# MELTING / SOLIDIFICATION CHARACTERISTICS OF PARAFFIN BASED NANOCOMPOSITE FOR THERMAL ENERGY STORAGE APPLICATIONS

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*The present work aimed to investigate the melting and solidification characteristics of nanoparticle enhanced phase change material (NEPCM). The NEPCMs were prepared using paraffin as the phase change material (PCM) and multiwall carbon nanotube (MWCNT) as the nanomaterial without using any dispersant. Thermal conductivity of the NEPCM was measured with respect to temperature and the measured data showed higher enhancement than the PCM both in liquid and solid state, due to inherent high conductive and the continuous networking of the MWCNT. A reduction in solidification and melting time of 42% and 29% was achieved in the case of NEPCM with 0.9% and 0.3% respectively. It is concluded that enhanced heat transfer characteristics of NEPCM is highly beneficial towards design and development of efficient TES system for various applications.*

Keywords: *Carbon nanotubes, Phase change material, Thermal energy storage, Melting, Solidification, Nucleating agent*

## 1. Introduction

Depletion of the fossil fuels and the exponential increase in energy demand due to urbanization and rapid industrial growth have made the researchers and policy makers to focus on the utilization of naturally available renewable resources. According to UN Intergovernmental Panel on Climate Change (UNIPCC), there is an increase in average global temperature of about 0.6 K and it is expected further increase in temperature by 1.4 – 4.5 K by year 2100 [1]. The major contribution for the global warming is due to exponential increase in the usage of thermal energy in the various sectors, particularly in the buildings [2], which demand the need for alternate energy resources. The renewable energy, particularly the solar energy, receives more importance for its clean, non-polluting, inexhaustible and cost free nature. However, the major problem associated with the solar energy is intermittent in nature and the energy demand for various applications is also time dependent, but in a different pattern and phase from the solar energy supply. The time gap between the supply and demand is to be matched dynamically through the integration of an energy storage system for effective utilization of solar energy.

Among the various energy storage systems, the thermal energy storage (TES) is of great significance, in particular, the latent heat thermal energy storage (LHTS) system, in which a greater energy density is stored using the phase change materials (PCMs) in a narrower operational temperature range. The LHTS system is utilized successfully in different applications such as energy

management in buildings [3], telecom shelter [4], food storage [5] and space cooling [6] in order to improve the overall system performance. Various types of PCMs are commercially used in the LHTS system, out of these the paraffins are more widely used in many applications, as they start to melt / solidify congruently without any sub-cooling. Moreover, paraffins possess high stability, better recycling, non-corrosive and water repellant along with relatively at lower cost. However, the inherent lower thermal conductivity of paraffin is the major drawback that increases the thermal resistance during the phase change process, as the liquid – solid interface moves away from the heat transfer surface. The increase in thermal resistance reduces the charging / discharging rate significantly. Different techniques like providing fins on the heat transfer surface [7, 8], insertion of a metal matrix [9, 10] and dispersion of high conductive solid particles at micron scale [11 - 13] have already been proposed to augment the heat transfer characteristics of the PCM. Though the results are encouraging, but limitations are evident like increase in weight and the volume of the storage system.

The above major problems in the PCM based TES system can be overcome with the recent pioneering developments in the field of nanotechnology, capable of dispersing high conductive solid particles at the nano-metric scale in the PCM [14], normally called nanoparticle enhanced PCM (NEPCM). The thermal transport properties and the melting / solidifying characteristics of the NEPCM with the dispersion of different nanoparticles such as alumina [15, 16], copper [17], copper oxide [18], silver [19] multiwall carbon nanotubes (MWCNT) [20 - 22], graphene [23] and graphite nanoplatelets [24] have been reported in the literature. Their results clearly indicated that the thermal transport properties such as thermal conductivity and thermal diffusivity enhanced in proportion with the concentration of the nanoparticles with negligible change in latent heat values. Among the various nanoparticles, the carbon nanotubes and graphite nanoplatelets are extensively used in preparing the NEPCM owing to its relatively lower density and inherent higher thermal conductivity compared to that of metal / metal oxide nanoparticles. The addition of above carbonaceous nanoparticles not only resulted with increase in thermal conductivity, but also acted as the nucleating agent to reduce the degree of sub-cooling in the PCM [25]. It is observed from the above literature that only few research works have been carried out regarding the influence of MWCNT on the melting / solidification characteristics of paraffin in the temperature range suitable for solar water / air - heating applications. Considering the pressing need to enhance the thermal performance of the PCM based thermal energy storage system and inherent high thermal transport properties of the MWCNT, the present research work aimed to explore the heat transfer characteristics of paraffin based NEPCM during melting and solidification.

## 2. Preparation of the NEPCM

In the present study, two-step method was adopted to prepare the NEPCM with paraffin wax as the base PCM and MWCNT as the nanomaterial. Considering the outlet temperature of water from the solar based water heating system using flat plate collectors, paraffin wax (Fisher Scientific) having the phase change temperature in the range of 50 °C to 59 °C was chosen as the PCM and the MWCNT was procured from Cheap Tubes, USA. The major thermophysical properties of the base PCM and the specifications of the MWCNT provided by the manufacturers are shown in table 1 and table 2 respectively.

**Table 1. Thermophysical properties of base PCM***

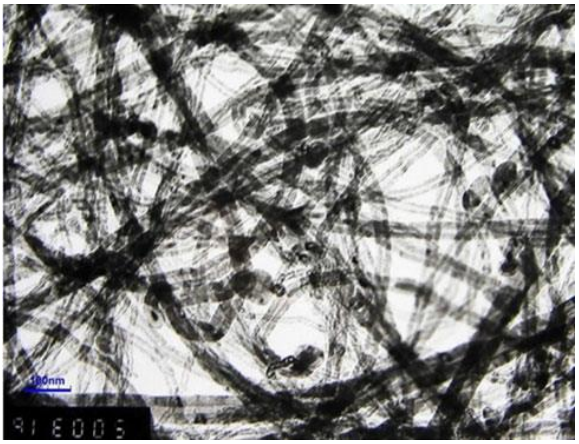
| Parameter | Value |
|---|---|
| Melting temperature | 50 °C – 59 °C |
| Density (Solid) | 0.915 kg / lit |
| Density (Liquid) | 0.88 kg / lit |
| Thermal conductivity (Solid at 30 °C) | 0.22 W / m K |
| Thermal conductivity (Liquid at 60 °C) | 0.16 W / m K |
| Latent heat | 140 - 145 kJ/ kg |

*Manufacturer data

**Table 2. Specifications of the MWCNT**

| Parameter | Value |
|---|---|
| Outer tube diameter | 30 – 50 nm |
| Inner tube diameter | 5 – 10 nm |
| Length | 10 – 20 nm |
| Specific surface area | 60 $m^2/g$ |
| True density | 2.1 $g/cm^3$ |
| Bulk density | 0.28 $g/cm^3$ |
| Electrical conductivity | > 100 S/cm |
| Purity | > 95 wt. % |

Figure 1 shows the TEM image of the MWCNT and the entanglements were noticed between the carbon nanotubes. In order to disentangle them, the ball milling of the MWCNT was carried out using tungsten carbide balls for 90 min, followed by ultra-sonication for a period of 30 min using an ultrasonicator (QSonica, USA). The solid PCM was initially melted to liquid state, followed by the addition of MWCNT into the liquid PCM and the mixture was stirred using a magnetic stirrer for period of 30 min at the temperature always greater than the phase change temperature of the paraffin (65 °C). The solution was then transferred to the water bath maintained at 65 °C in the ultrasonicator and the uniform dispersion of MWCNT in the PCM was achieved through the ultra-sonication for period of 90 min. Three different NEPCM with a mass concentration of 0.3, 0.6 and 0.9 wt. % were prepared and the diameter of the MWCNT in the NEPCMs was measured using scanning electron microscope (SEM). The diameter of MWCNT in the NEPCM sample with 0.3 wt. % is in the range of 31 to 60 nm as depicted in figure 2.



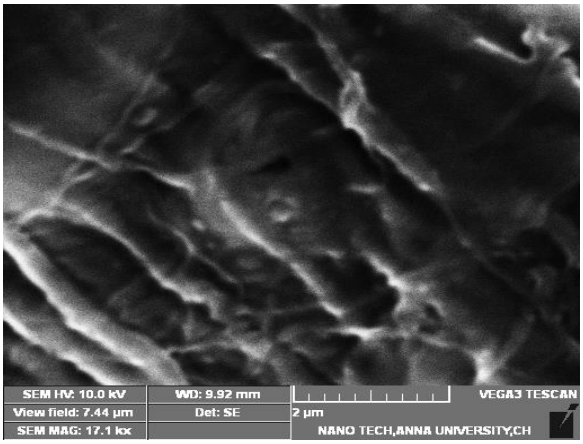



**Figure 1. TEM image of the MWCNT** **Figure 2. SEM image of the dispersed MWCNT**

## 3. Experimental methods

### *3.1 Thermal conductivity measurement*

It is essential to determine the variation in thermal conductivity of the PCM with respect to temperature to study the heat transfer characteristics of the PCM during energy charging / retrieving process. In the present study, the thermal conductivity of PCM and NEPCM was measured in both solid and liquid state with respect to temperature using a KD2 Pro thermal analyzer (Decan Devices Inc., USA), which works based on the transient hot-wire method. A sensor needle of 60 mm length and 1.2 mm diameter was used to measure the thermal conductivity of the NEPCM with an accuracy of ± 5%, while another sensor needle of 100 mm long and 2.4 mm diameter was used to measure the thermal conductivity of the NEPCM at the solid state with an accuracy of ± 10%. The desired temperature of the NEPCM was maintained using a refrigerated – heating circulator bath (Julabo, Germany) with a temperature stability of ± 0.01% and the thermal conductivity measurements were carried out in the range of 30 ºC – 80 ºC with a step size of 10 ºC. The liquid NEPCM was filled in a cylindrical glass container fitted with a nylon lid through which the sensor needle was inserted into the NEPCM. The sensor was always kept at the centre of the container for accurate measurements and a read time of 1 min and 4 min was configured during the measurements in the liquid and solid state respectively. The cylindrical container filled with the NEPCM was kept in the refrigerated – heating circulator bath and the measurements were carried out only after the NEPCM attained the desired temperature. Five experimental measurements were made at each temperature condition to ensure the repeatability of the data.

### *3.2 Experimental setup*

Figure 3a illustrates the schematic arrangement of the experimental setup to investigate the melting characteristics of the NEPCM. The melting setup consists of a thermally insulated stainless steel container of 15 L capacity, filled with water as the surrounding heat transfer fluid (HTF). A heating coil of capacity 4 kW, a proportionate temperature differential controller (PTDC) and a mechanical stirrer driven by an electrical motor are used to maintain the desired temperature of the surrounding heat transfer fluid (HTF). A cylindrical capsule with an outer diameter 50 mm and 2 mm thickness made up of copper was used to encapsulate the PCM. 11RTDs (class A) with accuracy of ±

0.15°C were located at various positions as shown in figure 3b with a considerable distance from the bottom of the capsule to avoid the end effects. All the RTDs were connected to a data logger (Agilent 34970A) to monitor and store the continuous temperature data during the melting experiments.

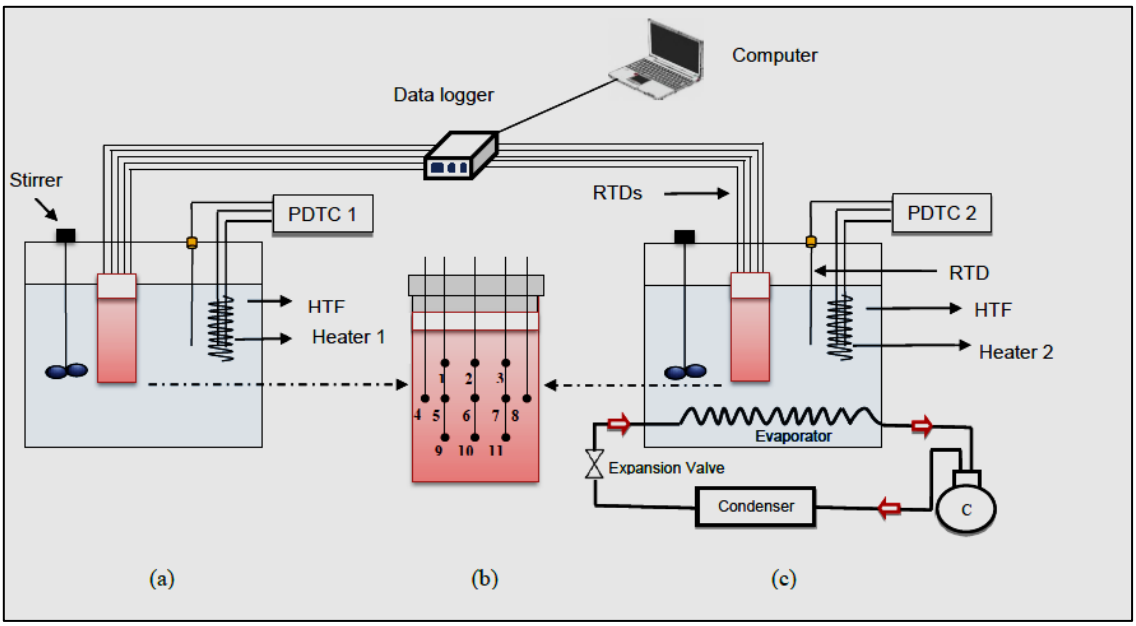



**Figure 3. Schematic arrangement of (a) Melting setup (b) Cylindrical capsule (c) Solidification setup**

A known mass of NEPCM (160 g) was initially melted and the liquid NEPCM was cautiously transferred to the cylindrical capsule, ensuring no air bubbles entrapped in the NEPCM. The top of the capsule was tightly sealed with a cap made up of nylon and the capsule was kept at room temperature (30 °C - 35 °C) for *5 h* to solidify the liquid NEPCM. The capsule was immersed at desired depth of the container and the transient temperature variation of the NEPCM at all eleven locations were continuously measured for every 10 s until the NEPCM attains the thermal equilibrium with the surrounding HTF. The uniform temperature of the surrounding HTF was achieved through continuous stirring during the entire period of experimentation. The capsule with melted NEPCM was immediately transferred to the solidification experimental set up and their schematic arrangement of the experimental set up is shown in figure 3c. The detailed arrangement and working of the experimental set up were presented in detail by Kumaresan et al [16]. The temperature of the surrounding HTF was maintained at 30°C and the transient temperature variation of the NEPCM during solidification was continuously measured and recorded for every 10 s until the NEPCM attains the thermal equilibrium with the surrounding HTF. The uncertainties associated with various measured data are presented in table 3.

**Table 3. Results of uncertainty analysis**

| Measured quantities | Uncertainty |
|---|---|
| Diameter of cylindrical capsule | ± 0.02 mm |
| Mass | ± 0.002 g |
| Temperature | ± 0.15 ºC |
| Thermal conductivity ( Liquid) | ± 5% |
| Thermal conductivity ( Solid) | ± 10% |

## 4. Results and discussion

### *4.1 Thermal conductivity enhancement*

The variation in thermal conductivity of the PCM and NEPCM with respect to temperature both in solid and liquid state is shown in figure 4. As perceived from the figure, the thermal conductivity of the NEPCM is evidently higher than the PCM at all the measured temperatures and also in proportion with the concentration of the MWCNT. The maximum thermal conductivity enhancement of~22% (T= 30 °C) and 29% (T = 80 °C) was noticed in the case of the NEPCM with 0.9 wt. % in solid and liquid state respectively. The inherent higher thermal conductivity and the continuous networking of the MWCNT that in turn provides faster heat transfer rate are the possible mechanisms for the enhancement in the thermal conductivity of the NEPCMs. Also, the higher thermal conductivity of the NEPCM near the phase change transition is highly beneficial to store and retrieve the thermal energy at the faster rate in the PCM based TES applications. However, the thermal conductivity of both PCM and NEPCM started to reduce appreciably in the liquid state, owing to the molecular disorder during the phase change transition from solid to liquid, which supress the augmenting effect even with the presence of MWCNT. The same trend of enhanced thermal conductivity was reported in different paraffins with the dispersion of MWCNT [21, 23, 26] and exfoliated graphite nanoplatelets [24]. The present experimental results of thermal conductivity enhancement are compared with the results of different enhancement techniques such as providing fins, addition of metal matrix and dispersion of high conductivity particles. The thermal conductivity of paraffin is augmented by 40%, 15%, 32% and 60% times with the addition of fins [8], spherical metal beads [10], expanded graphite [13] and high conductive aluminium powder at micron scale [12] respectively. Though the thermal conductivity enhancement is relatively higher in the above cases than the present study, the following major problems significantly reduce the thermal performance of LHTS system; (i) the presence of fins suppresses the natural convection during melting, (ii) the usage of metal matrix and beads occupy more volume in the encapsulation resulting proportional reduction in storage capacity per unit volume of LHTS system along with considerable increase in weight of the system, (iii) settlement of dispersed high conductivity particles at micron scale and the suppression of natural convection during melting.

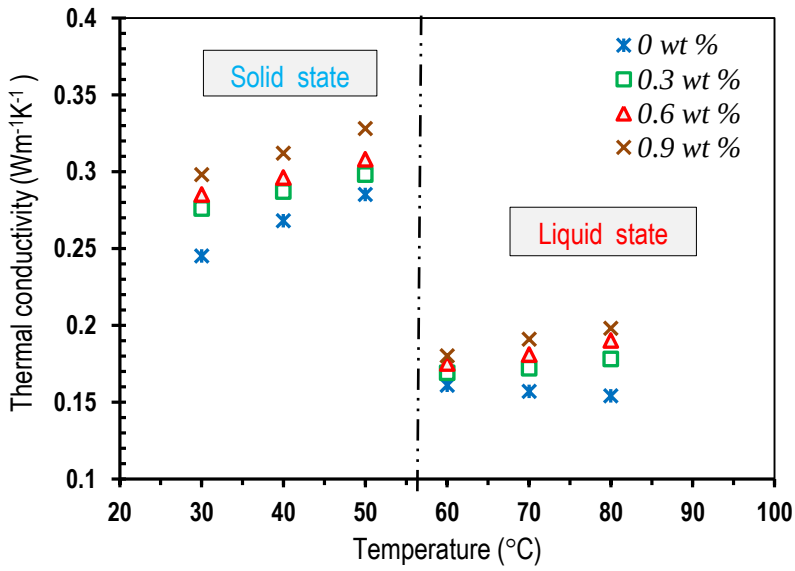


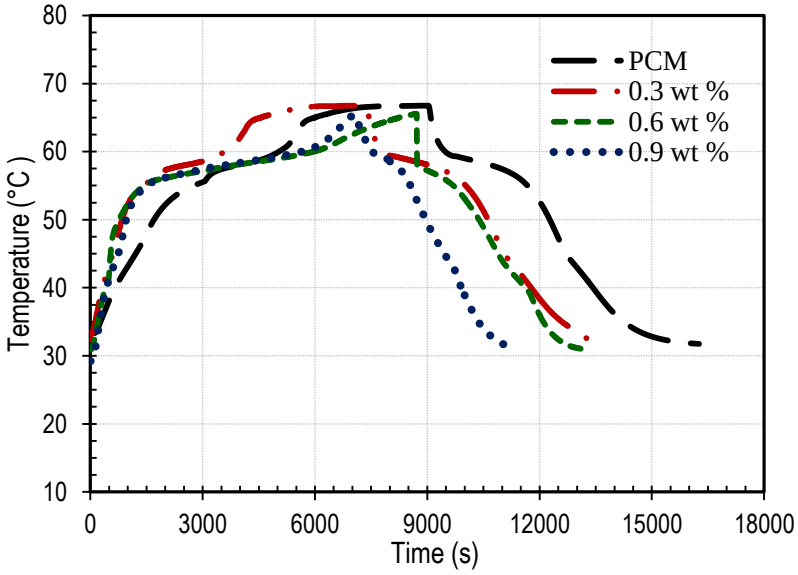

**Figure 4. Thermal conductivity of the NEPCM in solid and liquid state**

### *4.2 Transient temperature variation of the NEPCM*

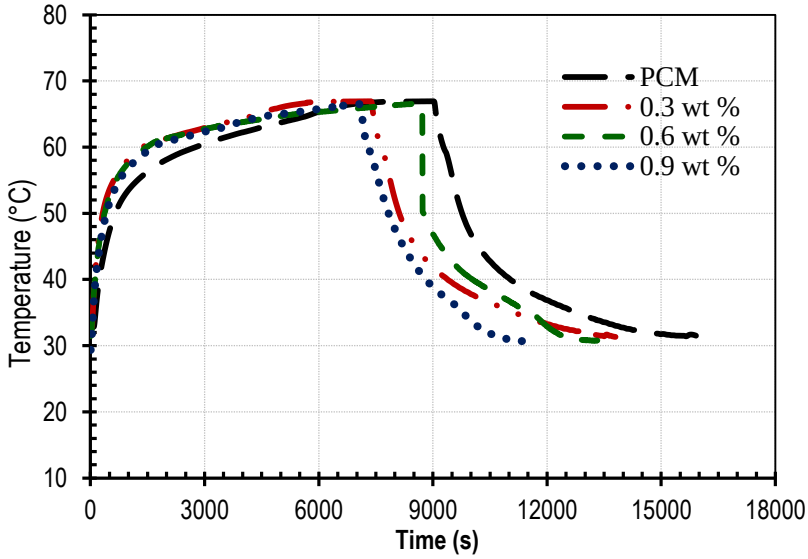
The transient temperature variation of the PCM and NEPCM at the center of the cylindrical capsule are shown in figure 5a during solidification and melting. Time taken by the PCM and NEPCM (0.3 wt.%) to attain the onset of melting (58 °C) from the initial temperature condition of 30 °C was 3960 s and 2520 s respectively. This reduction in time during the sensible heating is due to the enhanced thermal conductivity in the solid state and optimum percolation heat path provided by the high conductive MWCNT. However, the time taken was not further reduced in the case of the NEPCMs containing the MWCNT with the concentration greater than 0.3 wt. %. It could be explained by increase in interfacial thermal resistance between the CNTs and PCM with respect to increase in concentration, which in turn results with reduction in the heat transfer during sensible heating. During melting, the enhanced heat transfer characteristics of the NEPCM (0.3 wt. %) due to micro convection effects resulted with reduction in the melting time of 28.6% compared to that of the PCM. Nevertheless, the micro convection effects get suppressed with further addition of MWCNT that provides higher thermal resistance to the melting, owing to the predominant effect of increase in viscosity with respect to concentration of the MWCNT (though appreciable enhancement in thermal conductivity of the NEPCM was observed as discussed in section 4.1). The same trend of reduction in time also prevailed in the case of the NEPCM with 0.3 wt. % during liquid sensible heating.

The transient temperature behavior of the PCM and NEPCM at the center of the capsule are illustrated in the figure during solidification at the surrounding bath temperature of 30 °C. It is observed that the solidification time of the NEPCM considerably reduced in proportion with the concentration of MWCNT. A maximum reduction in the solidification time of 42% was achieved in case of NEPCM with 0.9 wt. % compared to that of the PCM due to its enhanced thermal conductivity. Also, the transient temperature behavior of the PCM and the NEPCM at various radial locations respectively at a distance of 22.5 mm (RTD 4) and 12.5 mm from the center (RTD 5) is shown in figure 5(b-c). As noticed from figure 5b, the PCM and NEPCM near the wall got melted / solidified at a faster rate due to negligible conductive resistance offered by the small quantity of liquid

and solid PCM respectively during melting and solidification. Nevertheless, the thermal conductive resistance increased significantly due to disordering of the solid molecules during melting and growing solidified solid PCM during solidification as shown in figure 5c. The results evidently showed that the PCM particularly the low thermal conductivity is subjected to different heating / cooling rates during its phase transition from liquid - solid and vice versa. Further, the present experimental results revealed that the addition of high conductive MWCNT in the base PCM augmented the heat transfer characteristics, which is very useful to store / retrieve the energy from the PCM based thermal energy storage system for various applications particularly solar water / air heating applications.




**(a)**

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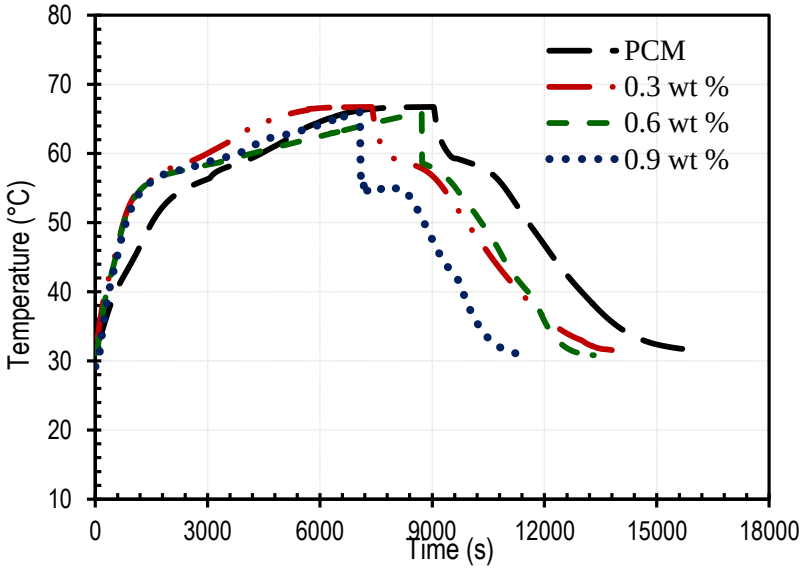


**(c)**

**Figure 5. Transient temperature variation of the NEPCM at (a) center (b) near the wall (22.5 mm from center) (c) between the wall and center (12.5 mm from center)**

## Conclusions

The following conclusions are made based on the present experimental investigation on melting / solidification behaviour of paraffin dispersed with MWCNT.

- The addition of high conductive MWCNT in the PCM resulted with appreciable enhancement in the thermal conductivity. A maximum enhancement of 22% and 29% was noticed respectively in solid and liquid state of the NEPCM containing 0.9 wt. % due to inherent higher thermal conductivity and continuous networking of the MWCNT.

- The maximum reduction in the melting time of 29 % was achieved in the NEPCM with 0.3 wt. % compared to that of the PCM. Further, the addition of MWCNT resulted with the suppression of micro convection effects due to the predominant increase in viscosity of the NEPCM in the liquid state.

- The solidification time was reduced considerably in proportion with the concentration of MWCNT and the maximum reduction in solidification time of 42% was achieved with the NEPCM containing 0.9 wt. % owing to the enhanced thermal transport properties of the NEPCM. Based on the present experimental results, further research works need to be carried out to optimize the concentration of the MWCNT towards the development of NEPCM based LHTS system for various solar thermal applications.

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