Analysis on thermal transport properties of carbon based NFPCM in different concentrations for CTES applications

A Sathishkumar, Mrithul S, K S Aditya Kashyap, and M Cheralathan

Department of Mechanical Engineering, SRM Institute of Science and Technology, Kattankulathur, Chennai 603 203, Tamil Nadu, India.
Email: cheralam@srmist.edu.in

Abstract:
Energy crisis is one of the major problems the world is currently facing. Many researches are happening around the world to tackle the problem. Some involve in discovering new sources and some, in improving the available ones. This study belongs to the second category. This study aims to reduce the time taken to reach a certain temperature in a chiller, thereby reducing the running time of the chiller. A lower running time means lower energy requirement. This is done using Graphene based NFPCM in different concentrations. Three DI water filled balls with SDBS surfactant were mixed with 0.15 wt.%, 0.3 wt.% and 0.45 wt.% of GNP respectively. Three RTD sensors were connected to the balls at the center, 10mm from the center and 20mm from the center which were then connected to a data logger. The experiment was performed in a solidification bath into which the balls were suspended. The experiment was done at a surrounding temperature of -8ºC and -9ºC. The results were displayed in temperature vs time graphs. It was noted that with the increase in the graphene content in the balls, the time that was taken to reach the temperature has been reduced.

1. Introduction:
Most of the air conditioning, refrigeration, electronic cooling, transportation, and manufacturing industries aim at achieving energy efficient cooling in various applications. Mostly 40% of the energy in the world is consumed by the building sector. Utilizing alternate energy resources has always been the real topic for conversation amongst the researchers and policy makers. The supply and demand of energy is need of the hour. The mismatch between the process draws our attention towards the requirement of thermal energy storage (TES) systems (Zalba et al., 2003), to revive or to store the hot and cool thermal energy in the form of latent/sensible heat using the most efficient or suitable system. Making the proper usage of CTES in the chiller helps with reduction in the electricity cost i.e. by using it in uniform intervals of the day. This is mainly implemented in large buildings where centralized air conditioning (Cheralathan et al., 2007), supermarkets etc. where cooling is highly recommended. In current scenario where designers first look for Nano-PCMs for warm energy stockpiling frameworks, for cooling micro electric framework, in save materials for human solace or for space warming of huge structures. Variety of PCM such as salt hydrates, paraffin based, vegetable based and water based are in the area of interest. PCM are incorporated with nanomaterial such as SiO2, Al, TiO2, Cu, Al2O3, KOH, NaOH, carbon nanofibers etc. The addition of nanoparticles, thermal-conductivity and major
phase change are properties of the PCM. These have to be checked at different thermal conditions. According to studies paraffin as base PCM with copper, carbon Nano fibers (CNF), alumina, graphene and carbon nanotubes (CNT) as the nanomaterial. Satishkumar et al. [2] investigated on freezing characteristic of nanofluid PCM for building applications. The focal point of the investigation was to show the improved thermo physical properties of the NFPCM, which are very helpful to run the cool warm vitality stockpiling (CTES) framework and the hardening conduct of water based NFPCM encased in a circular compartment. The analysis utilized various centralizations of graphene nanoparticles added to the PCM. It was seen that the base PCM demonstrated a 9.5% expansion in warm conductivity with expansion of 0.6% of graphene nanoplatelets because of increment in surface are and high-thermal-conductivity. The paper also talks about effect of density of the solution and shows that increase of density is not recommended. Vikram et al. [3] this paper explored the solidification conduct of de-ionized (DI) water as the base stage change material (PCM) scattered with different mass division of sodium chloride and D-sorbitol in a circular epitome. The cementing tests were completed at a shower temperature of - 7°C and DI water experiences a sub cooling of - 5.4°C. In any case, the sub cooling generously decreased to - 2.8°C for DI water with 0.5wt. % sodium chloride and 1 wt. % of D-sorbitol. The cooling rate is found to diminish regarding increment in convergence of the dispersants in sub cooling district, however at a specific focus both dispersants give the improved cooling rate to a given driving potential than DI water. It is inferred that decrease of sub cooling and incomplete charging of water based PCMs would be useful to improve the vitality productivity of the cool warm vitality stockpiling (CTES) framework. Refat al-shannaq et al. [22] this study aims at increasing the thermal conductivity of PCM which decide freezing and melting times. This study takes a unique method by using graphite sphere filled with PCM. It shows that melting and freezing times can be reduced by 44.4% and 53.7% respectively and it also shows that minimum super-cooling can also be achieved inlet temperature and volumetric flow rate has an effect on freezing rate. Kumaresan et al. [23] this study works on decreasing the time of solidification. In this study they have used multi wall carbon nanotubes (MWCNT) having base PCM as de-ionized water. It was seen that a significant reduction in solidification time of 14% was achieved with a maximum of 20.1%. It was also seen that MWCNT also act as a nucleating agent which shows a reduction in sub cooling. Ting zou et al. [24] in this study a composite PCM of CaCl2•6H2O is prepared using different concentration of urea, ethanol, SrCl2•6H2O and methyl cellulose. It shows that 15wt% urea and 5wt% ethanol gives an enthalpy of 127.2J/g, moreover addition of 2wt.% of SrCl2-6H2O reduced the super cooling to 0.95°C

2. Materials and methods

2.1 Selection of base PCM and Nanoparticle

The selection of the PCM depends on the thermal properties like high specific heat, high latent heat of fusion per unit, high thermal conductivity is essential for better thermal performance and heat transfer. Specific requirements depending on the situation like chemical properties. The PCM should be able to sustain phase change under cyclic thermal loading. Taking this into consideration DI Water is selected with a Thermal Conductivity of 0.608 W/mK for the research. DI water is characterized as the water where fundamentally all the particles are evacuated which incorporates a few cations, for example, iron, calcium, sodium and copper and a portion of the anions including chloride and sulfate. Table 1 shows the thermophysical properties of the DI water. Graphene nanoplatelets (GNP) selected as a nanomaterial due to its higher thermal conductivity for low density. Also, stability of the NFPCM purely based on the density of the nanomaterial used. The properties of the GNP purchased from Cheap Tubes, USA is listed in Table 2. Also, the TEM image of the GNP is shown in Figure 1.
Table 1 Thermo physical properties of water.

| Property                                | Value                        |
|-----------------------------------------|------------------------------|
| Liquid thermal conductivity at 20°C     | 0.598 W m⁻¹K⁻¹              |
| Solid k                                 | 2.2 W m⁻¹K⁻¹                |
| Solid density                           | 920 kg m⁻³                  |
| Liquid density at 4°C                   | 1,000 kg m⁻³                |
| Melting/freezing temperature            | 0 °C                         |
| Latent heat of melting                  | 334 kJ kg⁻¹                 |
| Specific heat water                     | 4.187 kJ kg⁻¹K⁻¹            |
| Specific heat ice                       | 2.108 kJ kg⁻¹K⁻¹            |

Table 2 Properties of Graphene Nanoplatelets (GNPs).

| Product Name                             | Graphene Nanoplatelets, 99% |
|------------------------------------------|------------------------------|
| Molecular Weight                         | 12.01 g/mol                  |
| Supplier                                 | Platonic Nanotech            |
| Particle Size (BET)                      | ≤10nm                        |
| Appearance                               | Powder                       |
| X-Ray Diffraction                        | Conforms                     |

2.2 Preparation of Nano fluid phase change material

Nanofluid stage change materials (NFPCM) planning comprises of a couple of successive advances when utilizing it as a working liquid in any CTES framework. NFPCM is simply not a blend of the nanoparticles and base PCM. The best possible blending, sonication of the nanoparticles is required to yield the best outcomes.

Figure 1 TEM image of the Graphene Nanoplatelets (Cheap Tube, USA)
Two-step method: In this method, first the nanoparticles are obtained by different methods and then are dispersed into the base liquid as per Fig. 2. A known mass of (SDBS: 1 wt. %) is blended in with a known volume of base PCM which is DI water. The volume of base PCM taken is 90% of the all-out volume encased inside the ball. The blend is then mixed for 15-20 minutes utilizing an attractive stirrer. Surfactants are mixes which diminish the surface pressure or the durable power between the fluid and strong. Surfactants may go about as cleansers, wetting operators, frothing specialists and dispersants. The graphene nanoparticles are then scattered in the above blend and the arrangement is mixed for another 30 mins. To get even scattering of the nanoparticles, the arrangement was ultrasonicated for 100 mins at a recurrence of 50 KHz.

![Methodology](image)

**Figure 2** Preparation method of NFPCMs

After observing and making sure that there is no sedimentation, formation of lumps or agglomeration in the NFPCM it is carefully taken out of the setup. One thing to be noted is that NFPCM should be prepared right before the experiment is conducted to get the best results. The size of dispersed nanoparticles in the base PCM was analyzed using a Scanning Electron Microscope(SEM). The SEM
image of NFPCM for maximum concentration is shown in Figure 3. After ensuring the above procedure is done sequentially and properly, the solidification experiments were conducted and discussed in the later sections.

3. Experimental Setup

The important components of experimental setup are explained below (Fig. 4). This system is suitable for changing the bath temperatures to get an apt study of the solidification and other relevant behaviors.

- Steel spherical capsule
- 3 RTD sensors (2 wire type)
- PTDC (Proportionate Differential Temperature Controller)
- Data logger (Agilent34970A)
- Heat transfer fluid
- Evaporator, Compressor, Condenser, Expansion valve
- Stirrer

The setup has many parts including a polyurethane insulated stainless steel tank of 12 litre capacity, filled with a mixture of 70 percent water and 30 ethylene glycol by volume which is usually used as an antifreeze. A heating coil of capacity 2000 watts and a chiller unit of capacity 5000 watts were also simultaneously used to set the required bath temperature in the tank. 30 percent ethylene glycol is mixed with water in the tank to prevent it from freezing at bath temperatures. Bath temperature was maintained through the PDTC with a range of ±0.15 C. The PDTC modulates the input power to the heater subject to the temperature of surrounding heat transfer fluid and HTFs temperature its continuously measured by a RTD (Resistance Temperature Detector) sensor which is incredibly sensitive. RTD positions are given in Fig. 5. A spherical ball was filled to the brim with the NFPCM leaving only 10 percent space to account for changes in volume due to solidification.

![Figure 4 Experiment Setup (Line diagram)]
Three RTDs are fixed at equal distances reference being the centre of the spherical ball. Due to the solidification behaviour of spheres, the RTD closest to the outer surface will experience higher subcooling rate when the entire setup is immersed in a -6C bath. RTD 101 reaching below 0 C indicates that the radial volume between the outer surface and the RTD position has solidified. This explains the solidification behaviour. The complete solidification of a 75 mm diameter spherical ball filled with 180ml of DI water took 86 mins approx. The same for a 70mm ball took 73 mins.

The chiller unit is operated at a constant load and to achieve the required temperature of bath, a PTDC was used that modulated the heating component output on the basis of the temperature of the bath gauged by the RTD sensor. Mechanical stirrer driven by a 9-watt electrical motor running at a speed of 1280 rpm was installed at the top to achieve a stable temperature of the bath in the tank. This setup is suitable for altering the various bath temperatures to give a better analysis of the solidification and its properties. The tank has constant temperature inside the bath area which helps the ball to solidify and give uniform results.

The three two wire RTD sensors are connected to a datalogger (Agilent 34970A). The time interval between capturing the readings can be changed accordingly. Lesser the time interval, more accurate will be the results. For our experimental study the time interval between two temperature recordings is fixed as 20 seconds.

4. RESULTS AND OBSERVATION

4.1 Measurement of Density

The density of both the water and NFPCM are estimated at air temperature by gauging a fluid example in a standard volumetric cup (Class An) of 25 ml and 50 ml, utilizing a high precision electronic parity (± 0.002 g) with isolated space compartment. The methodology is rehashed multiple times to accomplish greater precision. It is observed from the ‘Table 2’ the percentage of increasing the density is maximum for 1.05 wt. % of GNP. Also, the variation of density (minimum) will not affect the stability of NFPCM.

\[
\text{Density } \rho = \frac{m_t - mf}{V_{nf}}
\]

Where, \(m_t\) = mass of flask and NFPCM
\( m_{fl} = \text{mass of the flask} \)
\( V_{nf} = \text{volume of NFPCM in flask} \)

### Table 3 Density Measurement of different NFPCMs.

| Samples | Composition | \( m_t \) (kg) | \( m_{fl} \) (kg) | \( P \) (kg \( m^{-3} \)) | % of increase in density |
|---------|-------------|----------------|-----------------|----------------|-------------------------|
| S1      | DI water    | 0.2790         | 0.077           | 1010           | -                       |
| S2      | 0.4%        | 0.2798         | 0.077           | 1014           | 0.396                   |
| S3      | 0.8%        | 0.2806         | 0.077           | 1018           | 0.792                   |
| S4      | 1.2%        | 0.2814         | 0.077           | 1022           | 1.188                   |

### 4.2 Variation of Transient Temperature of NFPCMs

The variation of transient temperature of DI water is shown in Figure 6 to show the degree of subcooling and the onset of solidification at various locations radially inside the spherical capsule. It is seen that the maximum degree of subcooling of 3.8°C occurred at the middle of the capsule. The same trend of subcooling was reported by other authors and researchers who researched the related topics with water encapsulated in spherical hollow ball during their experiments.

![Figure 6 Variation of transient temperature of DI water (Tsurr = -6°C).](image-url)
The difference in subcooling between the ours and other’s results is because of the difference in capsule size, geometry and material of capsule. It is noticed from the figure that the outbreak solidification occurs at the same time in all the radial locations. This is due to latent heat releasing form the nucleation sites formed close to the surface, which is absorbed by the surrounding subcooled water. Further, in order to assess the effect of nucleating agent and surfactant (SDBS) during solidification, the experimentation trials were conducted with water + surfactants and at different concentration of GNP nanoparticles at the surrounding bath temperature of -6°C.

![Figure 7 Variation of transient temperature of NFPCMs (Tsurf = -6°C).](image)

Figure 7 shows that the maximum reduction in solidification time of 18.56% was achieved with NFPCM containing 1.2 wt %. From the graph we can see that the main problem of subcooling that exist in water is reduced with great margin with the addition of SDBS and reduced to a great extent with the addition of nucleating agent. Figure 7 depicts that the presence of GNP in water reduced the solidification time considerably by 19% at the surrounding bath temperature of -7°C due to its enhanced thermal transport properties.

It had already been shown that the subcooling was max at the middle of the capsule and hence the corresponding temperature-time history at this location. It has been noticed that the addition of nucleating agent or surfactant has no observable changes during the liquid sensible cooling region as well as in the onset of solidification. Nevertheless, the presence of surfactant and nucleating agent has a significant influence on the reduction of the subcooling from 3.2°C to 1.3°C and the presence of nucleating agent to a great extent eliminating the area of subcooling, when compared to that of water.

Considerable energy saving is possible in the chiller based CTES system due to increase in the operating temperature of the evaporator form -7°C by using the enhanced heat transfer characteristics of the
NFPCM during the solidification. This accelerated mode of charging, particularly with water as the PCM, is extremely helpful to alleviate the major problem of non-uniform charging/discharging encountered in the CTES system for various applications that demand uniform heat flux in a short duration.

![Variation of transient temperature of NFPCMs (Tsurr = -6°C).](image)

**Figure 8** Variation of transient temperature of NFPCMs (Tsurr = -6°C).

The elimination of subcooling in water due to the presence of nucleating agent facilitates to operate the evaporator of the refrigeration system at a relatively higher temperature. The experiments were also conducted five times to explore the effect of nanoparticle on the solidification characteristics of water + nucleating agent at both surrounding bath temperature.

Based on the present experimental results, further research works need to be carried out to optimize the concentration of the GNP towards the development of NFPCM based CTES system for various thermal and refrigeration applications. Figure 8 shows the variation of temperature at different locations for a surrounding temperature of -6°C.

5. DSC Analysis

The DSC curve describes the enthalpy variation for both freezing and melting. Figure 9 shows the change in enthalpy for both freezing and melting for DI water. The green color indicates melting of the solution which is above x-axis and the values are of positive sign. The blue color indicates freezing of the solution which is below x-axis and the values are of negative sign. This DSC curves are used to find the phase transition temperature. The area of the graph occupied depicts the enthalpy of the solution.
The change enthalpy of the DI water while melting is 325.5 J/kg. The change enthalpy of DI water while freezing is 277.8 J/kg. Now the enthalpy should be reduced. In order to reduce the enthalpy, change Nanoparticles are added.

**Enthalpies variation for both freezing and melting - 0.15 Wt. % GNP**

**Figure 9** DSC curve of DI water for both freezing and melting conditions.

**Figure 10** DSC curve of NFPCM (0.15 wt. %) water for both freezing and melting conditions.
Figure 10 describes about the DSC curve of NFPCM (0.15 wt. %) water for both freezing and melting conditions. Here the solution is DI water added with surfactant and 0.15 wt.%. The area occupied in this graph is reduced to some extent as impurities like GNP are added at a calculated percentage. The solution’s enthalpy changes while melting is 310.9 J/kg. The solution’s enthalpy changes while freezing is 261.2 J/kg. The difference between the enthalpies of freezing is 14.6 J/kg. The difference 36 between the enthalpies of melting is 16.6 J/kg. There is a minimal reduction in the enthalpy change.

![DSC curve of NFPCM (0.3 wt. %) water for both freezing and melting conditions.](image)

Figure 11 DSC curve of NFPCM (0.3 wt. %) water for both freezing and melting conditions.

Figure 11 depicts that the DSC curve of NFPCM (0.3 wt. %) water for both freezing and melting conditions. Here the solution is DI water added with surfactant and 0.30 wt% GNP. The area occupied in this graph is reduced to an extent as impurities are added at an increased volume. The solution’s enthalpy changes while melting is 281.4 J/kg. The solution’s enthalpy changes while freezing is 246.2 J/kg. The difference between the enthalpies of freezing is 29.5 J/kg. The difference between the enthalpies of melting is 15 J/kg. Figure 12 depicts that the DSC curve of NFPCM (0.45 wt. %) water for both freezing and melting conditions. The solution’s enthalpy changes while melting is 269.5 J/kg. The solution’s enthalpy changes while freezing is 241.1 J/kg. The difference between the enthalpies of freezing is 11.9 J/kg. The difference between the enthalpies of melting is 5.1 J/kg. There is a minimal reduction in the enthalpy change. In this manner if the concentration of GNP or impurity is increased then the change in enthalpy would also be reduced and better results would be obtained.
6. Conclusion
After performing the experiments on the characteristics of solidification of water based PCM with an incorporated nucleating agent, the following points have been concluded:

The addition of Graphene Nano-Platelets as nucleating agent for the initiation of solidification of NFPCM effected a complete reduction in supercooling. Maximum reduction of solidification time with the addition of GNP was achieved at 0.45 wt% of GNP and is 23.07% for $T_{surr} = -8^\circ$C and 18.29% for $T_{surr} = -9^\circ$C.

There is no appreciable improvement in density of the NFPCM. Enthalpy of the NFPCM is reduced with the addition of GNP (10 % for maximum concentration which is 0.45 wt% of GNP).

Acknowledgment
The authors are grateful to the DSC Laboratory, SRM Institute of Science and Technology, Kattankulathur Campus, Chennai, for supplying the required research facility.

References
[1] Refat Al-Shannaq, Mohammed M.Farid 2018 A novel graphite-PCM composite sphere with enhanced thermo physical properties of Applied Thermal Engineering 142(2018) 401-409.
[2] A.Miliozzi, R.Liberatore, T.Crescenzi, E.Veca 2015 Experimental analysis of heat transfer in passive latent heat thermal energy storage systems for CSP plants of ATI 2015-70th conference of the ATI Engineering Association, 730-736.
[3] R.Y. Sakr, Ahmed A.A. Attia, Ahmed A. Altohamy, Ismail M.M. Elsemary, M.F. Abd Rabbo 2017 Heat transfer enhancement during freezing process of Nano Phase Change Material (NPCM) in a spherical capsule of Applied Thermal Engineering 125 (2017) 1555–1564.

[4] Alibakhsh Kasaeiana, Leyli bahramia, Fathollah Pourfayaza, Erfan Khodabandehb, Wei-Mon Yan 2017 Experimental studies on the applications of PCMs and nano-PCMs in buildings: A critical review of Energy and Buildings 154 (2017) 96–112.

[5] Ahmed A. Altohamy, M.F. Abd Rabbo, R.Y. Sakr, Ahmed A.A. Attia 2015 Effect of water based Al2O3 nanoparticle PCM on cool storage performance of Applied Thermal Engineering 84 (2015) 331-338.

[6] P Chandrasekaran, M Cheralathan, V Kumaresan, R Velraj 2014 Solidification behavior of water based nanofluid phase change material with a nucleating agent for cool thermal storage system of international journal of refrigeration 41(2014)157-163.

[7] A Sathishkumar, V Kumaresan, R Velraj 2016 Solidification characteristics of water-based graphene nanofluid PCM in a spherical capsule for cool thermal energy 6 storage applications international journal of refrigeration 66(2016)73–83.

[8] V.Kumaresan, P.Chandrasekaran, Maitreyee Nanda, A.K. Maini, R.Velraj 2013, Role of 6 PCM based nanofluids for energy efficient cool thermal storage systems of International 8 journal of Refrigeration 36(2013) 1641-1647.

[9] Chan CW, Tan FL. Solidification inside a sphere- an experimental study. IntCommun Heat Mass Transfer 2006;33:335-41.