

1 Article

2 **Experimental Investigation of Freezing and Melting Characteristics of Graphene Based**  
3 **Phase Change Nanocomposite for Cold Thermal Energy Storage Applications**4 **Shaji Sidney<sup>1</sup>, Mohan Lal D<sup>1</sup>, Selvam C<sup>2</sup> and Sivasankaran Harish<sup>3,\*</sup>**5 <sup>1</sup> Department of Mechanical Engineering, Anna University, College of Engineering Campus, Chennai,  
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13  
14 **Abstract:** In the present work freezing and melting characteristics of water seeded with chemically functionalized  
15 graphene nano-platelets in a vertical cylindrical capsule was experimentally studied. The volume percentage of  
16 functionalized graphene nano-platelets was varied from 0.1% to 0.5% with an interval of 0.1%. The stability of the  
17 synthesised samples were carried out by zeta potential distribution. The thermal conductivity of the  
18 nanocomposite samples were experimentally measured using transient hot wire method. A maximum  
19 enhancement of ~24 % in the thermal conductivity was observed for the 0.5% volume percentage in the liquid state  
20 while a ~53 % enhancement in the solid state. Freezing and melting behaviour of water dispersed with graphene  
21 nanoplatelets were carried out using a cylindrical stainless steel capsule in a constant temperature bath. The bath  
22 temperatures considered for studying freezing characteristics were considered to be -6°C and -10°C, while to study  
23 the melting characteristics the bath temperature was set as 31°C and 36 °C. The freezing and melting time decreased  
24 for all the test conditions when the volume percentage of GnP increased. The freezing rate was enhanced by ~  
25 43% and ~32% for the bath temperatures of -6°C and -10°C respectively at 0.5 vol % of graphene loading. The  
26 melting rate was enhanced by ~42% and ~63% for the bath temperature of 31°C and 36 °C respectively at 0.5 vol %  
27 of graphene loading.28 **Keywords:** nanocomposite, melting, freezing, graphene, thermal conductivity  
2930 **1. Introduction**31 The world is facing a lot of challenges in storing and retrieving energy and in fulfilling the pressing  
32 demands for energy. Heat is the main form of energy which can be stored in the form of latent heat in phase change  
33 materials such as water or organic fluids. The oldest form of thermal energy storage (TES) probably involves  
34 harvesting ice from lakes and rivers and storing it in well-insulated warehouses throughout the year for use in  
35 almost all tasks that mechanical refrigeration satisfies today, including food preservation, cooling of drinks, and  
36 air-conditioning. A variety of TES techniques have been developed over the past decades. Today compressed-air  
37 storage and batteries are mostly used to meet many of the thermal energy storage requirements.38 Instead of storing electrical energy in a battery or as compressed air, thermal energy storage using water  
39 based ice is one of the most ancient modes of energy storage and is considered to be the most efficient and economic  
40 mode of energy storage, as it eliminates the recurring expenses incurred for the replacement of batteries. Water  
41 can be used as an effective thermal energy storage material due to its higher thermal conductivity and excellent  
42 freezing / melting characteristics. Cold energy stored in ice can be effectively used to remove heat from another  
43 fluid in a secondary circuit. Water acts as a good thermal energy storage material in various industries such as the  
44 dairy industry for chilling milk [1, 2], pharmaceutical [3] and chemical industries for transportation and storage  
45 without depending on batteries.46 The refrigeration sector has now evolved the use of DC powered compressors that directly utilise the use  
47 of solar energy eliminating inverters. Likewise, few researches have started using DC powered compressors  
48 without batteries autonomously depending on ice based thermal storage [1-4]. Per Henrik Pedersen and Ivan Katic  
49 (2016) validated that the energy content in ice produced by the DC compressor was higher than the energy content  
50 in a lead-acid battery, in terms of both volume and weight.

1 However further research has been going on to replace water with any other fluid or to choose the best  
2 additive so as to improve the freezing and melting characteristics to store more thermal energy than the existing  
3 ones and to have smaller thermal storage devices. One of the most suitable methods is to add highly thermal  
4 conductive material to the water. Among the materials, metal and metal oxides in nano metric sizes exhibit  
5 excellent thermal transport properties. Owing to the higher density of metal and metal oxide powders, carbon  
6 based nanomaterials are widely used due to their higher aspect ratio. Hence, adding carbon based nano materials  
7 is an effective way of increasing the thermal energy storage of water. Thus, this study deals with the experimental  
8 investigation on freezing and melting characteristics of graphene based water for thermal energy storage  
9 applications such as milk chilling, chemical industries etc.

10 Guruprasad et al. (2017) suggested that for medium and low temperature systems, the use of organic  
11 materials as PCM can be cost effective and will improve the thermal conductivity of thermal energy storage  
12 materials and play a major role in increasing the charging and discharging rate. They inferred that the thermal  
13 enhancement achieved with carbon based nanostructures is better than those with metallic and metal oxide. The  
14 maximum enhancement in thermal conductivity obtained by Sathish Kumar et al. (2016) was 9.5% for 0.6 wt. % of  
15 graphene nano platelets dispersed in DI water with the use of surfactants. A 24% reduction in the solidification  
16 time was observed for the nanocomposite with 0.6 wt. % of GnP. The experiments conducted by Ahammed et al.  
17 (2016) showed an increase of 5.23% in thermal conductivity of graphene–water nanocomposite, prepared using  
18 surfactant, when the volume concentration of nanoparticles is changed from 0.05% to 0.1% and 14.56%  
19 enhancement is observed when the volume concentration increases by three times. Harikrishnan et al. (2014)  
20 inferred that the latent heat of composite PCMs is lower than that of base material for both melting and freezing  
21 and the maximum changes are 3.56% and 3.82 %, respectively. The thermal conductivity of graphene–water  
22 nanocomposite is found to be higher when compared with that of the metal oxide nanoparticles and the same is  
23 lower when compared with that of pure metallic nanoparticles. However, the use of pure metallic nanoparticles  
24 in fluids causes the problem of stability. Hence Ahammed et al. (2016) suggested that instead of using a high-  
25 volume concentration of metal oxide and pure metal nanoparticles, a low volume concentration of graphene can  
26 be used as the heat transfer fluid to enhance thermal conductivity. Harish et al. (2015) treated graphene nano-  
27 particles with concentrated nitric acid to avoid the use of surfactants. A maximum thermal conductivity  
28 enhancement of ~230% was measured in lauric acid treated with the acid graphene nano inclusions for 1 vol %.

29 Due to the ever growing demand for energy, there is need for energy storage in PCMs. The PCMs usually  
30 are encapsulated in containers/capsules. Different researches have used different geometrical shapes for the  
31 capsules such as cylinders, spheres, pyramids, cones, rectangular and cuboids with different materials like stainless  
32 steel, aluminium, copper, polypropylene, and polyolefin for numerical and experimental studies. The material  
33 selection was based on the property of the PCM used and applications [11-16]. Yoon et al. (2001) studied the  
34 freezing properties of water in a circular cylinder kept horizontally. During the initial phase of freezing annular  
35 ice layer started growing on the surface of the cylinder at a higher rate. This was followed by the asymmetric ice  
36 layer at a medium cooling rate and finally was the instantaneous ice layer growing over the whole region at a low  
37 cooling rate. Kalaiselvam et al. (2008) performed analytical analysis in the freezing and melting process of different  
38 PCMs encapsulated in a cylindrical capsule. The presence of heat generation enhanced the freezing time it also  
39 hastened the melting. Total freezing time was subjected to Stefan's Number and heat generation parameter,  
40 whereas complete melting time depended on equivalent thermal conductivity.

41 Nanotechnology is being used in many applications to provide more efficient energy transfer. Application of  
42 nanocomposites in heat exchanging devices appears promising with these characteristics. In this context, the use  
43 of nano-particles in water provides a scope for performance improvement in thermal storage for an ice bank tank.  
44 The main objective of this work is to study the freezing and melting characteristics of water-graphene  
45 nanocomposite in a vertical cylindrical capsule and compare it with base fluid. Graphene has been widely accepted  
46 as it is a single-atom-thick sheet of hexagonally arrayed  $sp^2$ -bonded carbon atoms ever from its discovery by  
47 Novoselov et al. [19]. Graphene possesses remarkable thermophysical properties due to its large specific surface  
48 area (50–750  $m^2/g$ ) and extremely high thermal conductivity (3000–5000 W/m K) [20–28]. The thermo-physical  
49 properties of graphene nanocomposite such as thermal conductivity are also determined for the temperatures  
50 ranging from -10°C to 40°C.

51

## 52 2. Materials and Methods

53 The thermal conductivity of the functionalized water-graphene nanocomposites were measured  
54 experimentally. The study was carried out using chemically treated graphene nano platelets to avoid the use of  
55 surfactants which were used to improve stability of the nanocomposites.

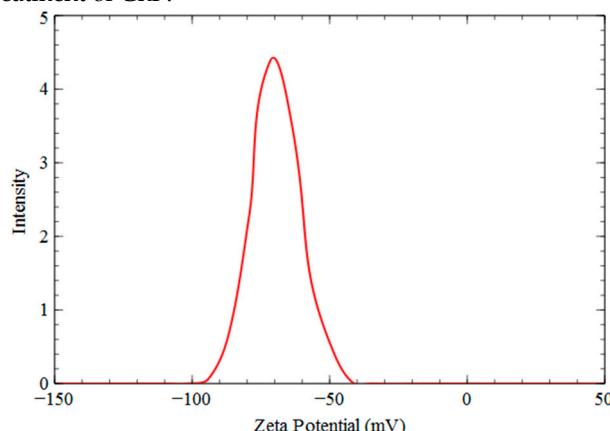
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## 2 2.1 Preparation of graphene nanocomposite

3 Nanocomposite was prepared prior to the experimental work using the two step method. The essential  
4 requirements for nanocomposites are: stable suspension, adequately durable, negligible agglomeration of  
5 particulates, no chemicals change of the particulates or fluid etc. The required quantity of graphene nano platelets  
6 was purchased from XG Sciences (USA). The GnP-H<sub>2</sub>O was prepared by covalent functionalization method. The  
7 GnPs were chemically functionalised with concentrated nitric acid (68 wt %) to improve the dispersion of the  
8 particles and to avoid the use of surfactants. 5g of graphene nano-platelets were dispersed in 250 ml of  
9 concentrated nitric acid taken in a conical flask and then refluxed at a temperature of 100°C for 2 hours. For  
10 uniform dispersion, the fluid was stirred using a magnetic stirrer. To maintain constant temperature during the  
11 process, the conical flask was placed in a constant temperature bath, which was maintained at 100°C. After 2 hours,  
12 the conical flask was taken out from the oil bath and allowed to cool down slowly to room temperature. The nano-  
13 platelets were filtered then washed with DI water and dried in a furnace at 160°C [10]. Nitric acid treatment was  
14 used to chemically modify the surface of graphene platelets in order to increase the surface-active sites for  
15 electrochemical reactions due to the hydrophobic nature of GnP. The nitric acid treatment introduced more  
16 oxygen/nitrogen-containing functional groups onto the graphene surface, and clearly enhanced the hydrophilicity  
17 of the graphene. This will promote the wettability of graphene when it is dispersed in DI water which is the base-  
18 fluid. For the experimental work, the volume percentage of GnP were 0.1%, 0.2%, 0.3%, 0.4% and 0.5%. Depending  
19 on the volume percentage, the required quantity of chemically functionalised GnP was added to the DI water and  
20 was stirred for 30 minutes using a magnetic stirrer. After stirring, the fluid was ultra-sonicated using a digital  
21 sonicator (Qsonica, USA) for 2 hours to enhance the stability. The graphene nanocomposites thus prepared were  
22 kept for observation and no particle sedimentation was observed at the bottom of the bottle even after two weeks.  
23

## 24 2.2 Stability analysis

25 Zeta potential measurement was carried out in order to ensure the stability of the prepared nanocomposite.  
26 The general reference of average zeta potential values are considered more negative than -30 mV or more positive  
27 than +30 mV in order to predict the stability of dispersion while poor stability shows a value below 20 mV [28, 29].  
28 The fig.1 shows that the stability of nanocomposite (0.5 vol. %) lies in the excellent stability region with a Zeta  
29 potential peak of -69.4mV. The nano particles are highly electronegative, and this indicates excellent stability of  
30 nanocomposite after acid treatment of GnP.



31 32 **Fig. 1.** Zeta potential distribution of nanocomposite at 0.5 vol. %

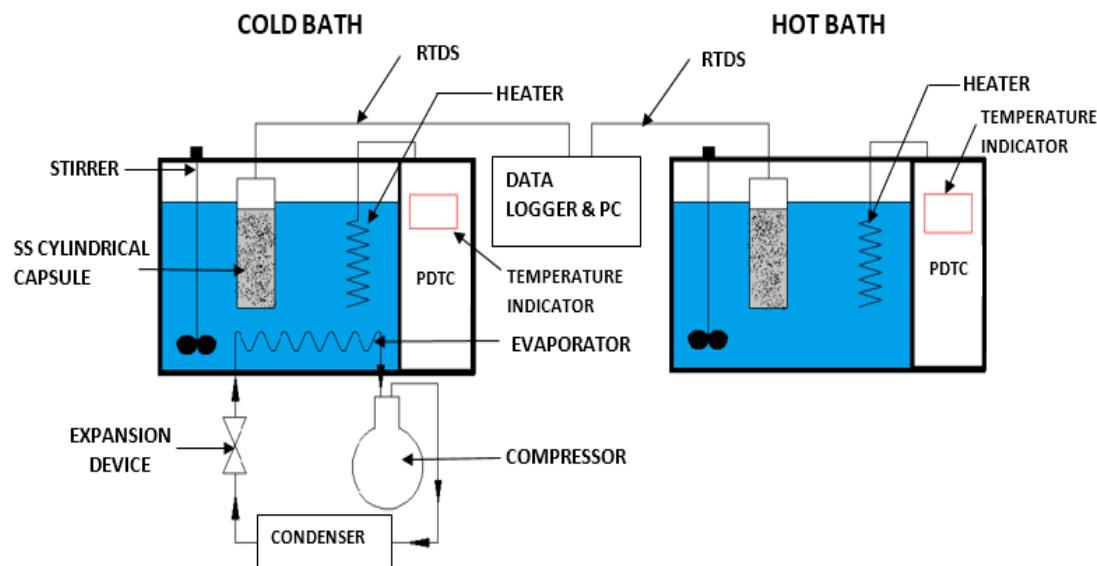
## 33 2.3 Thermal conductivity measurement

34 The thermal conductivity of the nanocomposite was measured in the temperature range of -10°C to 40°C  
35 using KD2 Pro thermal analyzer (Decagon devices, USA) which works on the principle of transient hot wire  
36 method. The nanocomposite sample was filled in a small container and the KS1 sensor probe was inserted at the  
37 center of the container. The desired test temperatures of the samples were achieved by immersing the container in  
38 a refrigerated/heating circulator bath system, which maintains the temperature of the surrounding fluid with an  
39 accuracy of  $\pm 0.03^\circ\text{C}$ . The sensor used to measure the thermal conductivity in the KD2 Pro apparatus was the KS-  
40 1 sensor (60mm long, 1.3mm diameter) with an accuracy of  $\pm 5\%$ . The sensor is integrated with a heating element  
41 and a thermo-resistor in the core and is connected to a microprocessor to control and conduct the measurements.  
42 The precise results were obtained by keeping the probe continuously for 20 minutes in the fluid sample, after  
43 attaining the desired equilibrium temperature. Five measurements were taken for each sample, to ensure the  
44 repeatability and accuracy of the result. While measuring the thermal conductivity in the solid phase of the

1 nanocomposite, a thermal grease was applied on the surface of the KS-1 sensor as per the instructions by the KD2  
 2 Pro thermal analyser manual. Holes were drilled on the solid nanocomposite then the KS-1 sensor with thermal  
 3 grease was inserted to measure the thermal conductivity.

#### 4 **2.4 Experimental test facility for freezing and melting characteristics**

5 Fig.2 shows the schematic representation of the experimental test facility which was used to study  
 6 the freezing/melting characteristics of the nanocomposite. The experiments consist of charging and discharging of  
 7 nanocomposite in a stainless steel cylindrical capsule. A cold bath was used for freezing/charging experiments and  
 8 a hot bath was used for the melting/discharging experiment. Experiments were carried out based on the test matrix  
 9 as given in section 2.5.



10 **Fig. 2. Experimental setup for the freezing/melting study**

11 A stainless steel cylindrical capsule was used to carry out the freezing and melting experiments as  
 12 in most of thermal storage systems. The capsule was made of SS as most of the food storage appliances are made  
 13 of SS [1]. The vertical cylindrical capsule had an inner diameter of 46 mm and height of 120 mm of a total capacity  
 14 of 200ml with a wall thickness of 1.5mm. The temperature sensor at the middle of the cylinder was considered for  
 15 the freezing and melting study. Nanocomposite was filled inside the capsule and then it was placed in the freezing  
 16 bath. The capsule was filled with only 80% of its full capacity i.e. 160ml to account for the volume of RTDs and the  
 17 expansion of water when it becomes ice. The experimental setup for freezing (Charging) consisted of a freezing  
 18 unit with an evaporator tank, a condensing unit, a PDTC (Proportional differential temperature controller), a  
 19 cylindrical capsule, a computer and a data logger. The cold bath was filled with a mixture of water and ethylene  
 20 glycol so that negative temperatures can be achieved without freezing the cold bath. The transient temperature  
 21 variations of the nanocomposites were measured and recorded continuously for every 30 seconds using a data  
 22 logger. The experimental setup for melting (Discharging) consists of a hot bath with a storage tank, a heating coil,  
 23 a PDTC (Proportional differential temperature controller), a cylindrical capsule, a computer and a data logger.  
 24

#### 25 **2.5 Test matrix and working procedure**

26 Freezing and melting experiments were carried out by placing a cylindrical SS capsule filled with  
 27 nanocomposite in a constant temperature bath. The bath temperatures considered were -6°C and -10°C for the  
 28 freezing the nanocomposite till -3 °C while 31°C and 36 °C were considered for the melting experimentations till  
 29 the nanocomposites reached 30°C. Table 1 shows the test matrix for freezing and melting experiments.  
 30  
 31  
 32  
 33  
 34  
 35  
 36

1

**Table1:** Freezing and melting test matrix

| Volume Percentage of functionalised GnP | Initial temperature of the sample | Bath temperatures for freezing | Sample temperature after freezing | Bath temperature for melting | Sample temperature after melting |
|---|-----------------------------------|--------------------------------|-----------------------------------|------------------------------|----------------------------------|
| 0%, 0.1%, 0.2%, 0.3%, 0.4% & 0.5%       | 32 °C                             | -6°C & -10°C                   | -3°C                              | 31°C & 36°C                  | 30°C                             |

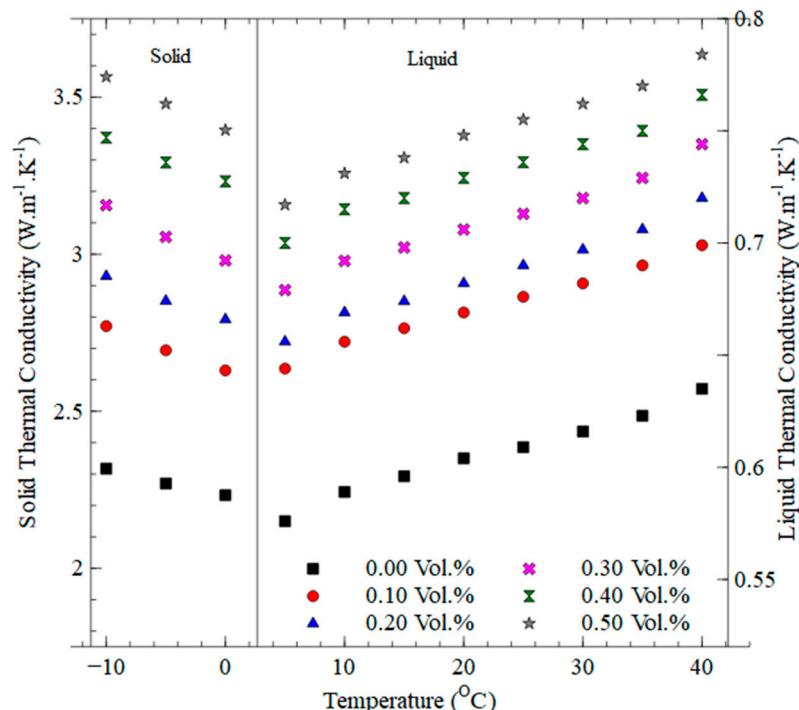
2 During the charging process, the test sample was placed inside the cold bath tank where the temperature  
 3 was maintained below the freezing temperature of the nanocomposite. In the beginning of the charging process,  
 4 the nanocomposite was sensibly cooled until it reached the freezing temperature. At freezing temperature, the  
 5 latent heat was absorbed by the nanocomposite and it underwent phase change from liquid to solid. After freezing,  
 6 the nanocomposite was again sensibly cooled till the bath temperature was achieved.

7 During the discharging process, the cylindrical capsule with fully solidified nanocomposite is placed  
 8 inside the storage tank where the temperature is maintained above the melting temperature of the nanocomposite.  
 9 In the beginning of the discharging process, the nanocomposite is sensibly heated until it reaches the melting  
 10 temperature. At the melting temperature, the latent heat is released by the nanocomposite and it undergoes phase  
 11 change from solid to liquid. After melting, the nanocomposite is again sensibly heated till the bath temperature is  
 12 achieved.

### 13 3. Results and Discussion

#### 14 3.1. Thermal conductivity

15 Initially, the thermal conductivity of pure DI water was experimentally measured at temperatures  
 16 ranging from -10 to 40°C. Then, the experimental data were compared with the standard data to validate the  
 17 measurement practice [30], [31], [32]. It was found that the measured values matched-up with the standard values.  
 18 The average percentage deviation of measured values from the standard values of the base-fluid was  $\pm 2\%$ .



19

1 Fig. 3: Variation of thermal conductivity with respect to temperature for different volume percentage

2 Fig. 3 shows the variation in thermal conductivity of nanocomposite in liquid state and it is observed that  
3 the graphene nanocomposite has higher thermal conductivity when compared to the base-fluid. The dispersion of  
4 GnP significantly improved the thermal conductivity of the nanocomposite. The reason behind this enhancement  
5 of thermal conductivity is the nano size of the GnP and the two-dimensional geometry of GnP that increases the  
6 exposure to the base-fluid.

7 By increasing the volume percentage of GnP, the thermal conductivity is found to increase. The average  
8 increase in thermal conductivity compared to base fluid are found to be 11.01%, 13.38%, 17.23%, 20.96% and 23.95%  
9 respectively for the considered volume percentage of GnP in the liquid state. The thermal conductivity for the  
10 0.5% volume percentage is 23.95% higher compared to that of the base fluid, whereas Selvam et al. (2016) obtained  
11 a thermal conductivity 16% higher than the base fluid at the same concentration. The superior thermal conductivity  
12 is due to the use of chemically functionalised GnP instead of dispersing surfactants in the base fluid for better  
13 stability. Whereas, in the solid state as shown in Fig.3, the average surge in thermal conductivity compared to  
14 base fluid are 18.67%, 25.7%, 34.75%, 45.08% and 53.05% respectively for the considered volume percentage of  
15 GnP.

16 Thermal conductivity in solid state was higher than in the liquid state. The reason for this sudden increase  
17 in thermal conductivity when fluid turns to solid state is due to the orderly solid structure that causes better  
18 accelerated molecular vibrations. The sudden fall in thermal conductivity when solid state changes to liquid state  
19 might be caused by the orderly stable microstructure in solid turning into a disorderly structure in liquid state.  
20 Table 2 shows the tabulated comparison of thermal conductivity of nanocomposite with respect to temperature  
21 and % volume fraction. The background for the thermal conductivity enhancement is an attribute to the high  
22 aspect ratio, 2-D geometry and stiffness of graphene.

23 The acid treatment of GnP plays a significant role in the enhancement of thermal conductivity in the  
24 nanocomposites. Instead of adding surfactant, Nitric acid treatment was used to chemically modify the surface of  
25 GnP in order to increase the surface-active sites for electrochemical reactions and also to improve the stability. As  
26 surfactants are not used, the effects of degradation in thermal conductivity while adding surfactant are completely  
27 avoided in this nanocomposite.

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52 surfactants are not used, the effects of degradation in thermal conductivity while adding surfactant are completely  
53 avoided in this nanocomposite.

1 Table:2 Thermal conductivity of nanocomposite with respect to temperature and vol%

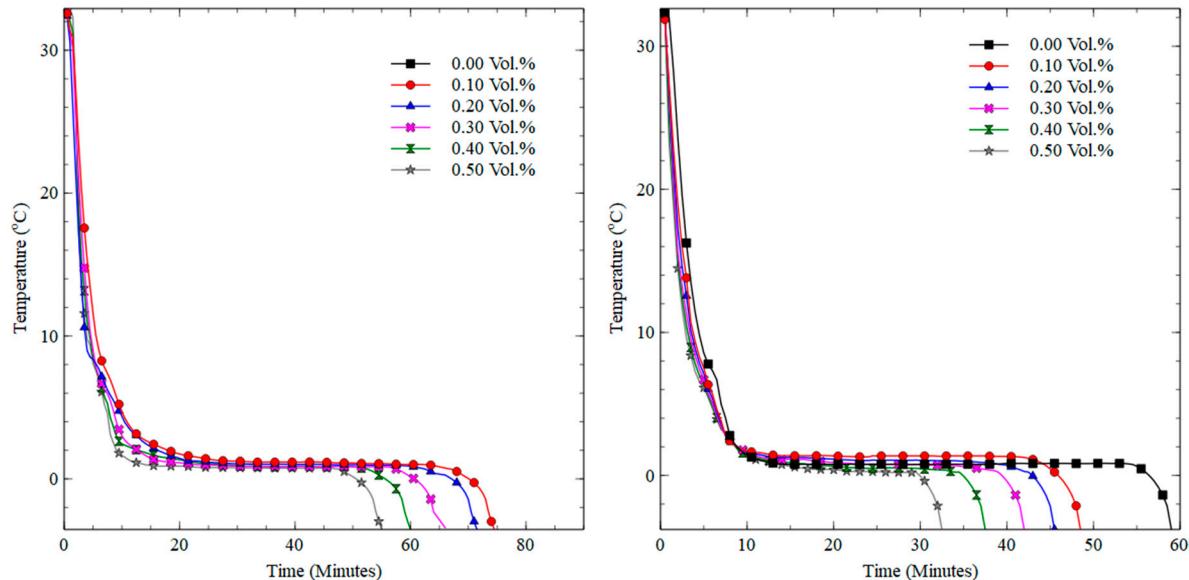
| Temp<br>(°C) | DI Water<br>Standard<br>K<br>(W/mK) | DI Water<br>Measured<br>K<br>(W/mK) | Nanocomposite (0.1%) |                               | Nanocomposite<br>(0.2%) |                               | Nanocomposite<br>(0.3%) |                               | Nanocomposite<br>(0.4%) |                               | Nanocomposite<br>(0.5%) |                               |
|--------------|-------------------------------------|-------------------------------------|----------------------|-------------------------------|-------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------|-------------------------------|
|              |                                     |                                     | K<br>(W/mK)          | Percentage<br>Increase<br>(%) | K<br>(W/mK)             | Percentage<br>Increase<br>(%) | K<br>(W/mK)             | Percentage<br>Increase<br>(%) | K<br>(W/mK)             | Percentage<br>Increase<br>(%) | K<br>(W/mK)             | Percentage<br>Increase<br>(%) |
| -10          | 2.30                                | 2.317                               | 2.771                | 19.59                         | 2.930                   | 26.46                         | 3.156                   | 36.21                         | 3.371                   | 45.51                         | 3.565                   | 53.87                         |
| -5           | 2.25                                | 2.27                                | 2.694                | 18.67                         | 2.851                   | 25.59                         | 3.055                   | 34.58                         | 3.292                   | 45.02                         | 3.479                   | 53.24                         |
| 0            | 2.22                                | 2.233                               | 2.63                 | 17.77                         | 2.792                   | 25.05                         | 2.980                   | 33.46                         | 3.232                   | 44.73                         | 3.395                   | 52.04                         |
| 5            | 0.57                                | 0.576                               | 0.644                | 11.80                         | 0.656                   | 13.87                         | 0.679                   | 17.8                          | 0.700                   | 21.53                         | 0.717                   | 24.42                         |
| 10           | 0.58                                | 0.589                               | 0.656                | 11.37                         | 0.669                   | 13.57                         | 0.692                   | 17.52                         | 0.715                   | 21.34                         | 0.731                   | 24.19                         |
| 15           | 0.589                               | 0.596                               | 0.662                | 11.07                         | 0.674                   | 13.03                         | 0.698                   | 17.1                          | 0.720                   | 20.83                         | 0.738                   | 23.85                         |
| 20           | 0.598                               | 0.604                               | 0.669                | 10.76                         | 0.682                   | 12.95                         | 0.706                   | 16.81                         | 0.729                   | 20.71                         | 0.748                   | 23.79                         |
| 25           | 0.607                               | 0.609                               | 0.676                | 11.00                         | 0.690                   | 13.33                         | 0.713                   | 17.05                         | 0.736                   | 20.85                         | 0.755                   | 23.94                         |
| 30           | 0.615                               | 0.616                               | 0.682                | 10.71                         | 0.697                   | 13.2                          | 0.720                   | 16.89                         | 0.744                   | 20.7                          | 0.762                   | 23.78                         |
| 35           | 0.623                               | 0.623                               | 0.690                | 10.75                         | 0.706                   | 13.3                          | 0.729                   | 16.95                         | 0.750                   | 20.45                         | 0.770                   | 23.54                         |
| 40           | 0.63                                | 0.635                               | 0.699                | 10.07                         | 0.720                   | 13.45                         | 0.744                   | 17.15                         | 0.766                   | 20.62                         | 0.784                   | 23.46                         |

2

## 3 3.2. Freezing and Melting Characteristics

## 4 3.2.1 Freezing Process

5 Initially the nanocomposite which is in the liquid phase at room temperature (32°C) gets sensibly cooled  
 6 to the freezing temperature by placing it inside the cold bath maintained at the desired temperature. After sensible  
 7 cooling, the nanocomposite begins to solidify starting from the outermost surface which is exposed to the heat  
 8 conducting surface. Due to this the outermost layer starts to solidify first. The solidification process continues until  
 9 the midpoint of nanocomposite solidifies. After complete solidification, sensible cooling of the solidified sample  
 10 takes place until the nanocomposite reaches -3°C. The bath temperatures for freeing experiments were -6°C and -  
 11 10°C.



1  
2 **Fig.5.** Freezing curves at from 32 °C to -3 °C with a bath temperature of -6 °C and -10 °C  
3

4 Fig.5 shows the freezing curve at -6 °C and -10 °C for the base-fluid and nanocomposites for different  
5 volume percentage of GnP from 32 °C to -3 °C. The time taken by the base-fluid to solidify is 77.5 minutes whereas,  
6 the time taken by 0.1%, 0.2%, 0.3%, 0.4% and 0.5% vol. fraction nanocomposites to solidify is 59 minutes, 52.5  
7 minutes, 49.5 minutes, 47 minutes and 44 minutes respectively. Thus, the addition of nano-particles aided to  
8 reduce the freezing time by 23.87%, 32.25%, 36.12%, 39.35% and 43.22% for 0.1%, 0.2%, 0.3%, 0.4% and 0.5% vol.  
9 fractions respectively.

10 Similarly, at the bath temperature of -10 °C the time taken to solidify the base fluid is 55.5 minutes  
11 whereas, 0.1%, 0.2%, 0.3%, 0.4% and 0.5% vol. fractions of nanocomposites the time taken is 46 minutes, 43.5  
12 minutes, 40 minutes, 36 minutes and 31 minutes respectively. Thus, the addition of nano particles reduced the  
13 freezing time by 12.25%, 15.48%, 16.12%, 25.16% and 31.61% for 0.1%, 0.2%, 0.3%, 0.4% and 0.5% vol. fractions  
14 respectively.

### 15 3.2.2 Melting Process

16 The solidified nanocomposite is sensibly heated up to the melting temperature when placed inside the  
17 hot bath. After sensible heating, the nanocomposite begins to melt starting from the outermost surface which is  
18 exposed to the heat conducting surface. Due to this, the outermost layer starts to melt first. The melting process  
19 continues until the midpoint of the nanocomposite melts completely. Then the sensible heating of the liquid  
20 sample takes place until it is in thermal equilibrium with the hot bath temperature. The melting experiment is also  
21 carried out for the base-fluid as well as the nanocomposites. The bath temperatures for the melting experiments  
22 are 31°C and 36°C respectively. The melting process was carried out till the nanocomposite sample reached 30°C.  
23

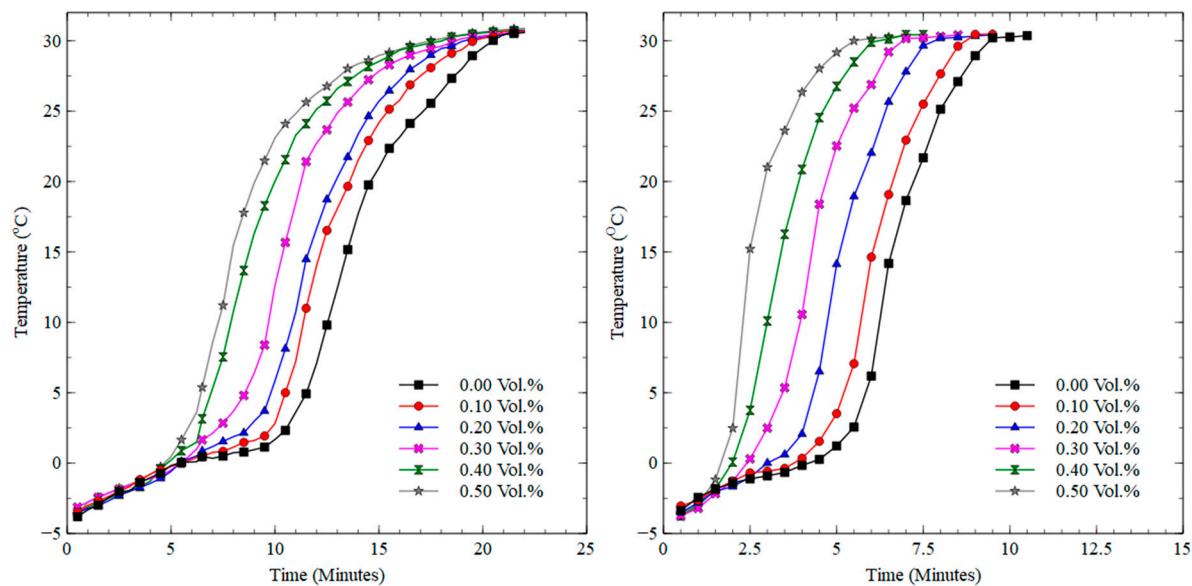


Fig.6. Melting curves from -3 to 30 °C with a bath temperature at 31°C and 36 °C

Fig.6 shows the comparison of melting curves from -3°C to 30°C for the base-fluid and nanocomposites kept at bath temperatures of 31°C and 36 °C. The sensible heating process is faster compared to the latent process. The time taken by the DI water to melt completely is 6 minutes whereas, time taken by 0.1%, 0.2%, 0.3%, 0.4% and 0.5% vol. fractions of nanocomposites is 5.5 minutes, 5 minutes, 4.5 minutes, 4 minutes, and 3.5 minutes respectively. Thus, the addition of nano-particles reduced the melting time by 8.33%, 17.67%, 25%, 33.33% and 41.67% for 0.1%, 0.2%, 0.3%, 0.4% and 0.5% vol. fractions respectively. The similar trends are observed when the samples are melted from -3 to 30 °C when kept in a hot bath at 36 °C. At this condition the time taken by DI water to melt completely is 4 minutes whereas 0.1%, 0.2%, 0.3%, 0.4% and 0.5% vol. fractions of nanocomposites the time taken is 3.5 minutes, 3 minutes, 2.5 minutes, 2 minutes and 1.5 minutes respectively. Thus, the addition of nano-particles reduced the melting time by 12.5%, 25%, 37.5%, 50% and 62.5% for 0.1%, 0.2%, 0.3%, 0.4% and 0.5% vol. fractions respectively.

During melting, the solidified fluid near the walls absorbs heat and starts to melt. Conduction is the dominant mechanism in the initial time when the thickness of the liquid layer is so thin. The thickness of the liquid layer increases and buoyancy force is developed with respect to time. The difference between the solid and liquid density causes the melted water to sink towards the bottom of the capsule and to consequently push up the ice. It intensifies the convection force and accelerates the melting rate. However, it can be noticed that the thermal conductivity of liquid is lower than solid and therefore, the heat conduction in liquid is lower than in solid. Thus, as the thickness of the liquid layer increases, the heat transfer conduction is reduced and on the other hand, natural convection is enhanced. So, melting is accelerated because of this natural convection in the liquid [33].

During freezing, the liquid near the walls rejects heat to the surrounding cold bath and starts to solidify. As time passes, the thickness of the solid layer increases. Water is denser than ice causing the ice to float. So, water gets accumulated at the bottom of the capsule. It can be seen that in the initial time, the solidification rate is great and conduction is the dominant mechanism of heat transfer between liquid and cold surfaces. As time progresses, more amount of liquid becomes solid and therefore the solid layer near the cold surfaces gets thicker. Although the thermal conductivity of solid is higher than liquid, the solid layer imposes thermal resistance for heat conduction from the cold surface to the warm liquid. Thus, heat conduction decreases by increasing thickness of solid layer. Solidification rate reduces gradually during the process, especially near the end of process where the solid layer covers the whole of the capsule except a small region [33]. In both freezing and melting experimentations, it was observed that addition of nano-particles enhanced the freezing and melting rates respectively, and the maximum enhancement was observed with the 0.5% volume percentage of GnP.

36 **4. Conclusions**

37 Water based graphene nanocomposites were prepared with chemically by the covalent functionalization  
38 method and their thermal conductivity were measured experimentally. The freezing and melting characteristic  
39 of the prepared nanocomposites were studied experimentally by varying the bath temperatures and volume  
40 percentage of GnP. The results showed that the addition of GnP nanoplatelets increased the thermal conductivity  
41 of all volume fractions and a maximum of 23.95% enhancement was observed for 0.5% volume fraction in the  
42 liquid state. Similarly, in the solid state, the maximum thermal conductivity enhancement was 53.05% for 0.5%  
43 volume fraction. The freezing and melting time decreased for all the test conditions when the volume percentage  
44 of GnP increased.

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46 Conceptualization S.H and D.M lal; Methodology, S.S. and C.S; Formal analysis, S.S. and C.S; writing—  
47 original draft preparation, S.S.; writing—review and editing, S.H., C.S and D.M. lal; supervision D.M. lal

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