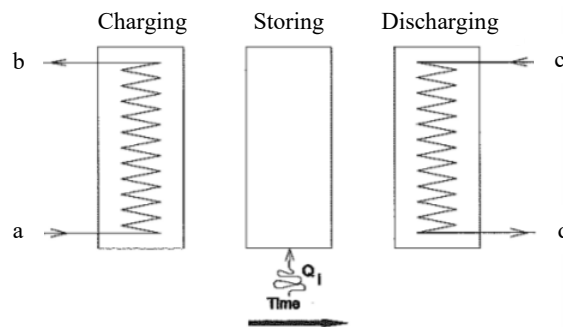


Figure 1. Basic principle of TES [3].

2.1. Latent heat

Latent heat is the energy absorbed by or released from a substance during a phase change. The phase is change either from a solid to a liquid or a gas or vice versa. Absorbing or charging energy to the substance from the surrounding environment or warmer substance will led to spread out the molecules into a larger phase volume i.e. solid into fluid phase change. In other words, a substance with lower density will gives off energy or discharging to change a phase with higher density, as the molecules come closer together and lose energy from motion and vibration.

In latent heat storage (LHS) system, phase change material is commonly employed as heat storage medium which consist storage capacity as below equations.

$$Q = m[C_{sp}(T_m - T_i) + a_m \Delta h_m + C_{1p}(T_f - T_m)] \quad (1)$$

$$Q = m[C_{sp}(T_m - T_i) + a_m \Delta h_m + C_{1p}(T_f - T_m)] \quad (2)$$

A constant temperature between absorbing and releasing the energy is the advantage of PCM in latent heat storage system as shown in Figure 2. In addition, the heat per unit per volume can be stored 5-14 times more than sensible storage materials [4]. Generally, LHS has low capital cost, higher storage density and low energy losses to the surroundings. However, the main drawbacks of LHS materials are corrosive to metallic walls and their phase segregation could result in super cooling [5]. Phase change materials (PCM) in the required temperature range, storage containment system and heat exchange mechanism for energy transfer are the three main basic criteria for LHS system [5].

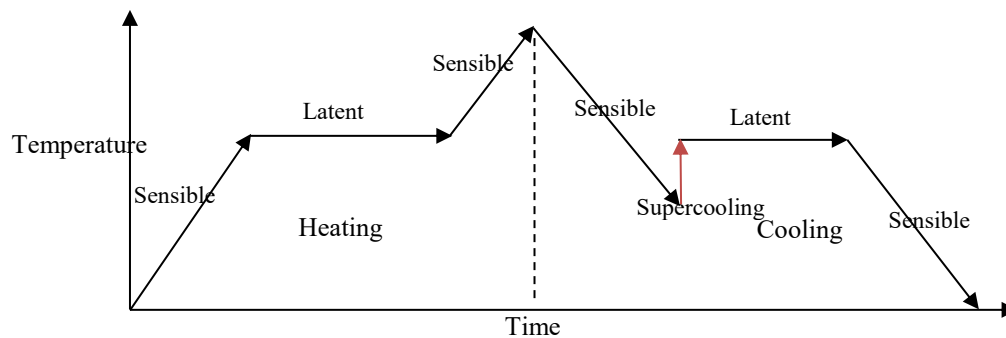


Figure 2. Sensible and latent heat phase change for solid-liquid-gas [6].

3. Phase Change Materials

The melting temperature and latent heat of fusion are the two components in identifying the suitable phase change material (PCM) for latent heat storage. The PCMs are classified as given in Table 1. Organics phase change materials such as Paraffins are commonly used as PCM for thermal energy storage system. The saturated hydrocarbons structure however has a low thermal conductivity which reduces their rate of heat charging and discharging during the melting and solidification cycles [7-10]. In contra, inorganic PCMs differs from organic PCMs in a number of important ways. Inorganics PCMs have greater phase change enthalpy which lead to have great thermal properties as shown in Table 2. Cabeza et al [11] observed significant differences between organic and inorganic PCMs. Therefore, reviewing inorganic PCM as latent heat storage materials in this paper is the main focus.

Table 1. Classification of PCMs [4].

Phase Change Materials	Organic	Paraffin Compounds Non-Paraffin Compounds
	Inorganic	Salt Hydrate Metallics
	Eutectic	Organic-Organics Inorganic-Inorganic Inorganic-Organic

Table 2. Comparison of organic and inorganic phase change materials [12,13,14].

	Advantages	Disadvantages
Inorganic	Greater phase change enthalpy	Supercooling
	Higher energy storage density	Phase segregation
	Higher thermal conductivity	Corrosive
	Non-flammable	Lack of thermal stability
	Inexpensive	
Organic	No corrosives	Lower phase change enthalpy
	Low or none supercooling	Low thermal conductivity
	Chemical and thermal stability	Flammability

3.1. Inorganics phase change materials

The potential inorganic PCMs substances in recent studies are shown as in Table 3 below. The substances are suit in class of low and high temperature applications. Various applications used appropriate inorganics PCM substance in order to obtain the accurate result. Mainly, the thermophysical properties are discussed in order to review the substances performance.

Table 3. Thermo-physical properties of salt hydrates (modified) [15].

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 ₂ O	8	253				[16]
KF.4H ₂ O	19	231	1.45		1.84	[17,18]
Mn(NO ₃) ₂ .6H ₂ O	25.8	125.9	1.60			[16]
CaCl ₂ .6H ₂ O	28	174	1.80	1.088	1.42	[11,16]
LiNO ₃ .3H ₂ O	30	256	1.58	0.820	1.80	[16,19]
Na ₂ SO ₄ .10H ₂ O	32.4	248	1.49			[20]
CaBr ₂ .4H ₂ O	34	115.5	1.52			[13]

3.1.1 Salt hydrate. Inorganic salts containing water of crystallization is known as salt hydrates. It is formulated generally as AB.nH₂O, where number of water molecules and salt composition represented. The phase transformation dehydration of the salt can be expressed as;

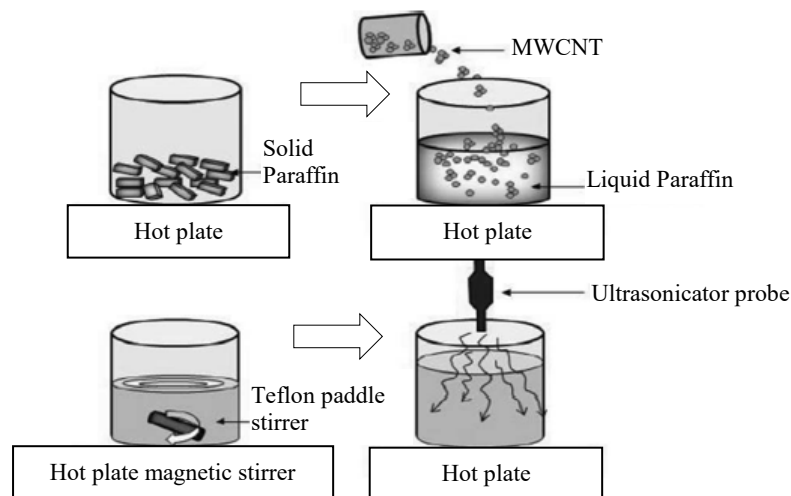
$$AB.nH_2O = AB + nH_2O - Q \quad (3)$$

$$AB.nH_2O = AB.mH_2O + (n - m)H_2O - Q \quad (4)$$

The salt hydrates can be classified into types of three which affected from its melting behaviour. Firstly, salt hydrates with congruent melting behaviour. This type of salt hydrate is soluble in the hydration water at the melting temperature. Secondly, salt hydrates with incongruent melting which is only partially soluble in the hydration water at the melting temperature salt is only partially soluble in the hydration water and thirdly, salt hydrates with semi-congruent melting which are in equilibrium have different compositions because of the transformation of the salt hydrate to a salt hydrate with a lesser amount of hydration water during the melting process of solid and liquid phases [4].

4. Preparation Methods

The specifications of the PCM used in the present studies influenced the preparation method of nano-PCM. Melting point of PCM is an important factor in determining the nano-PCM preparation method. Murugan et al [21] reported that nano-PCM with paraffin having the melting temperature range of 18–23°C and solidification range of 22–19°C as the base material appropriated to be prepared as shown in the schematic diagram in the Figure 3. A novel two-step method is adopted for the preparation of the nano-PCM. The homogeneous solution was prepared with dispersing the MWCNT in liquid paraffin using a magnetic stirrer for a period of 60 min.

**Figure 3.** Schematic diagram of nano-PCM preparation method [21].

Recent studies reported by Li et al [22] also support this two-step nano-PCM preparation method with implementation inorganic salt hydrate as the base material. The $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ material was obtained by dissolving and crystallized the industrial grade of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. The research conducted also deployed the two-step method of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ nanocomposite PCMs preparation. The solution was homogeneously stirred using a magnetic stirrer with added surfactant and nucleating agent, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ at 50°C for 20 min. 10 min continuously stirring while adding the nanoparticles. Finally, in order to ensure the dispersion stability of the mixture and minimize nanoparticle segregation and aggregation, ultrasonic vibration was applied to the preparation processes for another 30 min. The schematic preparation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ nanocomposite PCM is shown as Figure 4. Based on the review by the current study, this method is the best and commonly preparation method for PCM.

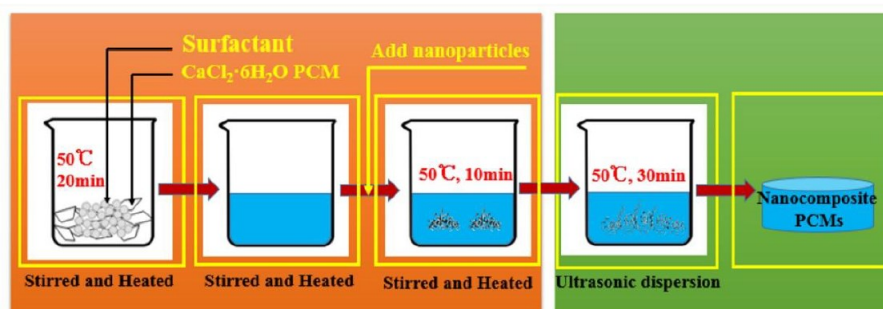


Figure 4. Schematic preparation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ nanocomposite PCMs [22].

5. Enhanced nano-PCM

5.1. Nanoparticle

Nanoparticle (NP) are tiny materials having size ranges from 1 to 100 nm. They can be classified into different classes based on their properties, shapes or sizes. The different groups include fullerenes, metal NP, ceramic NP, and polymeric NP. NP possess unique physical and chemical properties due to their high surface area and nanoscale size. Their optical properties are reported to be dependent on the size, which imparts different colors due to absorption in the visible region. Their reactivity, toughness and other properties are also dependent on their unique size, shape and structure. Due to these characteristics, they are suitable candidates for various commercial and domestic applications, which include catalysis, imaging, medical applications, energy-based research, and environmental applications. Hence, the NP is strongly recommended to be employed in PCM due to enhancement of thermo-physical properties of thermal energy storage.

5.2. Surface and size effect of nanoparticles

A key influence to enhance the thermal properties of the nano-PCM is a nanoparticles surface area and size effect. In case of graphene, a very large surface area as reported by Ma et al [23] by using volume fraction of filler (%). Figure 5 shows the theoretical surface area of fillers plotted as a function of volume fraction of filler under the assumption that fillers are dispersed uniformly in the composite. A large surface and size effect of nanoparticles will provide a large interface area between the nanoparticles and matrix.

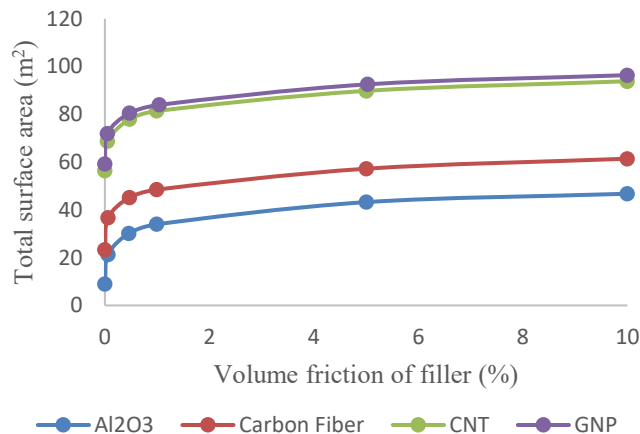


Figure 5. Total surface area of fillers in composites with varying filler contents [23].

The effectiveness of the nanoparticles size effect on thermophysical properties has been exemplified in a report by Chon et al [24]. Al₂O₃ nanofluid thermal conductivity normalized by the base fluid conductivity at each specified temperature and the experimental correlation for different nanoparticle sizes and volume concentrations are measured as shown in Figure 6. These experiments exhibit that a decreasing in nanoparticles sizes and volume ratio apparently functionalize to enhance the PCM thermophysical properties. In addition, the experiment resulted that the nanofluid conductivity increases with increasing nanofluid temperature. Therefore, large surface area and size effect are among the critical criteria to obtain the best thermal properties of enhanced nano-PCM.

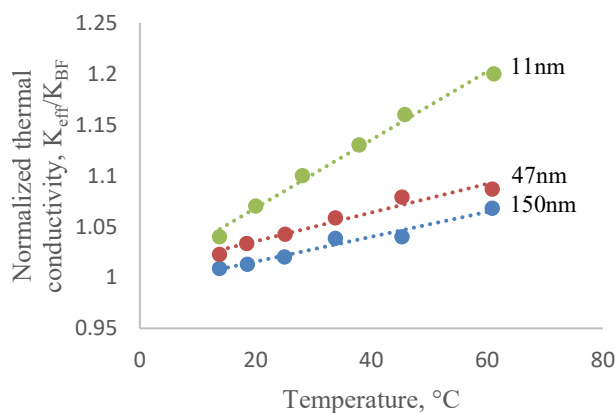


Figure 6. Temperature dependence of the thermal conductivity enhancement of three different Al₂O₃ nanofluids with 11-nm, 47-nm, and 150-nm sized nanoparticles at 1 and 4 vol% concentration, normalized by the thermal conductivity of the base fluid at the specific temperature [24].

5.3. Graphene nano-composite dispersion

Recent studies reported by Omer et al [25] described that the thermal conductivity of pentaethylene glycol-treated graphene nanoplatelets (PEG-GnP) and pentaethylene glycol thermally treated graphene (PEG-TGr) dispersed in distilled water nanofluids show the enhancement of 32% and 31%, respectively, at 50°C and 0.1% mass concentration. The higher thermal conductivity than that of pure stearic acid have been reported by Li et al [26], by adding different carbon additives included graphene. Their experiment summarized that by adding carbon additives (graphite based nano-composite), the thermal conductivity of the nano-composite increased by 12 times higher than that of pure stearic acid. This is certainly true in the studies by Yavari et al [27], which experimentally conducted in uniform dispersion of graphene flakes nanoparticles. Result shows that the thermal conductivity of graphene composite increased about 140% than that of pure 1-octadecanol without incurring a large reduction in phase change enthalpy. This was due to the expedition of the heat transfer and an effectiveness of phonon travel through the graphene fillers and between the flakes. Mehrali et al [28] reported that the thermal conductivity of a new form-stable composite phase change materials (PCMs) prepared by vacuum

impregnation of paraffin within graphene oxide (GO) sheets was significantly enhanced from 0.305 to 0.985 (W/m k).

In a similar case, Zhong et al [29] identified that the thermal conductivity of octadecanoic acid (OA) PCM consisting of graphene aerogel (GA) was highly improved about 2.635 W/m K which was 14 times larger than that of OA (0.184 W/m K). Another example of what is meant by enhancement the thermo physical properties is described by Kim and Dzar [30]. The thermal physical properties of paraffin wax with an exfoliated graphite nanoplatelets (xGnP) was experimentally studied. The thermal conductivity of paraffin/xGnP composite shows the increment with xGnP loading percentage of 1, 2, 3, 5 and 7 wt%. Surprisingly, the latent heat of paraffin/xGnP composite PCMs did not decrease as loading xGnP contents to paraffin.

Uniform and stable dispersion of nanoparticles in the PCM base solution are important driving factors of enhancing the thermal properties of the nano-PCM. However, a large surface area will lead nanoparticles more difficult in dispersing uniformly in PCM solution. According to Ma et al [23] an overwhelming problem in uniform dispersion would be occurred with an existing even a few nanometer thick interfacial region. In case of CNT reported by Choi et al [31], the small diameter in nanometer scale with high aspect ratio (>1000) [Choi et al, 2001], a large surface area will contribute a large interface area between the CNT and matrix which makes it more difficult to disperse uniformly.

5.4. Nucleation agent

The inorganic salts hydrated PCMs have received great attention in the field of energy storage technology due to higher heat storage capacity, constant phase transition temperature, non-flammable and etc. Even though the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ salt hydrated material is among the most preferred inorganic PCMs considering their low cost, accessibility, and high thermal storage performance [32], the material exhibits some problems such as supercooling which is up to 20°C, low heat transfer and so on in application of actual engineering. Therefore, the most frequently used method to make the improvement is adding some chemistry nucleating agent. Theoretically, the preferred nucleating agents should be close to the lattice parameter of the base materials. For instance, Borax is always notable as the most suitable nucleating agents for inorganic salt hydrated $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, which can decrease the supercooling degree about 12~13°C [33].

An example of this is the study carried out by Bilen et al [34] in which added 3wt% KNO_3 into $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ PCM system as a nucleating agent to prevent supercooling in the melting and solidification processes, resulted in obvious performance improvement. Another example of what is meant by effectively suppress the supercooling is as reported by Lane et al [35] which employed the strontium chloride hexahydrate, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ as a nucleating agent in $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ base PCM. In a similar case, Paris et al [36] made the comparison of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ as nucleating agents, and the results showed that the mixtures of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ with 3wt% $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ possess stable thermal behaviour than $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ with no supercooling occurs. Moreover, studies conducted by Dong and Yunlong [37] also showed that $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and borax acted as nucleating agent effectively can prevent the supercooling of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ PCM system. Sutjahja et al [38] illustrates this point clearly when the studies found that $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ exerted the best effect on $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, compared to other several nucleating agents used, (Ba_2CO_3 and K_2CO_3) and this result was consistence with research conducted by Li et al [39]. The degree of supercooling is within the range of 0.3–1.1°C and the complete solidification times were reduced by 17.84% when $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ contained with 1 wt% Al_2O_3 and consist of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ as nucleating agent as reported by Li et al [22].

6. Supercooling Degree

As was mentioned in the previous chapter, salt hydrate as inorganics PCM, possess superior properties such as better thermal conductivity, higher latent heat of fusion, and cheaper price to their organic counterparts. However, their extreme supercooling during freezing and phase segregation during melting have led to challenges in their applications to thermal energy storage. Prior studies that have noted the importance of reducing the supercooling of NEPCM in order to improve its thermophysical properties. However, very little was found in the literature on the question of reducing the supercooling

degree on inorganic NEPCM. Therefore, this is an initial objective of the future project which to identify the supercooling degree of inorganic NEPCM.

The effectiveness of the measurement of supercooling degree technique has been exemplified in a report by Li et al [22] which studies conducted on nanocomposite phase-change materials (PCMs) based on calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) with gamma aluminium oxide ($\gamma\text{-Al}_2\text{O}_3$) nanoparticles to characterize the supercooling degree of the nanofluid. Results demonstrate that the supercooling of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ nanocomposite PCMs are significantly suppressed with the degree of supercooling is within the range of 0.3-1.1°C. The schematic diagram of experimental set-up to obtain the values of the supercooling and heat storage (release) curves were gathered using the twin-bath setup as shown in Figure 7.

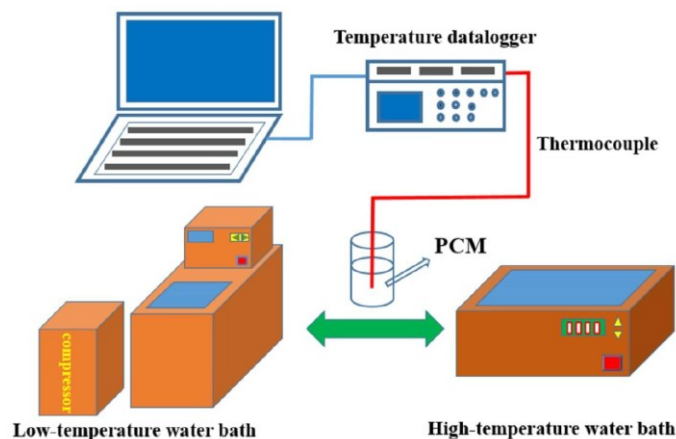


Figure 7. Schematic diagram of experimental set-up [22].

Another example of this is the study carried out by Liu et al [40] in which aimed to study the supercooling degree and nucleation behavior of nanofluids phase change material resulting that the supercooling degree can be reduced by 69.1%, and the nucleation was started in advance, shorting the time by 90.7%. This study demonstrates the need for better strategies for graphene oxide nanofluids to have more potential to be used as PCMs in cold storage applications because of their low supercooling degree and rapid nucleation behavior. Figure 8 shows the experimental setup of supercooling degree test system for nanofluid PCM. It consists of a thermostatic waterbath and a data acquisition system. The data acquisition system consists of a data collecting instrument (Agilent 34970A), a computer and a copper-constantan thermocouple (T type). Temperature of the nanofluids inside the cylindrical glass beaker is measured by the thermocouple which is set in the middle of the glass beaker. The internal diameter of the cylindrical glass beaker is 48 mm. The precision of the thermocouple was $\pm 0.2^\circ\text{C}$ and the average relative error was less than 3% when the temperature changing from -15°C to 15°C . The thermocouple was calibrated by a high precision thermometer. The glass beaker with sample nanofluids is placed in the ethylene glycol solution whose temperature is controlled at -15°C by the thermostatic waterbath during the whole freezing process. Therefore, the stated overviews regarding supercooling degree measurement are the effective and commonly method used by current researchers.

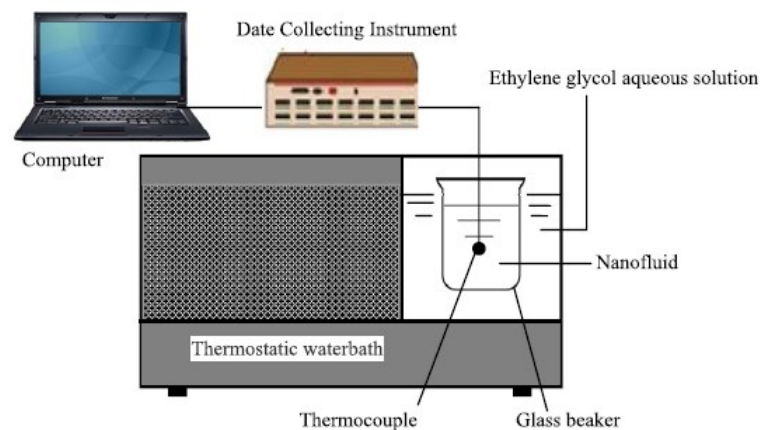


Figure 8. Schematic diagram of supercooling degree test system [40].

7. Results and Discussions

7.1. Supercooling degree of graphene oxide nanofluids

The experimental system was tested with deionized water prior to the employment of graphene oxide nanosheets [40]. The result with the deionized water serves as the basis for comparison with the results of nanofluids. Cooling process begins at the same temperature of 15°C. From the result shown in Figure 9, graphene oxide nanosheets affect the nanofluids supercooling degree. In addition, graphene oxide nanosheets also have enormous influences on the onset nucleation time nanofluids. In conclusion, graphene is the best candidate in suppressing phase change material supercooling drawback.

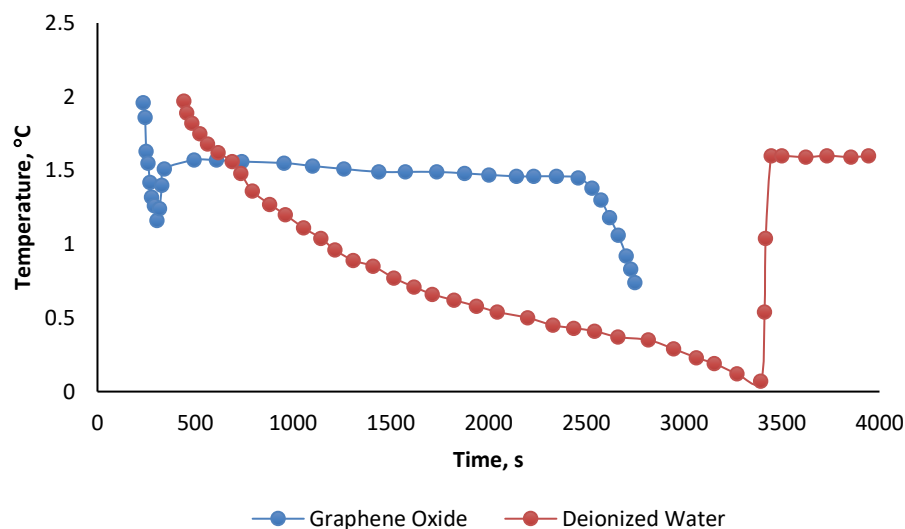


Figure 9. The cooling curve of nanofluids vs deionized water

8. Conclusions and Recommendations

In this review, an overview about NEPCM, their methodology on preparation and enhanced thermal properties were discussed. The relevance of employing inorganic salt hydrate PCM is clearly supported by the current findings which have significant merits among phase change materials for latent heat storage. It is worth noting that the excellent performance of salt hydrate PCMs has been concluded on the basis of thermal physical classification, properties, problems, and possible solutions in this paper. Suggested solutions are developed continuously in order to improve some of disadvantages that may limit their application in certain aspects.

The enhancement thermal conductivity and supercooling degree reduction of PCM can be obtained by employment of nanoparticles. Highly stable PCMs are being increasingly applied to different sectors. Constructions sector, air condition, and solar heating systems are offering great demand to the low phase change temperature range and rational cost which designate to salt hydrates. However, operational thermal cycling and technical performance of salt hydrates which may cause the decreasing of temperature and enthalpy should be paid a careful attention.

The tiny size of graphene causes it to possess a large surface area, which appoints it to be the best candidate to improve the thermo physical properties of NEPCM. The specific morphology, size and magnetic properties of NPs can be controlled by the NP synthesis techniques. Besides, the dispersion of nanoparticle in PCM also can be improved by nucleation process.

Based on the review, some recommendations can be made for future works regarding improving the reaction parameters of nanoparticle synthesis methods. Parameters such as temperature, pressure, time, and pH can be the important factors in controlling the physical structure of nanoparticle materials as there have been limited study conducted about the synthesis, characterization and modification process of nanoparticle. As a result, optimization and specific characteristics of a product can be attained. In addition, the invented synthesis method will be the route for the property study of specific characterization techniques throughout a large number of experimental works. Therefore, the study of synthesized nanoparticles is very meaningful and valuable for the development of new invented phase change materials.

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